SEMMELWEIS UNIVERSITY
PHARMACEUTICAL FACULTY

DEPARTMENT OF ORGANIC CHEMISTRY

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Collection of Organic chemical problems

Budapest
2016

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ISBN ISBN 978-963-12-8996-1

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Preface

This Collection of organic chemical problems was assembled for pharmacy students at Year II. Topics of the Collection are closely linked to the contents of the main lectures; it gives an overview of the more important compound families, with some special Chapters. The Collection tries to facilitate learning of the theoretical material, through basic and typical examples on the undergraduate level. The problems discussed in the Collection are partially derived from other school books, but is also based on the educational experience of two decades, as a conclusion of consultations, midterm tests as well as exams. The special problems are built on each other, following the internal logics of the subject. The usual arrangement of the problems are the following (Chapter by Chapter): nomenclature; preparation; chemical reactions, then essay question(s) connected to the given reactions. The nomenclature problems are based on the following handbook: József Nyitrai, József Nagy: Guide to the *IUPAC*-nomenclature of organic compounds (Association of Hungarian Chemists, Budapest, 1998). Mainly basic questions are involved in the Collection, related to preparations or chemical reactions, using different substituted derivatives as starting material. Answers for the essay questions are short, comprised definitions or key points, providing examples how to summarise the students' knowledge.

Problems in this Collection will be useful for learning other special pharmaceutical subjects. Since size of the Collection is limited, some themes are not involved, e.g., there is no Chapter for Spectroscopic problems. Students learn these missing topics at lectures and practices of spectroscopy, through solving attached spectroscopic problems. The Collection can be effectively used in seminars, as well. Names and structures of organic functional groups and compound types are added to the end of Collection, supporting learning and applications of functional groups for Pharmaceutical Chemistry. The Collection consists of 16 Chapters, the Answers are shown just after the Problems, respectively.

Main purpose of the Collection is to facilitate learning of Organic chemistry for the exams. Therefore problem solving of the Collection is useful together with lectures, seminars and practices, throughout the whole Academic Year.

I must say thanks to *dr. János Wölfling* (Associate Professor), since he helped to finalise the manuscript by his well-based, precise work, as well as by his valuable suggestions. I must say thanks to *dr. Péter Mátyus* (Professor) for the careful lectoring.

Dr. Péter Tétényi (Assistant Professor) and *dr. Ruth Deme (*Assistant Lecturer) carried out the translation to English, thanks to them for it.

Dr. Gábor Krajsovszky

Dear Respected User of the Collection:

Please forward your remarks and suggestions related to the Collection to the author of Collection. This feature would improve utilisation of the Collection in the educational work.

Thanks for your efforts.

CONTENT

Semester I.

Semester II.

I. Molecular orbital theory of organic compounds

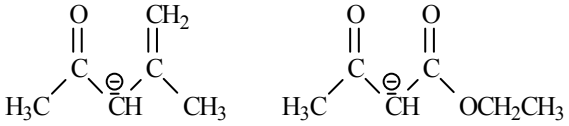
1. Define the following terms:
   A/ electron orbital
   B/ nodal plane
   C/ atomic orbital
   D/ molecular orbital.

2. Draw the π-orbital system of the allylic cation, of the allylic anion and of 1,3-butadiene. Give the number of electrons on each orbital. Which is the HOMO and which is the LUMO orbital?

3. Draw the π-orbital system of 3-methylenepenta-1,4-diene, how many electrons are on each shell?

4. Define the terms of kinetic as well as thermodynamic control.

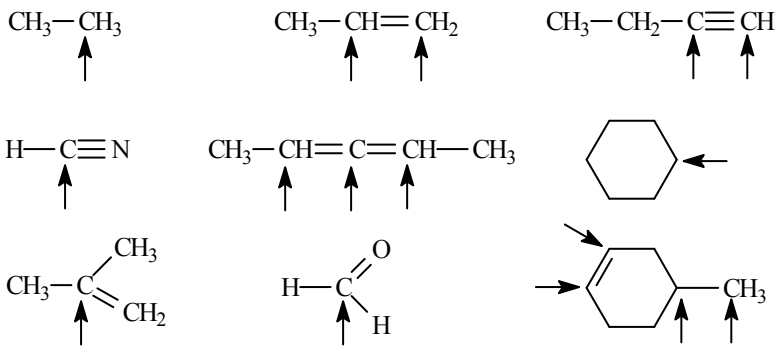
5. Draw the other two-two mesomeric structures of the following anions:



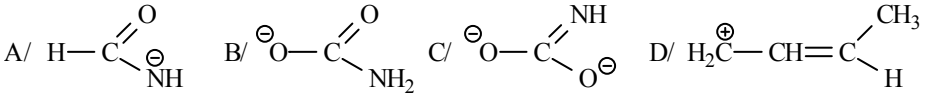
A/ B/

6. Define the terms of promotion and hybridisation (using the example of carbon atom). How do the hybridisation property of the atoms change by the function of electronegativity?

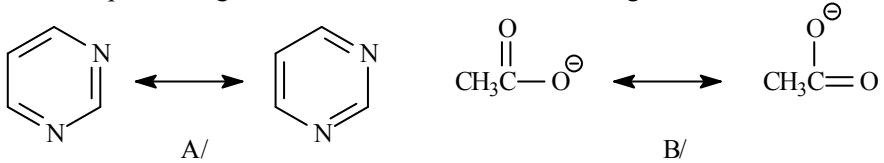
7. Determine hybridization states of the carbon atoms marked by arrows in the following compounds:



8. Draw any further resonance structures of the following species. How many electrons do participate in the construction of the *delocalised* system?

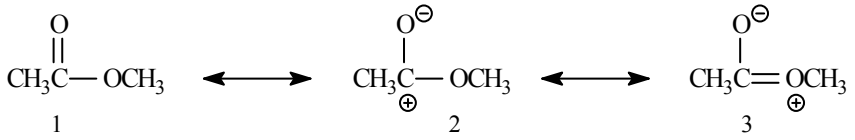


9. Draw the arrows representing the electron shifts in the following structures:



A/ B/

10. Which resonance structure(s) would be the closest one to the real structure of the given species?

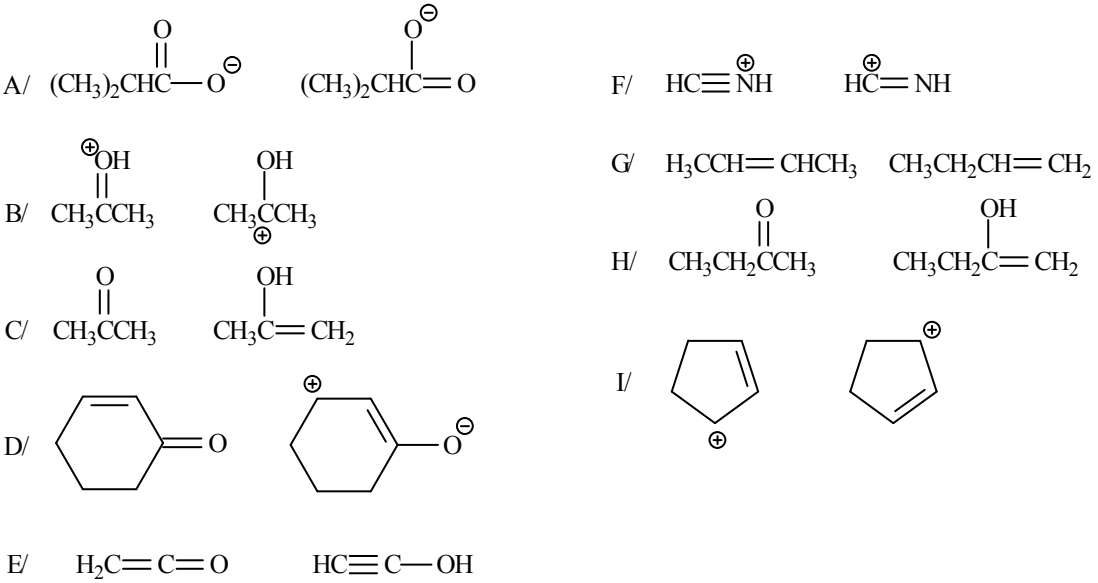


1 2 3

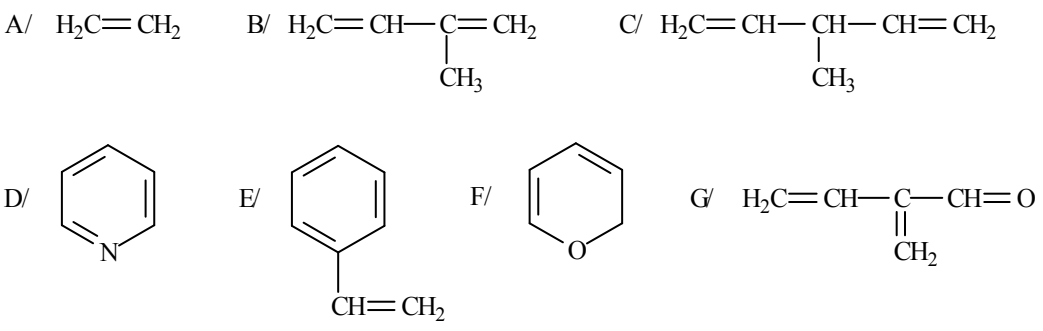
11. Draw the structural formulas of the following compounds, marking the *p*-orbitals forming the π-bonds at the drawing (mark the σ-bonds by lines):

$(CH_3)_2C{=}C(CH_3)_2$ A/ $CH_3C{\equiv}CCH_3$ B/

12. Determine whether the following pairs of species belong to resonance structures, to tautomeric structures or to structural isomers. Explain your decision.



13. Define the term of delocalised bond. Select the π-delocalised systems from the following structures:



14. A/ When does a molecular nonbonding orbital set?
B/ Which other orbital has simylar energy level than of this orbital?
C/ *P*-orbitals of which centres do participate in the construction of the nonbonding orbital?
D/ Do the energy level of this molecular orbital depend on the electron loading of the orbital?

I. ANSWERS

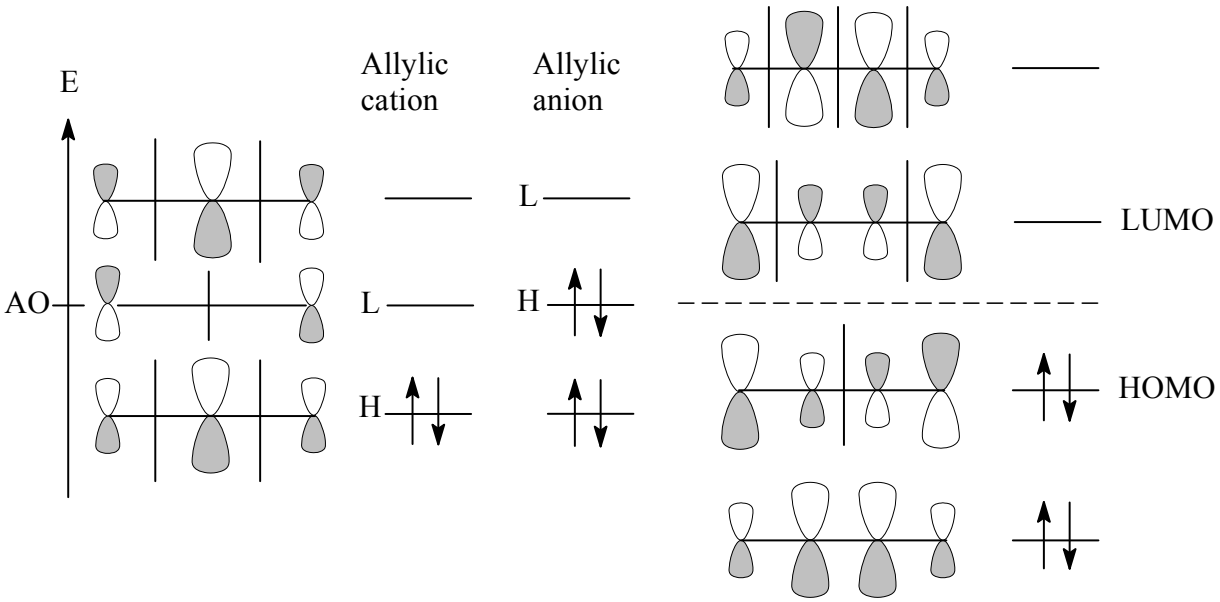
1. A/ Electron orbital: graphic representation of the wave function describing the wave properties of the electrons.

B/ Nodal plane: part(s) of the electron orbital, where - besides the nuclei- probability of finding electrons is zero.

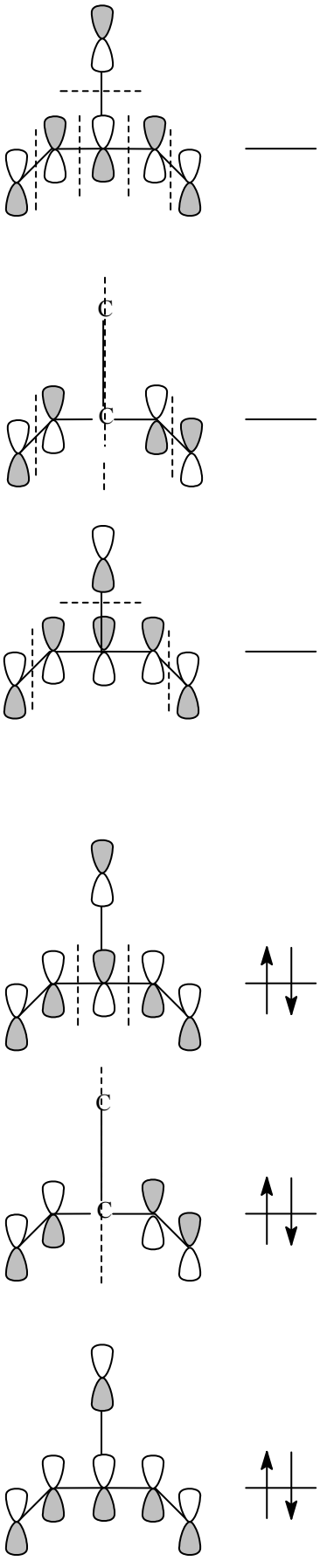
C/ Atomic orbital: electron orbital surrounding one nucleus, wave function of electron(s) moving within the field of *one* atom, where the electron can be found with probability of 90%.

D/ Molecular orbital: electron orbital surrounding two or more nuclei, wave function of electron(s) moving within the field of *two or more* atoms, where the electron can be found with probability of 90%.

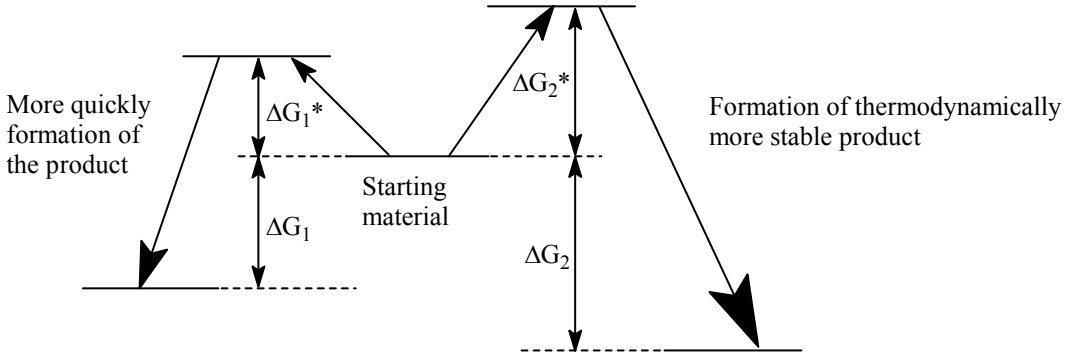
2. Π-orbital system, electron loading, HOMO (H) and LUMO (L) orbitals of allylic cation, allylic anion and of 1,3-butadiene:



3. Orbital system and electron loading of 3-methylenepenta-1,4-diene:



4. Kinetic control: the products are formed according to their *rates of formation*, i.e., the main product is formed in the faster reaction, since its activation free enthalpy is less ($\Delta G_1^* < \Delta G_2^*$).
Thermodynamic control: the products are formed according to their *stability, i.e.,* the main product is the more stable, since its heat of formation is greater ($\Delta G_1 < \Delta G_2$).



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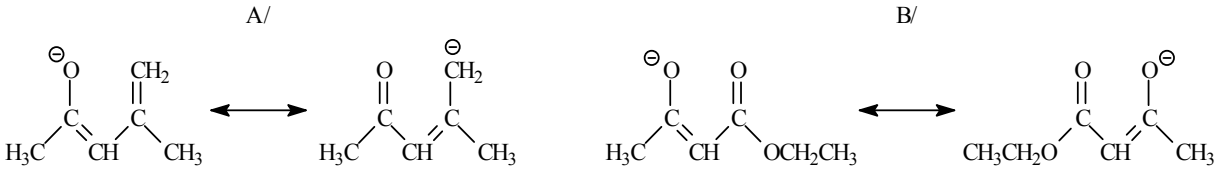
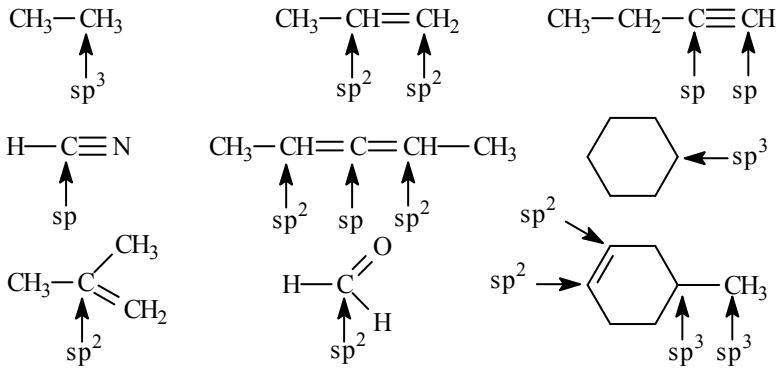


6. Promotion: a process preceding hybridisation, when a 2*s* electron is transferred to the 2*p* orbital.
Hybridisation: combination of 2*s* and 2*p* electron orbitals (a hypothetic process), when equivalent orbitals are generated. The abylity for hybridisation is decreased with increasing electronegativity.

7.



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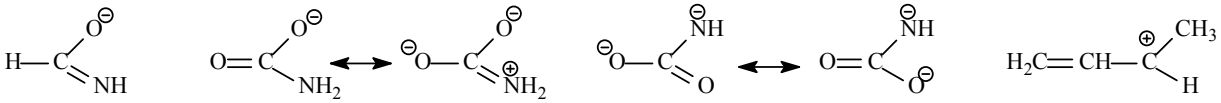
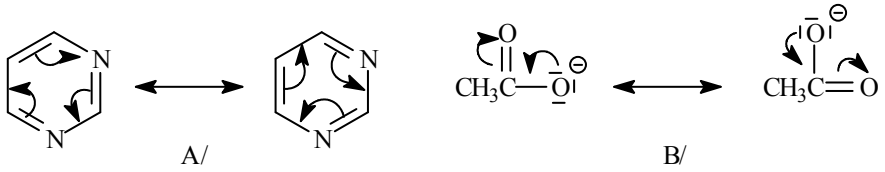


A/ 4 electron B/ 6 electron C/ 6 electron D/ 2 electron

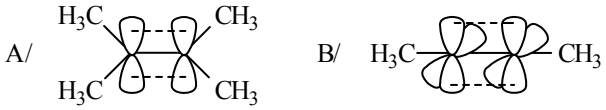
9.



A/ B/

10. The structure *1* is the closest to the real structure, since each carbons and oxygens are with electron octet and none of these atoms have charge. The structures *2* and *3* are farther from the real structure, since there is charge separation, and moreover, the structure *2* has a carbon atom without electron octet.

11.



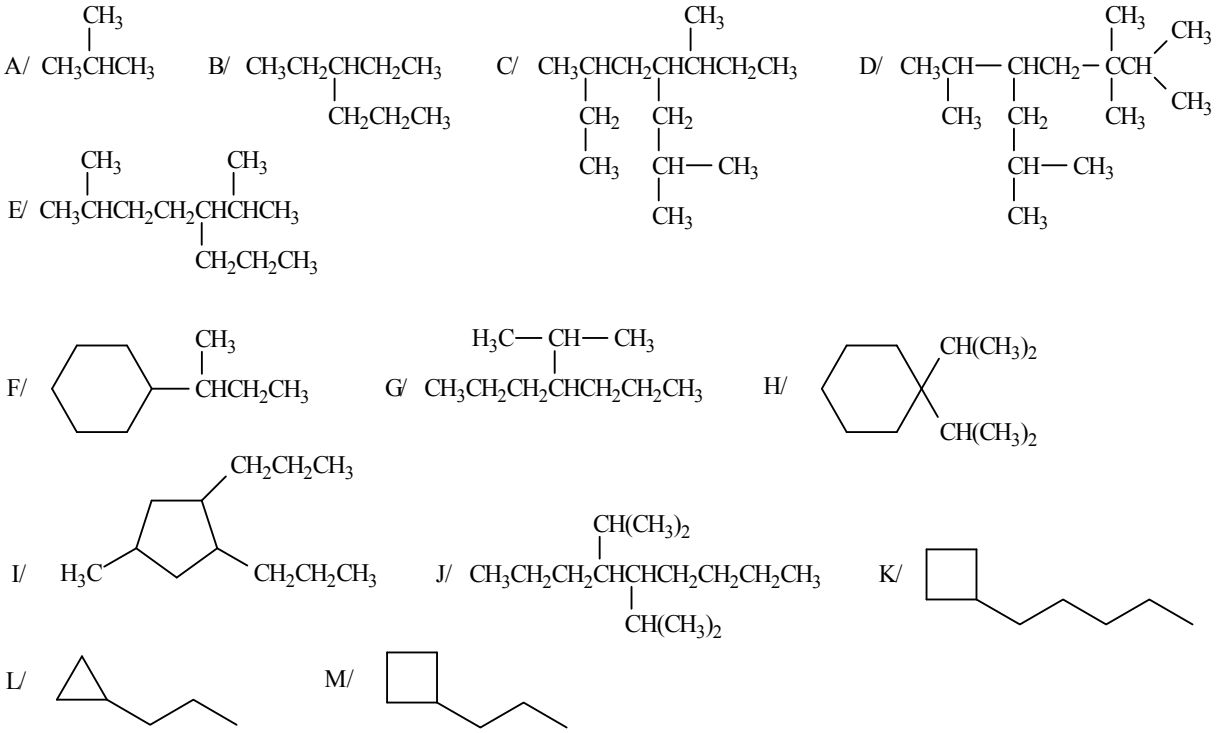
12. A/, B/, D/, F/, I/: differing only in the electron distribution and charges from each other, therefore these are *mesomeric* (resonance) structures.
G/ differing in the position of a double bond and of a hydrogene atom from each other, therefore these are *structural isomers*. Structures C/, E/, H/ are called as tautomers, since the hydrogene atom is a *mobyle* hydrogene. In tautomeric systems, there is equylibrium.

13. If the formed π molecular orbitals belong to 3 or more nuclei, the new bond is called *delocalised bond*. Π-delocalised systems are the followings: B/, D/, E/, F/, G/.

14. *Molecular nonbonding orbitals are formed, if*
A/ the number of combining atomic orbitals is odd.
B/ it is simylar to the energy level of the atomic orbital.
C/ The *p*-orbitals derived from the odd centres.
D/ it is independent of the number of electrons; e.g., the energy content of allylic cation, allylic radical and allylic anion are approximately the same.

II. Saturated hydrocarbons (alkanes, cycloalkanes)

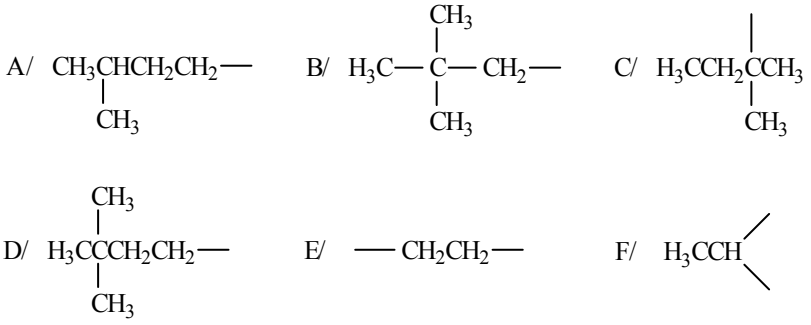
1. Name the following compounds:



2. Draw the structural formulas of the following compounds:

A/ 3-ethylheptane
B/ 4-ethyl-5-methylnonane
C/ propylcyclohexane
D/ isobutylcyclohexane
E/ 4-*tert*-butyloctane
F/ 4-(1,1-dimethylethyl)-2,3,6,8-tetramethylnonane
G/ 3,4-diethyl-2,8-dimethyl-5-(1-methylethyl)-nonane
H/ 1,3,5-triethylcyclohexane
I/ 4-ethyl-3-methylheptane
J/ 3,3-diethylhexane

3. Give the names of the following hydrocarbone groups:

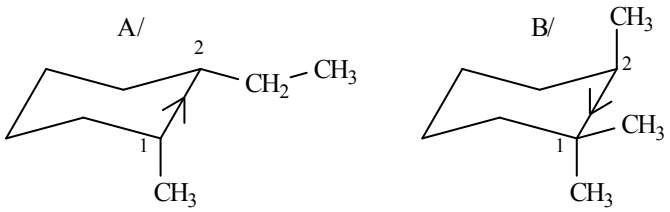


4. Draw the structural formulas of the following hydrocarbone groups:
   A/ 1-propyl B/ *sec*-propyl C/ *n*-butyl
   D/ *sec*-butyl E/ isobutyl F/ *tert*-butyl

5. Draw the structural formulas of the hydrocarbone structural isomers with general formulas of
   A/ C_5H_{12}
   B/ C_6H_{14}

6. Draw the structural formulas of the saturated cycloalkane structural isomers with general formulas of
   A/ C_5H_{10}
   B/ C_6H_{12}

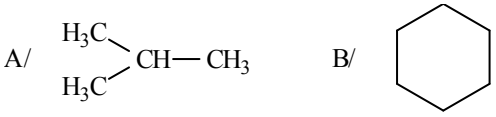
7. Draw the Newman projection of the following compounds, along the C^1-C^2 bond looking from the directions shown:



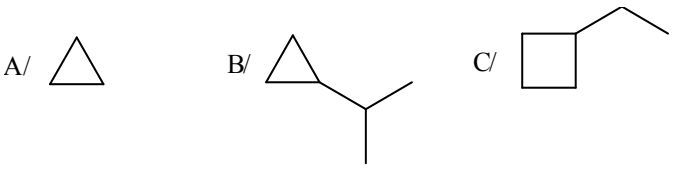
8. Draw the more stable conformer of A/ *cis* 1-*tert*-butyl-2-methylcyclohexane
   B/ *trans* 1-isopropyl-2-methylcyclohexane
   in chair conformer and draw its Newman projection along the C^1-C^2 bond.

9. Draw the stereoisomers of A/ 1,2-dimethylcyclohexane
   B/ 1,4-dimethylcyclohexane
   in chair conformer in decreasing order of stabilities.

10. Prepare the following compounds by Kishner-Wolff reduction:



11. Prepare the following alicyclic compounds by ring closure reaction:



12. What kind of reaction does take place, when ethane is brominated photocatalytically? Draw structures of the possible products.

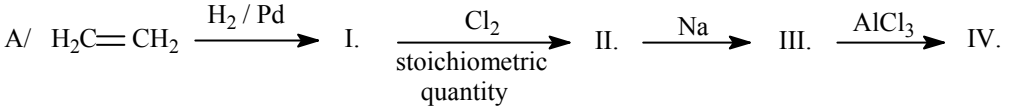
13. Prepare the following compounds by Wurtz synthesis
   A/ 3,4-dimethylhexane
   B/ 2,3-dimethylbutane
   from such a starting material, that the desired products would be formed avoiding any side products (other paraffine hydrocarbone must not be formed).

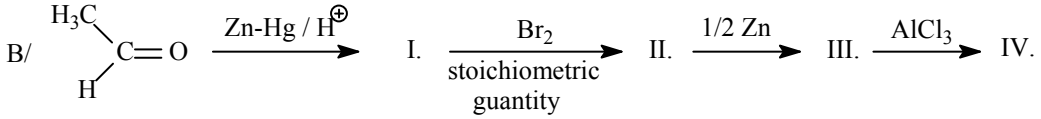
14. Prepare

A/ isobutane from *n*-butane

B/ neopentane from *n*-pentane.

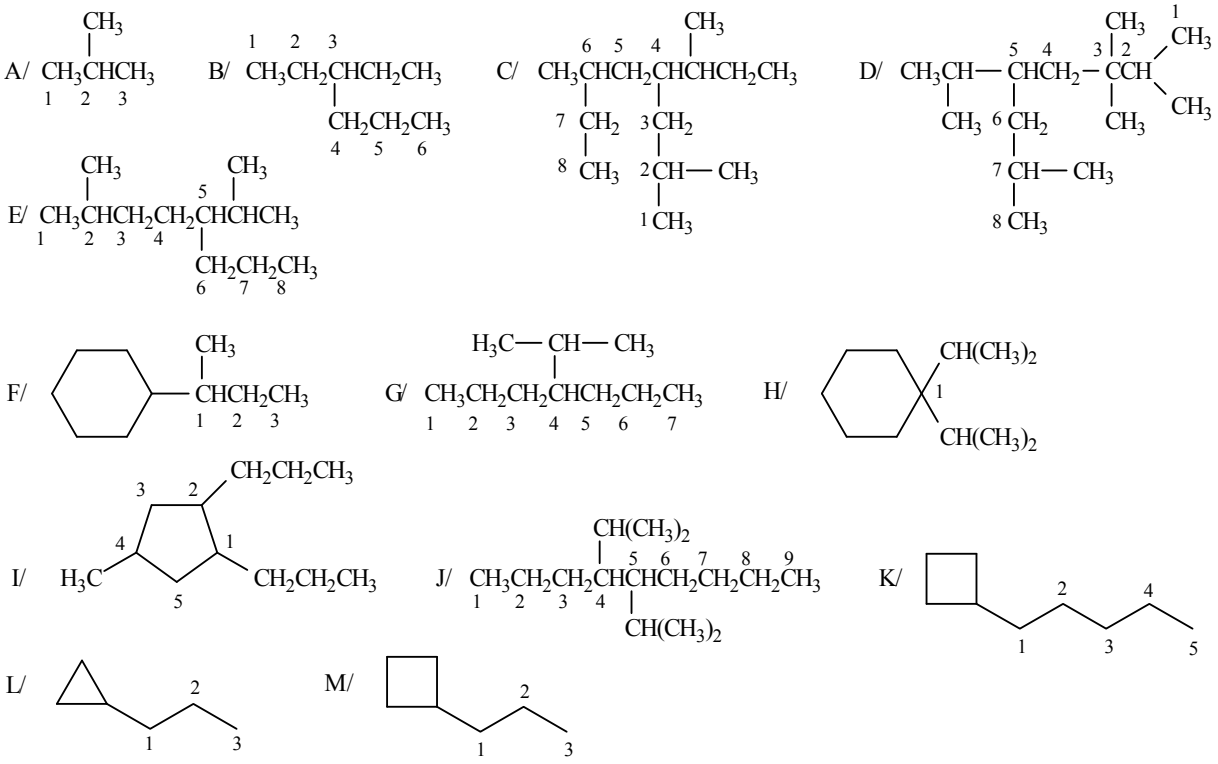
15. Draw the following reaction sequences:





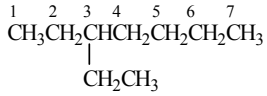
II. ANSWERS

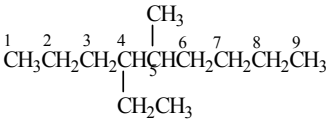
1.

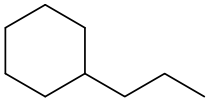


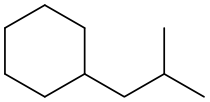
A/ 2-methylpropane
B/ 3-ethylhexane
C/ 2,6-dimethyl-4-(1-methylpropyl)-octane
D/ 2,3,3,7-tetramethyl-5-(1-methylethyl)-octane [5-isopropyl-2,3,3,7-tetramethyloctane]
E/ 2-methyl-5-(1-methylethyl)-octane [5-isopropyl-2-methyloctane]
F/ (1-methylpropyl)-cyclohexane
G/ 4-(1-methylethyl)-heptane [4-isopropylheptane]
H/ 1,1-diisopropylcyclohexane [1,1-bisz(1-methylethyl)-cyclohexane]
I/ 4-methyl-1,2-dipropylcyclopentane
J/ 4,5-diisopropylnonane [4,5-bisz(1-methylethyl)-nonane]
K/ pentylcyclobutane
L/ propylcyclopropane
M/ propylcyclobutane

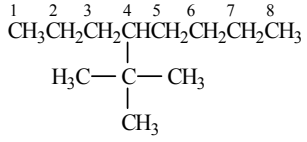
2.

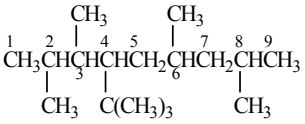
A/ 

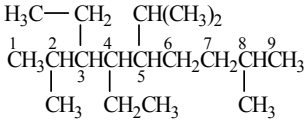
B/ 

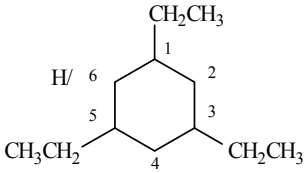
C/ 

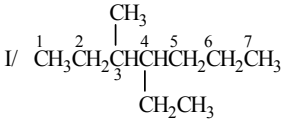
D/ 

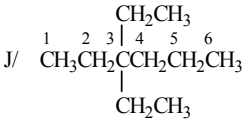
E/ 

F/ 

G/ 

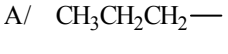
H/ 

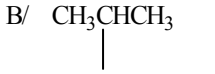
I/ 

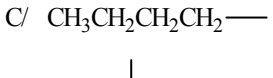
J/ 

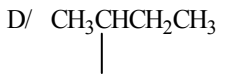
3. A/ isopentyl B/ neopentyl C/ *tert*-pentyl
D/ 3,3-dimethylbutyl E/ ethylene D/ ethylidene

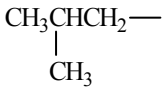
4.

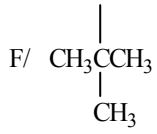
A/ 

B/ 

C/ 

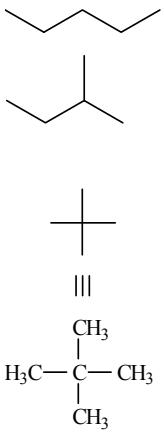
D/ 

E/ 

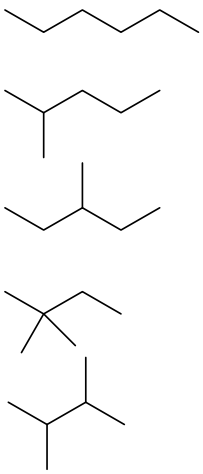
F/ 

5.

C_5H_{12} (3)

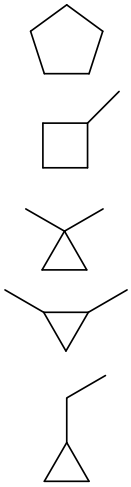


C_6H_{14} (5)

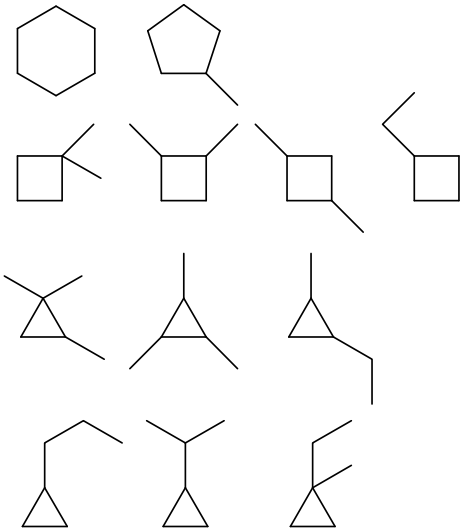


6.

C_5H_{10} (5)

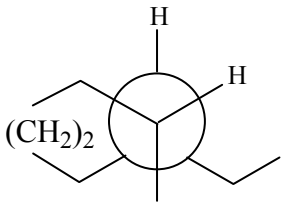


C_6H_{12} (12)



7.

A/



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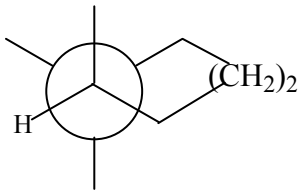
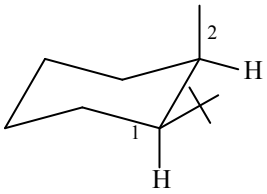
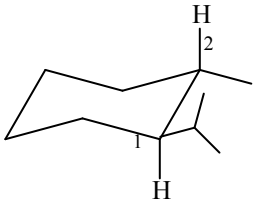


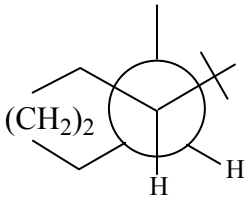
8.

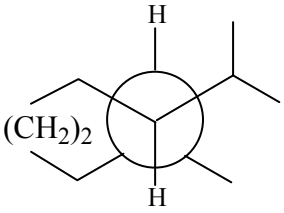
A/



B/

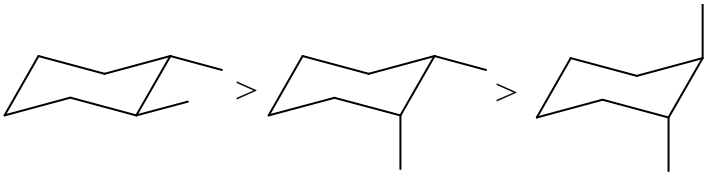




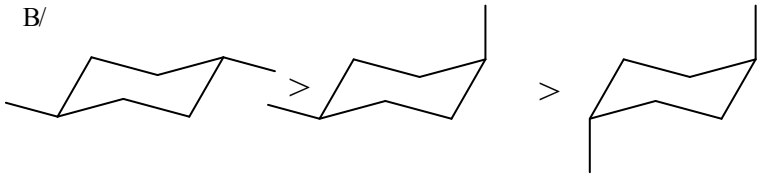


9.

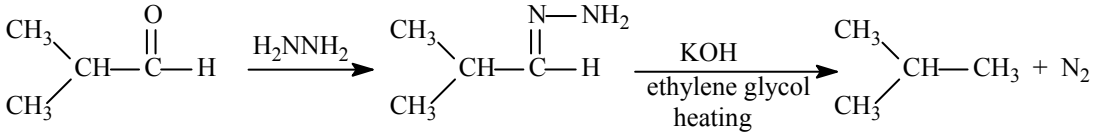
A/

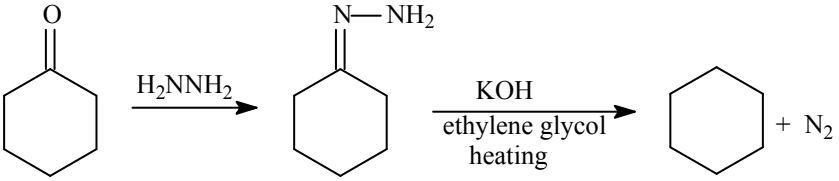


B/

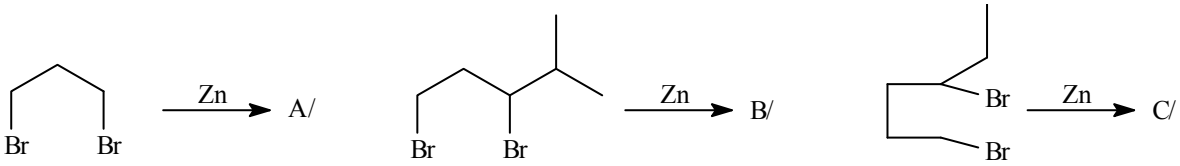


10.

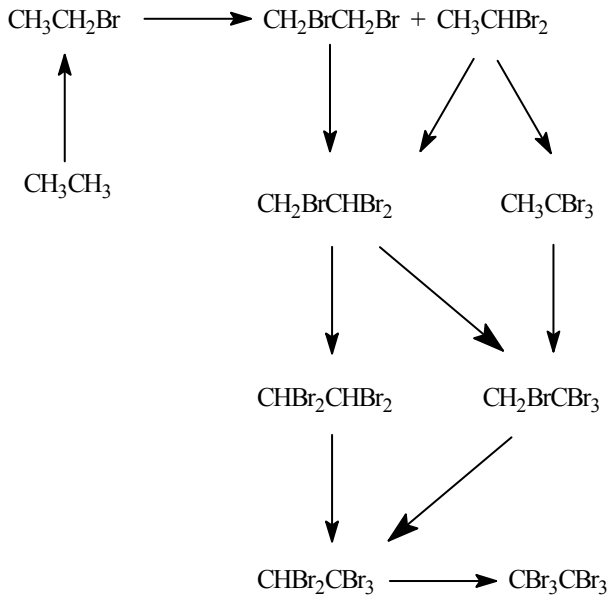
A/ 

B/ 

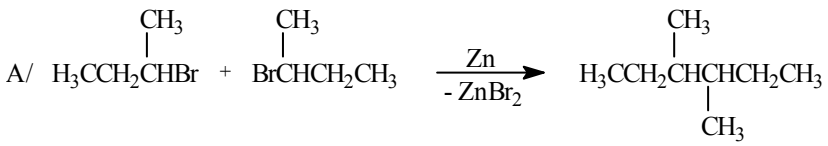
11.

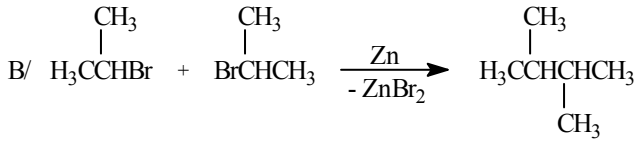


12. It takes place by radical substitution reaction. 9 different products can be formed in the reaction.

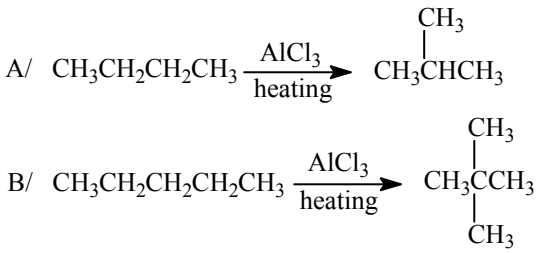


13.

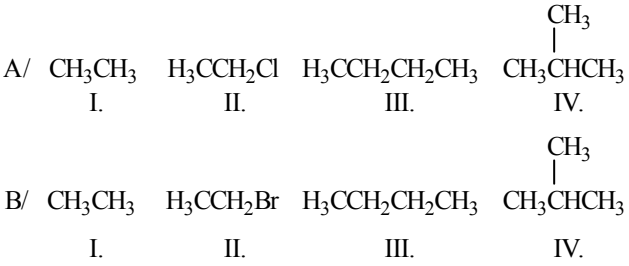




14.


A/ CH3CH2CH2CH3 AlCl3 heating CH3CHCH3
CH3
B/ CH3CH2CH2CH2CH3 AlCl3 heating CH3CCH3
CH3
CH3

15.


A/ CH3CH3 H3CCH2Cl H3CCH2CH2CH3 CH3CHCH3
CH3
I. II. III. IV.
B/ CH3CH3 H3CCH2Br H3CCH2CH2CH3 CH3CHCH3
CH3
I. II. III. IV.

III. Unsaturated hydrocarbones (alkenes, alkynes)

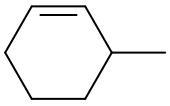
1. Give the names of the following unsaturated hydrocarbone groups:

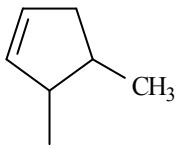
A/ $H_2C{=}CH{-}$

B/ $H_2C{=}CHCH_2{-}$

C/ $H_3CCH{=}CH{-}$

D/ $H_2C{=}C(CH_3){-}$

E/ 

F/ 

G/ $HC{\equiv}CH{-}$

H/ $HC{\equiv}CCH_2{-}$

I/ $H_3CC{\equiv}C{-}$

2. Draw the formulas of the following hydrocarbone groups:
   A/ pent-4-en-1-yn-1-yl B/ pent-1-en-4-yn-1-yl
   C/ isopropenyl D/ 1-methylprop-2-en-1-yl

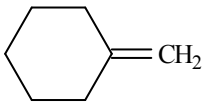
3. Name the following compounds:

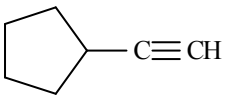
A/ $CH_3CH_2CH_2CH{=}CHCH_3$

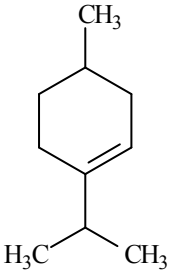
B/ $H_2C{=}CHCH_2C{\equiv}CH$

C/ $CH_3CH_2CH{=}CHCH_2C{\equiv}CCH_3$

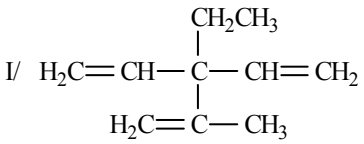
D/ $HC{\equiv}CCH{=}CH{-}CH{=}CH_2$

E/ 

F/ 

G/ 

H/ $CH_3C{\equiv}C{-}CH_2CH(CH_2CH{=}CH_2){-}CH{=}CHCH_2CH_3$

I/ 

J/ $CH_3C{\equiv}CCH(CH_2CH{=}CH_2){-}CH{=}CHCH_3$

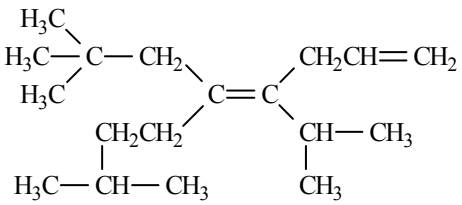
K/ $HC{\equiv}CCH_2CH(CH_2CH{=}CH_2){-}CH{=}CHCH_3$

L/ $HC{\equiv}CCH_2CH_2CH_2CH(CH_2CH{=}CH_2){-}CH{=}CHCH_3$

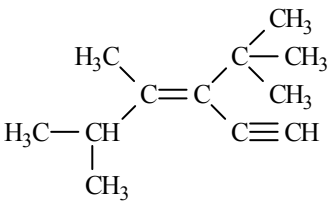
M/ $HC{\equiv}CCH_2CH_2CH_2CH(CH{=}CH_2){-}CH{=}CHCH_3$

4. Name the following compoundset, give the geometric isomerism:

A/

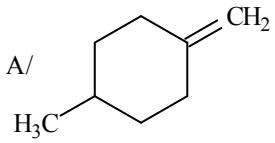


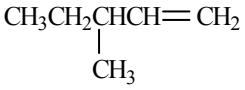
B/

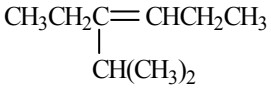


5. Draw structural formulas of the following compounds:
   A/ 3-(3-methylbutyl)-hept-2-en-5-yne
   B/ (*E*)-4-methyl-3-(2-methylpropyl)-hexa-1,3-diene
   C/ *cis* 4,5-dimethylcyclohex-1-ene
   D/ *trans* 4-ethyl-3-methylcyclopent-1-ene

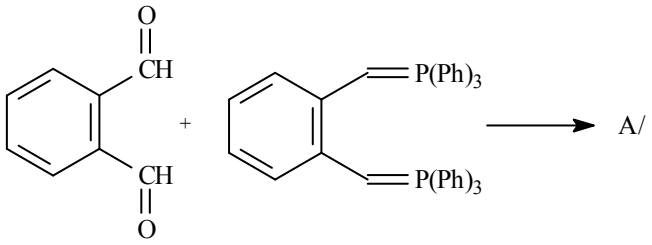
6. Prepare the following compounds by Wittig reaction:

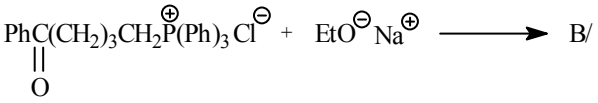
A/ 

B/ 

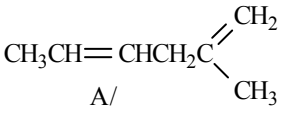
C/ 

7. How do the following pairs of compounds react with each other in Wittig reactions?

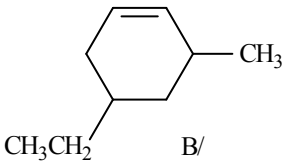




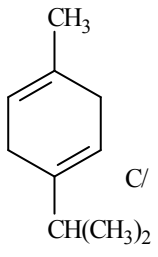
8. What kind of products are formed from the following compounds I/ by reductive ozonolysis II/ oxydative ozonolysis?



A/

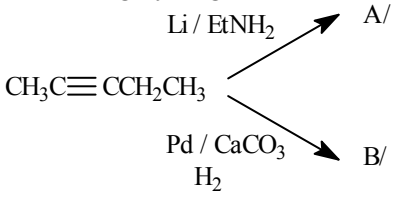


B/

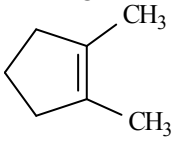


C/

9. What are the main products of the following hydrogenation reactions?

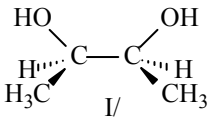


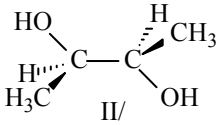
10. How does the following compound react with potassium permanganate
A/ at room temperature B/ by heating?



11. How would you prepare the following three pairs of compounds, from the same starting alkene (pairwise), but by different reaction conditions?

A/ by oxidation:





B/ by addition reaction:

I/ propan-2-ol

II/ propan-1-ol

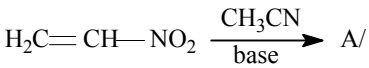
C/ by addition reaction:

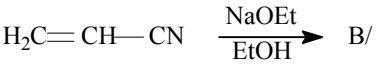
I/ 2-bromobutane

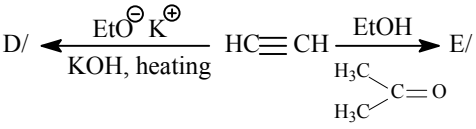
II/ 1-bromobutane

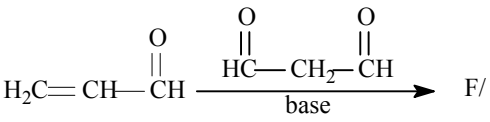
12. How does 3-methylbut-1-ene react in the following reactions?
A/ Br_2 / CCl_4
B/ Br_2 / H_2O
C/ CH_3COOH / mineral acid
D/ HCl
E/ HCN

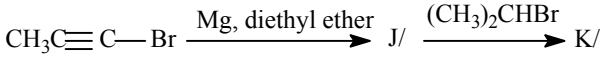
13. What products are formed in the following reactions:

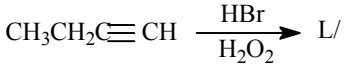










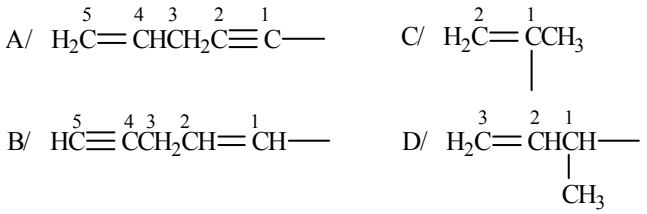


14. A/ Draw the structural formulas of the alkene structural and geometrical isomers with general formulas of C_5H_{10} (with 1 double bond)
B/ Draw the structural formulas of the alkyne structural isomers with general formulas of C_5H_8

III. ANSWERS

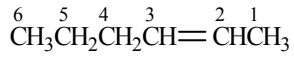
1. A/ ethenyl (vinyl)
   B/ prop-2-en-1-yl (allyl)
   C/ prop-1-en-1-yl
   D/ 1-methylethenyl
   E/ cyclohex-2-en-1-yl
   F/ 5-methylcyclopent-2-en-1-yl
   G/ ethynyl
   H/ prop-2-yn-1-yl (propargyl)
   I/ prop-1-yn-1-yl (propynyl)

2.

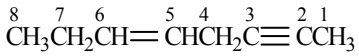


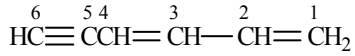
(2C/ and 1/D are identical groups)

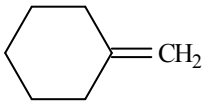
3. A/ hex-2-ene
   B/ pent-1-en-4-yne
   C/ oct-5-en-2-yne
   D/ hexa-1,3-dien-5-yne
   E/ methylenecyclohexane
   F/ ethynylcyclopentane
   G/ 1-isopropyl-4-methylcyclohex-1-ene
   H/ 5-(but-2-yn-1-yl)-nona-1,6-diene
   I/ 3-ethyl-2-methyl-3-vinylpenta-1,4-diene
   J/ 4-(prop-1-yn-1-yl)-hepta-1,5-diene
   K/ 4-(prop-2-yn-1-yl)-hepta-1,5-diene
   L/ 6-(prop-2-en-1-yl)-non-7-en-1-yne
   M/ 6-vinylnon-7-en-1-yne

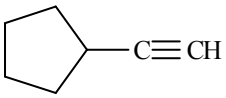
A/ 

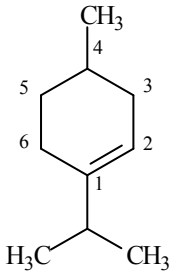
B/ 

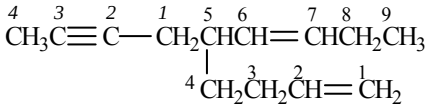
C/ 

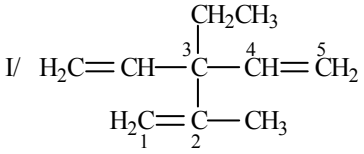
D/ 

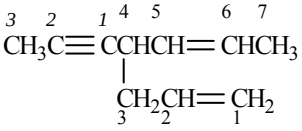
E/ 

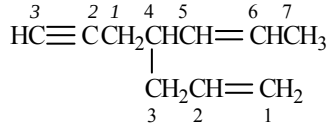
F/ 

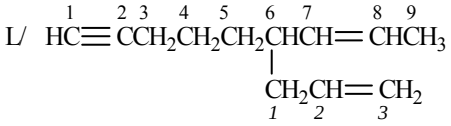
G/ 

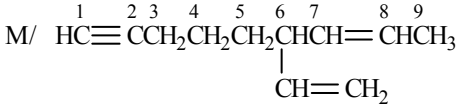
H/ 

I/ 

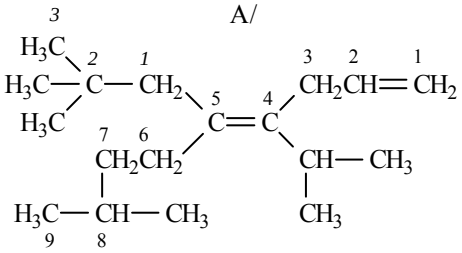
J/ 

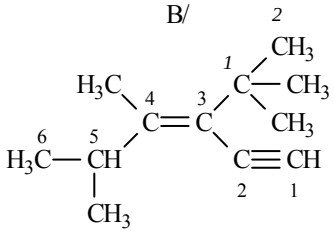
K/ 

L/ 

M/ 

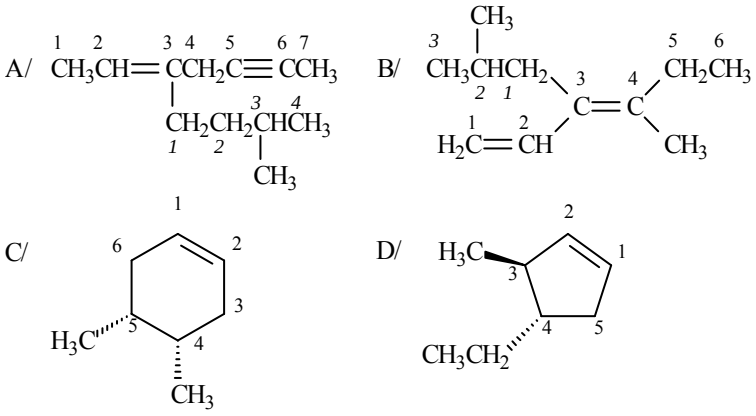
4.

A/ 

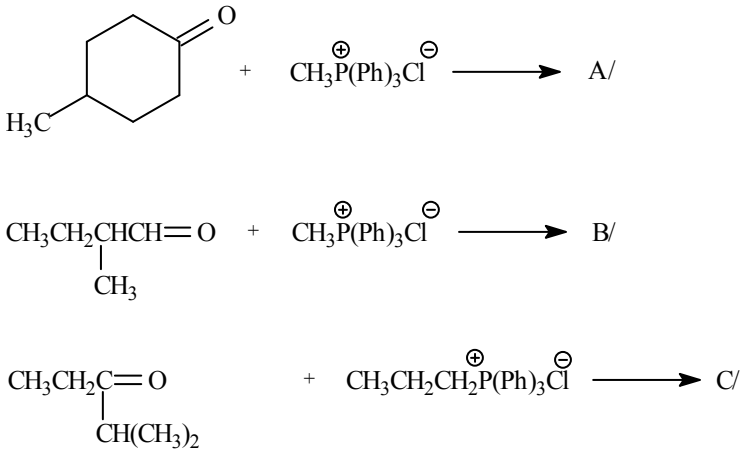
B/ 

A/ (*E*)-5-(2,2-dimethylpropyl)-4-isopropyl-8-methylnona-1,4-diene
B/ (*Z*)-3-(1,1-dimethylethyl)-4,5-dimethylhex-3-en-1-yne

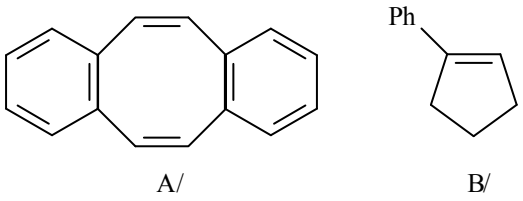
5.



6. These are the precursors of Wittig reaction:

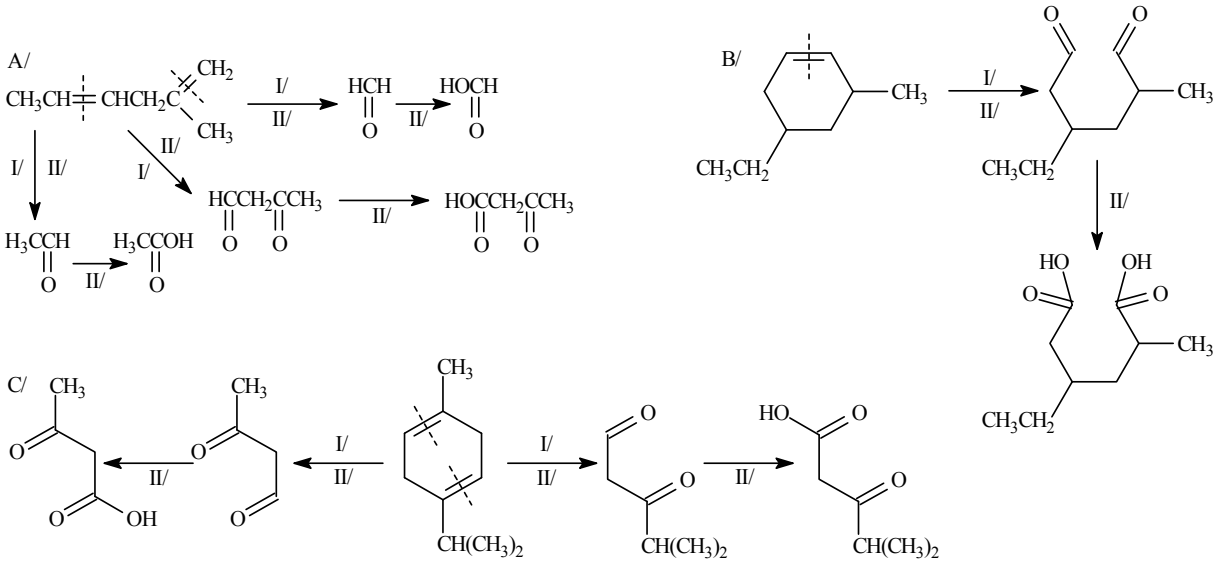


7.

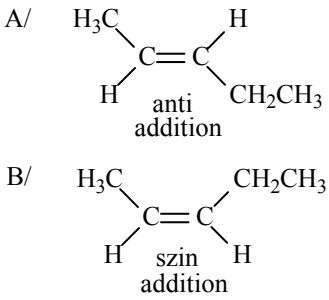


A/ intermolecular Wittig reaction
B/ intramolecular Wittig reaction

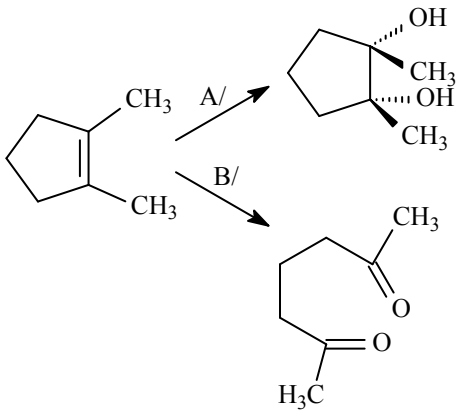
8.



9.



10.



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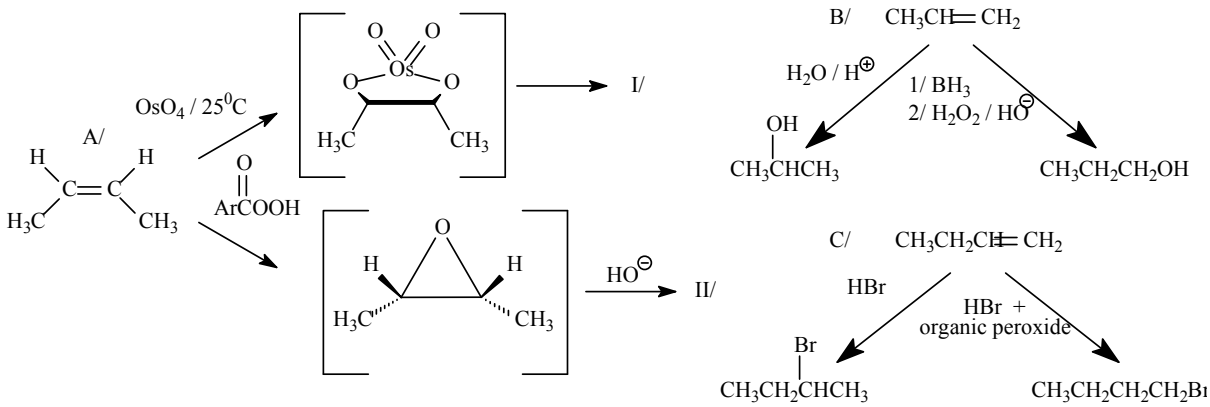

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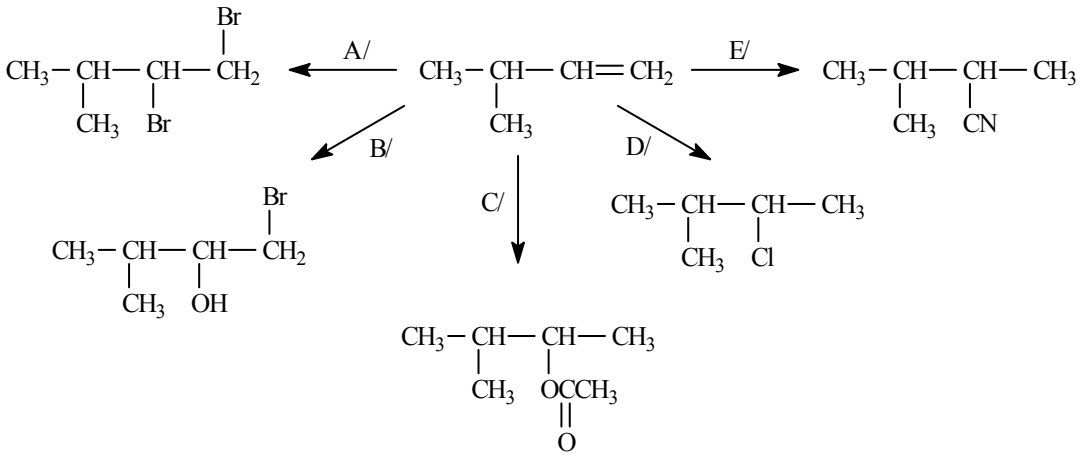


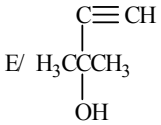
13.

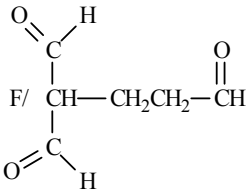
A/ $NC-CH_2CH_2CH_2NO_2$

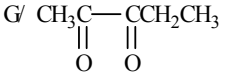
B/ $EtO-CH_2CH_2-CN$

C/ $(CH_3)_2N-CH=CH-COOEt$

D/ $H_2C=CH-OEt$







H/ CH_3COOH I/ CH_3CH_2COOH

J/ $CH_3C\equiv C-Mg$

K/ $CH_3C\equiv C-CH(CH_3)_2$

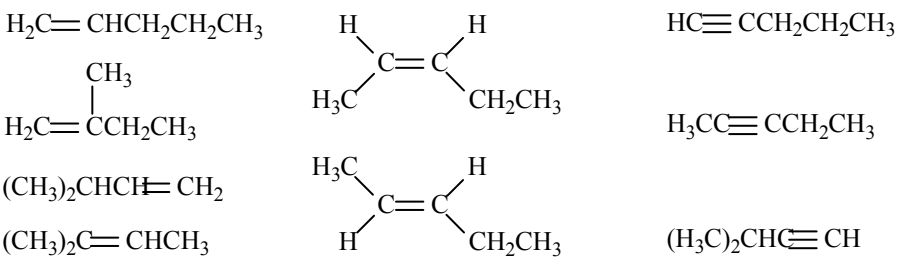
L/ $CH_3CH_2CH=CHBr$

(A/ - F/: nucleophilic addition reactions)

14.

A/ $H_3CCH{=}CHCH_2CH_3$ B/

geometric isomers:



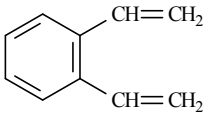
A/ C_5H_{10}: there are 5 structural isomers, one of them exists as *1 pair* of geometriai isomers (only the latter pair is possible).

Conditions of geometrical isomerism: there can not be two of the same substituents attached to carbons of C=C bond *(like 2 hydrogenes, 2 methyl groups, etc.),* but there can be identical substituents attached to different carbons of C=C bond.

B/ C_5H_8: there are 3 structural isomers

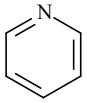
IV. Aromatic hydrocarbones (monocycles and condensed derivatives)

1. Choose 1/ aromatics
2/ antiaromatics
3/ non-aromatics
among the following compounds. Explain your decision.

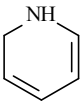


A/


B/

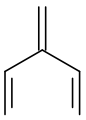


C/



D/


E/


F/

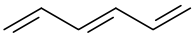

G/


H/

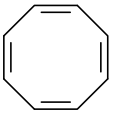

I/


J/

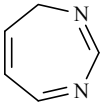

K/


L/

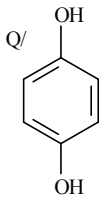

M/


N/

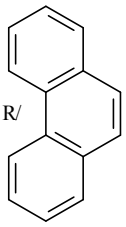

O/



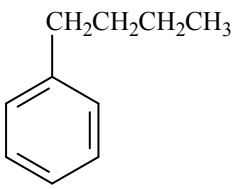
P/



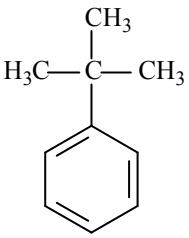
Q/


R/

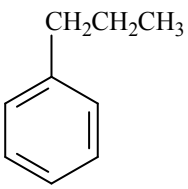
2. Prepare the following aromatic hydrocarbons from benzene, using selective methods:



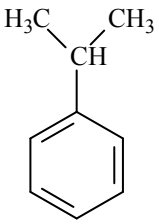
A/



B/

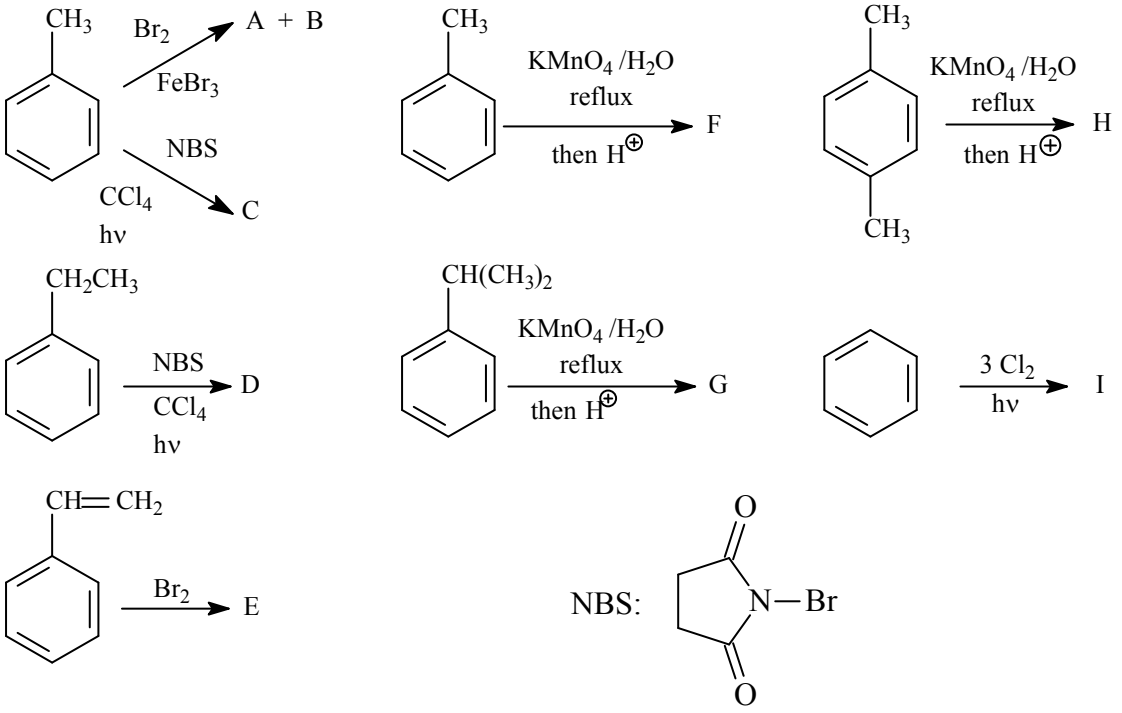


C/

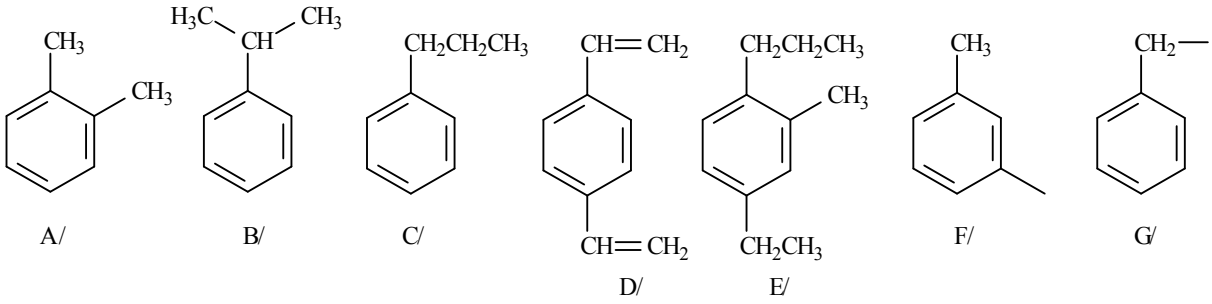


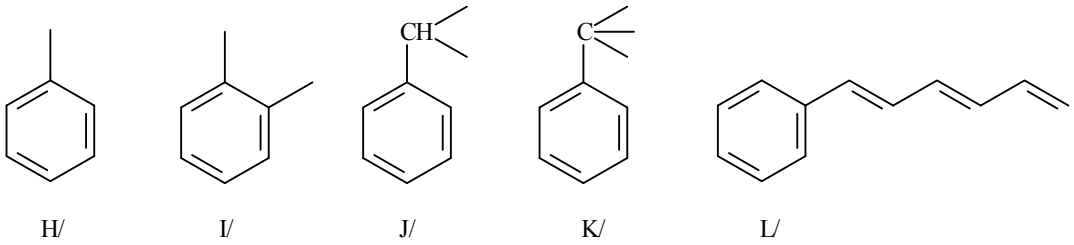
D/

3. What are the products of the following reactions:



4. Give names of the following aromatic hydrocarbones, or hydrocarbone groups:

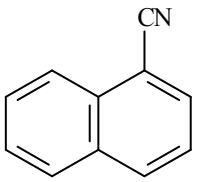




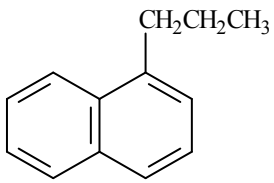
5. How does naphthalene react in the following reactions?

A/ V_2O_5 / heating in air
B/ Br_2
C/ HNO_3 / H_2SO_4, heating
D/ cc. H_2SO_4, 80^OC
E/ cc. H_2SO_4, 160^OC
F/ CH_3COCl, $AlCl_3$, CS_2, -15^OC
G/ CH_3COCl, $AlCl_3$, nitrobenzene, 40^OC
H/ Na / NH_3, EtOH
I/ H_2 / Ni
J/ CrO_3 / CH_3COOH

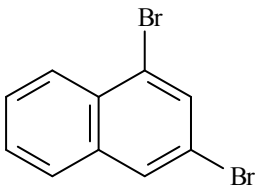
6. Prepare the following compounds from naphthalene:



A/



B/



C/

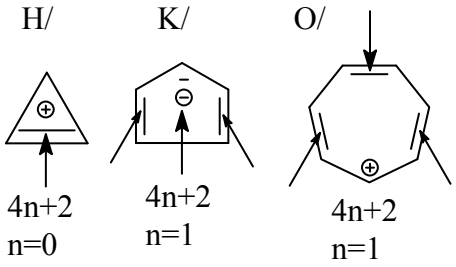
7. List the ^{1}H NMR spectroscopic characteristics of A/ Aromatic compounds
B/ antiaromatic compounds

IV. ANSWERS

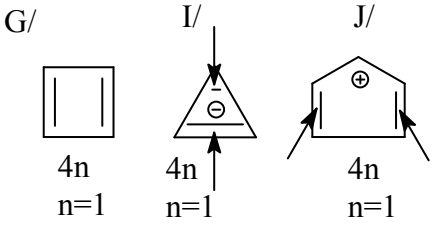
1. *Classification:*
1/ Aromatic compounds: A/, C/, H/, K/, O/, Q/, R/.
2/ Antiaromatic compounds: G/, I/, J/
3/ Nonaromatic compounds: B/, D/, E/, F/, L/, M/, N/, P/.

Proves (taking into consideration definitions of the aromatic, and antiaromatic systems):

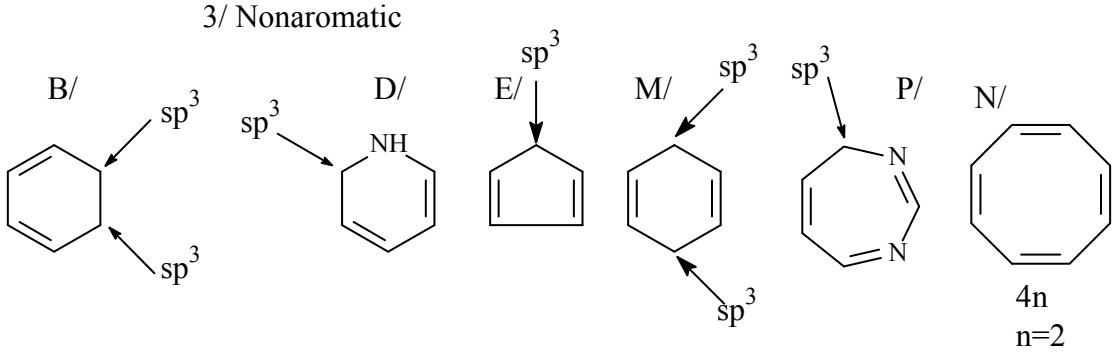
1/ Aromatic



2/ Antiaromatic



3/ Nonaromatic

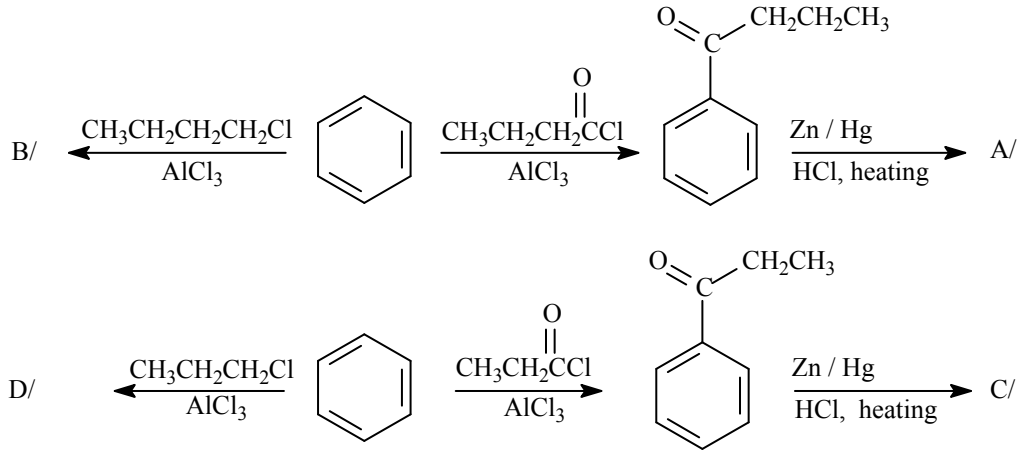


1/ <u>Aromatic</u>: A/ 1,4-divinylbenzene (a *benzene* derivative)
C/ hetero*aromatic* compound
Q/ 1,4-hydroquinone (a *benzene* derivative)
R/ (4n+2) π-electrons (n=3)

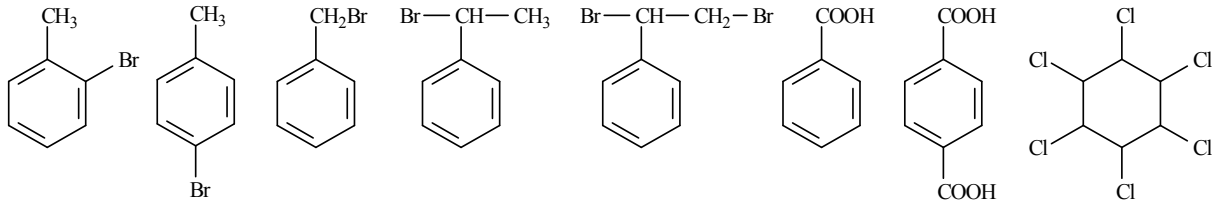
2/ <u>Antiaromatic</u>: G/ (4n) π-electrons (n=1)

3/ <u>Nonaromatic</u>: B/, D/, E/, P/ are cyclic compounds, but with *linear delocalisation*
F/ each atom is with sp^2 hybridisation, but with *branched delocalisation*
L/ *linear delocalised* system
M/ diolefine with isolated double bonds (cyclic compound, but with isolated double bonds)
N/ (4n) π-electrons (n=2), but the ring is not coplanar (the ring carbons are twitched)

2.



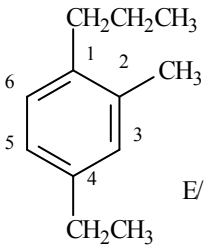
3.



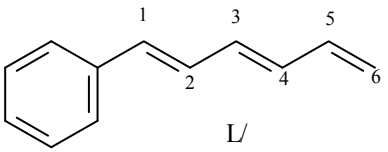
A/ B/ C/ D/ E/ F/ és G/ H/ I/

4.

A/ 1,2-dimethylbenzene [*o*-xylene]
B/ isopropylbenzene [cumene]
C/ propylbenzene [isocumene]
D/ 1,4-divinylbenzene
E/ 4-ethyl-2-methyl-1-propylbenzene
F/ *m*-tolyl
G/ benzyl
H/ phenyl
I/ *o*-phenylene
J/ benzylidene (benzal)
K/ benzylidyne (benzotri)
L/ hexa-1,3,5-trien-1-ylbenzene

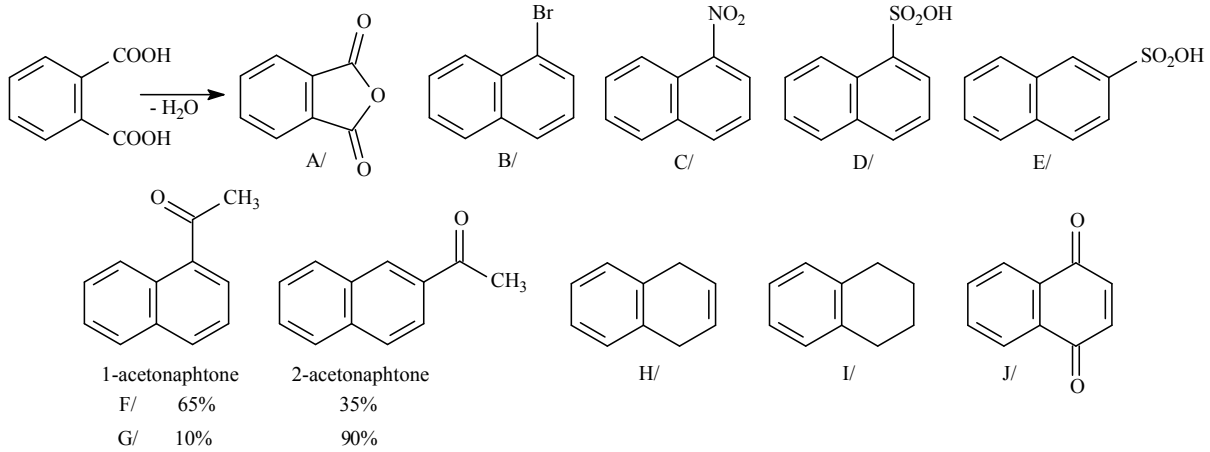


E/

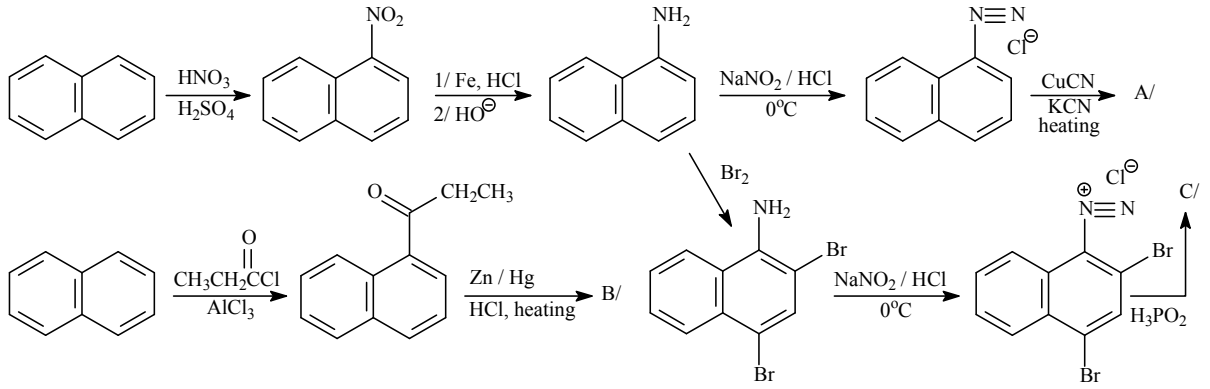


L/

5.



6.

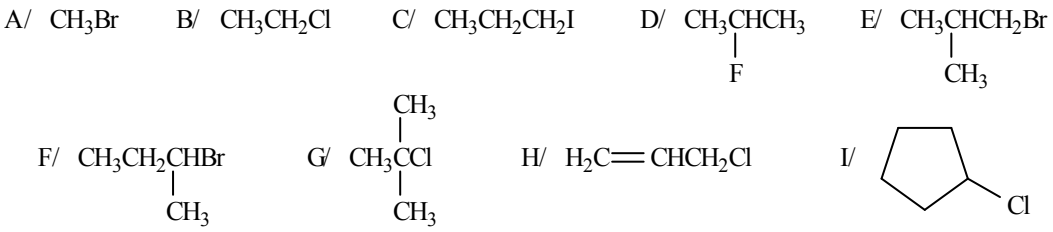


7.

	Aromatic compounds	**Antiaromatic** compounds
out-of-cycle	paramagnetic shift	diamagnetic shift
within-cycle	diamagnetic shift	paramagnetic shift

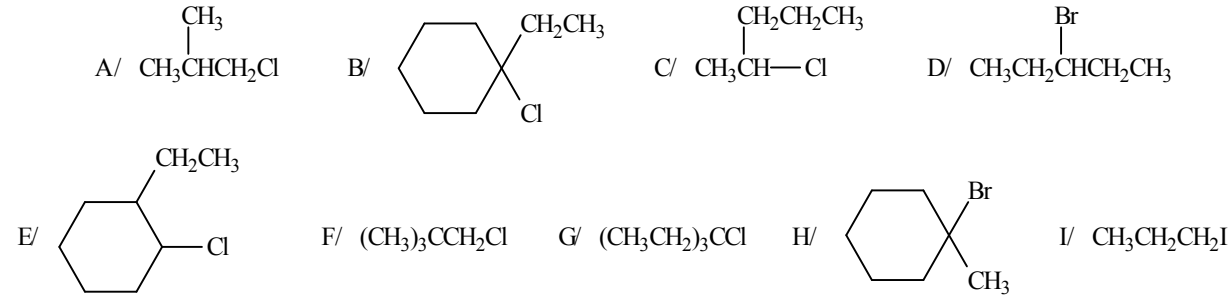
V. Aliphatic halogene compounds

1. Name the following compounds according to substitution as well as radicofunctional nomenclature:

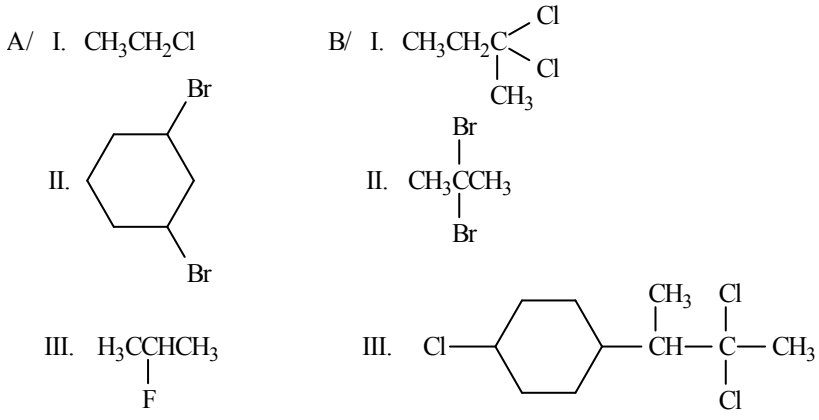


2. Draw the structural formulas of the following groups and compounds:
A/ chloromethyl B/ 2-chlorobutyl C/ 3-chlorobutyl D/ 3-chloro-2-methylbutyl
E/ iodomethylcyclohexane F/ benzyl iodide (Aromatic) G/ 1-bromo-1-methylcyclopentane H/ bromomethylcyclopentane I/ 1,3-dibromobutane

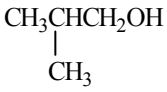
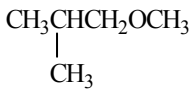
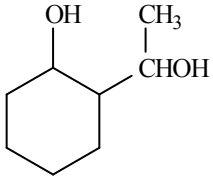
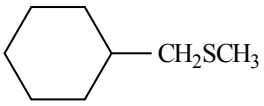
3. Classify the following alkyl halogenides according to their order:

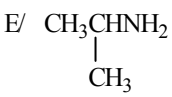
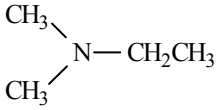
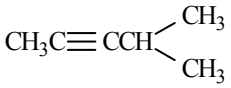
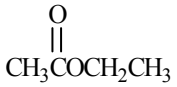


4. Prepare the following halogene compounds, starting A/ from the appropriate alcohol;
B/ from the appropriate – and substituted, if it is necessary - carbonyl compound.



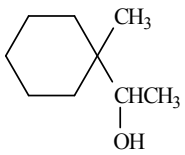
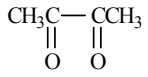
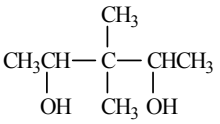
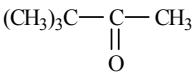
5. Prepare the following compounds, starting from alkyl halogenides:

A/  B/  C/  D/ 

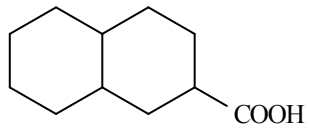
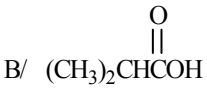
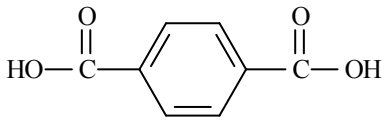
E/  F/  G/  H/ 

6. How does propyl iodide react with the following reagents?
A/ Ph_3P [triphenyl-phosphine] B/ NaN_3 C/ KCN D/ AgCN E/ $NaNO_2$
F/ $AgNO_2$ G/ NaH H/ $H_2C(COH)_2$ [propanedial] / $NaOCH_2CH_3$

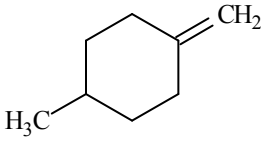
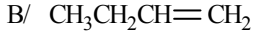
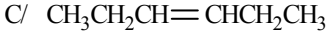
7. Prepare iodoform from the following compounds. Draw the intermediates, as well.

A/  B/  C/  D/  E/ 

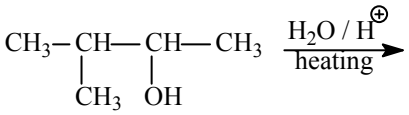
8. Which methyl ketones can be the starting material in order to prepare the following carboxylic acids by haloform reaction?

A/  B/  C/ 

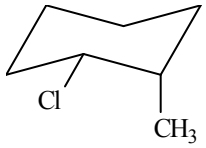
9. Prepare the following compoundset from such a starting material *elimination* reaction, resulting in mainly the desired alkenes:

A/  B/  C/ 

10. What alkene will be the main product in the following *elimination* reaction?

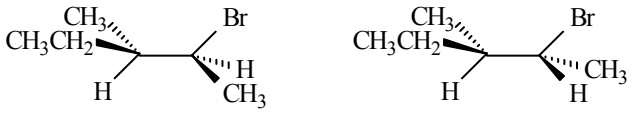


11. What kind of *alkene* product is formed from the given compound by E2 dehydrohalogenation (-HCl) reaction? What is the steric condition of the reaction?



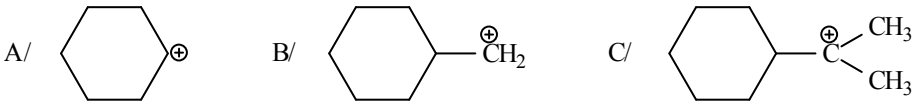
12. What is prepared from the following compounds with basic E2 elimination, or by S_N2 substitution reactions?

A/ B/

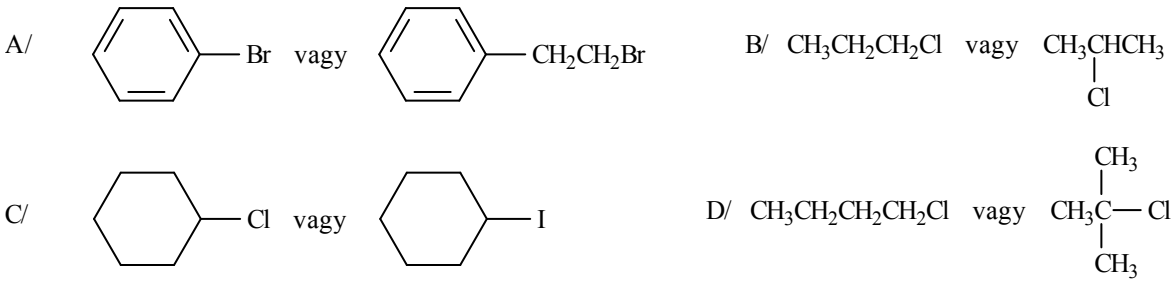


13. Draw the structural formulas of Hofmann, or Zaitsev products from the following compounds in E2 reactions:
A/ 3-bromo-2-methylpentane
B/ 1-chloro-1-methylcyclohexane.

14. Arrange the following carbocations into increasing stability order:



Which react faster from the following pairs of compounds by nucleophilic reagent in S_N2 reaction? Explain your answer.

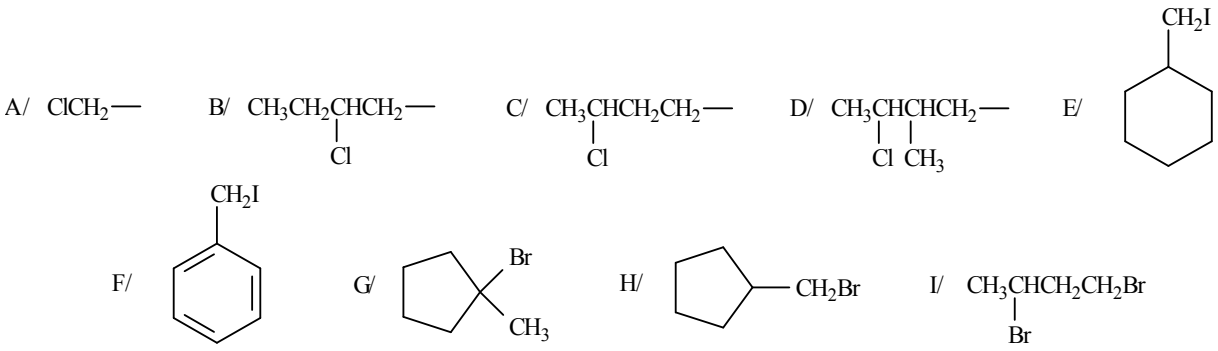


V. ANSWERS

1.

	Substitution name	*Radicofunctional* name
A/	bromomethane	methyl bromide
B/	chloroethane	ethyl chloride
C/	1-iodopropane	propyl iodide
D/	2-fluoropropane	isopropyl fluoride
E/	1-bromo-2-methylpropane	isobutyl bromide
F/	2-bromobutane	*sec*-butyl bromide
G/	2-chloro-2-methylpropane	*tert*-butyl chloride
H/	3-chloroprop-1-ene	allyl chloride
I/	chlorocyclopentane	cyclopentyl chloride

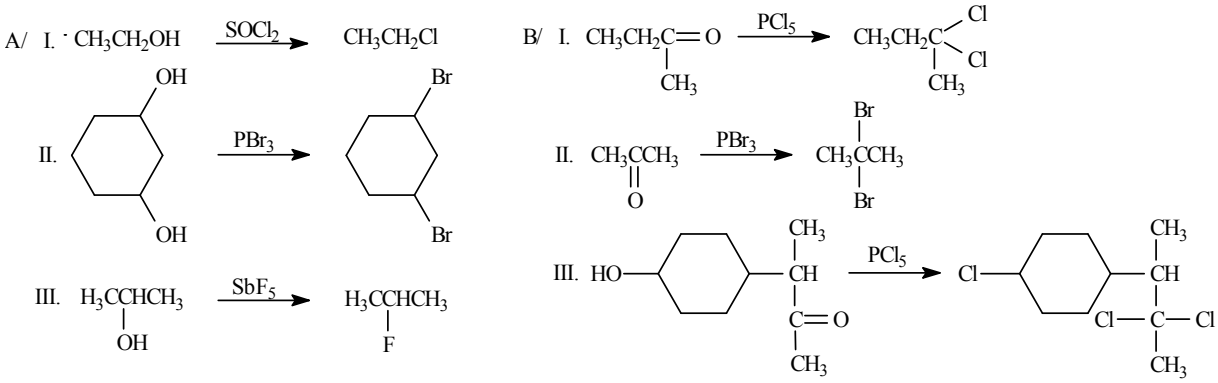
2.



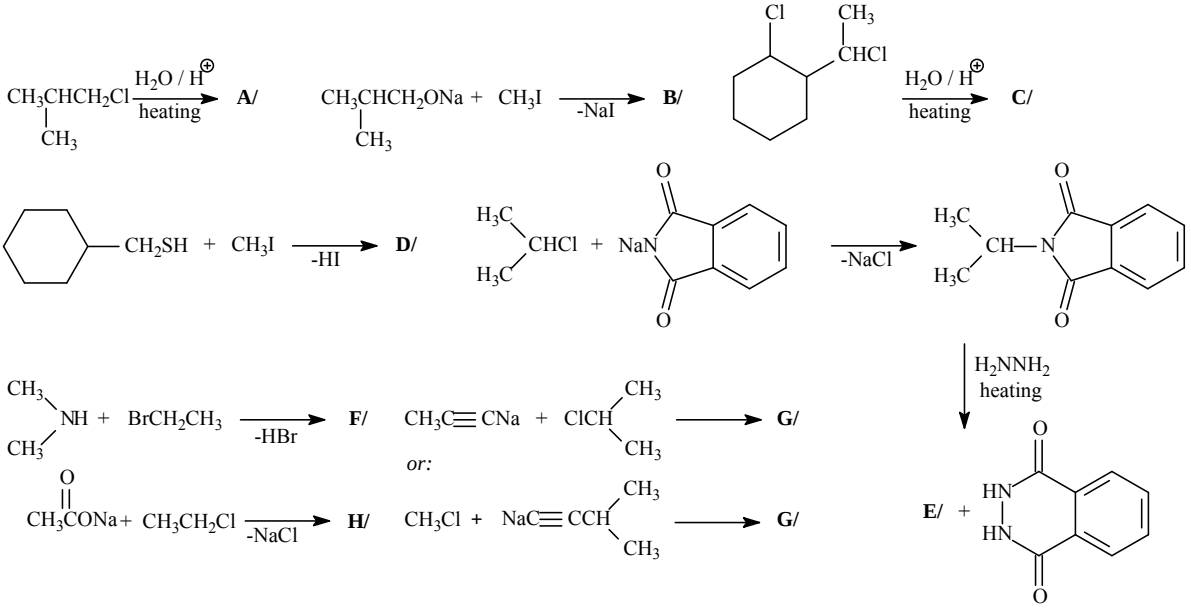
3.

1^0	2^0	3^0
A, F, I	C, D, E	B, G, H

4.



5.

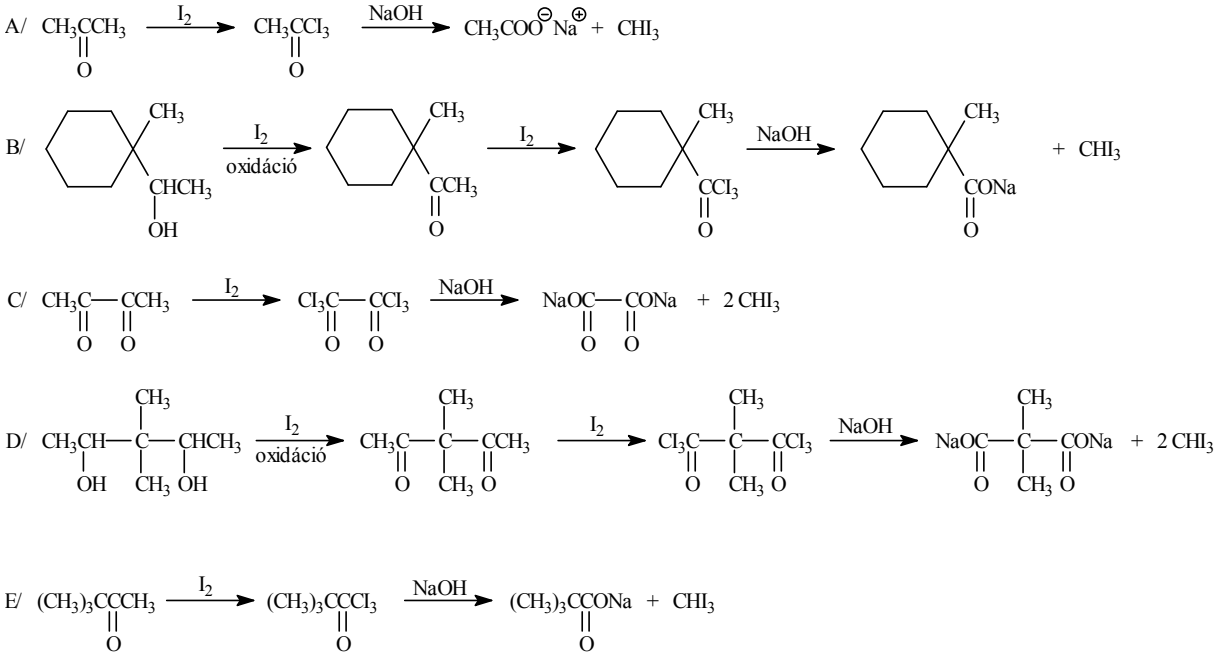


6.

A/ $CH_3CH_2CH_2\overset{\oplus}{P}(Ph)_3\ \overset{\ominus}{I}$ B/ $CH_3CH_2CH_2N_3$ C/ $CH_3CH_2CH_2CN$ D/ $CH_3CH_2CH_2NC$

E/ $CH_3CH_2CH_2NO_2$ F/ $CH_3CH_2CH_2ONO$ G/ $CH_3CH_2CH_3$ H/ $CH_3CH_2CH_2CH(COH)_2$

7.



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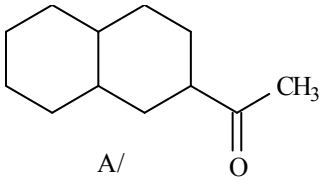
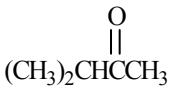
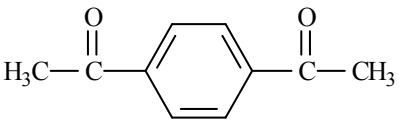


A/

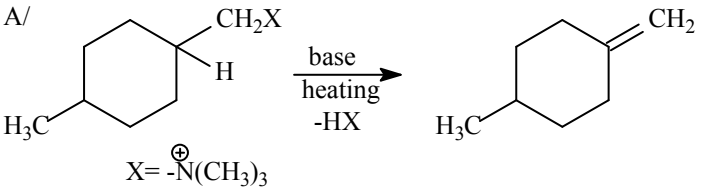


B/

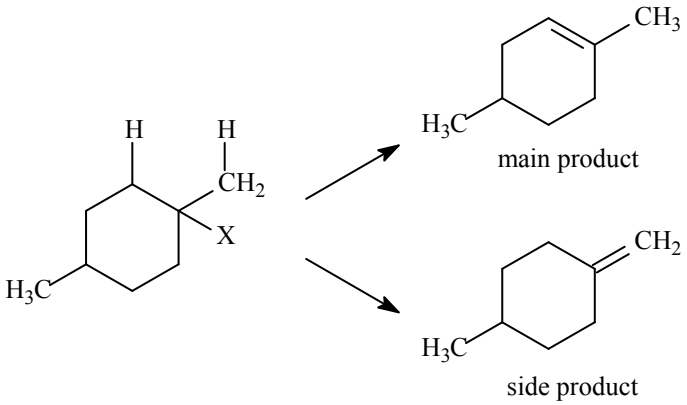


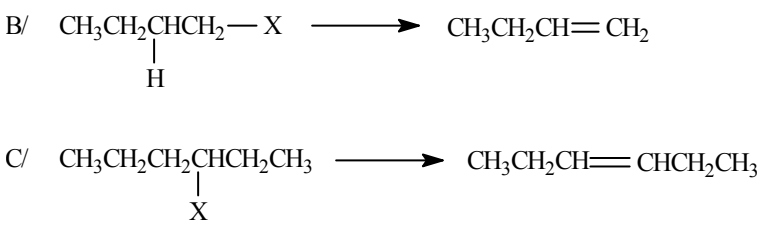
C/

9.

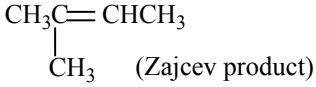


The functional group must be located to the side chain, otherwise two propducts are formed in comparable ratio:



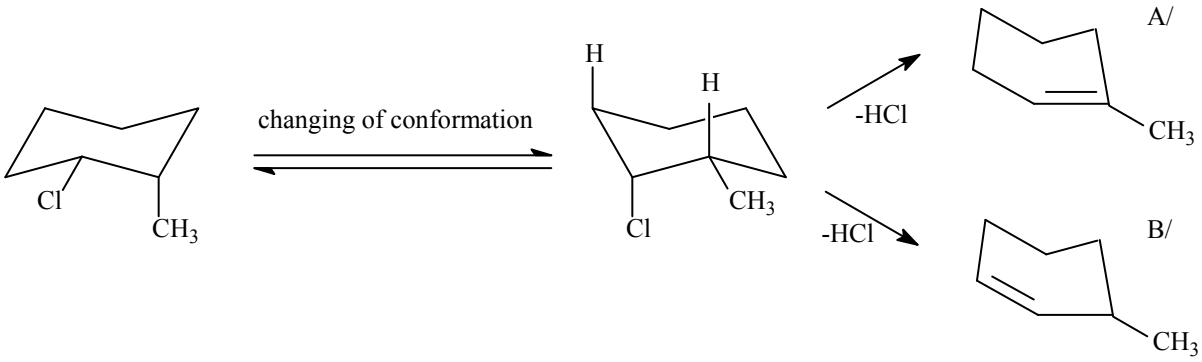


10.



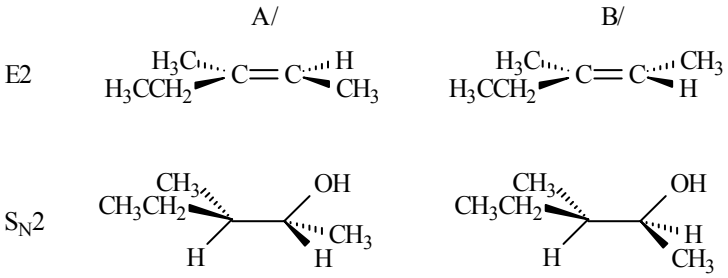
(Zajcev product)

11.

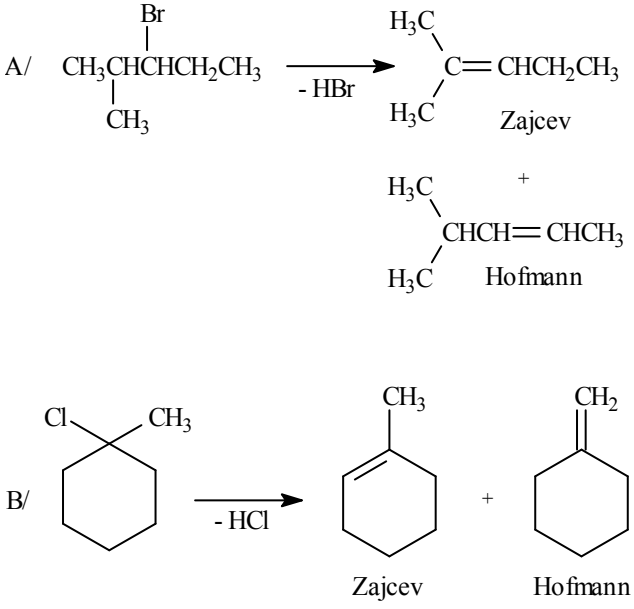


A/ the main product (the alkene bond is substituted with more alkyl groups)
B/ the side product (the alkene bond is substituted with less alkyl groups)
Steric condition of the reaction: the leaving groups (H, Cl) must be in *antiperiplanar* position.

12.



13.



14. B/ < A/ < C/

15. A/ 1-Bromo-2-phenylethane reacts more quickly, since bromobenzene (it is an aryl halogenide) does not react in S_N2 reaction.

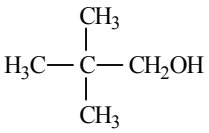
B/ Propyl chloride reacts more quickly, since it is a primary alkyl halogenide, therefore its transition state is less hindranced.

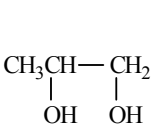
C/ Iodocyclohexane reacts more quickly, since iodine is a better leaving group, than chlorine, because iodine is more polarisable.

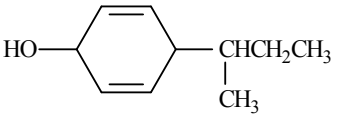
D/ Butyl chloride reacts more quickly with nucleophiles, since it is a primary alkyl halogenide, therefore its transition state is less hindranced. Tertiary alkyl halogenides do not react in S_N2 reactions.

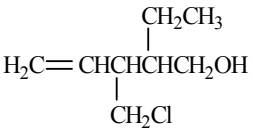
VI. Alcohols, phenols, ethers

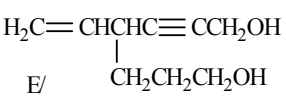
1. Name the following compounds:

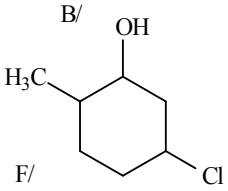

A/

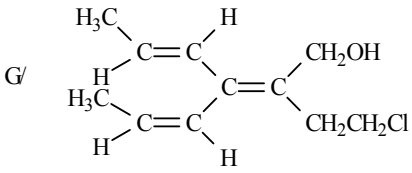

B/

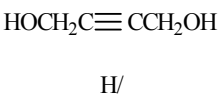

C/


D/


E/

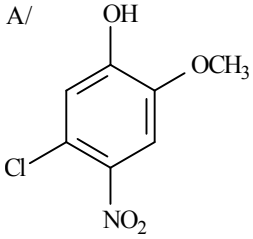

F/

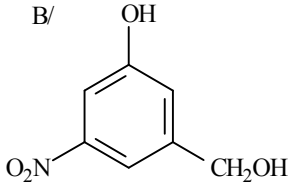

G/


H/

2. Draw structural formulas of the following compounds:
   A/ 2-methylbutane-2-ol
   B/ cyclohex-2-en-1-ol
   C/ *trans* 4-ethylcyclohexane-1-ol
   D/ 4-cyclohexylhepta-1,6-diene-4-ol
   E/ 2-hydroxymethylheptane-1,6-diol
   F/ cyclopentanemethanol
   G/ 6-bromo-4-chloromethylhexa-2,5-diyn-1-ol

3. Name the following compounds:


A/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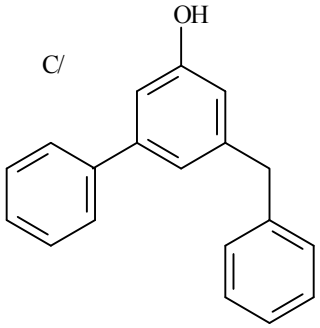
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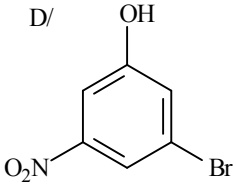
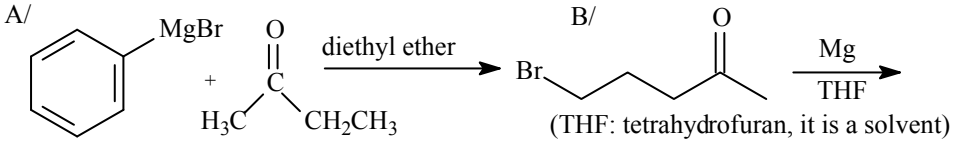

D/

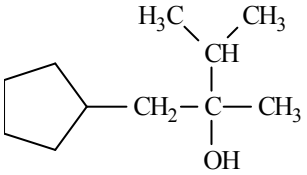
4. Draw structural formulas of the following compounds:
   A/ pyrocatechol
   B/ resorcinol
   C/ hydroquinone
   D/ *p*-benzoquinone
   E/ *m*-cresol
   F/ hydroxy-hydroquinone
   G/ diisopropyl ether
   H/ phenyl-methyl-ether

5. Which starting materials the following alcohols can be prepared from by Grignard reaction?
   A/ *n*-butanol
   B/ *sec*-butanol
   C/ *tert*-butanol

6. How do the following pairs of compounds react at the condition of Grignard reaction?



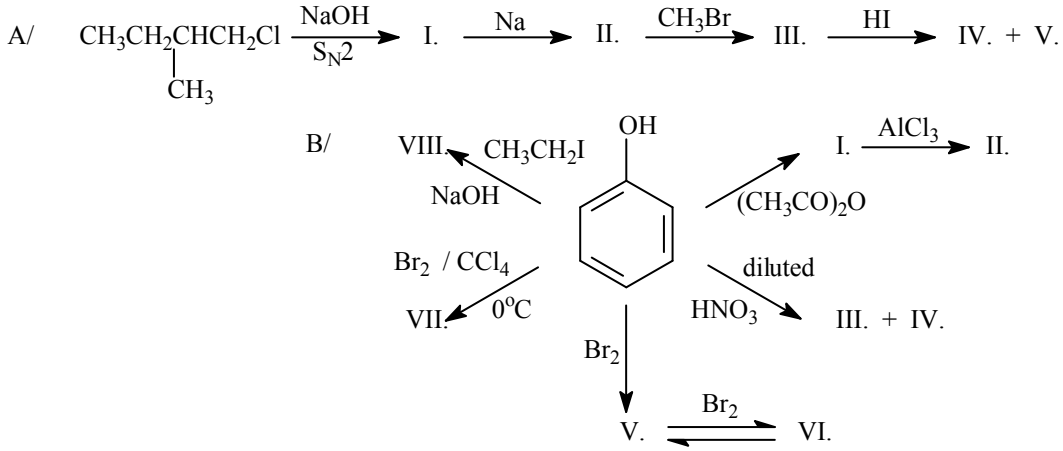
7. Desribe the three alternatives for the preparation of the following compound by Grignard reaction:



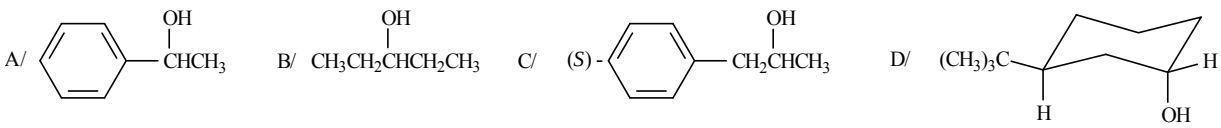
8. Prepare:

A/ isopropyl alcohol from *n*-propanol
B/ isopropyl alcohol from acetone
C/ phenol from the appropriate arylsulfonic acid
D/ 2-naphthol from an aromatic amine

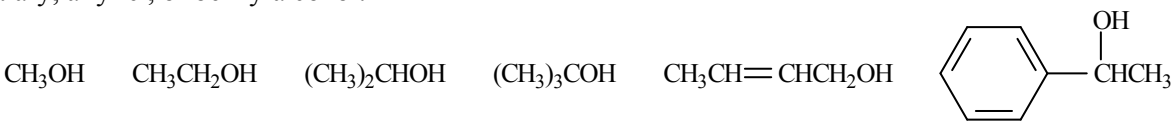
9. Draw the missing products of the following reactions!



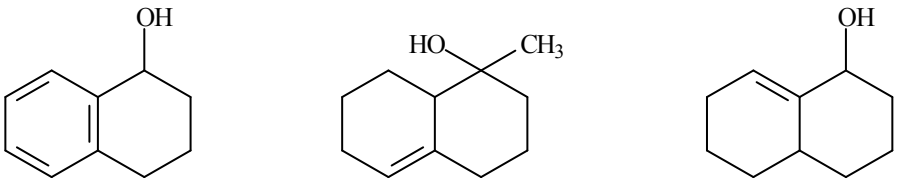
10. What kind of alkyl halides are needed for the preparation of the following alcohols by S_N2 reaction?



11. Classify the following alcohols according to the following terms: methyl, primary, secondary, tertiary, allylic , or benzylalcohol:



A/ B/ C/ D/ E/ F/



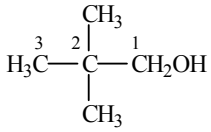
G/ H/ I/

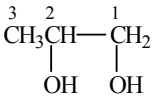
12. I/ Prepare
A/ salicylic acid
B/ salicylic aldehyde
C/ phenyl propionate
D/ salicylic alcohol
E/ 2-(dimethyl-aminomethyl)-phenol
from phenol.

II/ Prepare ethanol from methanol by method of increasing length of carbon chain, utilising 2 molecules of methanol to get 1 molecule of ethanol.

VI. ANSWERS

1. A/ 2,2-dimethylpropane-1-ol
   B/ propane-1,2-diol
   C/ 4-*sec*-butylcyclohexa-2,4-dien-1-ol
   D/ 2-ethyl-3-chloromethylpent-4-en-1-ol
   E/ 4-vinylhept-2-yn-1,7-diol
   F/ 5-chloro-2-methylcyclohexane-1-ol
   G/ (2*E*, 4*Z*)-2-(2-chloroethyl)-3-[(*E*)-prop-1-en-1-yl]-hexa-2,4-diene-1-ol
   H/ but-2-yn-1,4-diol


A/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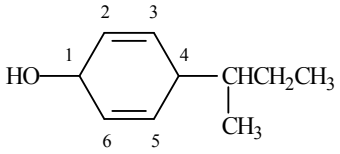
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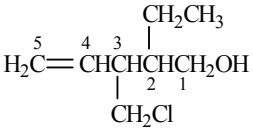
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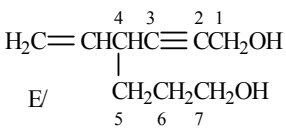
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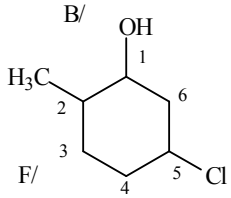
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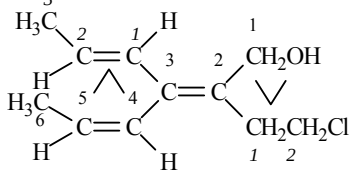
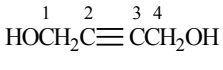
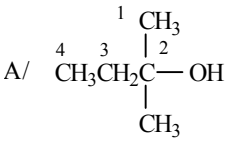
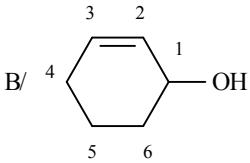
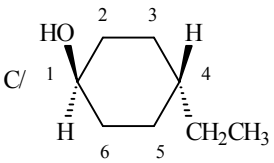

G/

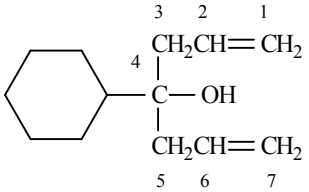

H/

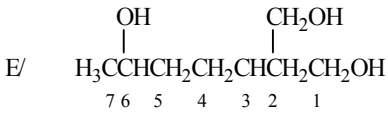
2.


A/


B/


C/


D/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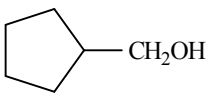
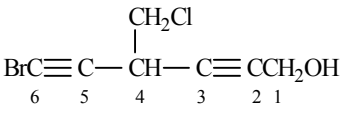
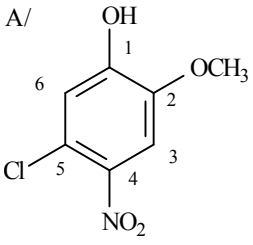
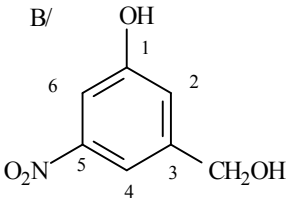

F/


G/

3. A/ 5-chloro-2-methoxy-4-nitrophenol
   B/ 3-hydroxymethyl-5-nitrophenol
   C/ 3-benzyl-5-phenylphenol
   D/ 3-bromo-5-nitrophenol


A/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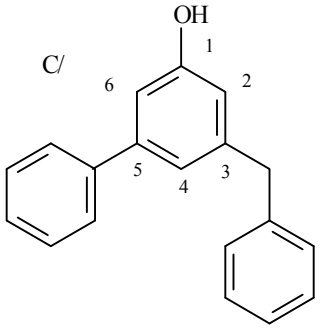
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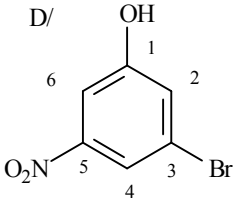
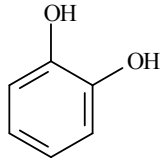
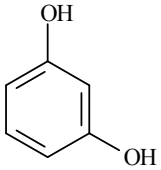

D/

4.


A/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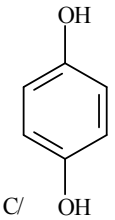
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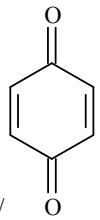
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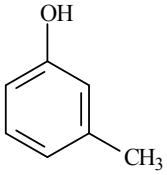
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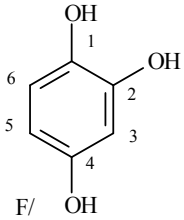
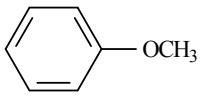

F/

G/ $CH_3CHOCHCH_3$ (CH_3, CH_3)

H/ 

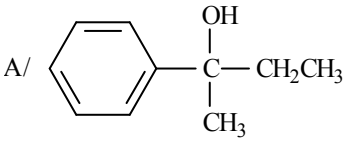
5.

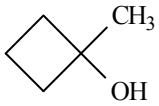
A/ $CH_3CH_2CH_2Br + HCHO$

B/ $CH_3CH_2Br + CH_3COCH_3$ vagy: $CH_3CH_2CHO + CH_3Br$

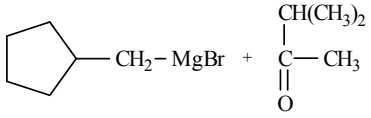
C/ $CH_3Br + (CH_3)_2CO$

6.


A/


B/

7.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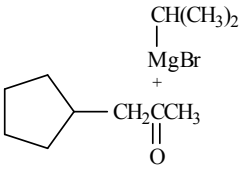
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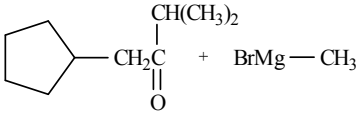
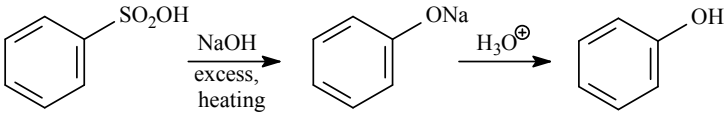
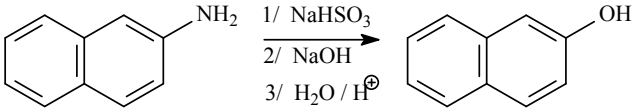

C/

8.

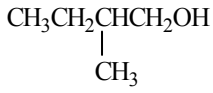
A/ $CH_3CH_2CH_2OH \xrightarrow[180^oC]{H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3CH(OH)CH_3$

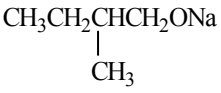
B/ $CH_3COCH_3 \xrightarrow[2/\ H_3O^{\oplus}]{1/\ NaBH_4} CH_3CH(OH)CH_3$

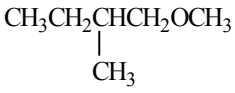
C/ 

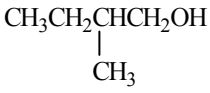
D/ 

9.

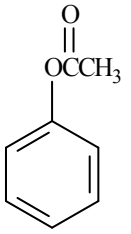
A/  I.

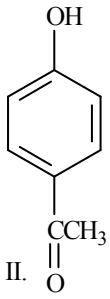
 II.

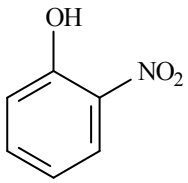
 III.

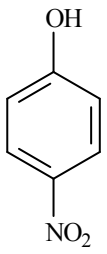
 IV.

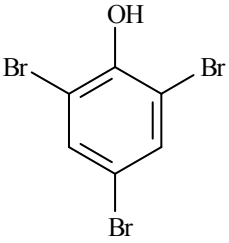
 V.

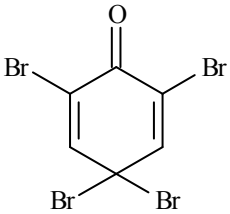
B/  I.

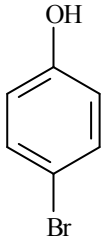
 II.

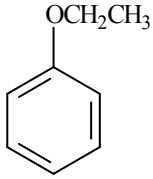
 III.

 IV.

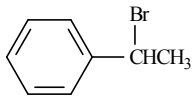
 V.

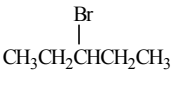
 VI.

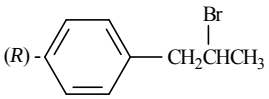
 VII.

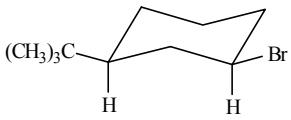
 VIII.

10.

A/ 

B/ 

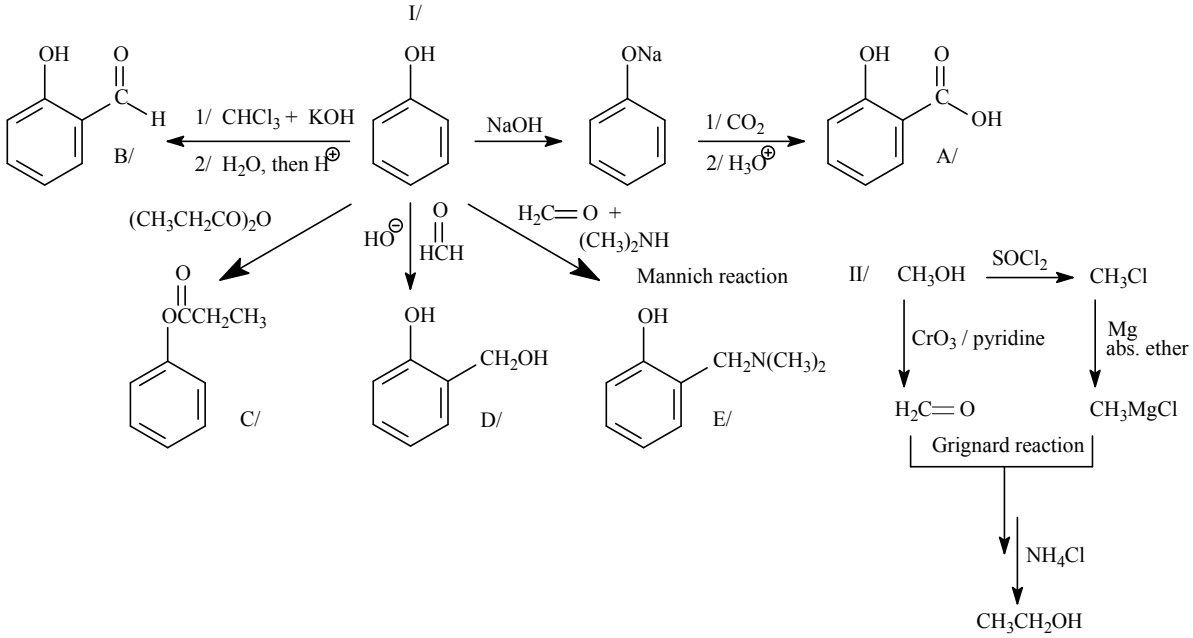
C/ 

D/ 

11.

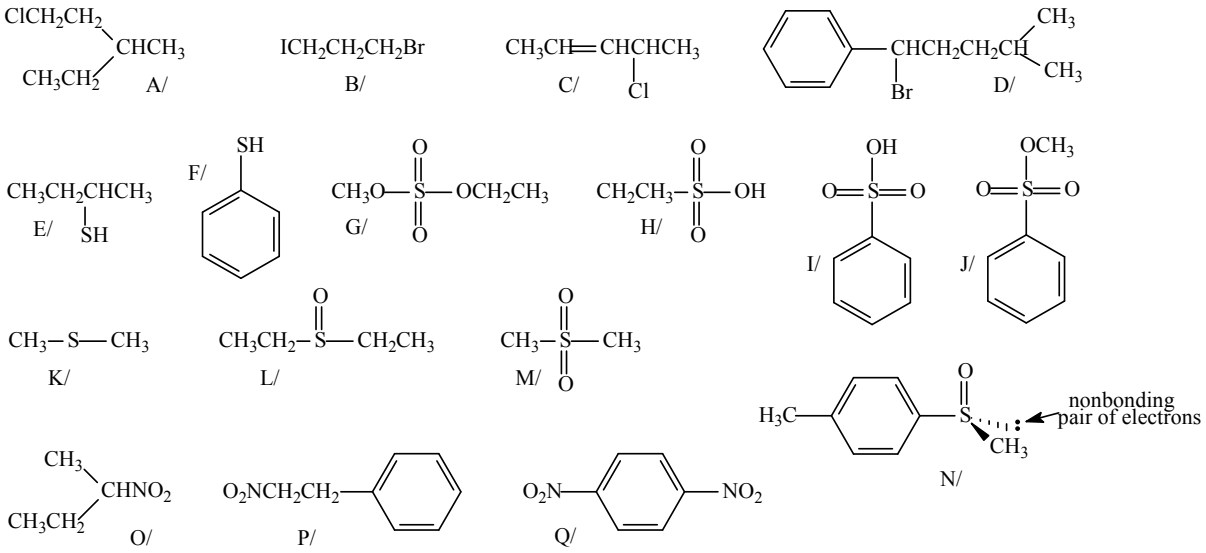
A/ methyl alcohol
B/ primary (1^o)
C/ secondary (2^o)
D/ tertiary (3^o)
E/ allylic alcohol type (1^o)
F/ benzylalcohol type (2^o)
G/ 2^o, benzyl
H/ 3^o (but not allylic)
I/ 2^o, allylic

12.

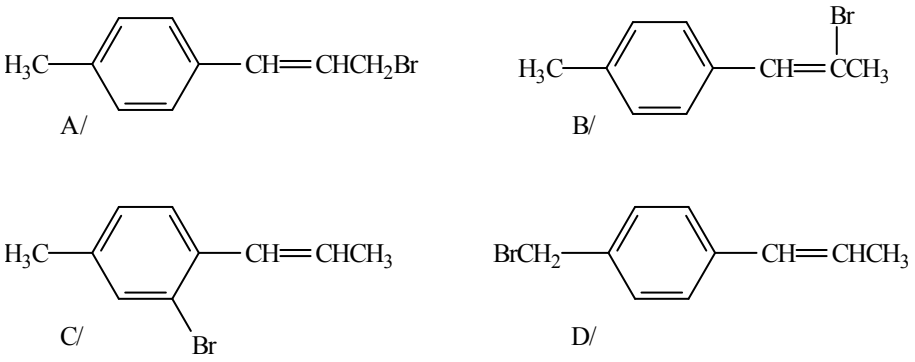

I/
OH
O
C
H
B/
1/ CHCl3 + KOH
2/ H2O, then H⊕
OH
NaOH
ONa
1/ CO2
2/ H3O⊕
OH
O
C
OH
A/
(CH3CH2CO)2O
HO⊖
O
HCH
H2C═O +
(CH3)2NH
Mannich reaction
O
OCCH2CH3
C/
OH
CH2OH
D/
OH
CH2N(CH3)2
E/
II/
CH3OH
SOCl2
CH3Cl
CrO3 / pyridine
Mg
abs. ether
H2C═O
CH3MgCl
Grignard reaction
NH4Cl
CH3CH2OH

VII. Aromatic halogene compounds, compounds with carbon-sulfur bond, aliphatic and aromatic nitrocompounds

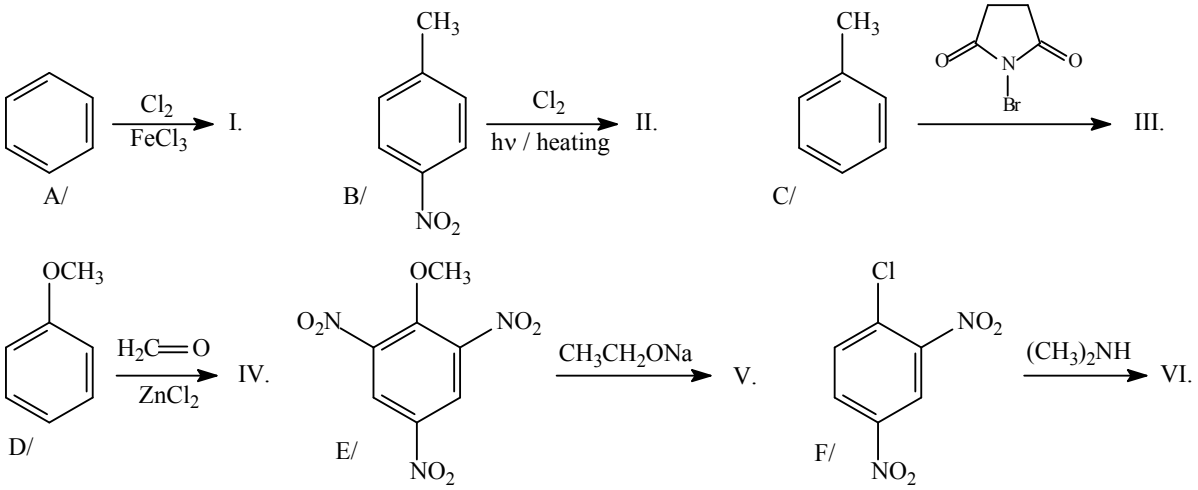
1. Name the following compounds:



2. Classify the following compounds according to the following terms: vinyl halogenides, allylic halogenides, benzyl halogenides, aryl halogenides:



3. Draw the following reactions:



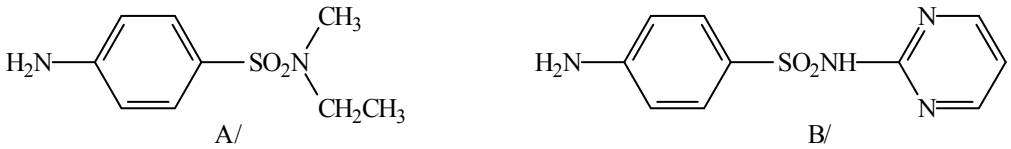
4. Prepare:

A/ 2-naphthol

B/ naphthalene-2-carboxylic acid

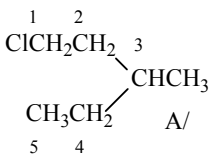
from naphthalene through the appropriate aromatic sulfonic acid derivative.

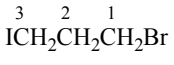
5. Prepare the following compound starting from acetanilide:

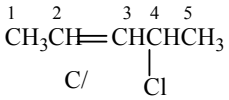


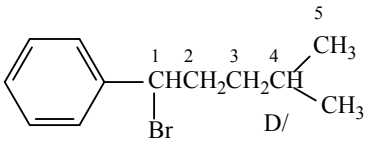
VII. ANSWERS

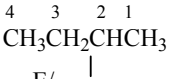
1.

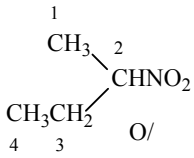

A/

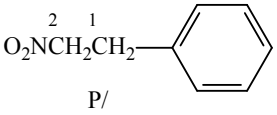

B/

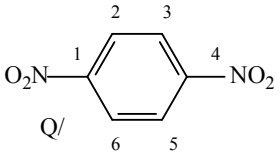

C/


D/


E/


O/


P/

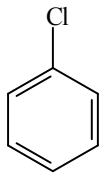

Q/

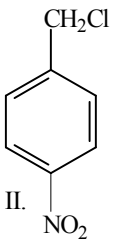
A/ 1-chloro-3-methylpentane
B/ 1-bromo-3-iodopropane
C/ 4-chloropent-2-ene
D/ 1-bromo-4-methyl-pentylbenzene
E/ butane-2-thiol
F/ thiophenol
G/ methyl ethyl sulfate
H/ ethanesulfonic acid
I/ benzenesulfonic acid
J/ methyl benzenesulfonate
K/ dimethyl sulfide
L/ diethyl sulfoxyde
M/ dimethyl sulfone
N/ (*S*)-methyl-4-tolyl-sulfoxide
O/ 2-nitrobutane
P/ 2-nitro-ethylbenzene
Q/ 1,4-dinitrobenzene

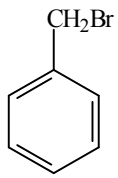
2.

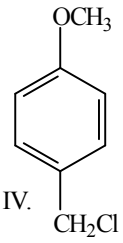
A/ allylic halogenid
B/ vinyl-halogenid
C/ aryl-halogenid
D/ benzyl-halogenid

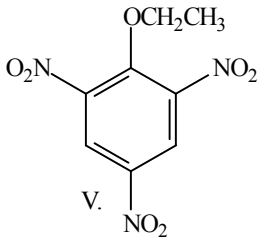
3.

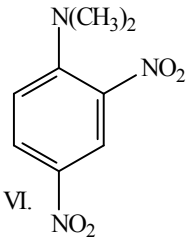

I.


II.

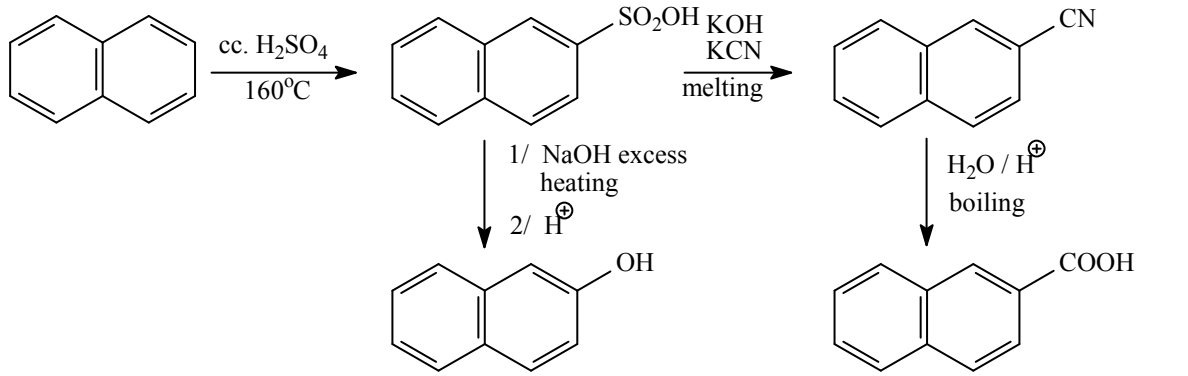

III.


IV.


V.

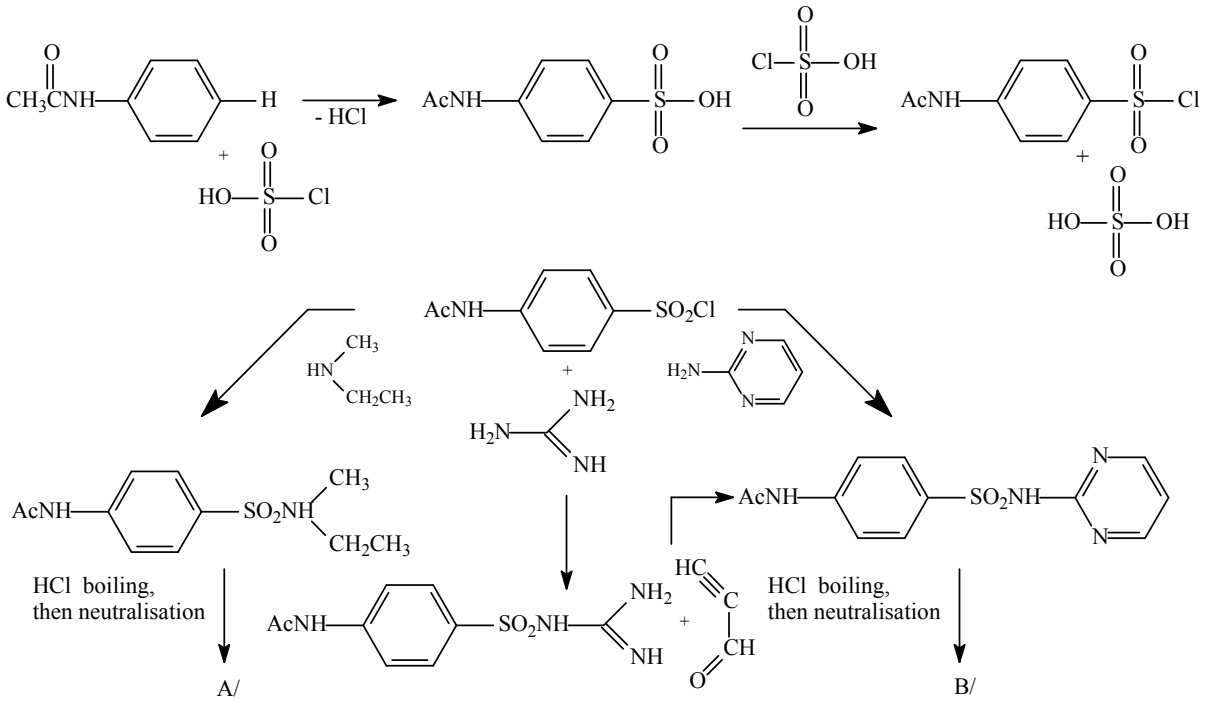

VI.

4.



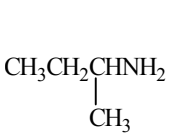
2-naphtol naphtalene-2-carboxylic acid

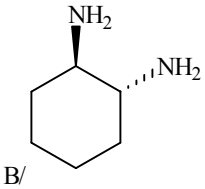
5.

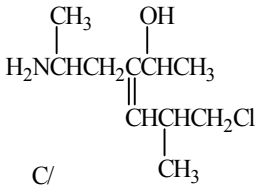


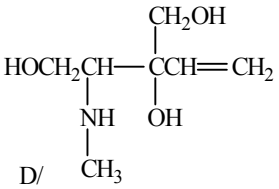
VIII. Aliphatic és aromatic amines, aromatic diazo- and azocompounds, diazomethane

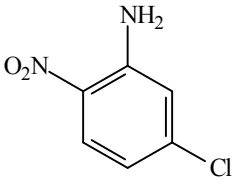
1. Name the following compounds:

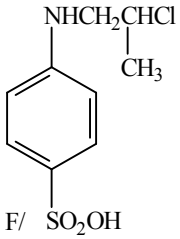

A/

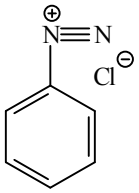

B/

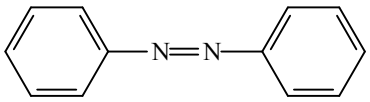

C/


D/


E/


F/

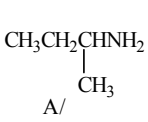

G/

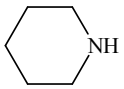

H/

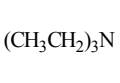
2. Draw structural formulas of the following compounds, or groups:

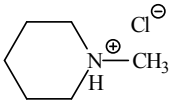
A/ 2-methylbutyl-1-amine
B/ ethyl isopropylamine
C/ pentane-1,2,5-triamine
D/ 2-bromo-3-(3-methoxy-5-nitrophenyl)-propyl-1-amine
E/ 3-nitro-*N*-methylaniline
F/ 1,3-bis(dimethylamino)-propane
G/ aminomethyl
H/ methylamino
I/ diethyl aminomethyl

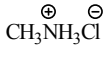
3. Classify the following compounds according to the following point of views:
primary (1^o), secondary (2^o), tertiary (3^o) amine
salt of primary (1^o), secondary (2^o), tertiary (3^o) amine
quaternary ammonium salt.

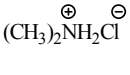

A/

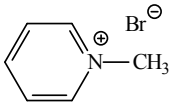

B/


C/


D/


E/

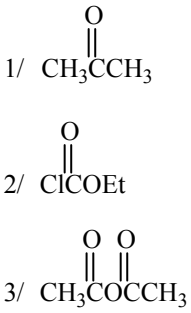

F/

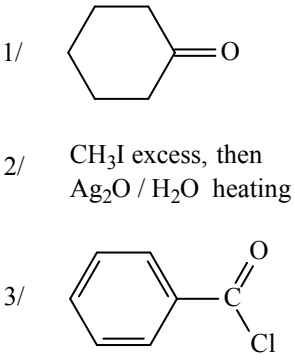

G/

4. Prepare by selective methods:

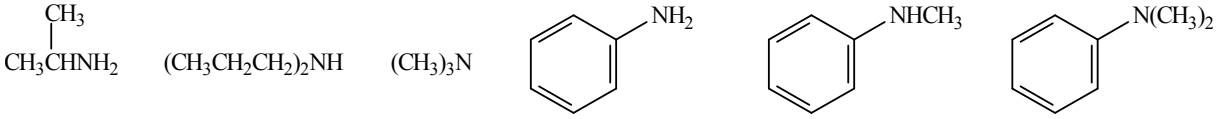
A/ propyl-1-amine
B/ diisopropyl-amine
  1/ from alkyl halogenide
  2/ from carbonyl compound
C/ *N,N*-dimethylbutyl-1-amine
D/ *N*-(1-butyl)-piperidine
  by Leuckart-Wallach type reductive alkylation
E/ 2-phenylethyl-1-amine from benzyl chloride
F/ 1-phenylethyl-1-amine from carbonyl compound.

5. How does A/ ethylamine B/ *N*-methyl-*N*-propylamine react with the following compounds?



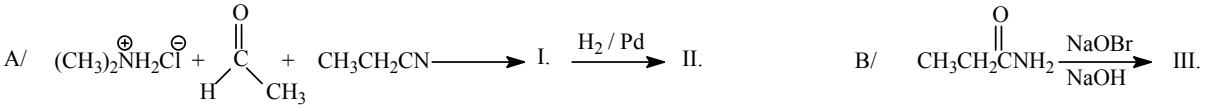


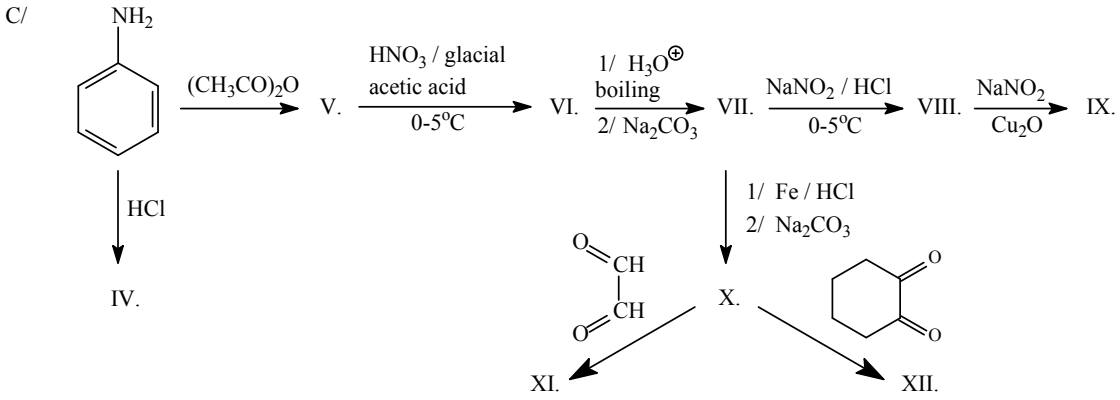
6. How do the following compounds react with nitrous acid?



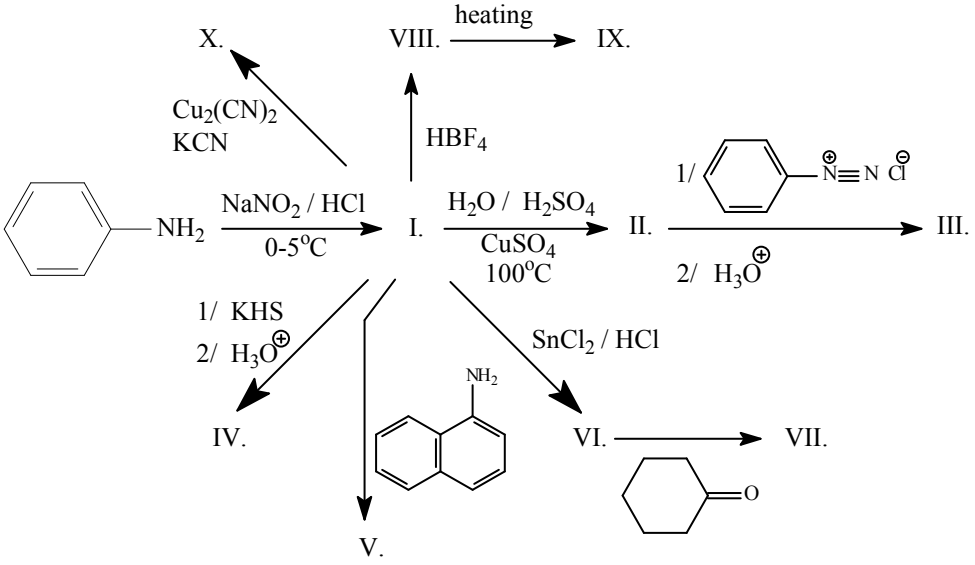
A/ B/ C/ D/ E/ F/

7. Draw the following reaction sequences:

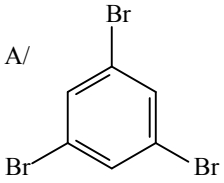




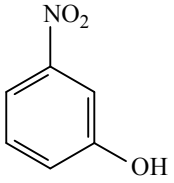
8. Draw products of the following reactions:



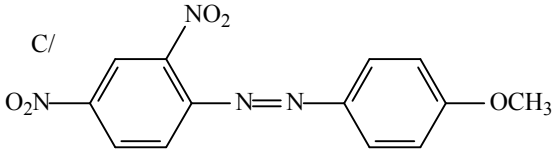
9. Prepare the following compounds through diazonium salt:

A/ 

from aniline

B/ 

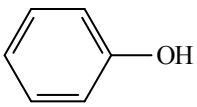
from nitrobenzene

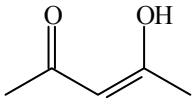
C/ 

from the appropriate pair of compounds, by coupling reaction

10. How does diazomethane react with the following compounds?

A/ 

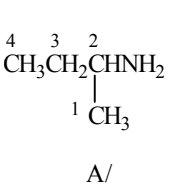
B/ 

C/ 

D/ CH_3CH_2OH

VIII. ANSWERS

1.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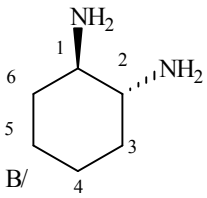
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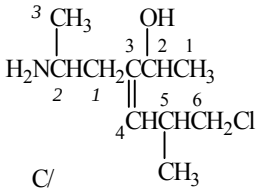
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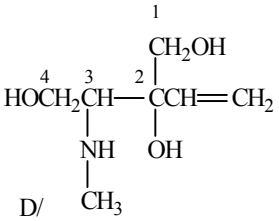
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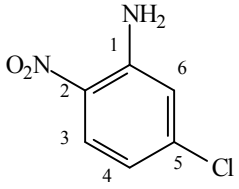
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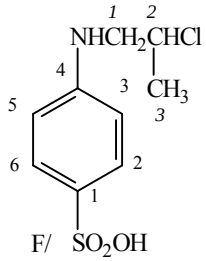
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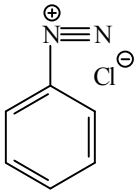
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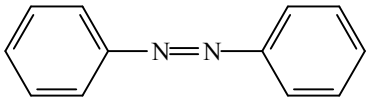
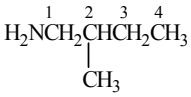

H/

A/ *sec*-butylamine
B/ *transz*-cyclohexan-1,2-diamine
C/ 3-(2-aminopropyl)-6-chloro-5-methylhex-3-en-2-ol
D/ 3-methylamino-2-vinylbutane-1,2,4-triol
E/ 5-chloro-2-nitroaniline
F/ 4-(2-chloro-propylamino)-benzenesulfonic acid
G/ benzenediazonium chloride
H/ azobenzene

2.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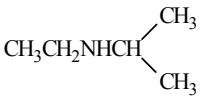
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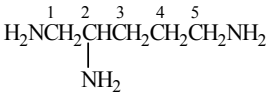
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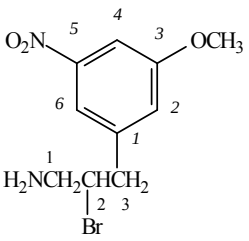
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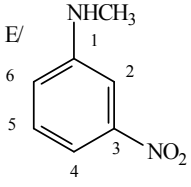
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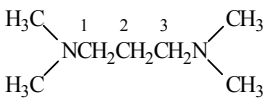
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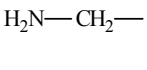
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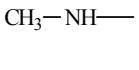
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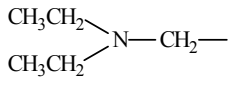
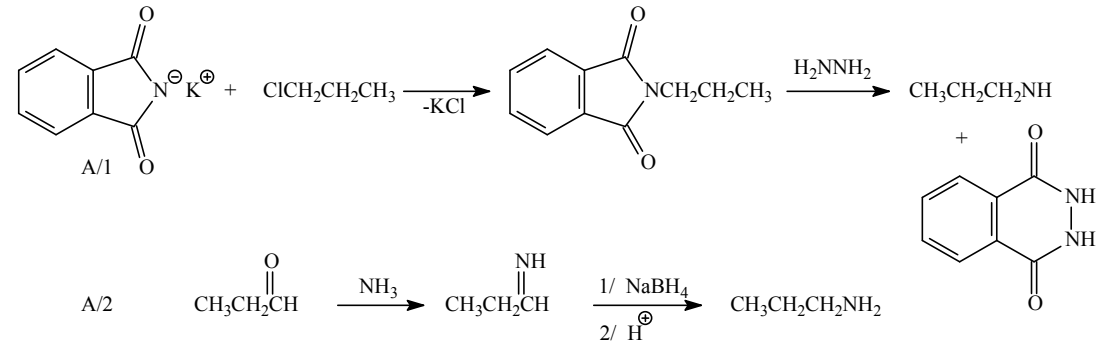

I/

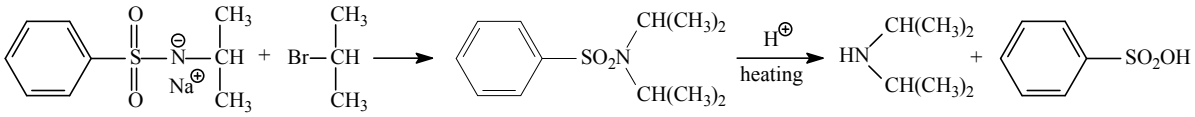
3.

A/ primary amine
B/ secondary amine
C/ tertiary amine
D/ tertiary ammonium salt
E/ primary ammonium salt
F/ secondary ammonium salt
G/ quaternary ammonium salt

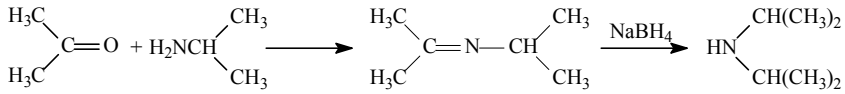
4.



B/1



B/2



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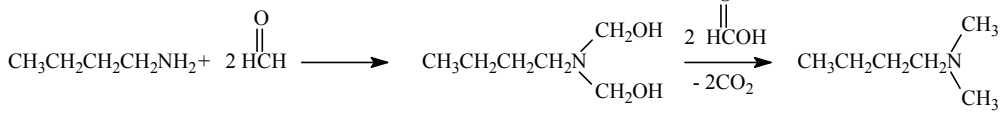

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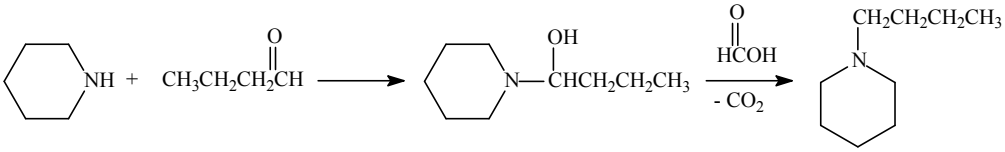

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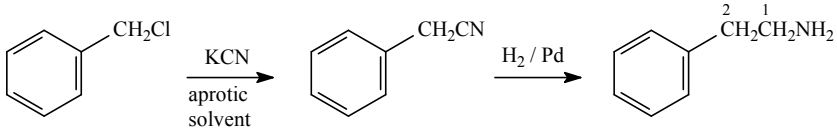

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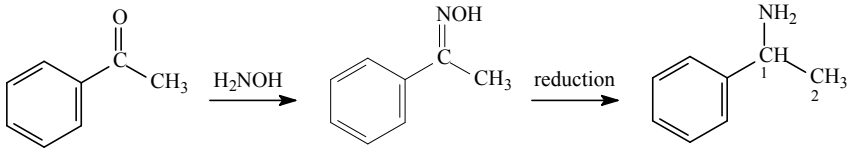


5.

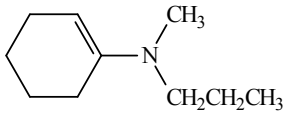
A/ $CH_3CH_2NH_2$

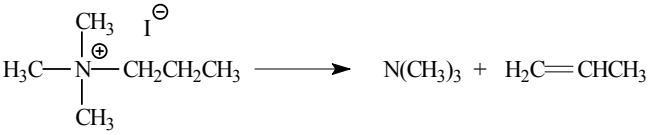
1/ CH_3CCH_3 = NCH_2CH_3

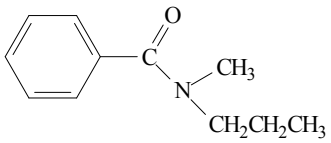
2/ $CH_3CH_2NHCOEt$

3/ $CH_3CH_2NHCCH_3$ (O)

B/ $H_3CNHCH_2CH_2CH_3$

1/ 

2/ 

3/ 

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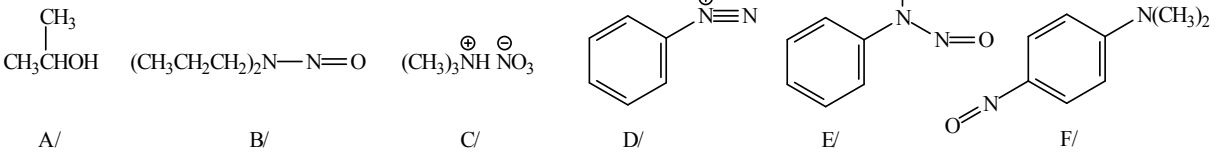
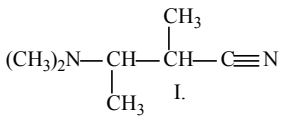


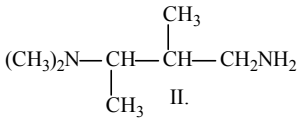
A/ B/ C/ D/ E/ F/

7.



I.

(product of Mannich reaction)

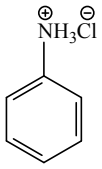


II.

$CH_3CH_2NH_2$

III.

(product of Hofmann degradation)



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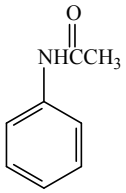

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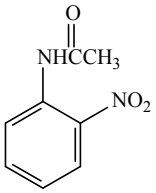

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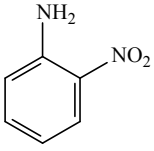

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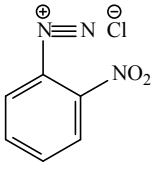

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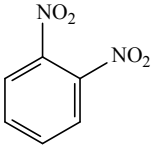

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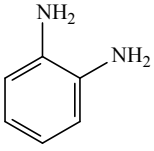

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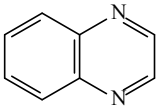
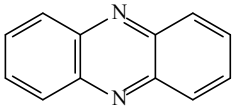
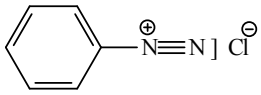


XI.



XII.

8.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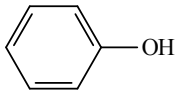
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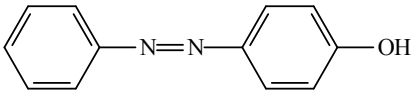
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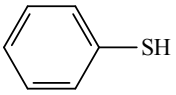
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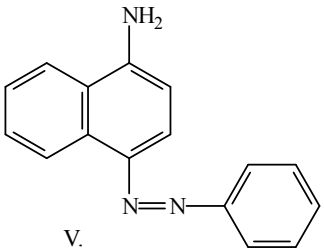
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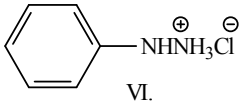
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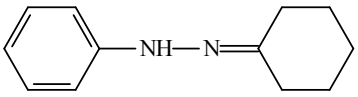
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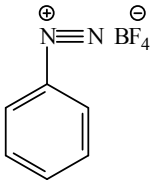
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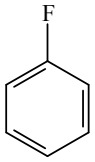
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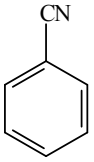
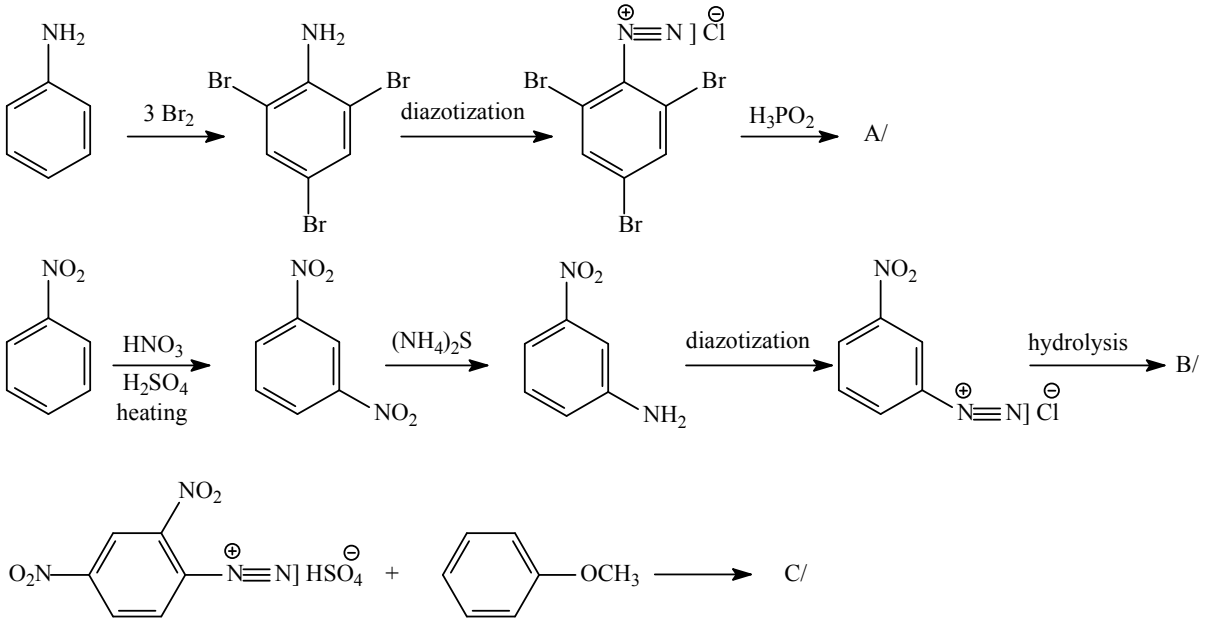
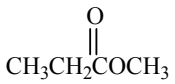
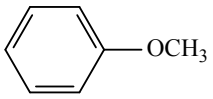

X.

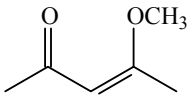
9.



10.

A/ 

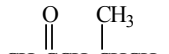
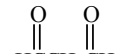
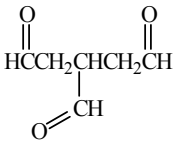
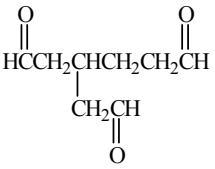
B/ 

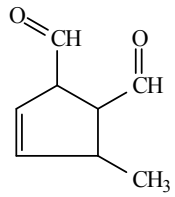
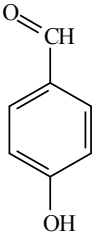
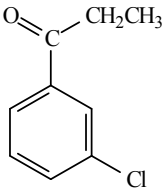
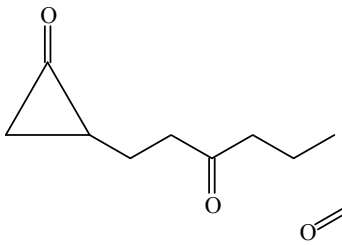
C/ 

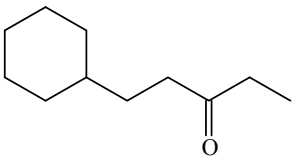
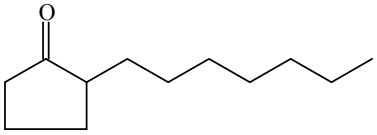
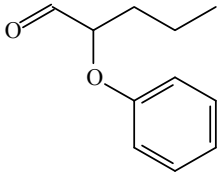
D/ There is no reaction, since acidity of the alcohol is too low.

IX. Aliphatic and aromatic carbonyl compounds (aldehydes and ketones)

1. Name the following compounds:

A/ 
B/ 
C/ 
D/ 
E/ 

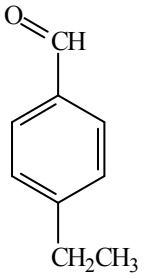
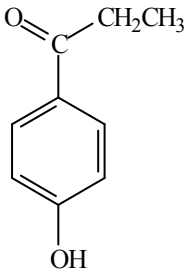
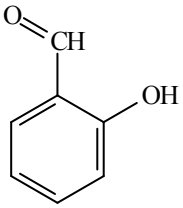
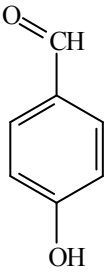
F/ 
G/ 
H/ 
I/ 

J/ 
K/ 
L/ 

2. Draw structural formulas of the following compounds:
A/ 5-bromohexane-2-one
B/ diacetyl
C/ 3-acetylcyclohexane-1-carbaldehyde
D/ butanedial
E/ salicylic aldehyde
F/ 2-acetonaphthone

3. Prepare A/ butan-2-one
B/ butanal
from the same starting material with triple bond, by addition reaction.

4. Prepare the following compounds:

A/ 
B/ 
C/ 
D/ 

A/ from an aromatic carboxylic acid derivative
B/ from phenol, by two different methods
C/ starting from phenol
D/ starting from phenol

5. How do the following compounds react in each reaction:

I/ acetaldehyde

A/ CH_3CH_2OH excess / $H^{\oplus}$

B/ $HOCH_2CH_2OH$ / $H^{\oplus}$

C/ $(CH_3)_2CHNH_2$

D/ $HCH=O$ + $(CH_3)_2NH$

II/ cyclohexanone

A/ $NaBH_4$, then $H^{\oplus}$

B/ CH_3NO_2 / base

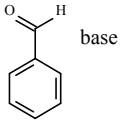
C/ $HO-NH_2$

D/ $(CH_3CH_2)_2NH$

III/ acetophenone

A/ Br_2 / $H^{\oplus}$

B/ I_2 / $HO^{\ominus}$

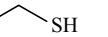
C/  base

D/ $NaHSO_3$

E/ $H_2N-NHCNH_2$ (O)

IV/ benzaldehyde

A/ CH_3CH_2MgBr, then $H^{\oplus}$

B/ 1/ 

2/ $CH_3CH_2CH_2CH_2Li$ / THF

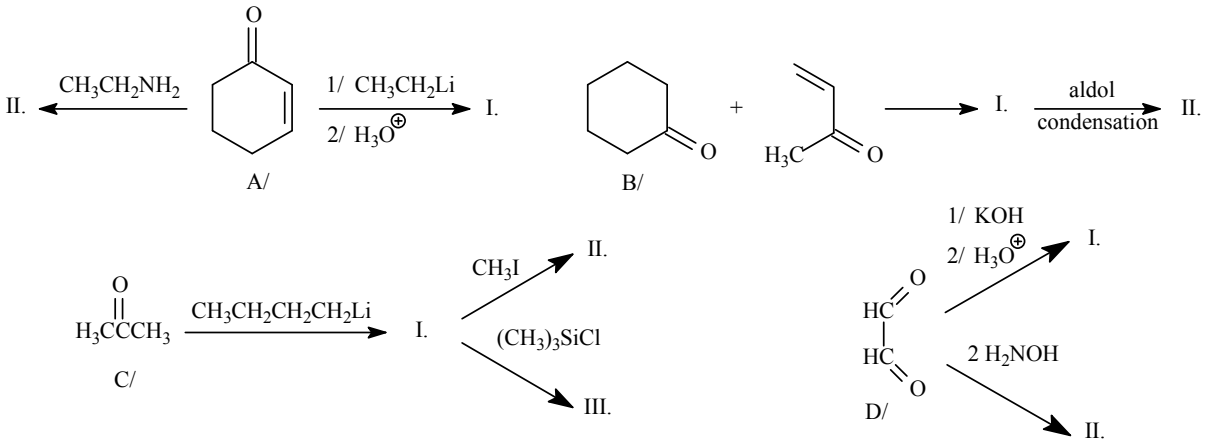
3/ CH_3CH_2Br

C/ 1/2 KCN, H_2O

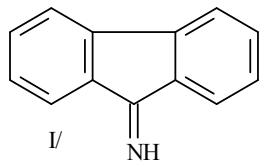
D/ HCN

E/ cc. KOH, then $H^{\oplus}$

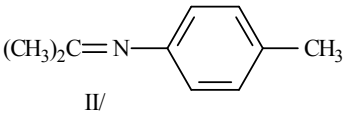
6. What products are formed in the following reactions:



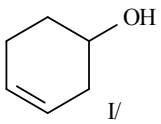
7. How would you prepare:
A/ the following imines from a carbonyl compound;
B/ the following alcohols from a carbonyl compound;
C/ the following carbonyl compounds through enamine?

A/ 

I/



II/

B/ 

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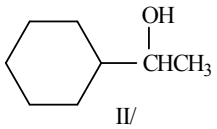
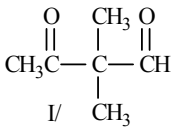


II/

C/ 

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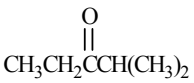
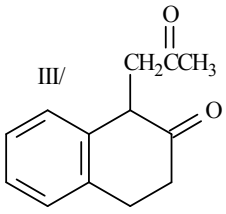
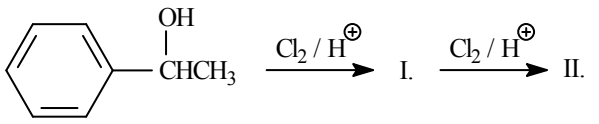
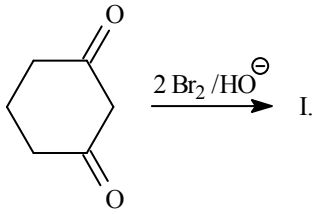


II/

III/ 

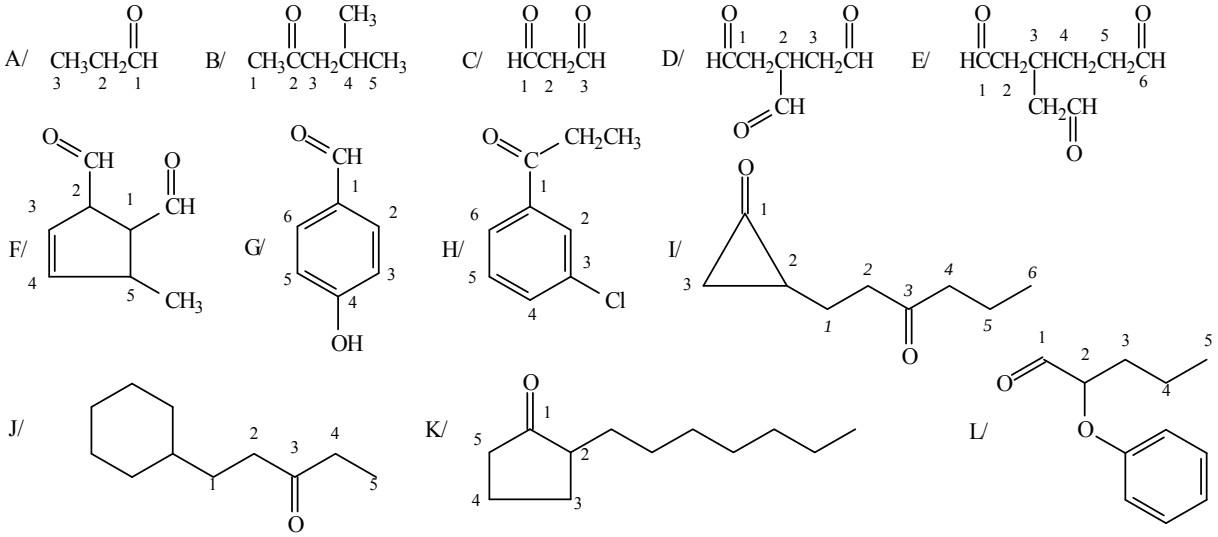
8. What are the products of the following reactions?

A/ 

B/ 

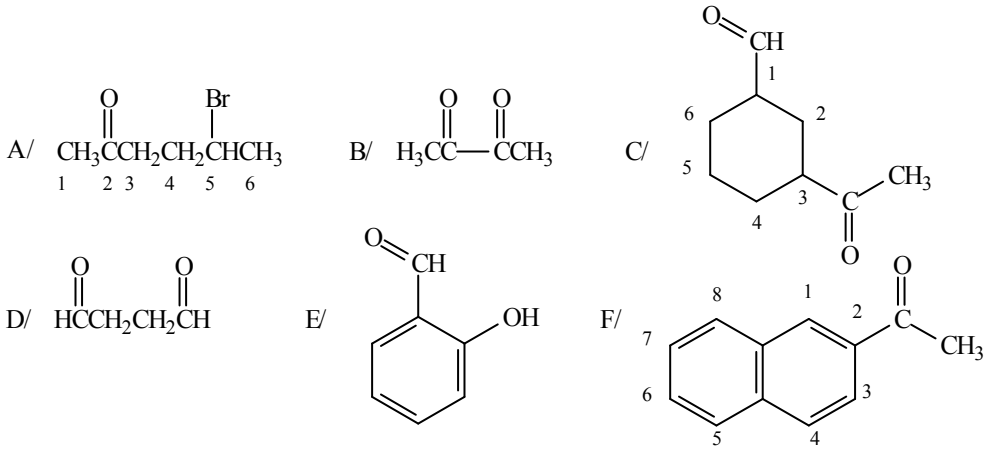
IX. ANSWERS

1.



A/ propanal
B/ 4-methylpentane-2-one
C/ propanedial
D/ propane-1,2,3-tricarbaldehyde
E/ 3-(formylmethyl)-hexanedial
F/ 5-methylcyclopent-3-en-1,2-dicarbaldehyde
G/ 4-hydroxybenzaldehyde
H/ 3-chloropropiophenone
I/ 2-(3-oxohexyl)-cyclopropane-1-one
J/ 1-cyclohexylpentane-3-one
K/ 2-heptylcyclopentane-1-one
L/ 2-phenyloxypentanal

2.



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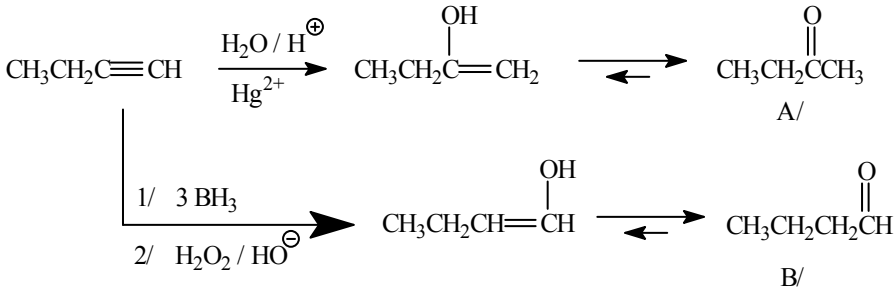

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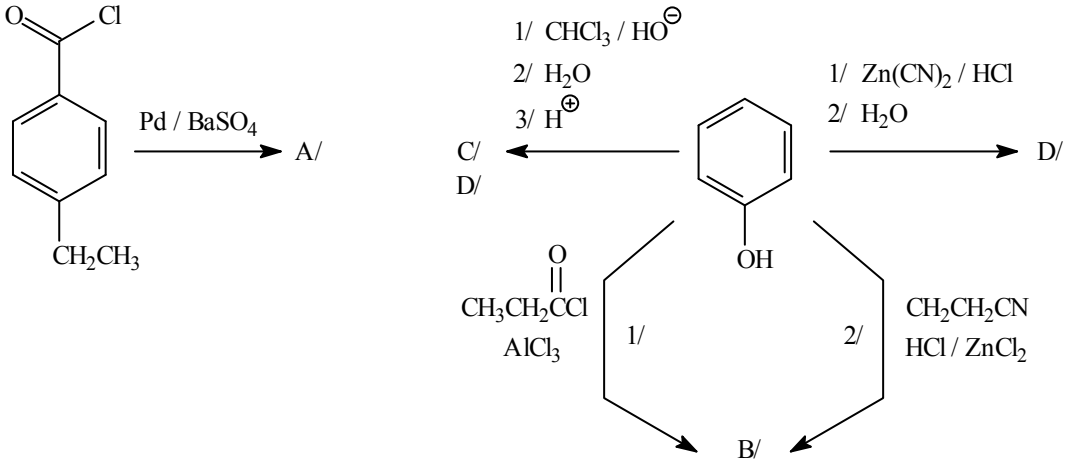


A/ reduction reaction

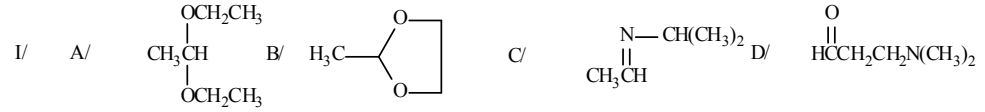
B/ 1/ There is acylation of the ring carbon, in the presence of $AlCl_3$ (there is acylation of the oxygen if $AlCl_3$ is absent)

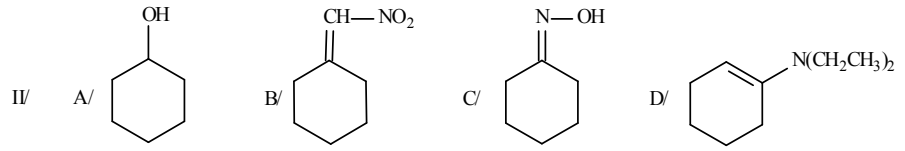
2/ Houben-Hoesch reaction

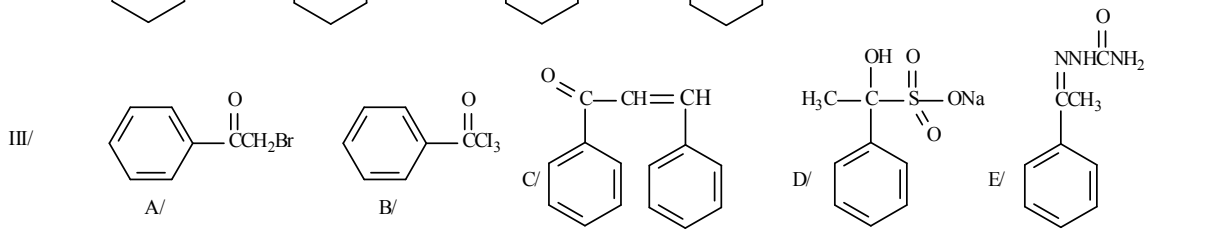
C/ Reimer-Thiemann-synthesis

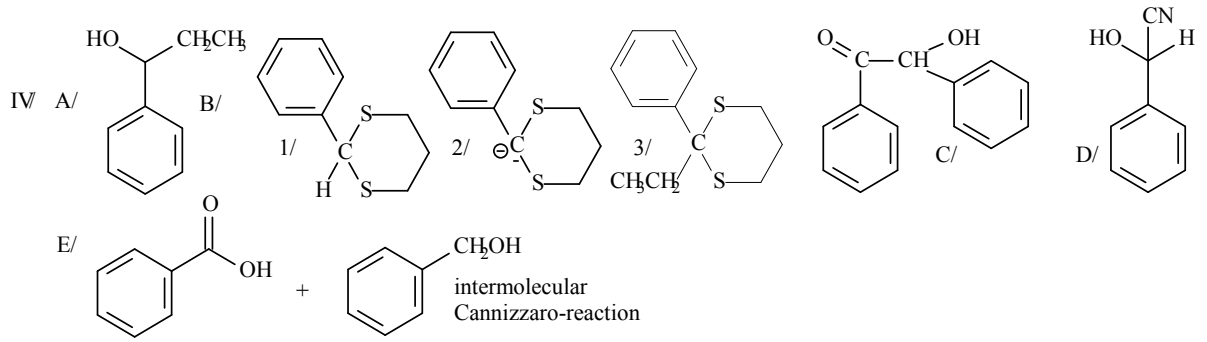
D/ Gattermann reaction

5.

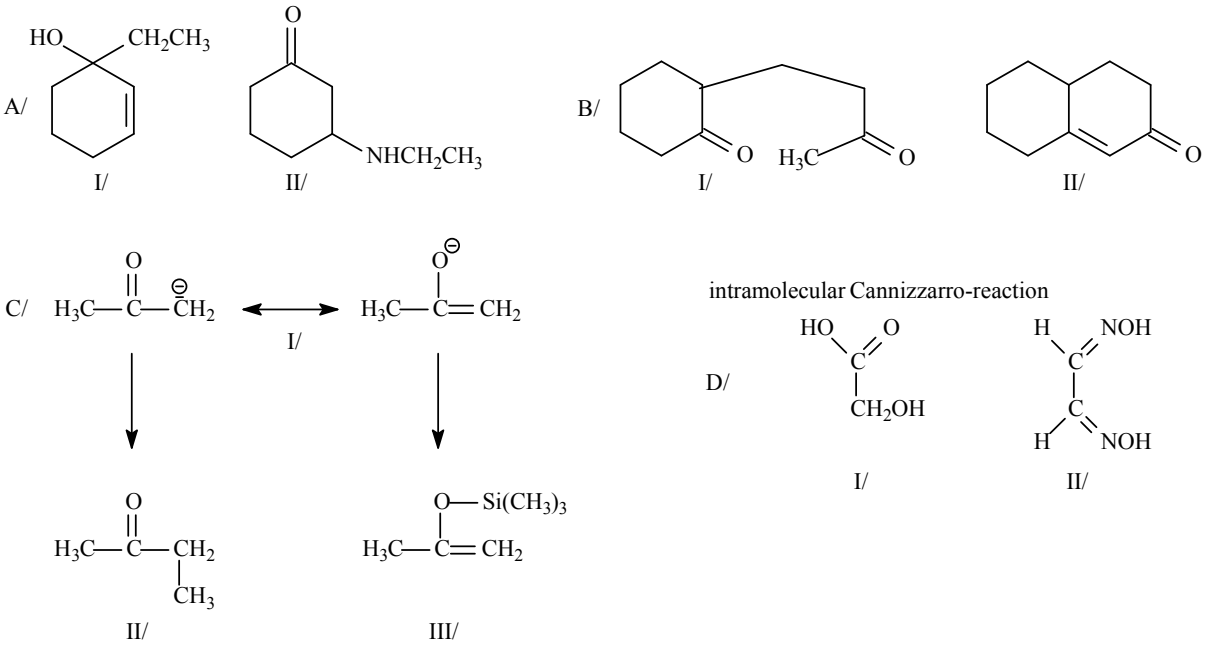

I/ A/ OCH2CH3 CH3CH OCH2CH3 B/ H3C O O C/ N CH(CH3)2 CH3CH D/ O HCCH2CH2N(CH3)2


II/ A/ OH B/ CH NO2 C/ N OH D/ N(CH2CH3)2

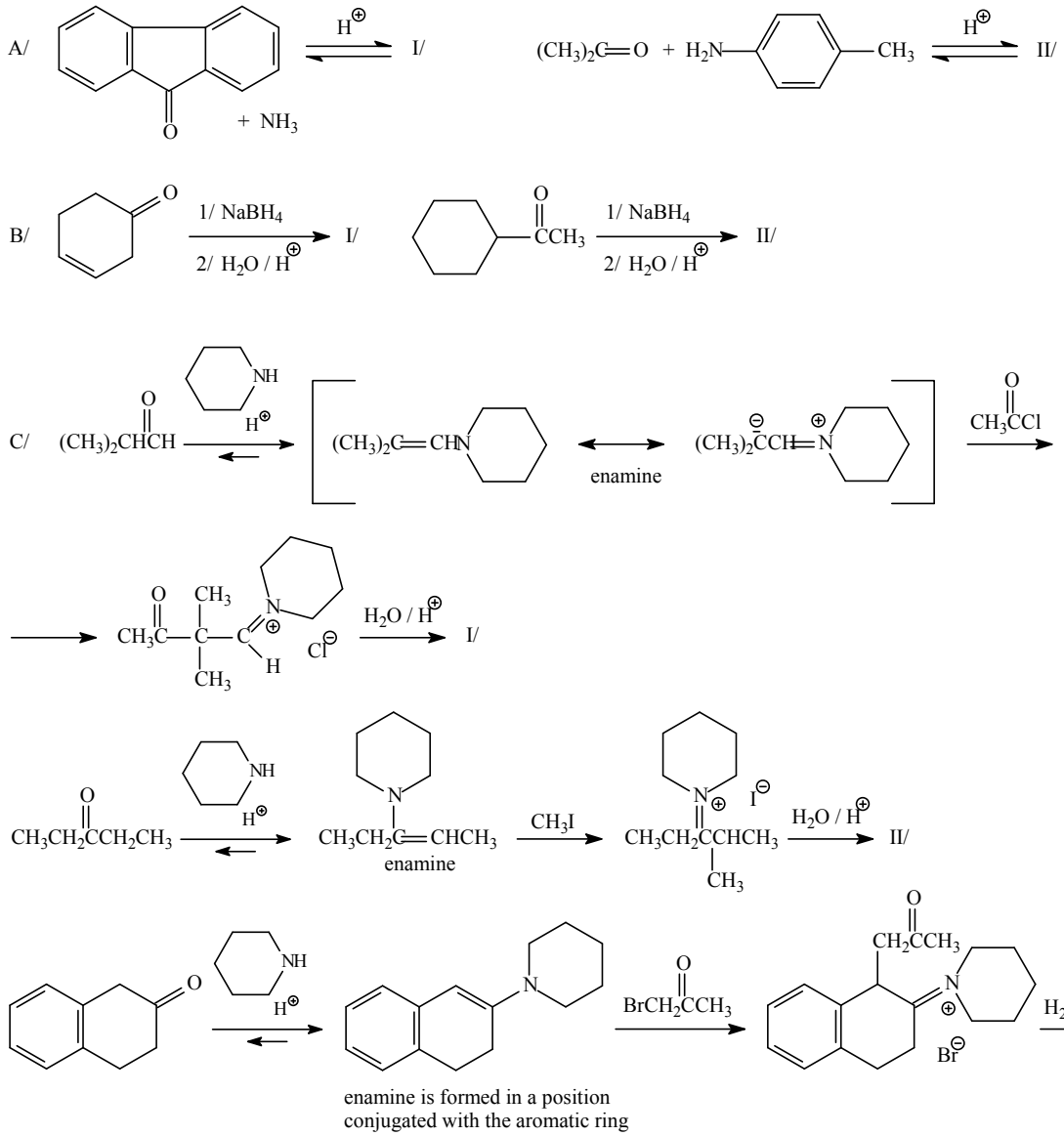

III/ O CCH2Br A/ O CCl3 B/ O C CH CH C/ OH O H3C C S ONa O D/ O NNHCNH2 CCH3 E/


IV/ A/ HO CH2CH3 B/ 1/ S C H S 2/ S C S 3/ S C CH3CH2 S O C CH OH C/ CN HO H D/ E/ O OH + CH2OH intermolecular Cannizzaro-reaction

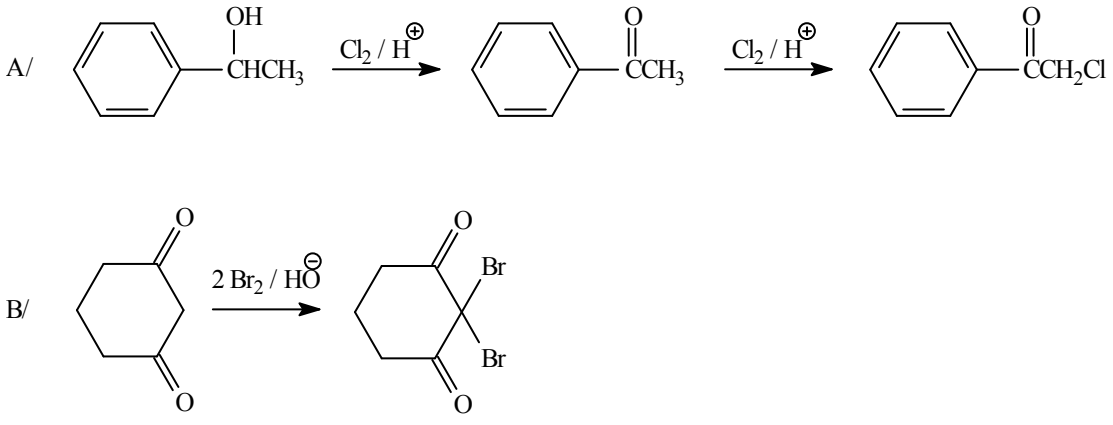
6.


A/ HO CH2CH3 I/ O NHCH2CH3 II/ B/ O H3C O I/ O II/ C/ O H3C C CH2 I/ H3C C CH2 O H3C C CH2 CH3 II/ O Si(CH3)3 H3C C CH2 III/ intramolecular Cannizzaro-reaction D/ HO O C CH2OH I/ H NOH C C H NOH II/

7.

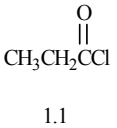

A/
+ NH3
I/
(CH3)2C=O + H2N
CH3
II/
B/
1/ NaBH4
2/ H2O / H
I/
CCH3
1/ NaBH4
2/ H2O / H
II/
C/
(CH3)2CHCH
(CH3)2C=CHN
enamine
(CH3)2CCH=N
CH3CCl
CH3C
CH3
CH3
Cl
H2O / H
I/
CH3CH2CCH2CH3
CH3CH2C=CHCH3
enamine
CH3I
CH3CH2CCHCH3
CH3
I
H2O / H
II/
BrCH2CCH3
CH2CCH3
Br
H2O / H
III/
enamine is formed in a position
conjugated with the aromatic ring

8.


A/
OH
CHCH3
Cl2 / H
CCH3
Cl2 / H
CCH2Cl
B/
2 Br2 / HO
Br
Br

X. Aliphatic and aromatic carboxylic acids and their derivatives

1. Name the following compounds: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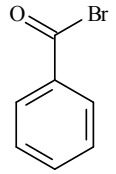
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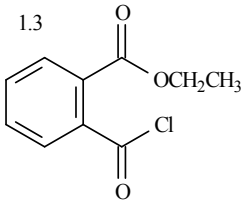
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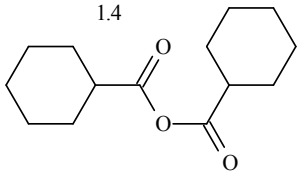
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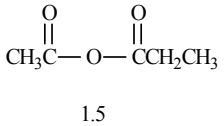
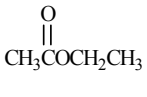

1.5


1.6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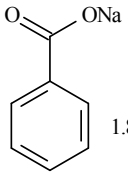
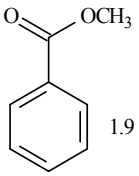

1.8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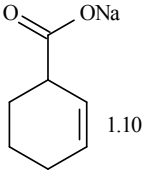
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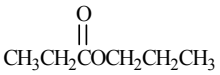
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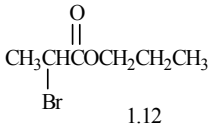
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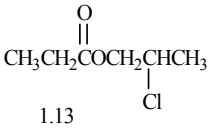
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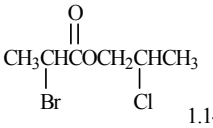
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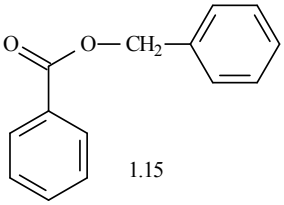
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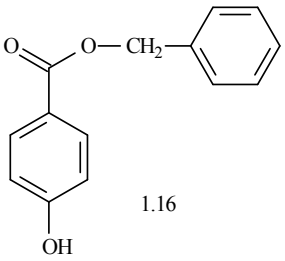
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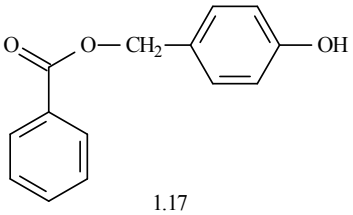
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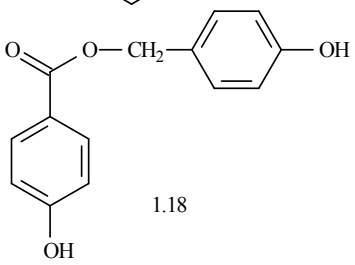
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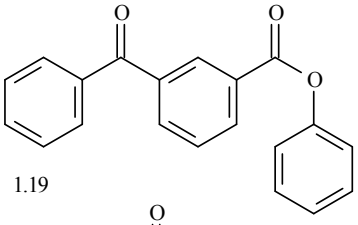
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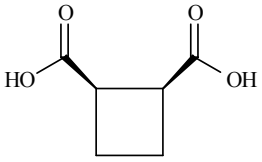
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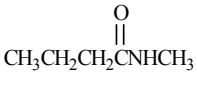
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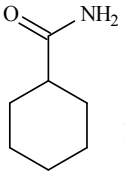
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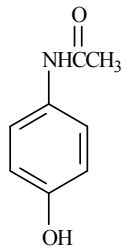
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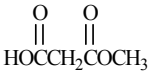
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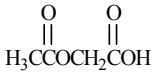
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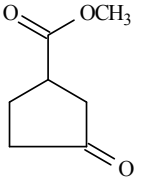
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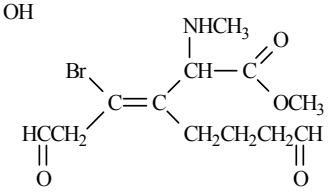
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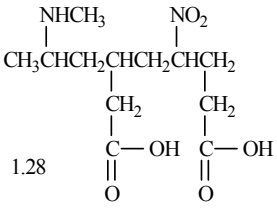
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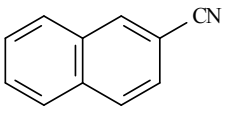
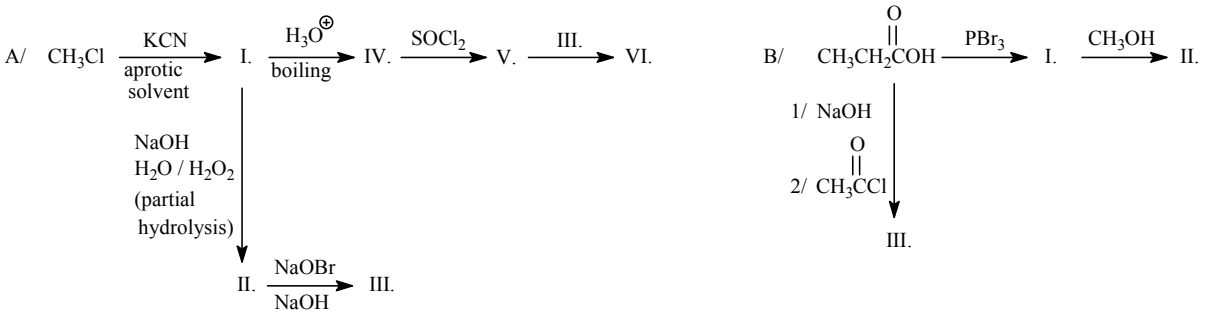
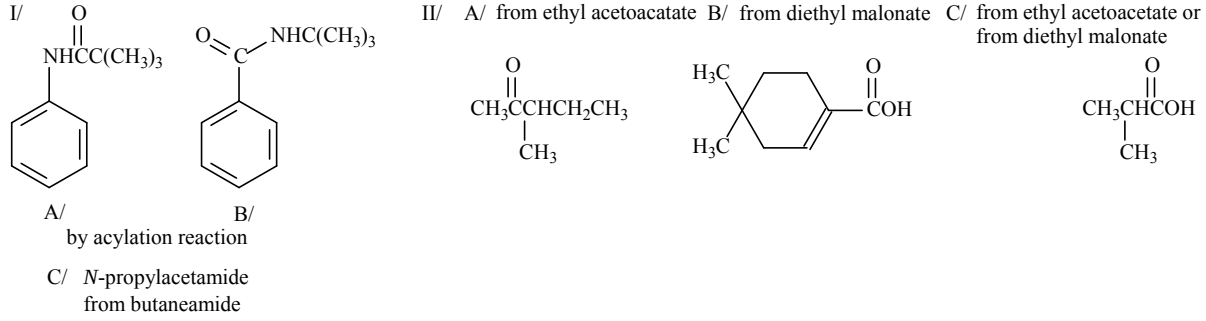

1.29

2. Draw structural formulas and IUPAC names of the following compounds:
   A/ crotonic acid
   B/ isocrotonic acid
   C/ phthalic acid
   D/ isophthalic acid
   E/ terephthalic acid
   F/ salicylic acid
   G/ pyruvic acid

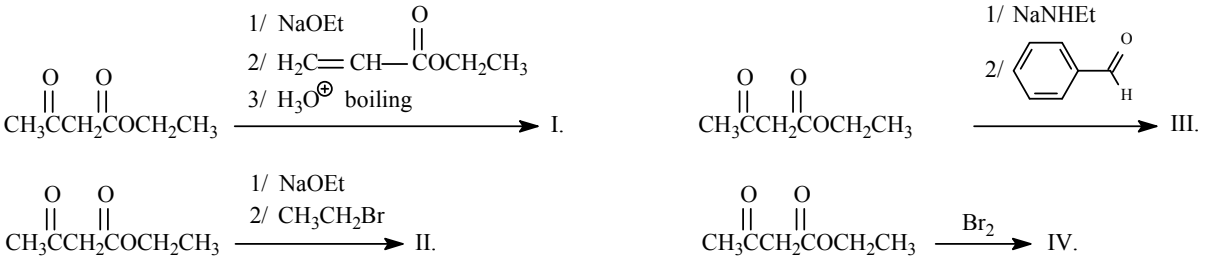
3. Draw the following reactions:



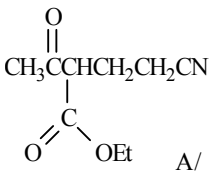
4. Prepare the following compounds:



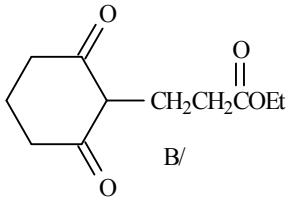
5. How does ethyl acetoacetate react in the following reactions:



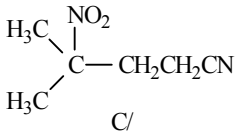
6. How would you prepare the following compounds by Michael addition?



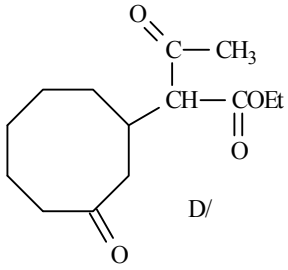
A/



B/

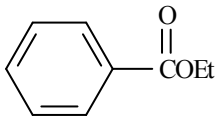


C/

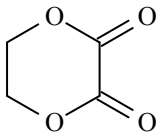


D/

7. Draw the saponification equations of the following esters by aqueous sodium hydroxyde:



A/



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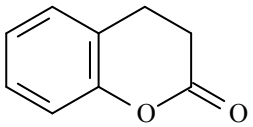
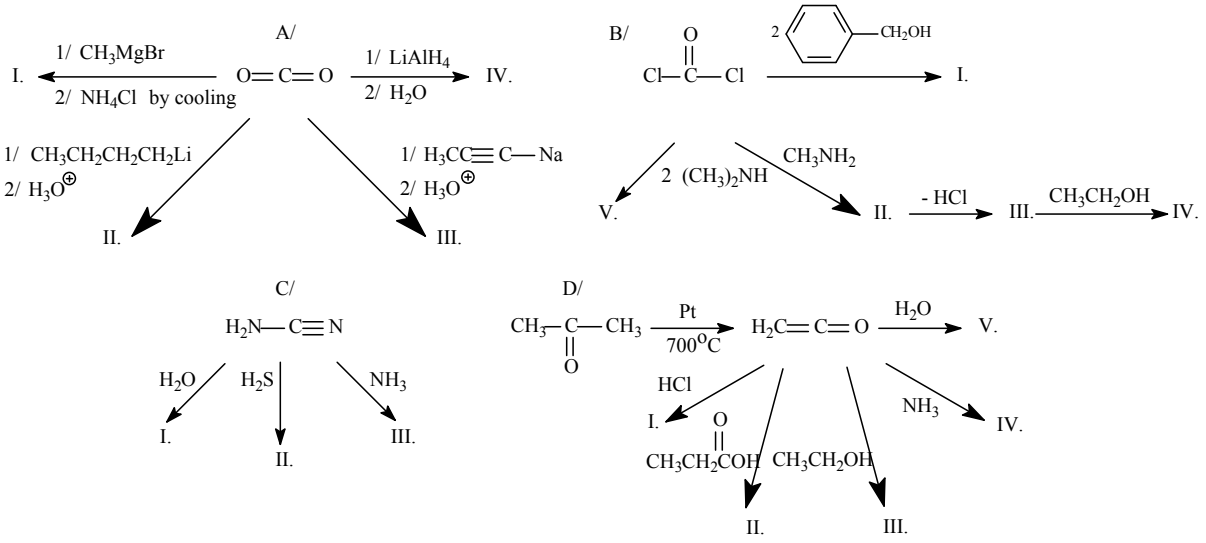


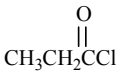
C/

8. Draw the following reactions:



X. ANSWERS

1.



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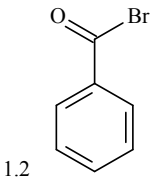

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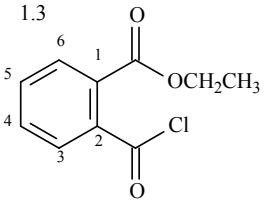

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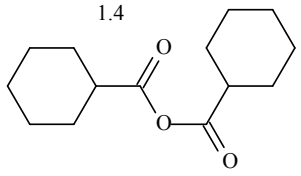

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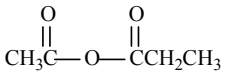

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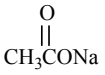

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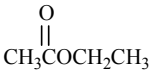

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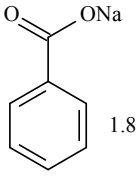

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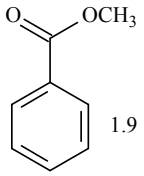

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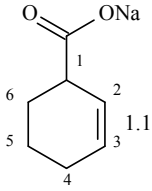

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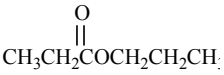

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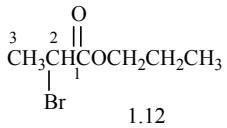

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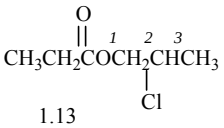

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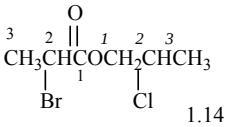

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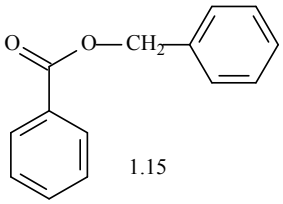

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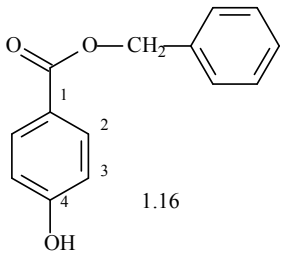

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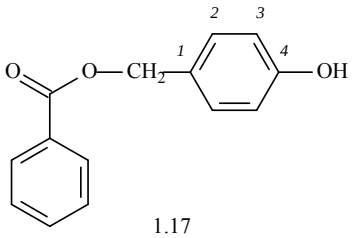

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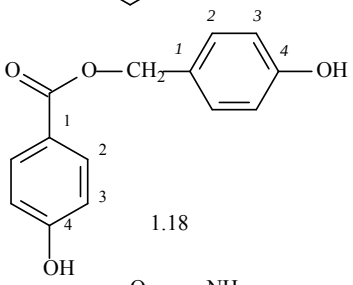

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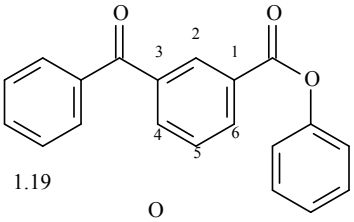

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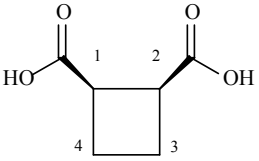

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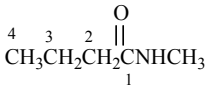

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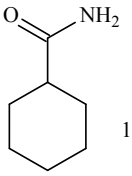

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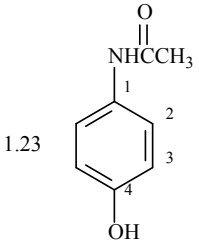

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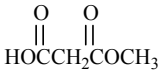

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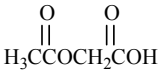

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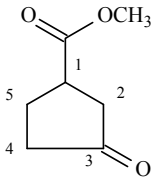

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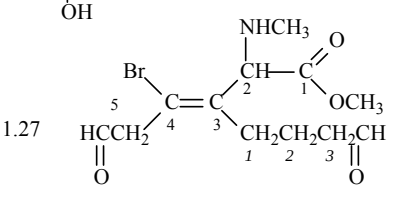

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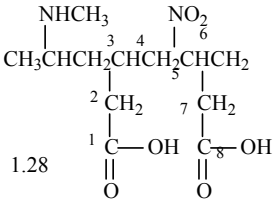

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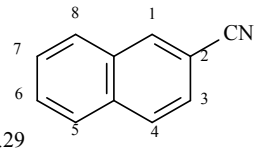
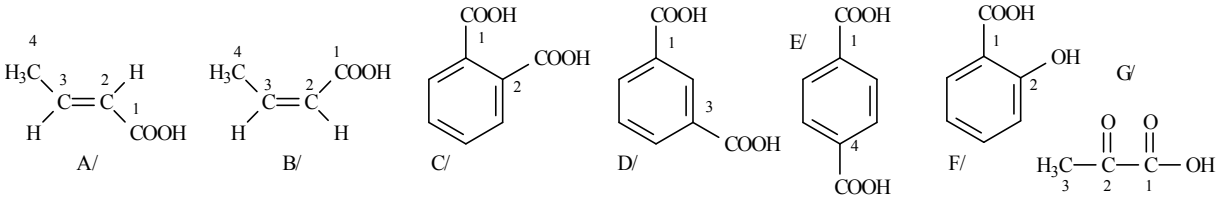


1.29

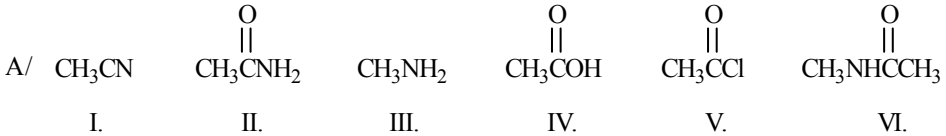
1.1 propionyl chloride
1.2 benzoyl bromide
1.3 ethyl 2-(chlorocarbonyl)benzoate
1.4 cyclohexanecarboxylic anhydride
1.5 acetic acid-propionic acid anhydride
1.6 sodium acetate
1.7 ethyl acetate
1.8 sodium benzoate
1.9 methyl benzoate
1.10 sodium cyclohex-2-encarboxylate
1.11 propyl propionate
1.12 propyl-2-bromo propionate
1.13 (2-chloropropyl) propionate
1.14 (2-chloropropyl) (2-bromopropionate)
1.15 benzyl benzoate
1.16 benzyl (4-hydroxybenzoate)
1.17 (4-hydroxybenzyl)benzoate
1.18 (4-hydroxybenzyl)-(4-hydroxybenzoate)
1.19 phenyl-(3-benzoylbenzoate)
1.20 *cis*-cyclobutane-1,2-dicarboxylic acid
1.21 *N*-methylbutanamide
1.22 cyclohexanecarboxamide
1.23 4-hydroxyacetanylide
1.24 methoxycarbonylacetic acid
1.25 acetoxyacetic acid
1.26 methyl-(3-oxocyclopentanecarboxylate)
1.27 (*Z*)-methyl-4-bromo-5-formyl-3-(3-formylpropyl)-2-methylamino-pent-3-en-1-oate
1.28 3-(2-methylaminopropyl)-5-nitrooctandioic acid
1.29 naphthalene-2-carbonitryle

2.

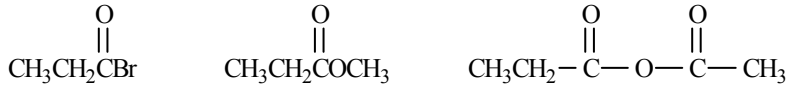


A/ (*E*)-but-2-enoic acid
B/ (*Z*)-but-2-enoic acid
C/ benzene-1,2-dicarboxylic acid
D/ benzene-1,3-dicarboxylic acid
E/ benzene-1,4-dicarboxylic acid
F/ 2-hydroxybenzoic acid
G/ 2-oxopropanoic acid

3.

A/ 

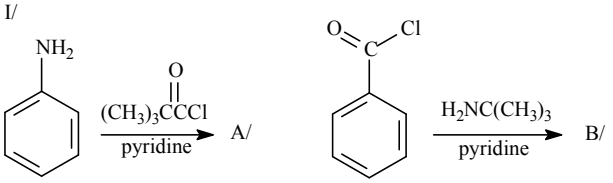
I. II. III. IV. V. VI.

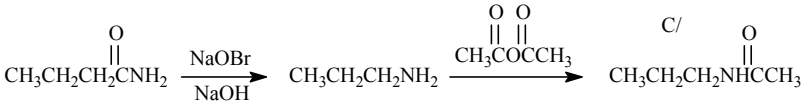
B/ 

I. II. III.

4.

I/





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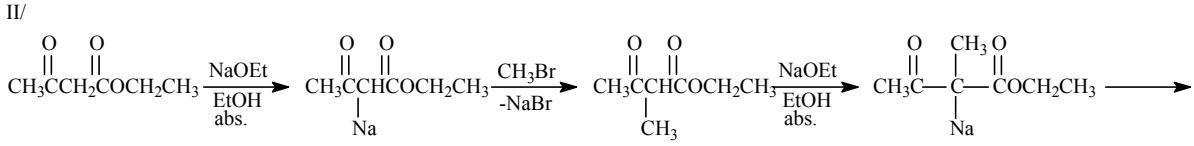

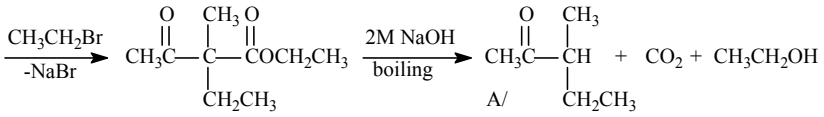

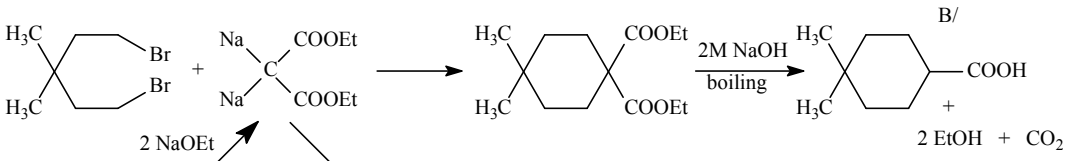

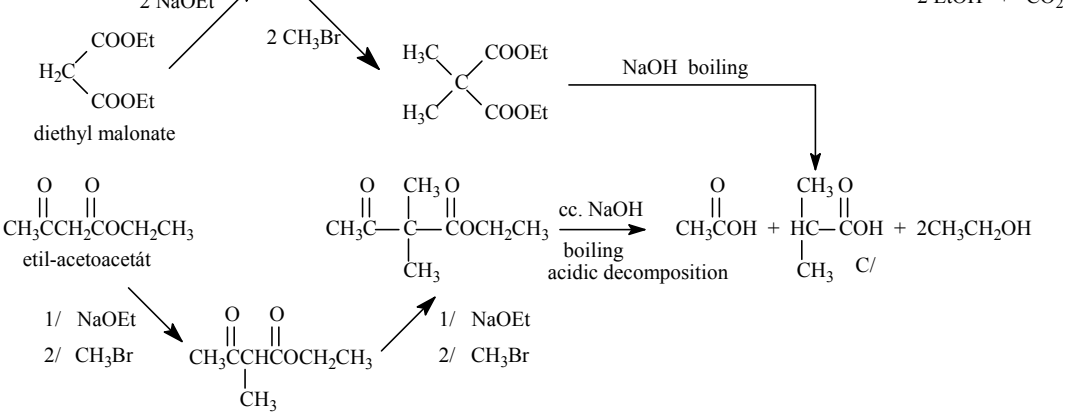

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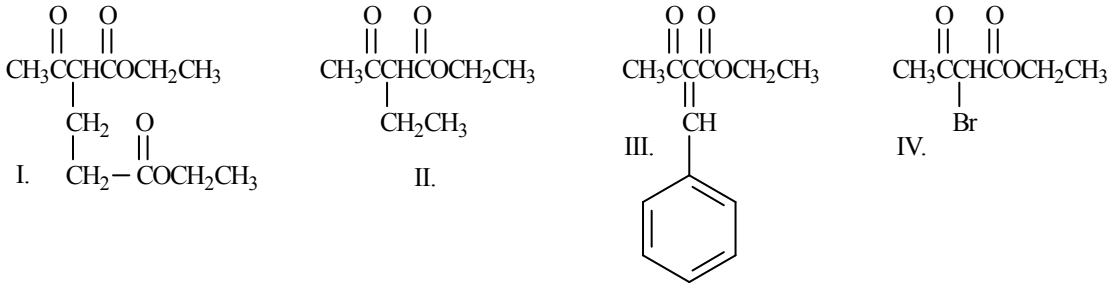

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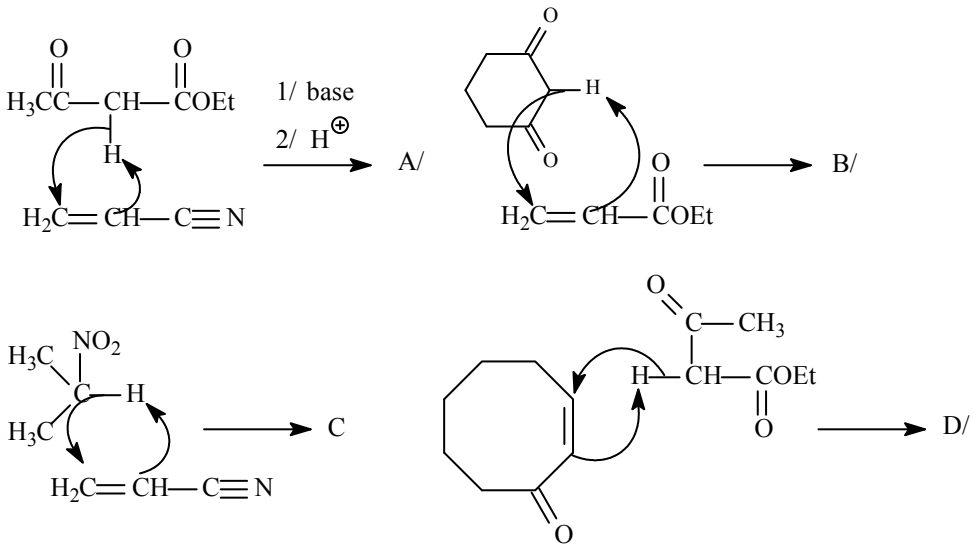

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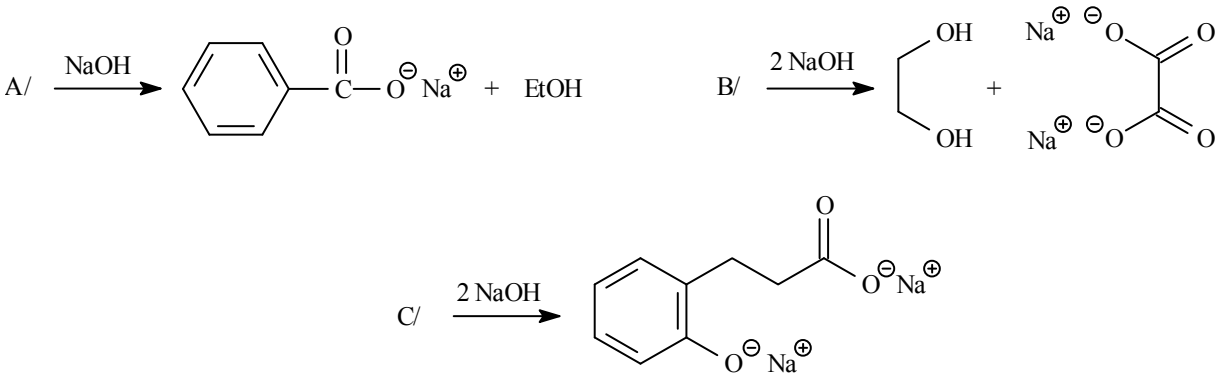

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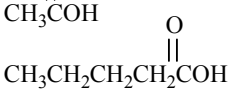
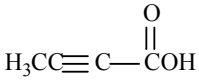
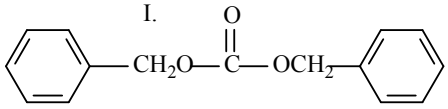
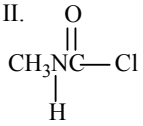
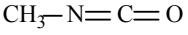
II. 

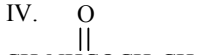
III. 

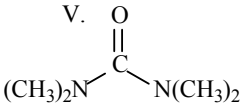
IV. CH_3OH

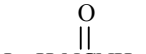
B/ I. 

II. 

III. 

IV. 

V. 

C/ I. 

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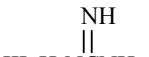
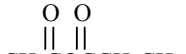
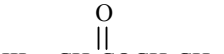
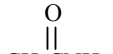
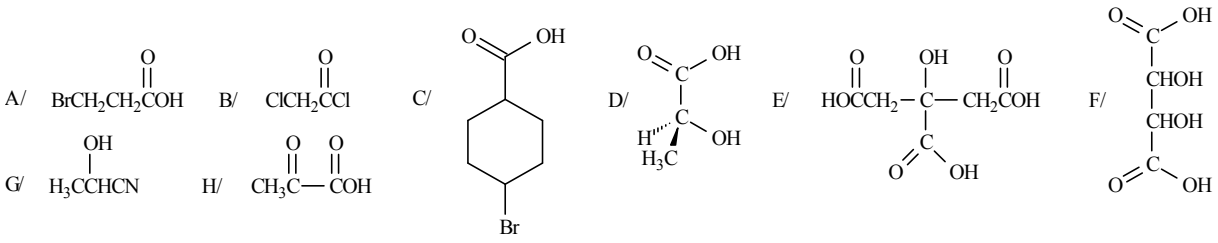
III. 

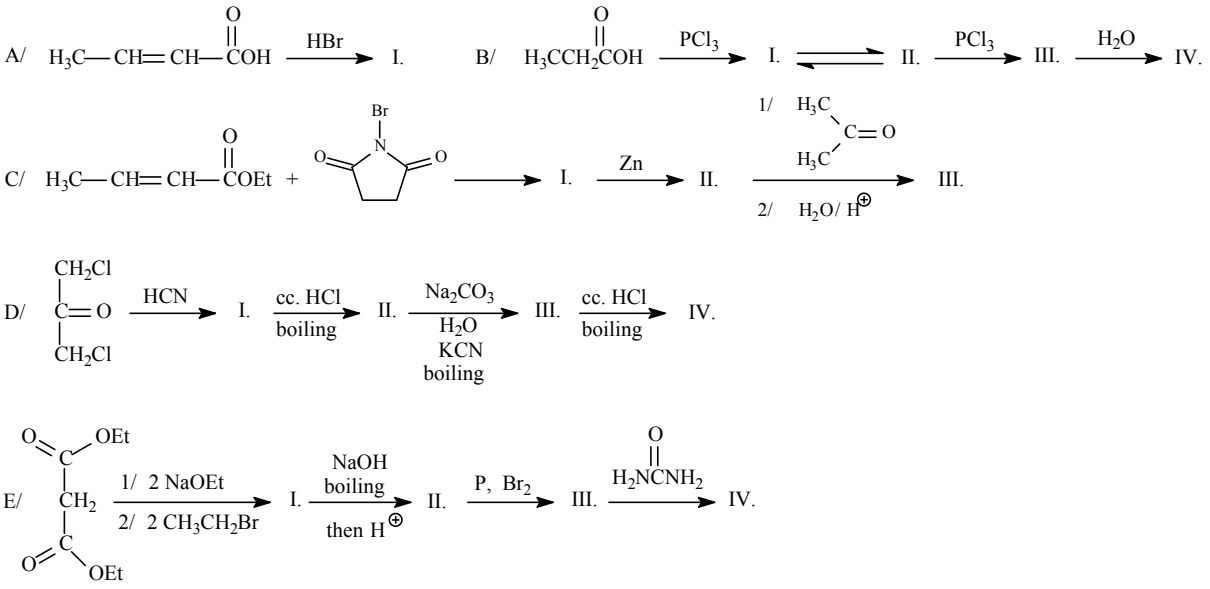
D/ I.  II.  III.  IV.  V. 

XI. Substituted carboxylic acids and substituted carboxylic acid derivatives (halogenated carboxylic acids, hydroxy-carboxylic acids, oxo-carboxylic acids, and their derivatives)

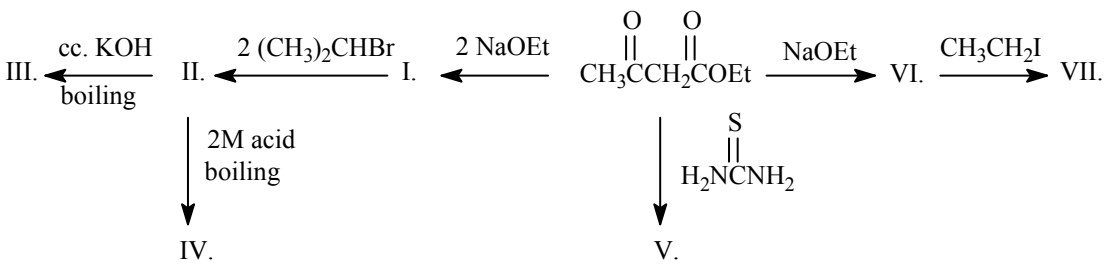
1. Give the IUPAC name of the following compounds!



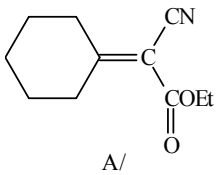
2. Draw the main products of the following reactions!

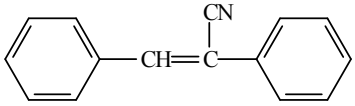


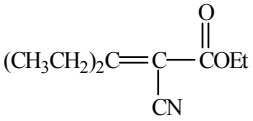
3. A/ Prepare racemic tartaric acid by cianohydrine synthesis from the appropriate carbonyl compound.
   B/ How does ethyl acetoacetate react in the following reactions?

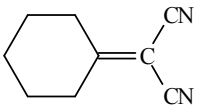


4. Prepare the following compounds by a reaction of a Knoevenagel type:

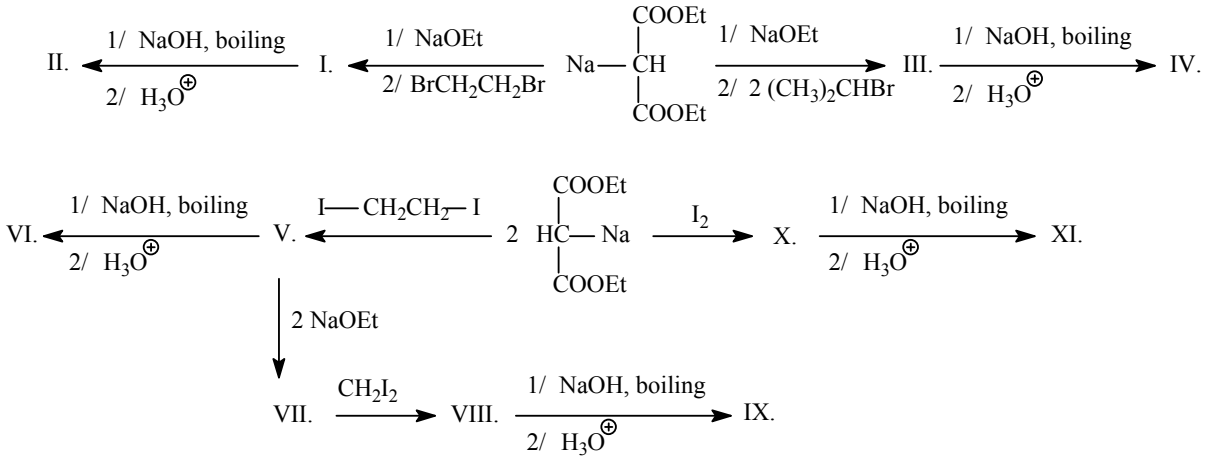

A/


B/

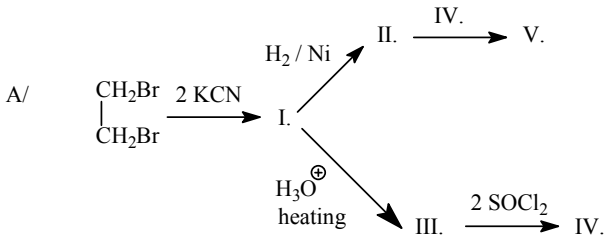

C/

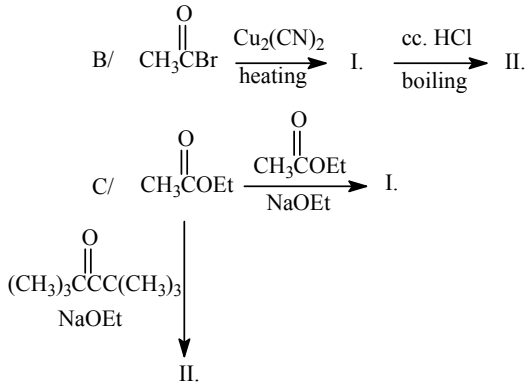

D/

5. How does the monosodium salt of diethyl malonate react in the following reactions?



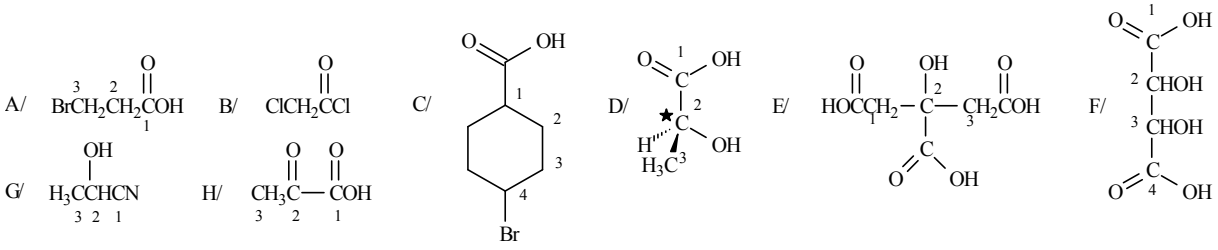
6. Draw the following reaction sequences:





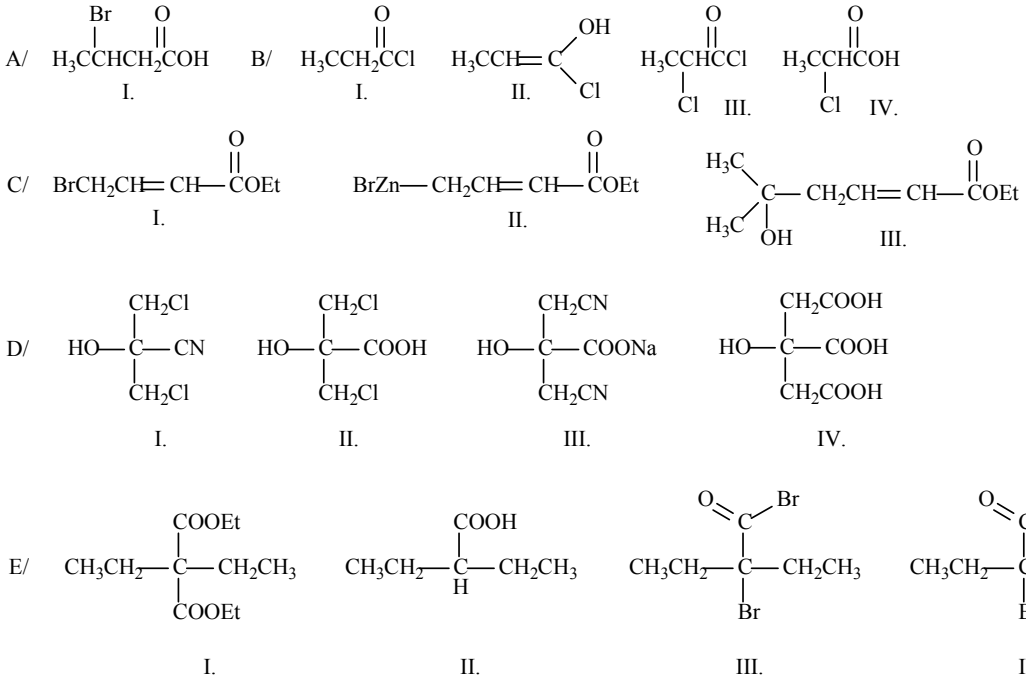
XI. ANSWERS

1.



A/ 3-bromopropionic acid, or 3-bromopropanoic acid
B/ chloroacetyl chloride
C/ 4-bromocyclohexanecarboxylic acid
D/ (*S*)-2-hydroxypropionic acid
E/ 2-hydroxypropane-1,2,3-tricarboxylic acid
F/ 2,3-dihydroxybutanoic acid
G/ 2-hydroxypropionitryle
H/ 2-oxopropionic acid

2.



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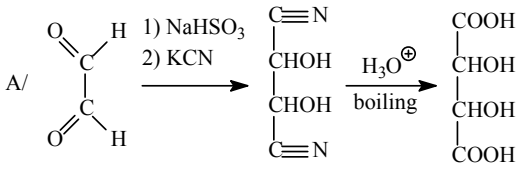
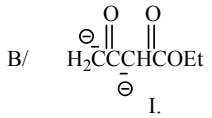
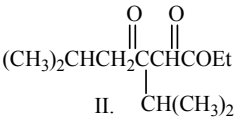




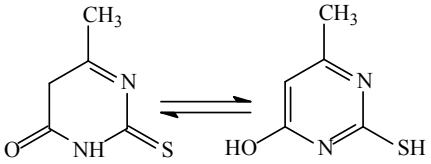
I.



II.

III.

IV.



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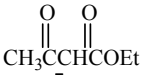

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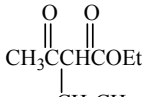
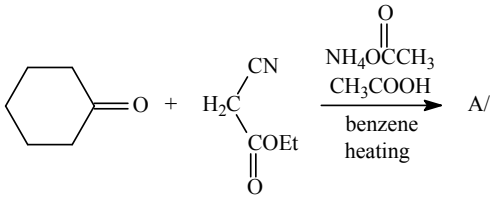
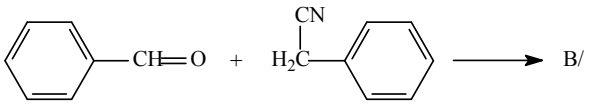
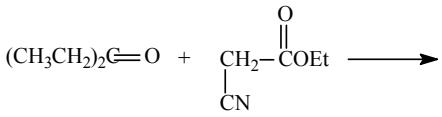


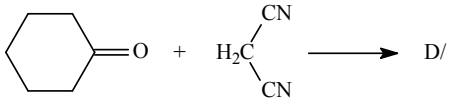
VII.

4.









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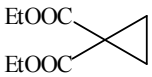

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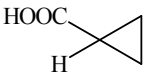

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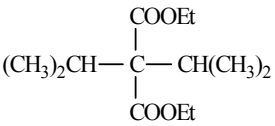

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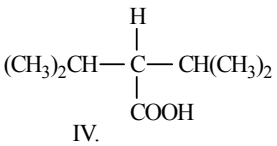

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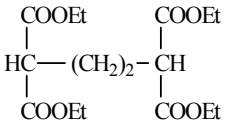

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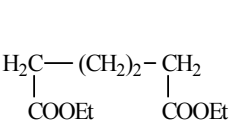

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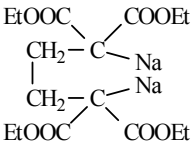

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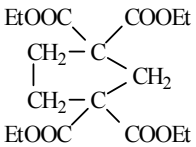

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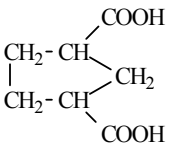

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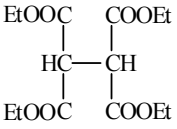

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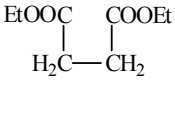
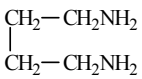
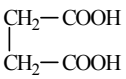


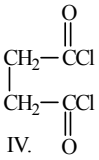
XI.

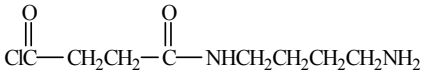
6.

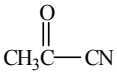
A/  I.

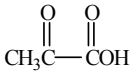
 II.

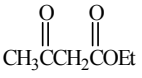
 III.

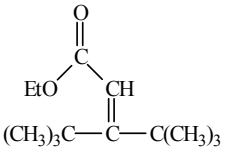
 IV.

 V.

B/  I.

 II.

C/  I.

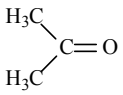
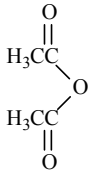
 II.

XII. Natural compounds

1. Draw the Haworth-Boeseken formulas of the following monosaccharides! What is their stereoisomer relationship (enantiomer, diastereomer, anomer) to each other?

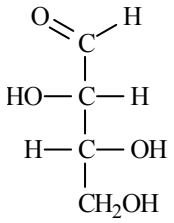
A) β-D-glucopyranose
B) α-D-glucopyranose
C) α-L-glucopyranose
D) β-L-glucopyranose

2. How does β-D-glucopyranose react in the following reactions?

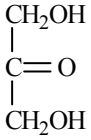
A/ $CH_3OH / H^{\oplus}$ B/ Br_2 / H_2O C/ $(C_6H_5)_3CCl$ / pyrirdine D/  in acidic medium E/  F/ HNO_3 / H_2O 100°C

G/ $NaBH_4$, then $H^{\oplus}$ H/ 3 $C_6H_5-NHNH_2$

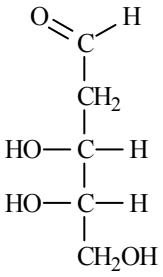
3. Classify the following monosaccharides (e.g., it is an aldohexose):



A/



B/

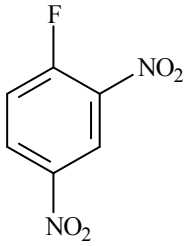


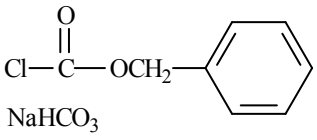
C/

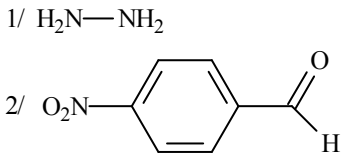
4. Prepare and name by IUPAC name the following amino acids:

A/ DL-isoleucine from diethyl malonate
B/ DL-phenylalanine by azlactone synthesis
C/ DL-alanine by Gabriel synthesis from the appropriate halogenated carboxylic acid
D/ DL-valine by Strecker synthesis from the appropriate aldehyde.

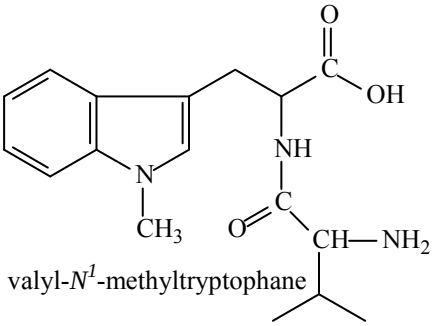
5. How does alanine react in the following reactions?

A/ 

B/ 

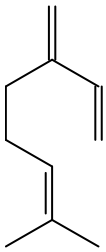
C/ 

6. Prepare valyl-N^1-methyltryptophane from the proper amino acid derivatives (functionalization of amino acids, coupling, cleavage of protecting groups):

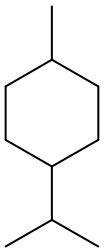


valyl-N^1-methyltryptophane

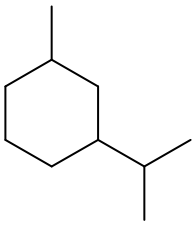
7. Draw and name types of joining of the isoprene units in the following compounds:



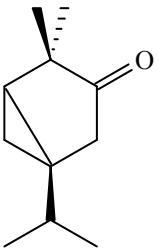
A/



B/



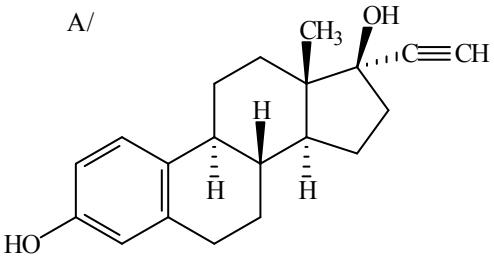
C/



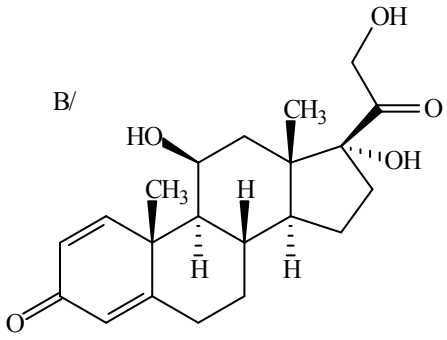
D/

8. Name the following compounds:

A/

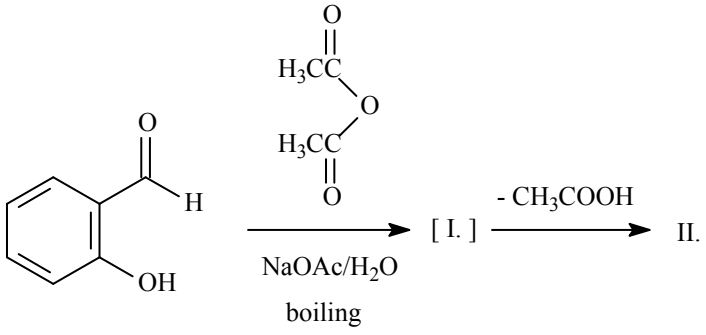


B/

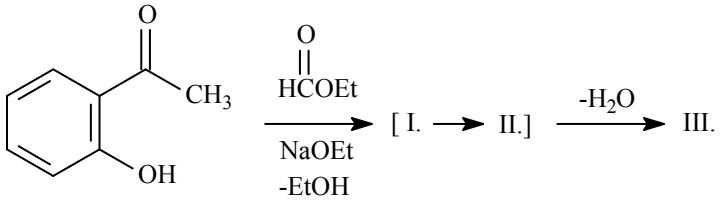


9. What compounds are formed in the following reactions?

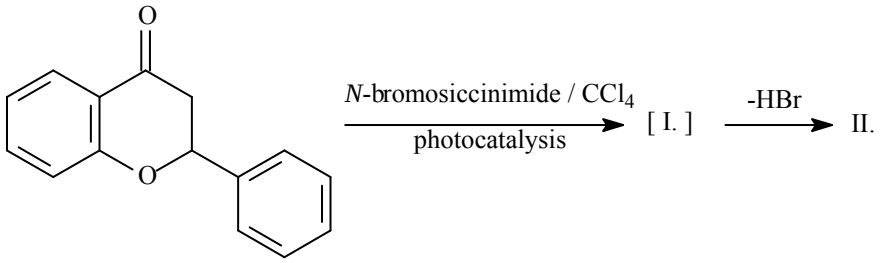
A)



B)

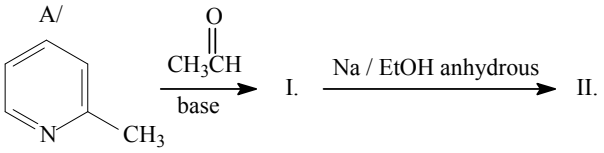


C)

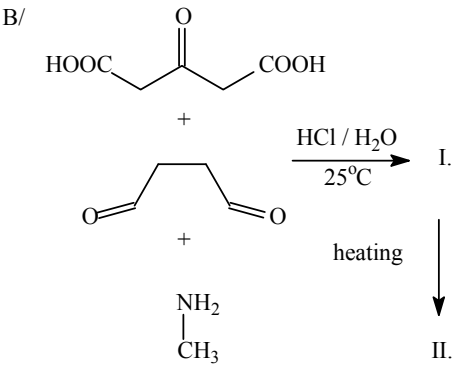


10. Draw the following reaction sequences:

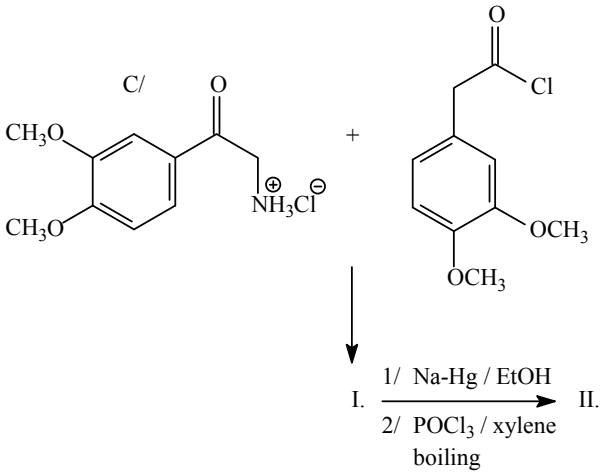
A/



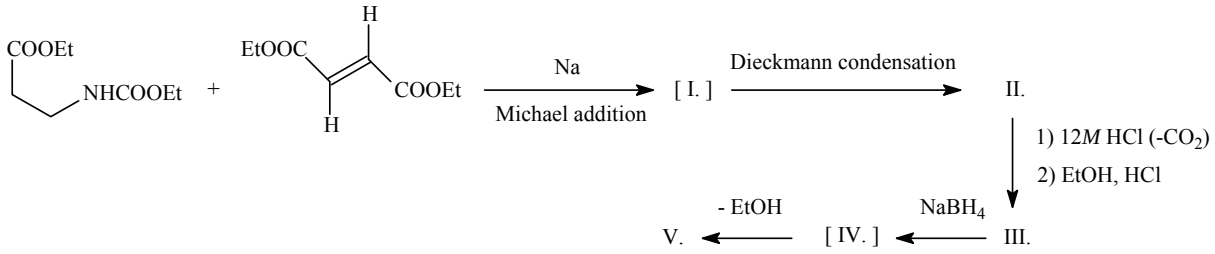
B/



C/

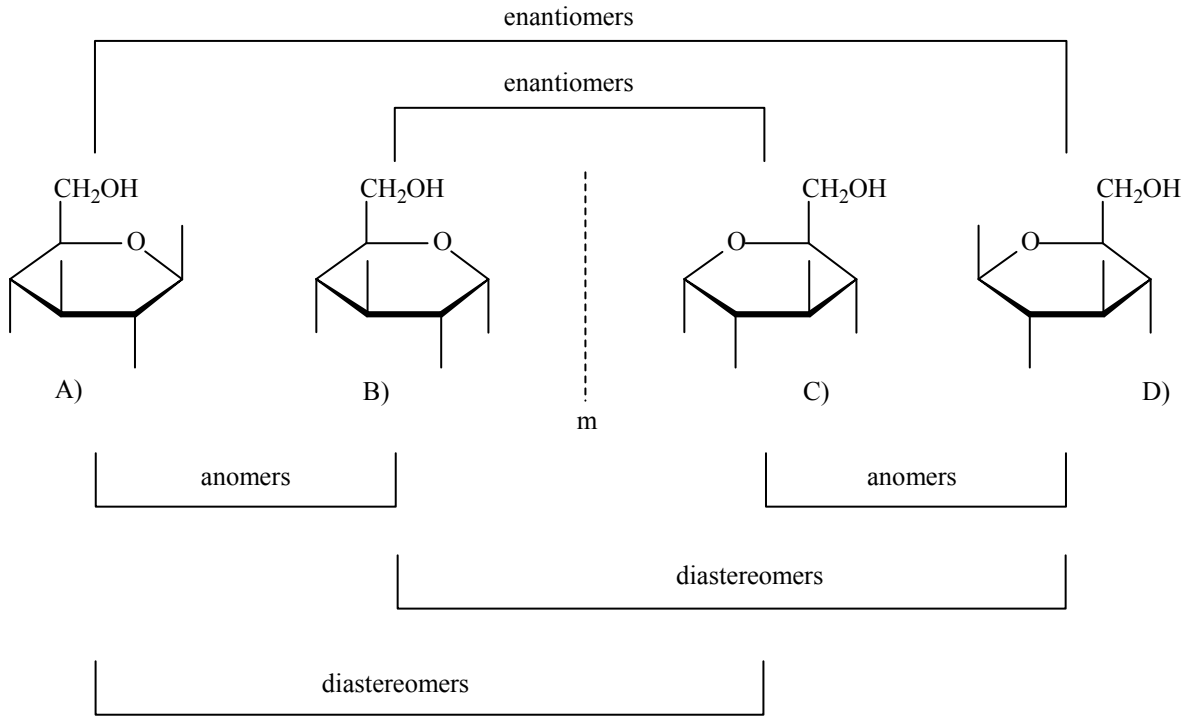


11. Draw the missing compounds in the following reaction sequence:

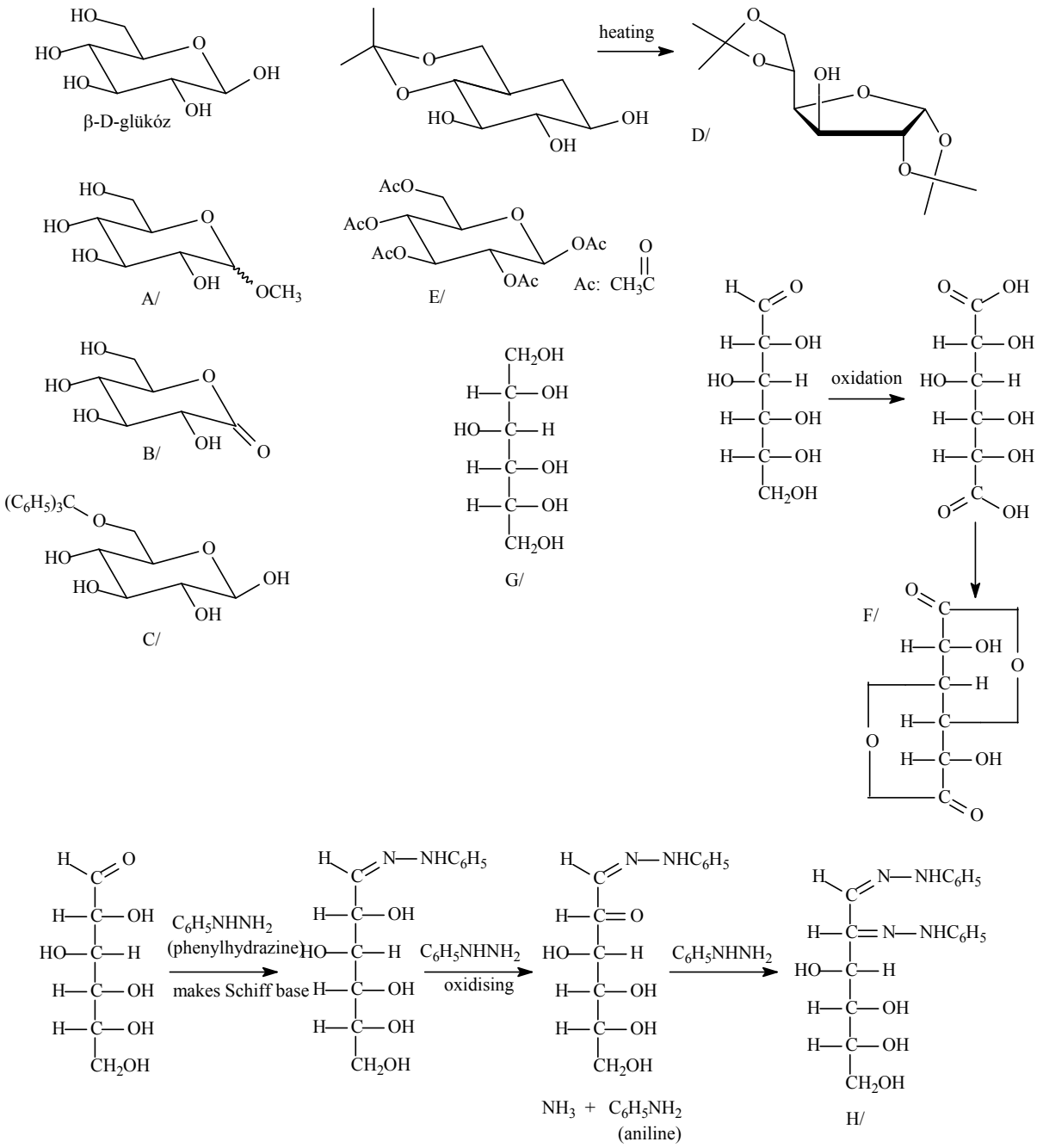


XII. ANSWERS

1.

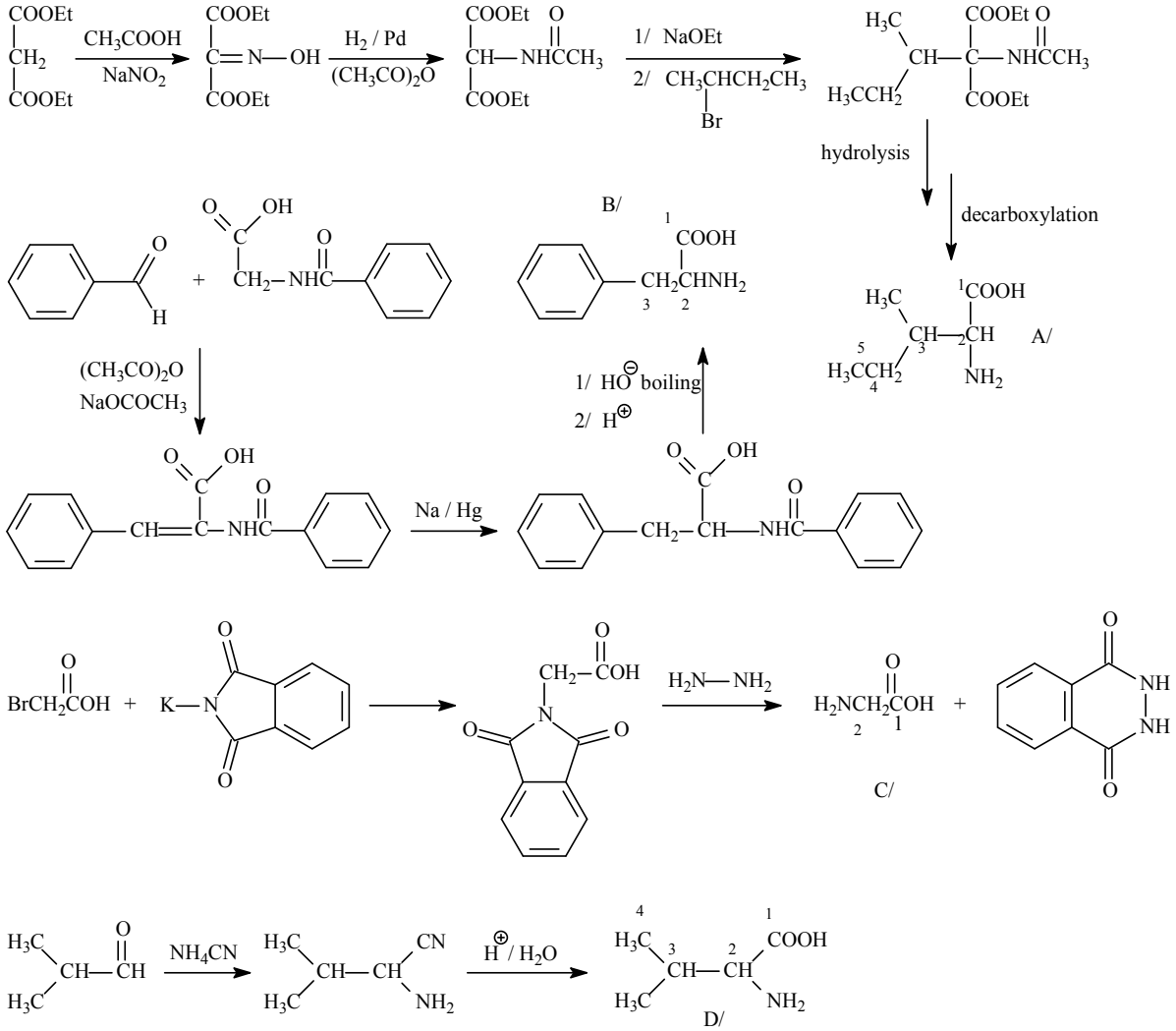


2.



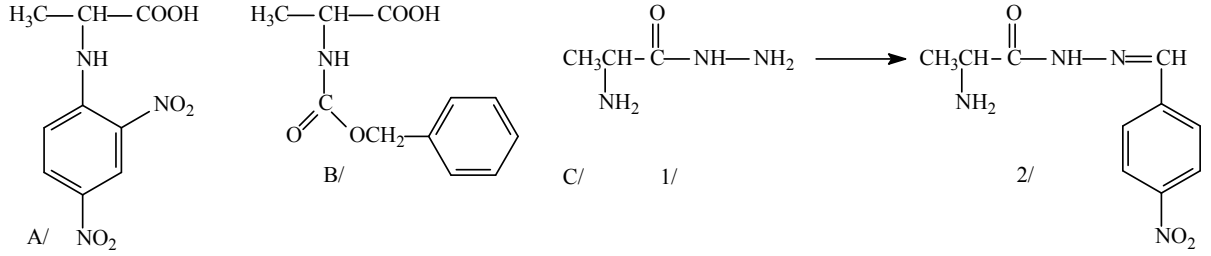
3. A/ aldotetrose
   B/ ketotriose
   C/ aldopentose

4.

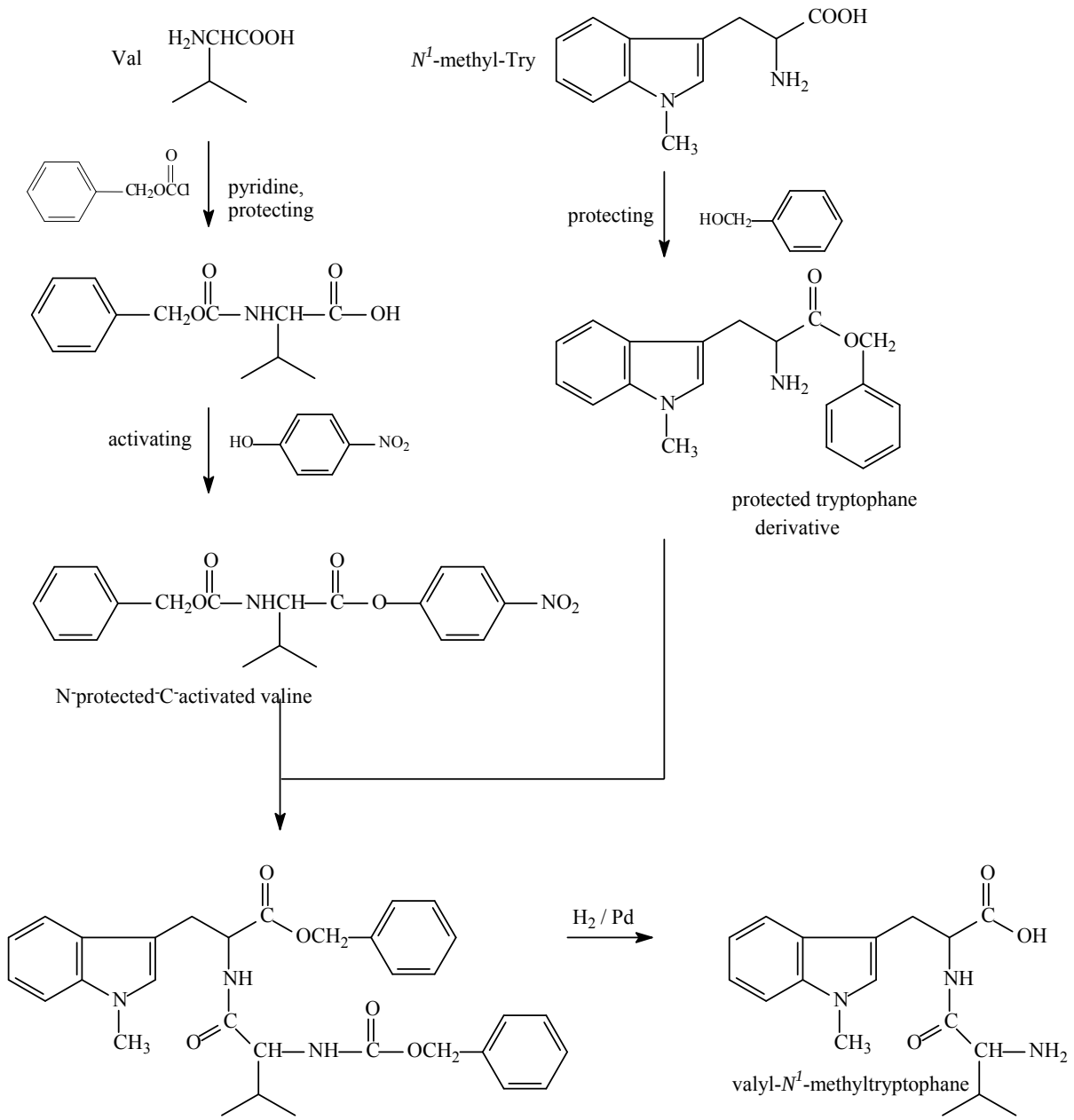


A/ 2-amino-3-methylpentanoic acid
B/ 2-amino-3-phenylacetic acid
C/ 2-aminoacetic acid
D/ 2-amino-3-methylbutanoic acid

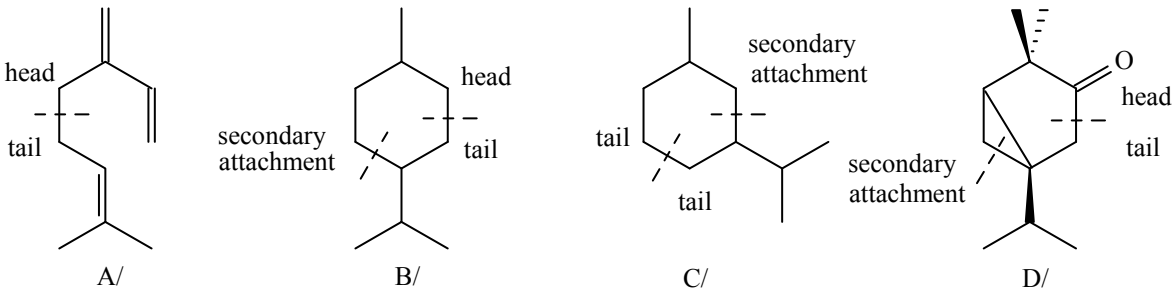
5.



6.

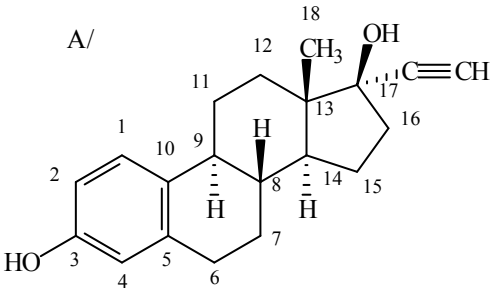

Val
H2NCHCOOH
N1-methyl-Try
COOH
NH2
N
CH3
pyridine,
protecting
protecting
HOCH2
activating
HO
NO2
OCH2
protected tryptophane
derivative
N-protected-C-activated valine
H2 / Pd
OH
valyl-N1-methyltryptophane

7.

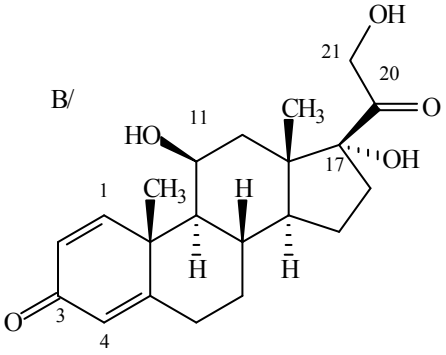

head
tail
A/
secondary
attachment
head
tail
B/
secondary
attachment
tail
tail
C/
O
head
tail
secondary
attachment
D/

8.

A/



B/

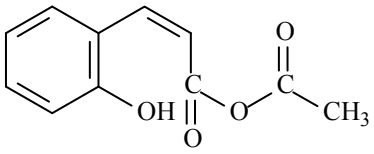


A/ 17α-ethynylestra-1,3,5(10)-trien-3,17β-diol

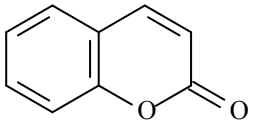
B/ 11β,17α,21-trihydroxypregna-1,4-dien-3,20-dione

9.

A)

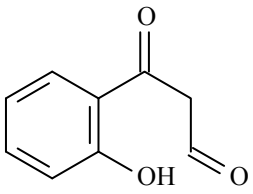


I. mixed anhydride

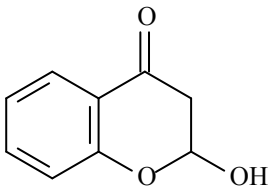


II. cumarine

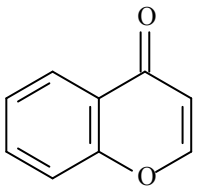
B)



I.

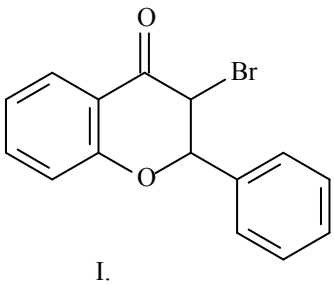


II.

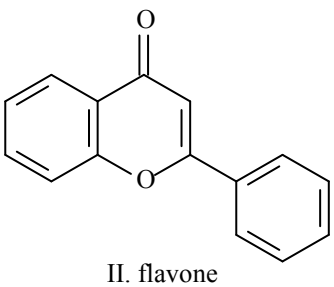


III. chromone

C)

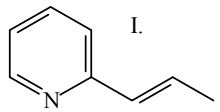


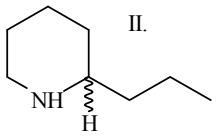
I.

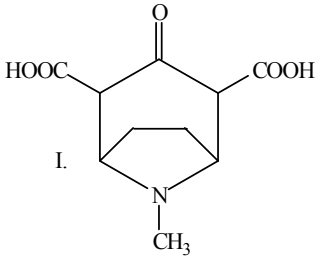


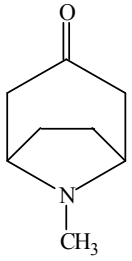
II. flavone

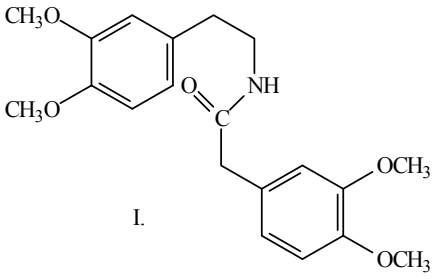
10.

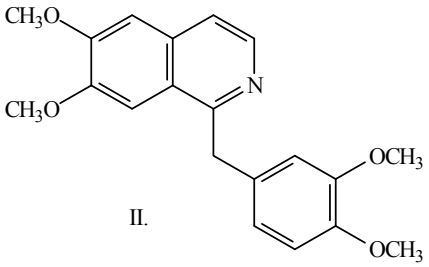
A/  I.

 II.

B/  I.

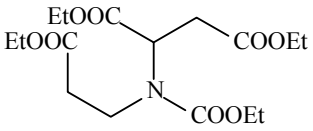
 II.

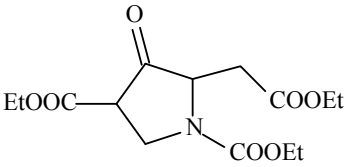
C/  I.

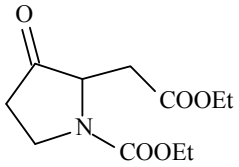
 II.

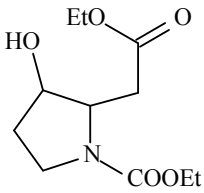
A / II. (±)-coniine
B / II. tropinone
C / II. papaverine

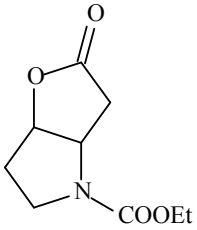
11.

 I.

 II.

 III.

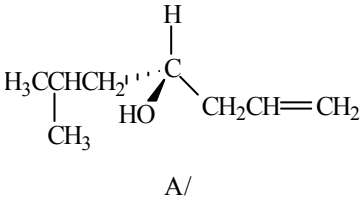
 IV.

 V.

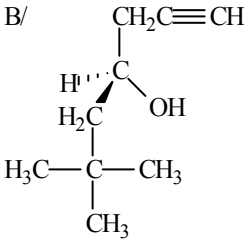
XIII. Isomerisms, acid-base properties, Principle of Retaining Orbital Symmetry (*Woodward-Hoffmann Rules*)

1. Draw the 3D structural formulas of
   A/ *(R)*-3-hydroxy-3-methylhex-5-en-1-al
   B/ *(S)*-6-hydroxy-5-methylhex-2-en-1-al

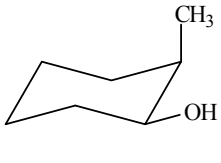
2. Name the following compounds:



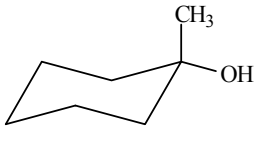
A/

B/ 

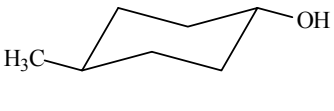
3. Select the chiral ones among the following compounds:



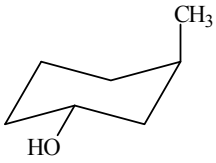
A/



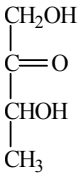
B/



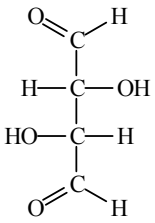
C/



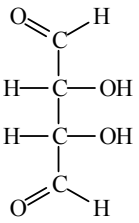
D/



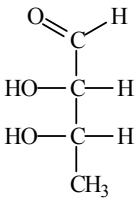
E/



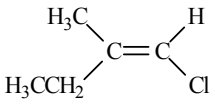
F/



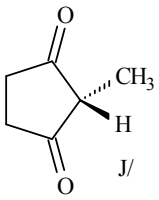
G/



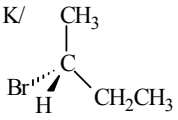
H/



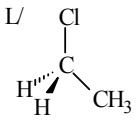
I/



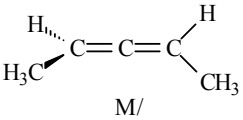
J/



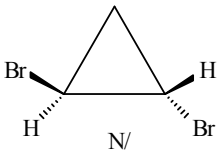
K/



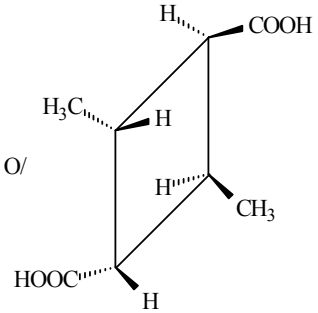
L/



M/

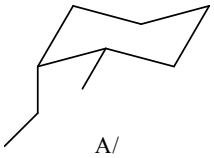


N/

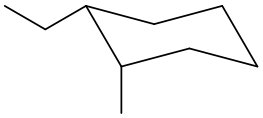


O/

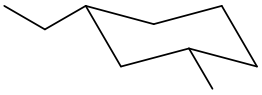
4. Determine the type of isomerism (constitutional, conformational, configurational) of the following pairs of structures (A:B, A:C, A:D, B:C, B:D, C:D relationships):



A/



B/

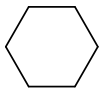


C/

D/

5. Choose the isomers from the following pairs of compounds, determine the type of isomerism:

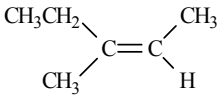
A/ $CH_3CH_2CH_3$ $CH_3CH{=}CH_2$

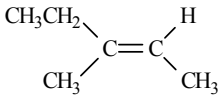
B/ $CH_3CH{=}CH_2$ 

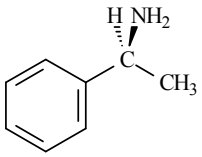
C/ $CH_3CH_2CH_2CH_3$ $CH_3CH(CH_3)$

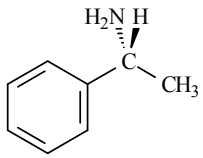
D/ $CH_3CH_2CH{=}CH_2$ $CH_3CH{=}CHCH_3$

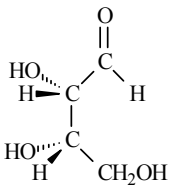
E/ $CH_3CH(Cl)CH_3$ $CH_3CH_2CH_2Cl$

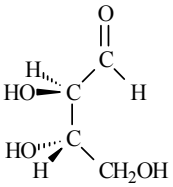
F/ 



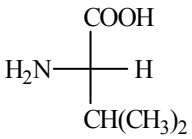
G/ 



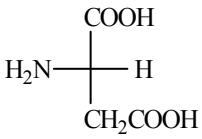
H/ 



6. Draw 3D structural formulas for the following amino acids drawn by Fischer projection:

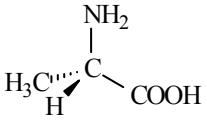


Val

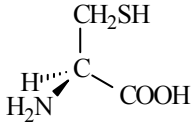


Asp

7. Draw Fischer projections for the following amino acids drawn by 3D structural formulas:

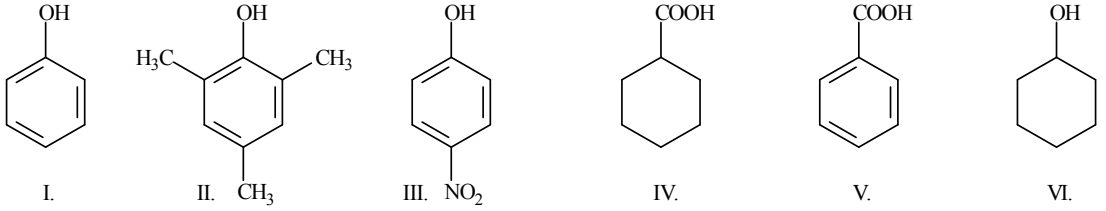


Ala

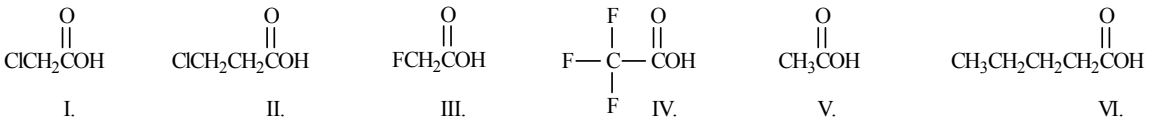


Cys

8. Make increasing acidity order of the following compounds (in aqueous solutions):

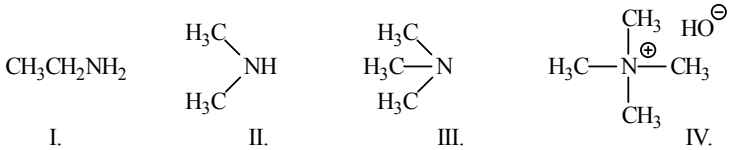
A/ 

I. II. III. IV. V. VI.

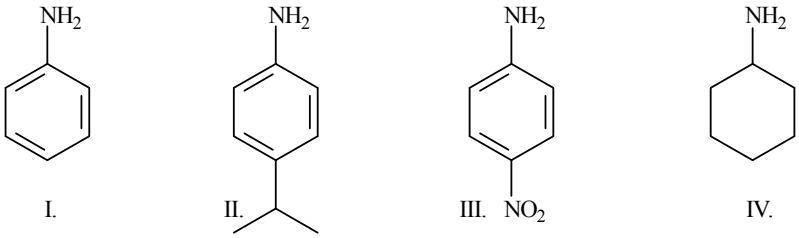
B/ 

I. II. III. IV. V. VI.

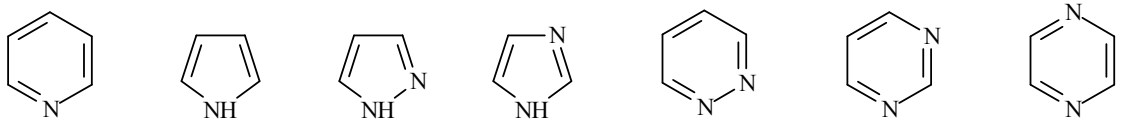
9. Make increasing basicity order of the following compounds (in aqueous solutions):

A/ 

I. II. III. IV.

B/ 

I. II. III. IV.

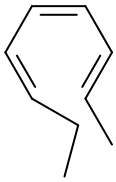
C/ 

I. II. III. IV. V. VI. VII.

10. Draw the structural formula of the product formed during the electrocyclisation reaction of:
A/ from (2*E*,4*E*)-hepta-2,4-diene by photochemical catalysis (hν);
B/ from (2*Z*,4*E*)-hepta-2,4-diene by thermal catalysis (Δ).

I/ How do you call the previous reactions?
II/ How many electrons contribute in these reactions?
III/ Which elements of symmetry should we examine the *orbitals participating in the reaction*?

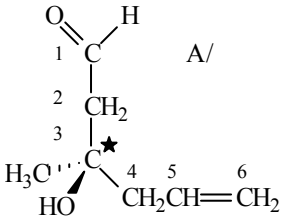
11. What is produced from the following compound:



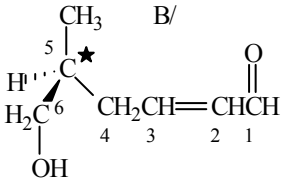
A/ by photochemical reaction;
B/ by thermal reaction?
Do the processes run by conrotation or disrotation?

XIII. ANSWERS

1.

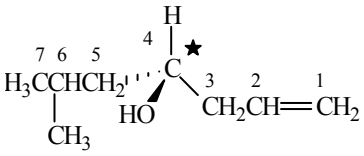


A/

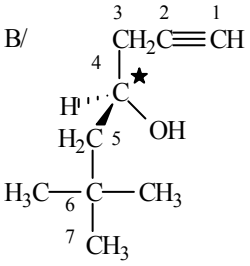


B/

2.



A/



B/

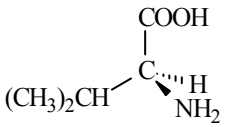
A/ *(R)*-6-methylhept-1-en-4-ol
B/ *(S)*-6,6-dimethylhept-1-yn-4-ol

3. A/ D/ E/ F/ H/ K/ M/ N/: chiral molecules.

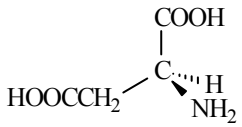
4.
A:B conformational B:C constitutional
A:C constitutional B:D configurational
A:D configurational C:D constitutional isomers.

5.
A/ not isomers (different general formulas)
B/ not isomers (different general formulas)
C/ structural isomers- different carbon skeletons (straight or branched chains)
D/ structural isomers- positional isomers (there is a difference in the position of a double bond)
E/ structural isomers- positional isomers (there is a difference in the position of a chlorine atom)
F/ stereoisomers - geometric (configurational) isomers (*Z*, or *E* isomers)
G/ stereoisomers – configurational enantiomers (*S*, or *R* optical isomers)
H/ stereoisomers – configurational diastereomers (optical isomers) (they are differing in the configurations of less, than all stereogenic centres)

6.

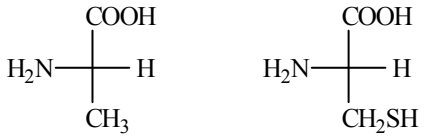


Val



Asp

7.

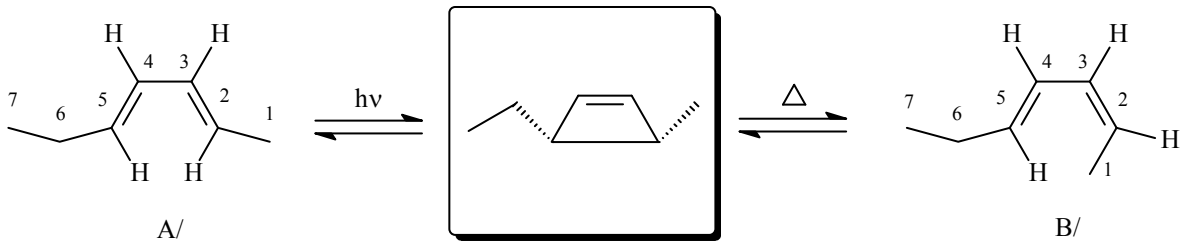


Ala Cys

8. A A/ VI < II < I < III < IV < V
   B/ VI < V < II < I < III < IV

9. A/ III < I < II < IV
   B/ III < I < II < IV
   C/ II < VII < VI < V < III < I < IV
   pK_a (conjugated acid, 9. C/): (-0.27) < 0.65 < 1.30 < 2.33 < 2.47 < 5.23 < 6.95

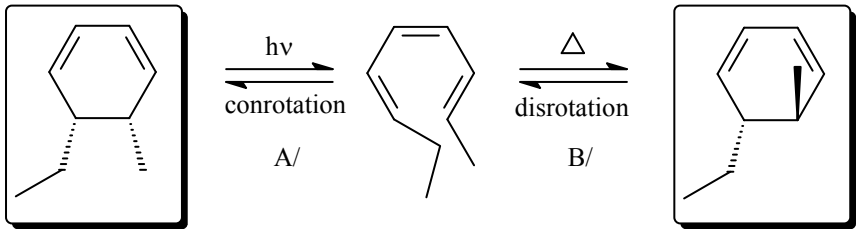
10.



A/ B/

I/ Pericyclic reaction
II/ 4 electrons are participating in them
III/ A/ to the symmetry plane (m)
B/ to the symmetry axis of C_2

11.

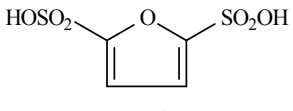


A/ B/

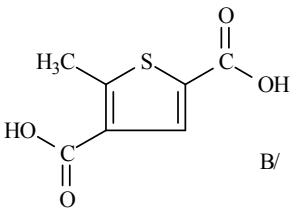
A/ by conrotation
B/ by disrotation

XIV. Heterocyclic compounds I. 5-membered heteroaromatic compounds with π-electron excess and their derivatives

1.Name the following compounds:

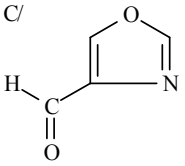


A/

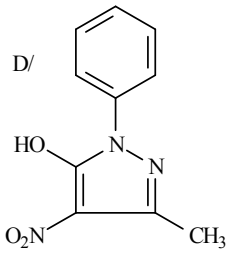


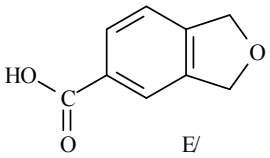
B/

C/

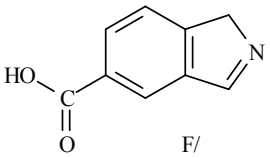


D/

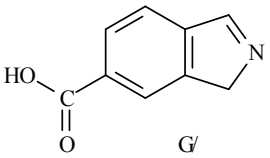




E/

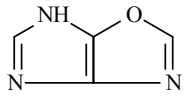


F/

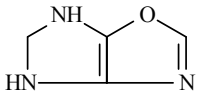


G/

H/

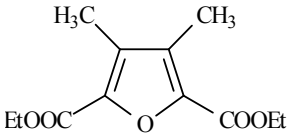


I/

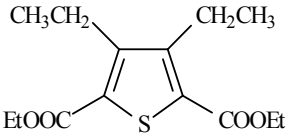


2. Draw structural formulas of the following heterocyclic compounds:
   A/ 3-methyl-2(3*H*)-oxofuran-4-carboxylic acid
   B/ methyl-2-formylfuran-3-carboxylate
   C/ 1*H*-5-ethylpyrrol-3-carbaldehyde
   D/ 1*H*-benzo[*c*]pyrazole
   E/ 1*H*,4*H*-pyrrolo[2,3-*d*]imidazole
   F/ 6*H*-furo[2,3-*c*]pyrrole-3-carbaldehyde
   G/ 3*H*-furo[3,4-*b*]pyrrole

3. Prepare the following compounds by ring synthesis:

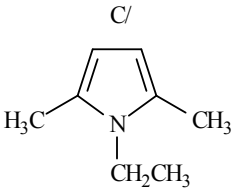


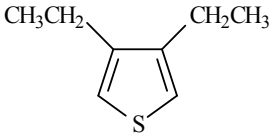
A/



B/

C/

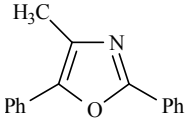




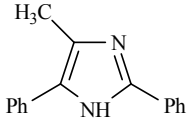
D/

A/ and B/ from a 1,2-diketone
C/ and D/ from a 1,4-diketone

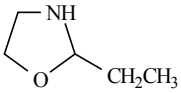
4. Prepare the following heterocyclic compounds by cyclisation:



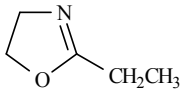
A/



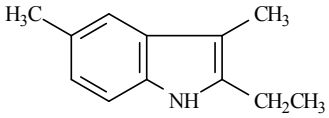
B/



C/



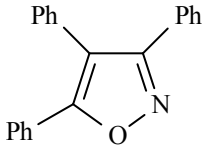
D/



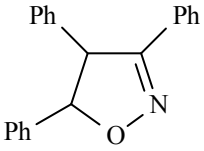
E/

Ph: phenyl group

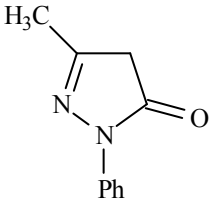
5. Prepare the following compounds:



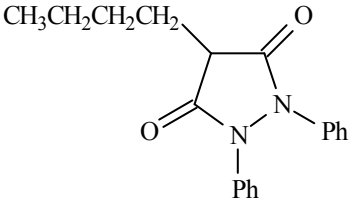
A/



B/



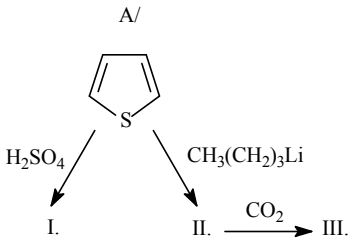
C/

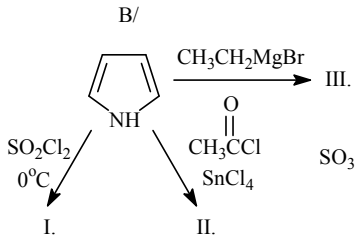


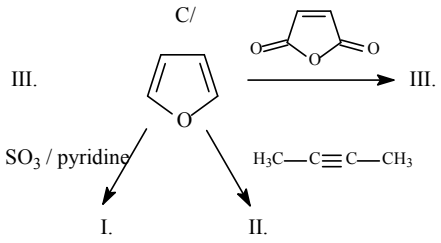
D/

A/ and B/ by 1,3-dipolar cycloaddition
C/ starting from ethyl acetoacetate
D/ starting from diethyl malonate substituted appropriately.

6. Draw products of the following reactions:

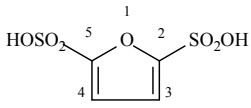




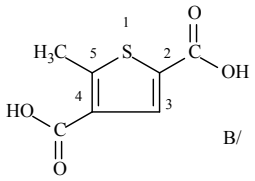


XIV. ANSWERS

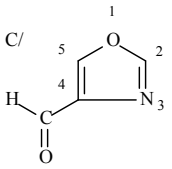
1.



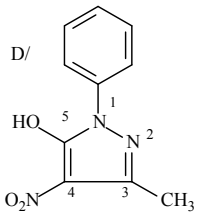
A/



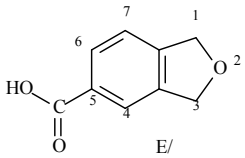
B/



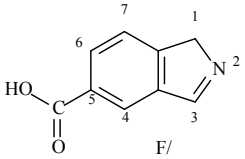
C/



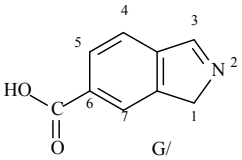
D/



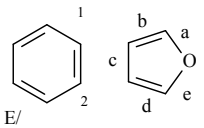
E/



F/



G/



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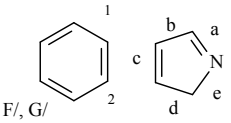
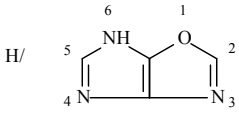
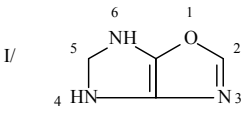


F/, G/

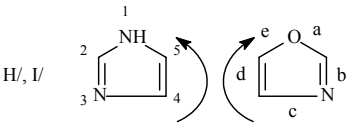
(we regularly do not write the locant for benzene, in such case)



H/



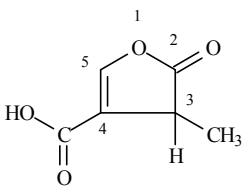
I/



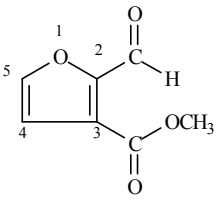
H/, I/

A/ furan-2,5-disulfonic acid
B/ 5-methylthiophene-2,4-dicarboxylic acid
C/ oxazol-4-carbaldehyde
D/ 1-phenyl-3-methyl-4-nitro-1*H*-pyrazol-5-ol
E/1,3-dihydrobenzo[*c*]furan-5-carboxylic acid
F/ 1*H*-benzo[*c*]pyrrole-5-carboxylic acid
G/ 1*H*-benzo[*c*]pyrrole-6-carboxylic acid
H/ 6*H*-imidazo[4,5-*d*]oxazol
I/ 5,6-dihydro-4*H*-imidazo[4,5-*d*]oxazol

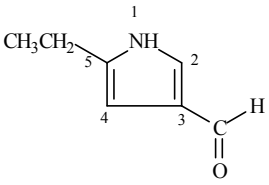
2.



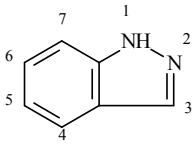
A/



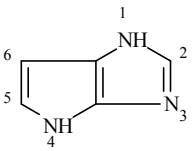
B/



C/



D/



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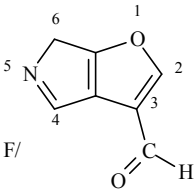

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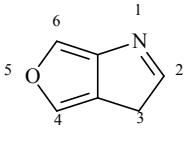
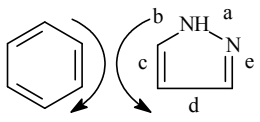
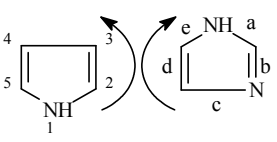
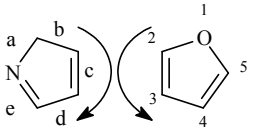
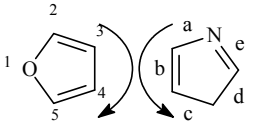


G/









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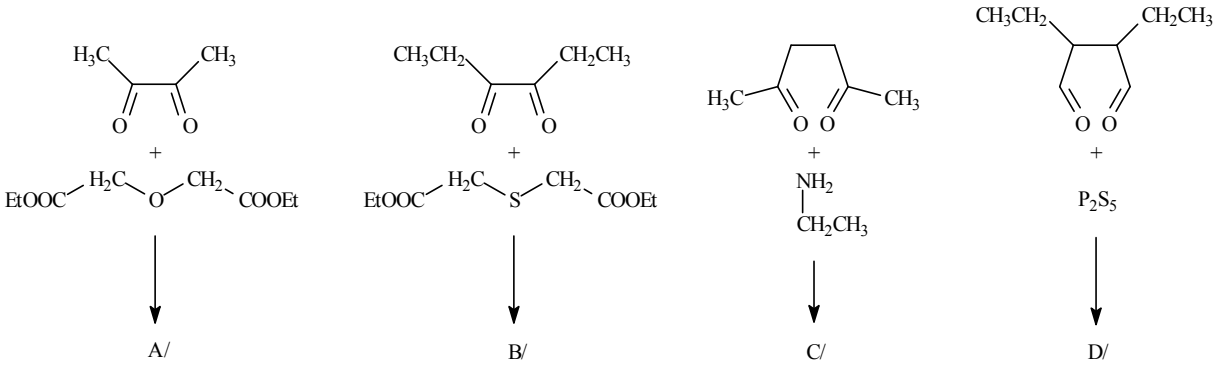

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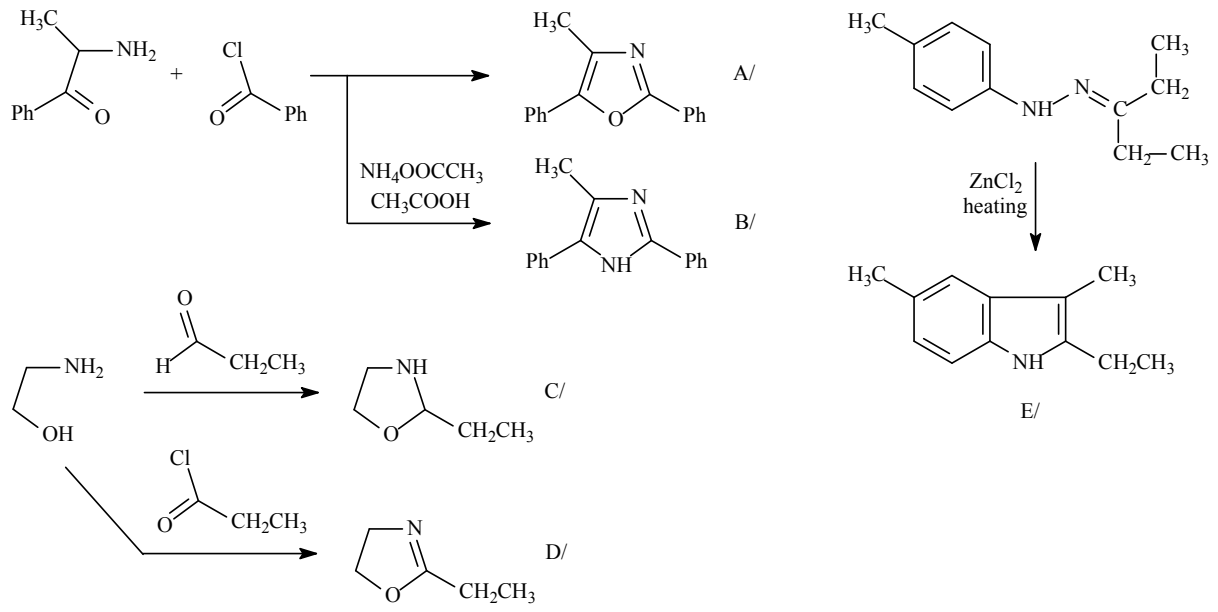

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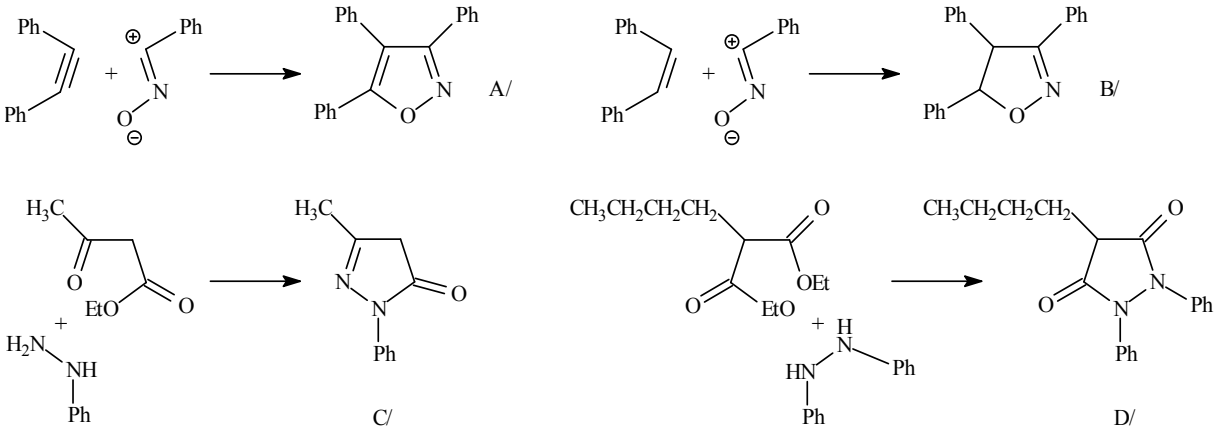

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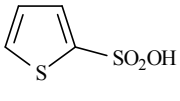
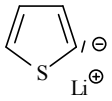
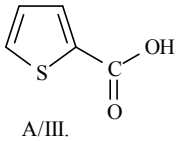


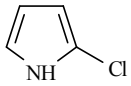
A/I.



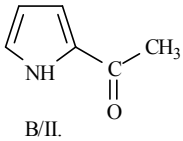
A/II.



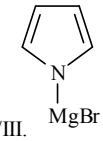
A/III.



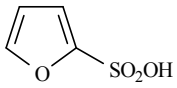
B/I.



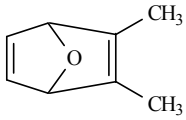
B/II.



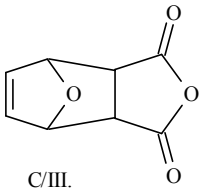
B/III.



C/I.



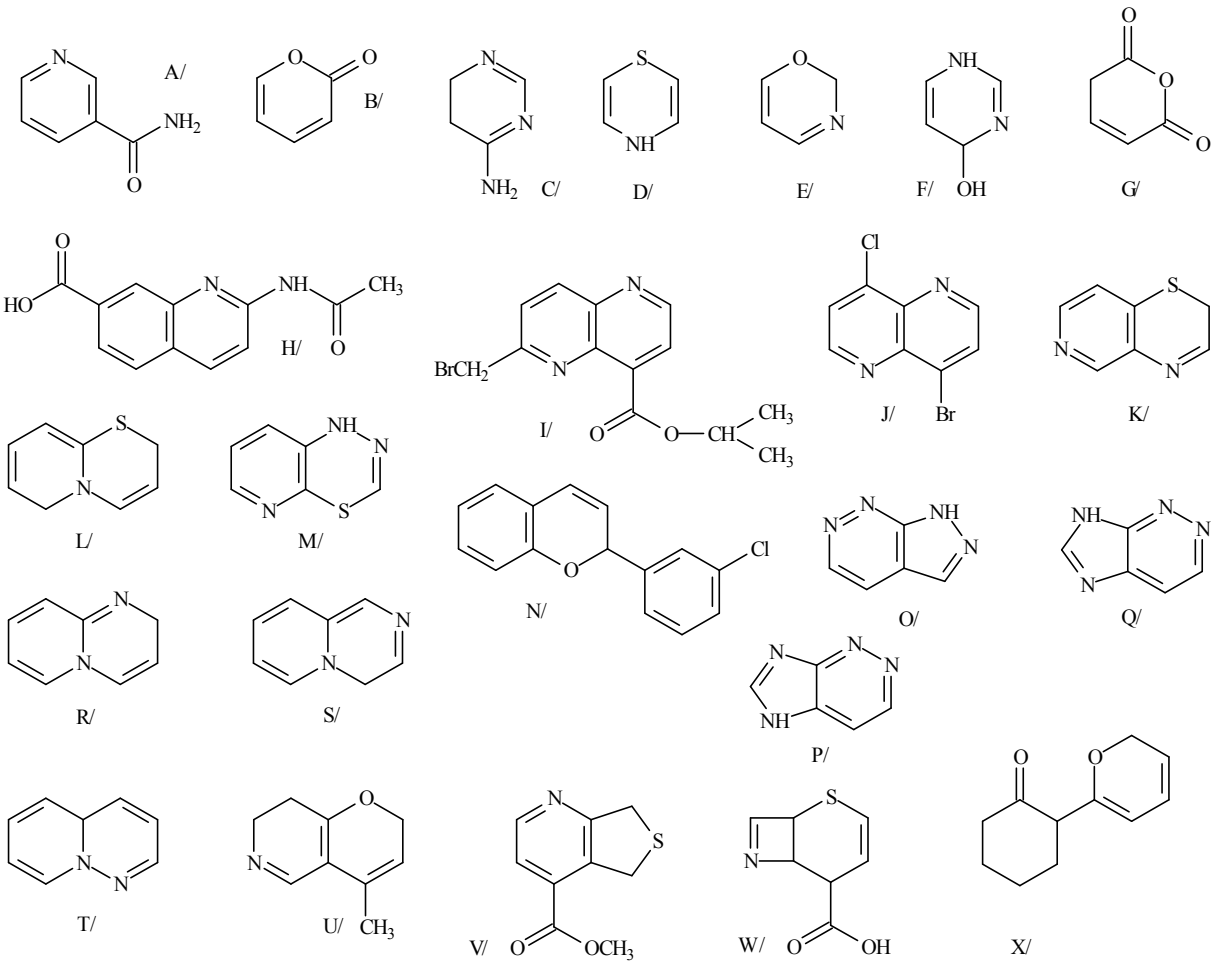
C/II.



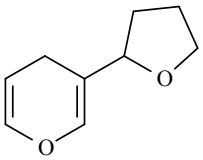
C/III.

XV. Heterocyclic compounds II. 6-membered heteroaromatic compounds with π-electron deficiency and their derivatives

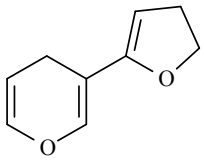
1. Name the following compounds:



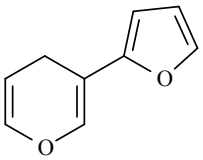
2. Name the following isolated bicyclic compounds:



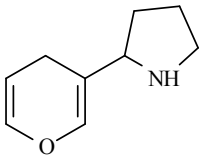
A/



B/



C/



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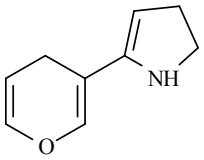

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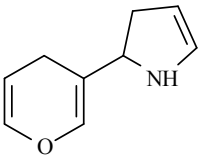

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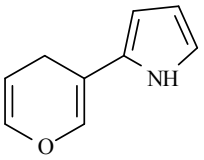

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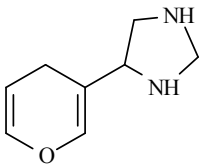

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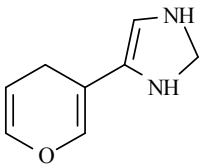

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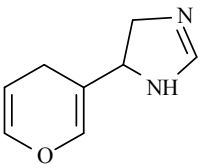

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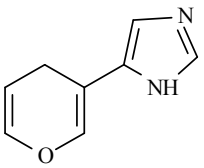

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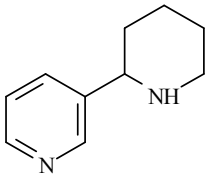

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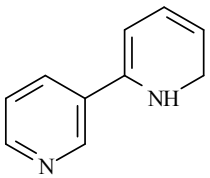

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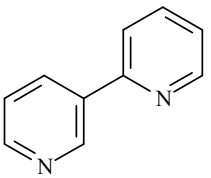

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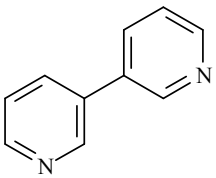

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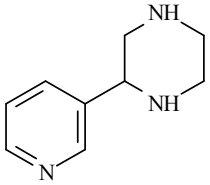

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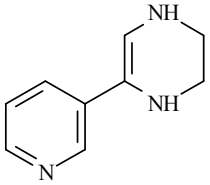

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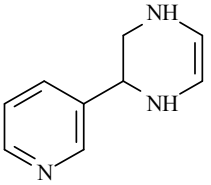

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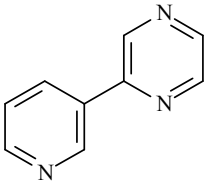
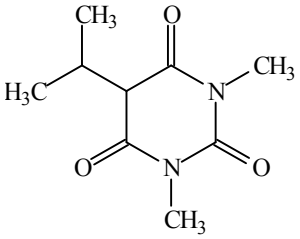


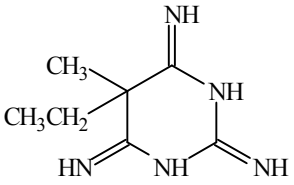
S/

3. Draw structural formulas of the following heterocyclic compounds:
A/ methyl-4-chloromethylisoquinoline-7 carboxylate
B/ sodium-6-aminomethylquinoline-4 carboxylate
C/ 6-ethylaminopyrido[3,4-*b*]pyridine-4-carbaldehyde
D/ pyrido[3,4-*c*]pyridazine
E/ pyrido[3,2-*d*]pyrimidine-6-carbonitryle
F/ 1*H*-pyrazolo[3,4-*b*]pyrazine

4. Prepare the following compounds by cyclisation:



A/



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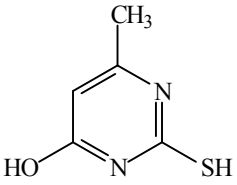

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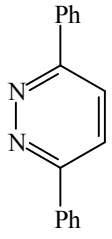

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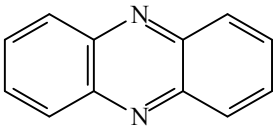

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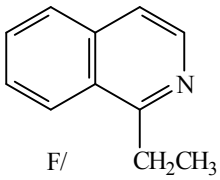

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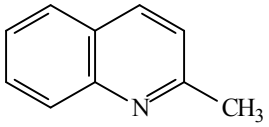
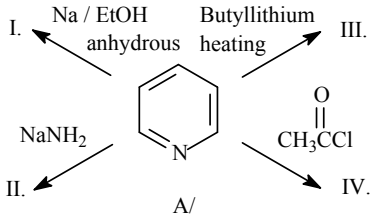
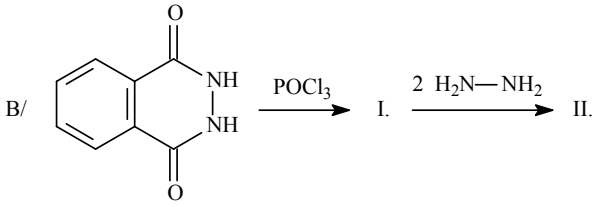


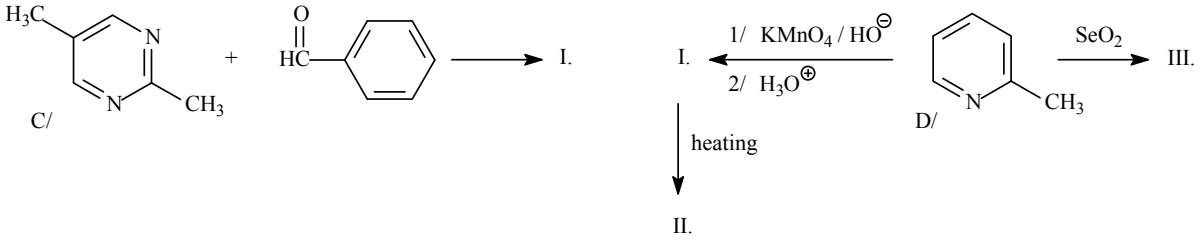
G/

5. Draw products of the following reactions:

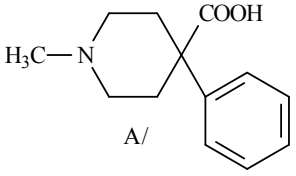


A/

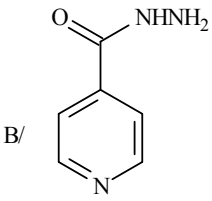




6. Suggest a synthetic pathways for the preparations of the following drugs:



A/



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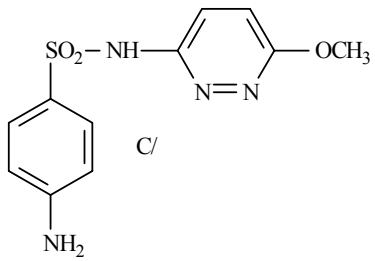
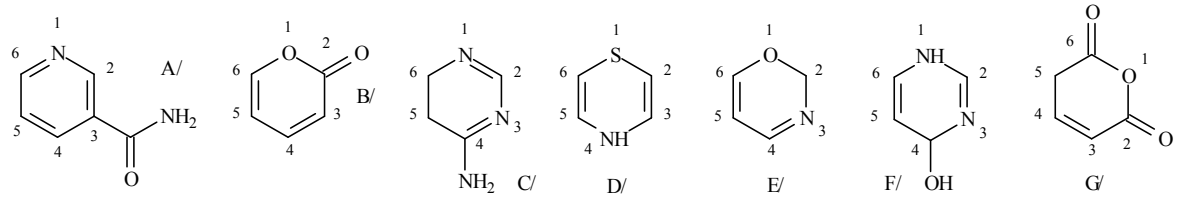


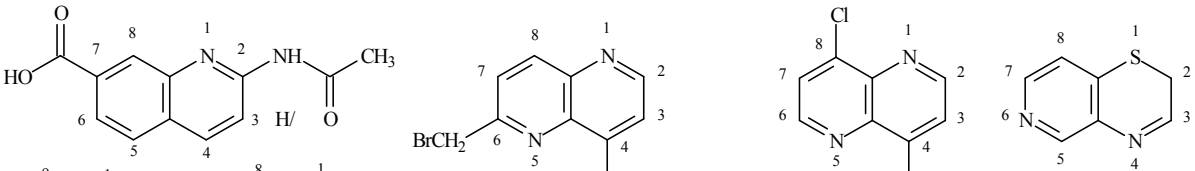
C/

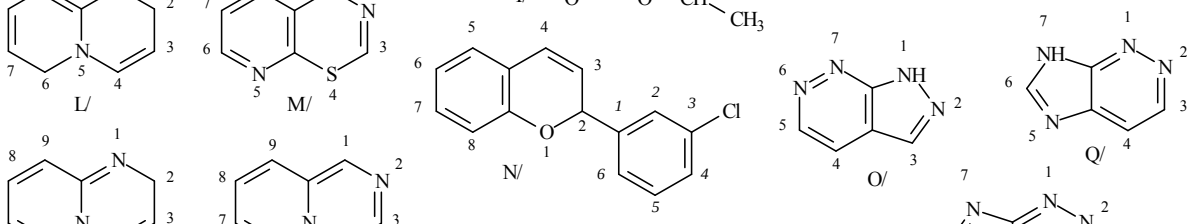
A/ by cyclisation
B/ starting from 4-methylpyridine
C/ starting from sulfanylamide

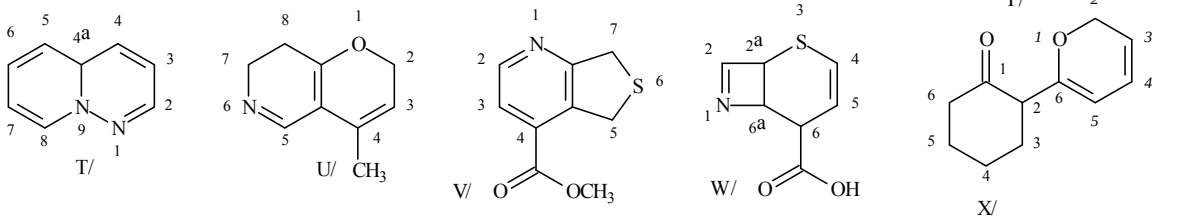
XV. ANSWERS

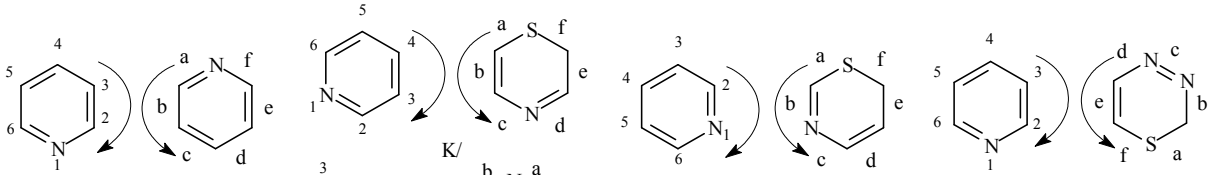
1.

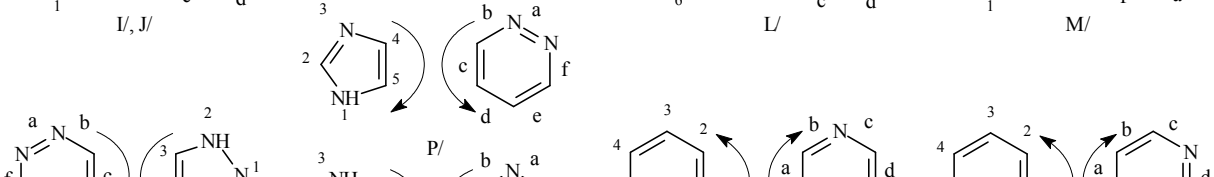


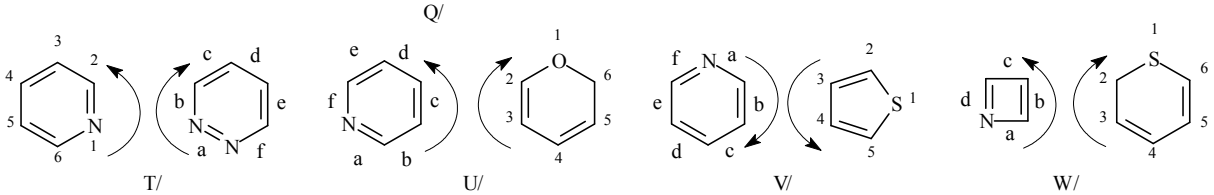






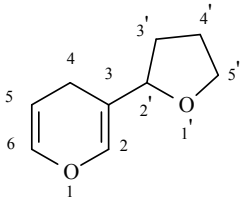




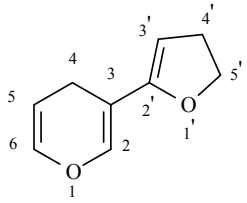


A/ pyridin-3-carboxamide
B/ 2*H*-pyran-2-one
C/ 5,6-dihydropyrimidin-4-amine
D/ 4*H*-1,4-thiazine
E/ 2*H*-1,3-oxazine
F/ 1,4-dihydropyrimidin-4-ol
G/ pent-2-en-dioic acid anhydride or: 2*H*-piran-2,6(5*H*)-dione
H/ 2-acetylaminoquinoline-7-carboxylic acid
I/ isopropyl-6-bromomethylpyrido[3,2-*b*]pyridin-4 carboxylate
J/ 4-bromo-8-chloropyrido[3,2-*b*]pyridin
K/ 2*H*-pyrido[4,3-*b*][1,4]thiazine
L/ 2*H*,6*H*-pyrido[2,1-*b*][1,3]thiazine
M/ 1*H*-pyrido[3,2-*e*][1,3,4]thiadiazine
N/ 2*H*-2-(3-chlorophenyl)-chromene
O/ 1*H*-pyrazolo[3,4-*c*]pyridazine
P/ 5*H*-imidazo[4,5-*c*]pyridazine
Q/ 7*H*-imidazo[4,5-*c*]pyridazine
R/ 2*H*-pyrido[1,2-*a*]pyrimidine
S/ 4*H*-pyrido[1,2-*a*]pyrazine
T/ 4a*H*-pyrido[1,2-*b*]pyridazine
U/ 7,8-dihydro-4-methyl-2*H*-pirano[3,2-*c*]pyridine
V/ methyl 5,7-dihydro-thieno[3,4-*b*]pyridin-4-carboxylate
W/ 6,6a-dihydro--2a*H*-thiapyrano[3,2-*b*]azet-6-carboxylic acid
X/ 2-(2*H*-pyran-6-yl)-cyclohexanone

2.



A/



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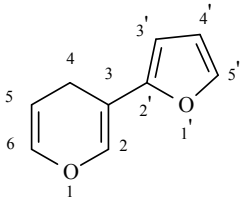

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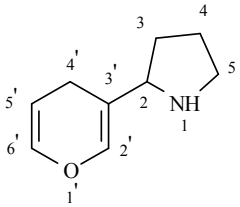

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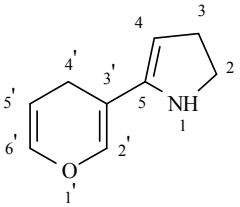

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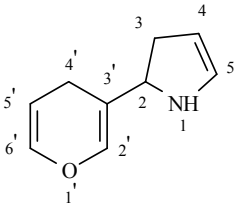

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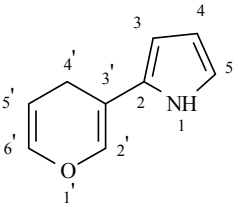

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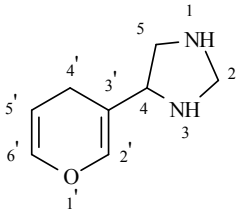

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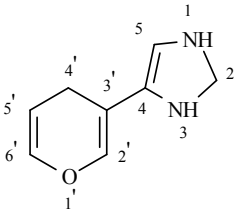

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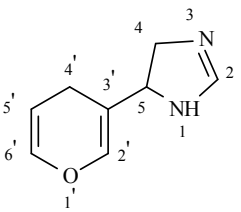

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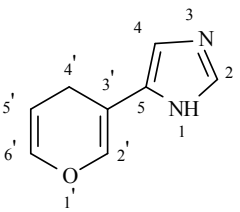

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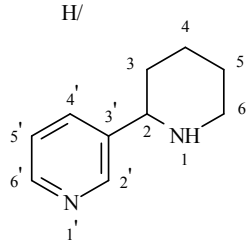

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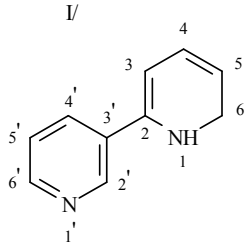

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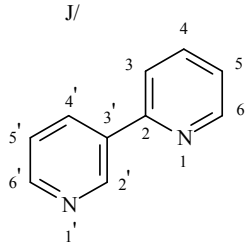

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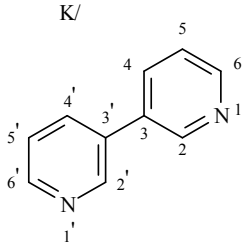

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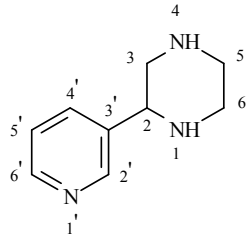

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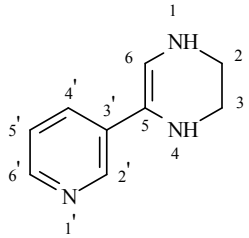

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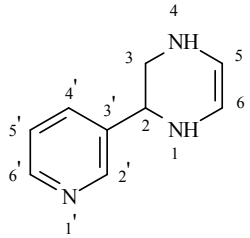

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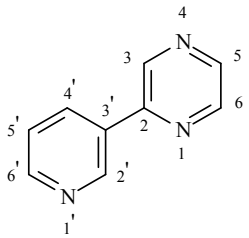
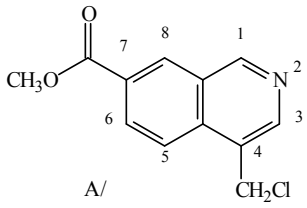


S/

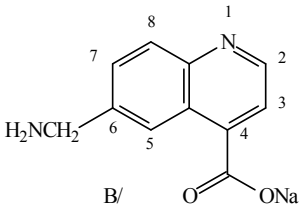
A/ 3-(tetrahydrofuran-2-yl)-4*H*-pyrane
B/ 3-(4,5-dihydrofuran-2-yl)-4*H*-pyrane
C/ 3-(furan-2-yl)-4*H*-pyrane
D/ 2-(4*H*-pyran-3-yl)-pyrrolidine
E/ 5-(4*H*-pyran-3-yl)-2,3-dihydro-1*H*-pyrrole
F/ 2-(4*H*-pyran-3-yl)-2,3-dihydro-1*H*-pyrrole
G/ 2-(4*H*-pyran-3-yl)-1*H*-pyrrole
H/ 4-(4*H*-pyran-3-yl)-imidazolidine
I/ 4-(4*H*-pyran-3-yl)-2,3-dihydro-1*H*-imidazole
J/ 5-(4*H*-pyran-3-yl)-4,5-dihydro-1*H*-imidazole

K/ 5-(4*H*-pyrane-3-yl)-1*H*-imidazole
L/ 1,2,3,4,5,6-hexahydro-[2,3']bipyridinyl
M/ 1,6-dihydro-[2,3']bipyridinyl
N/ [2,3']bipyridinyl
O/ [3,3']bipyridinyl
P/ 2-(pyridin-3-yl)-piperazine
Q 5-(pyridin-3-yl)-1,2,3,4-tetrahydropyrazine
R/ 2-(pyridin-3-yl)-1,2,3,4-tetrahydropyrazine
S/ 2-(pyridin-3-yl)-pyrazine

3.



A/



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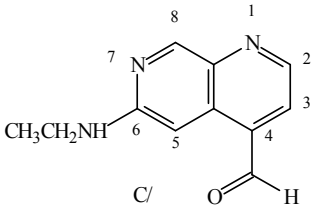
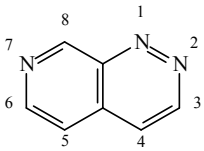
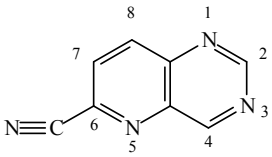
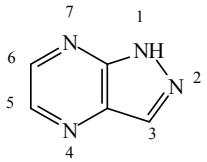


C/

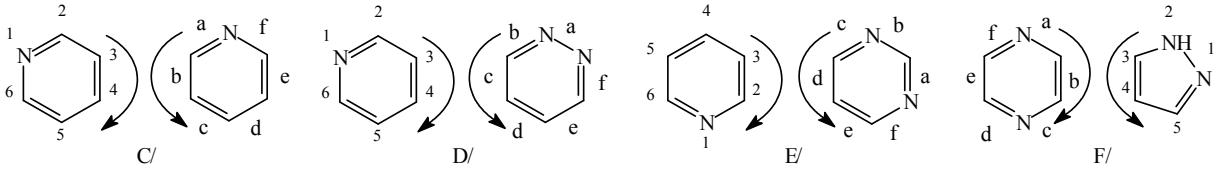

D/



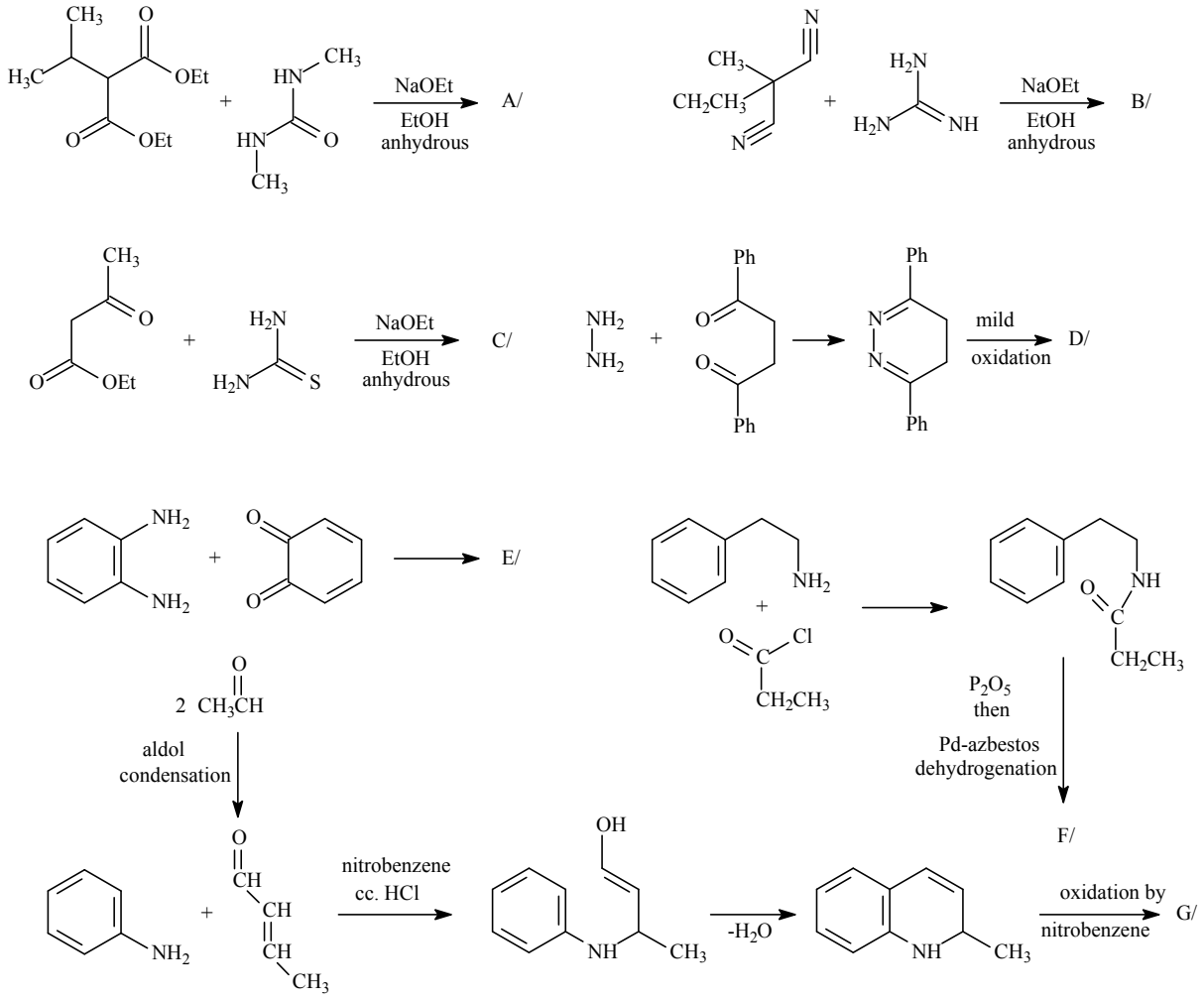
E/



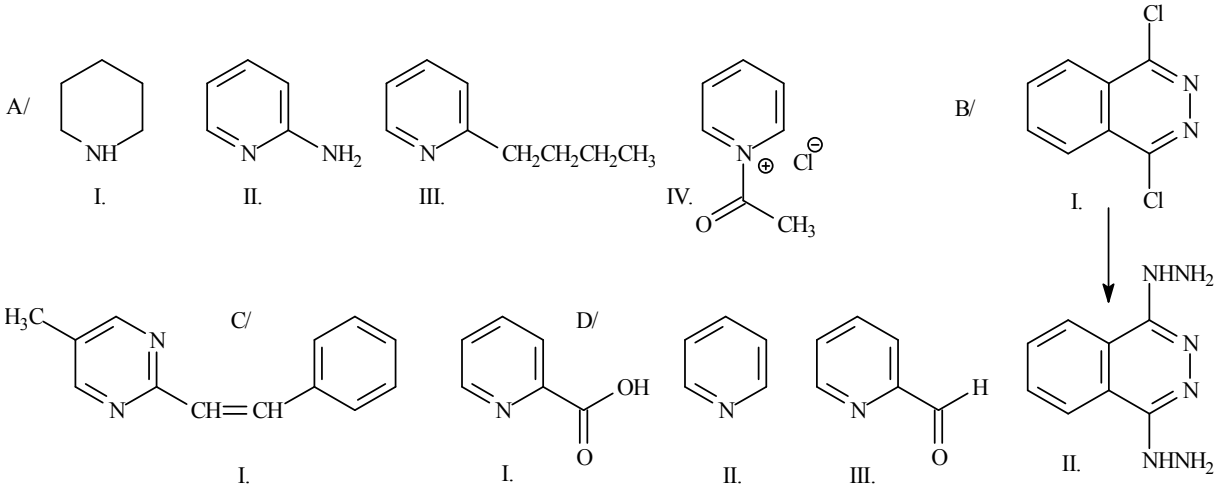
F/


C/ D/ E/ F/

4.


NaOEt
EtOH
anhydrous
A/
B/
C/
mild
oxidation
D/
E/
2 CH3CH
aldol
condensation
P2O5
then
Pd-azbestos
dehydrogenation
F/
nitrobenzene
cc. HCl
-H2O
oxidation by
nitrobenzene
G/

5.



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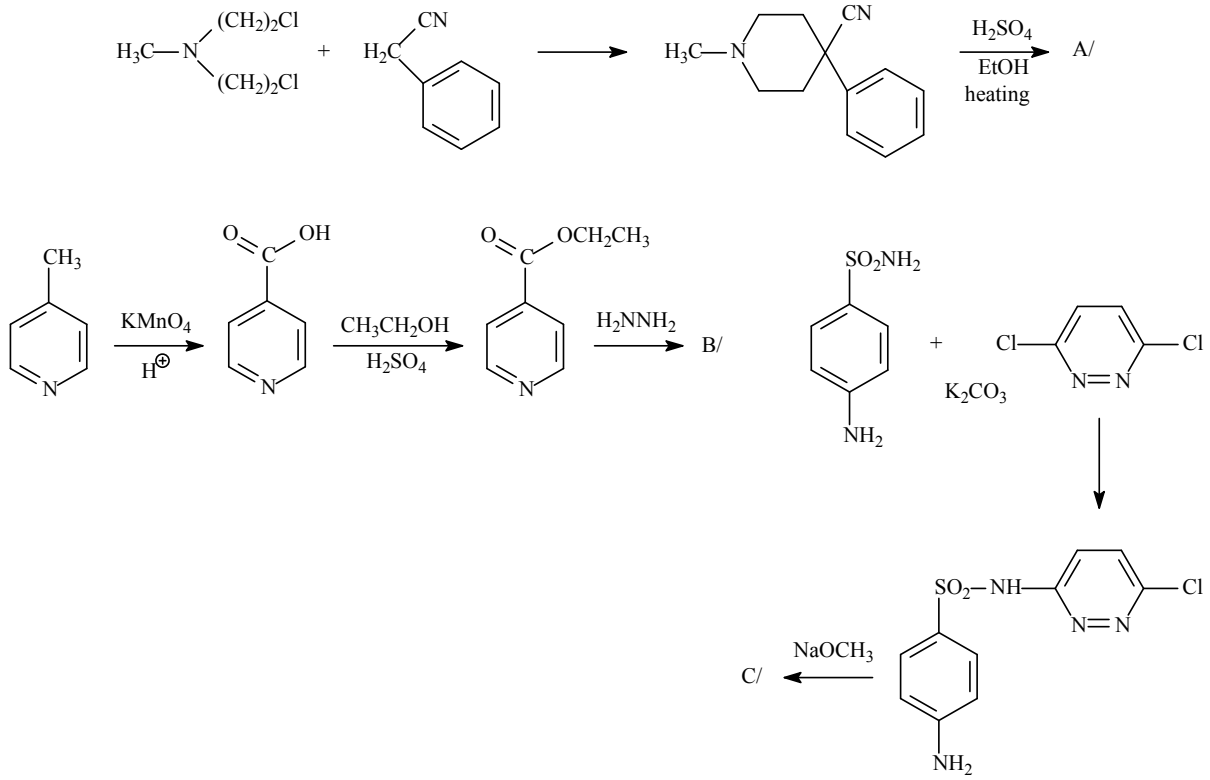
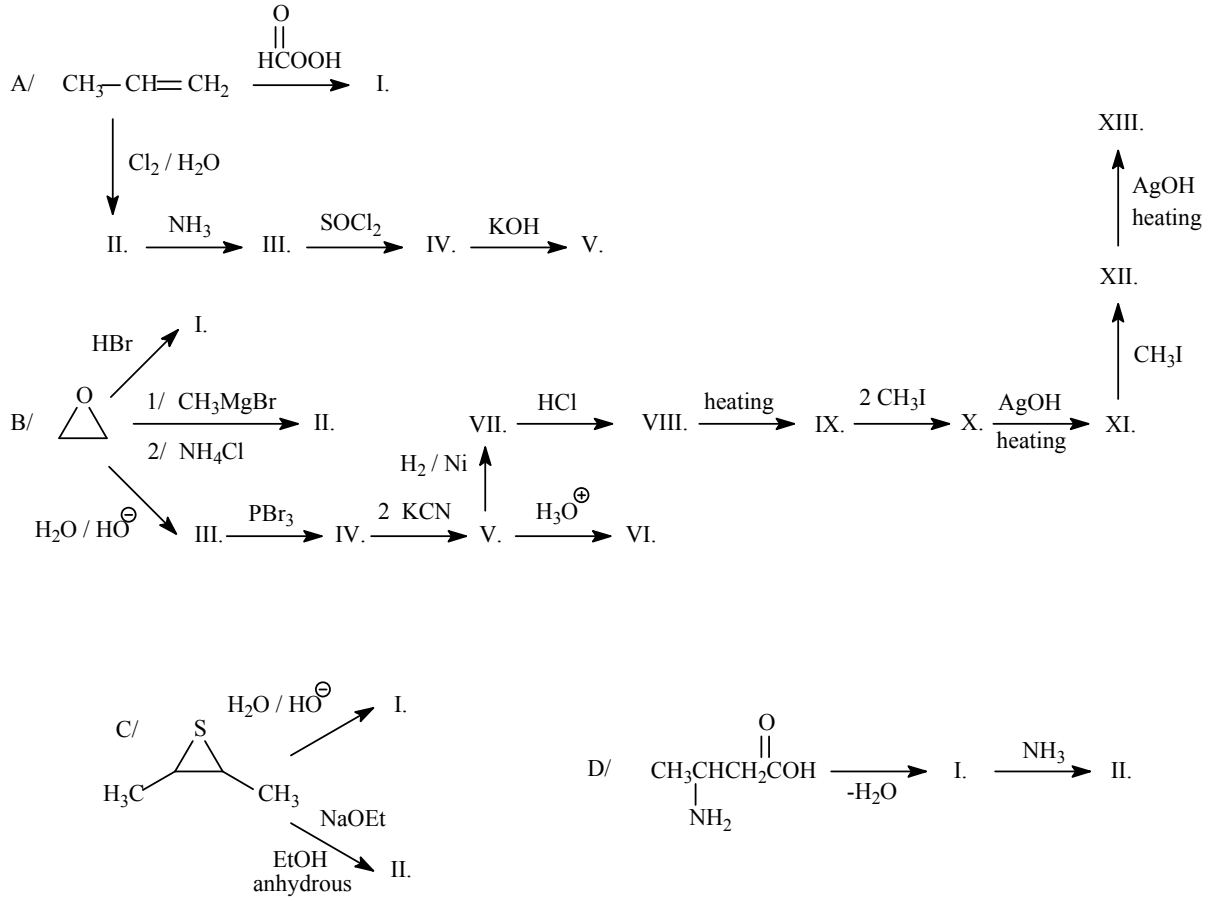
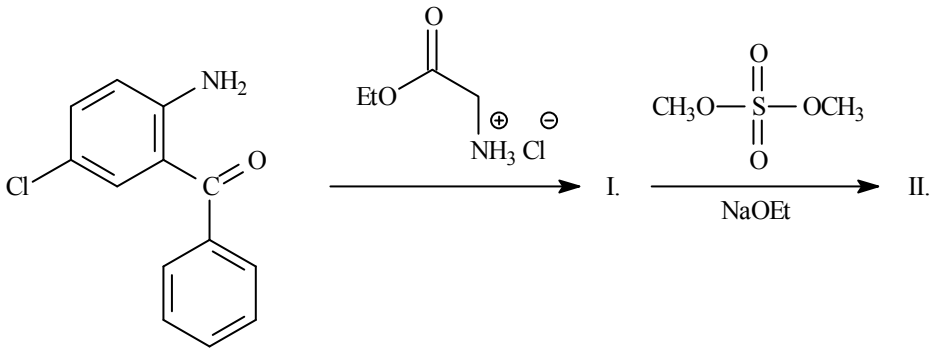


XVI. Heterocyclic compounds III. 3, 4 and 7 membered heterocyclic compounds and their derivatives

1. Draw the following reactions:

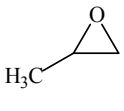


2. Draw the missing compounds of the following drug synthesis:



XVI. ANSWERS

1.

A/ 

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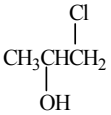
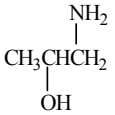


II.



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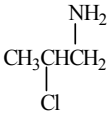

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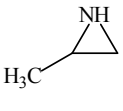
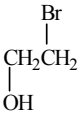


V.

B/ 

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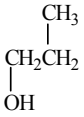

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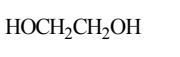

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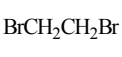
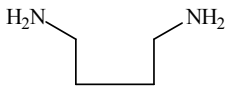


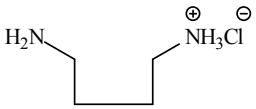
IV.

V.

VI.

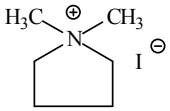


VII.



VIII.

IX.



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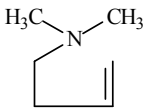
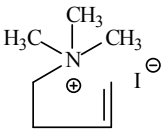
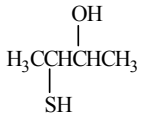


XI.



XII.

XIII.

C/ 

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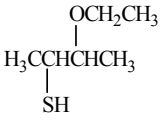

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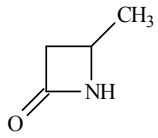
D/ 

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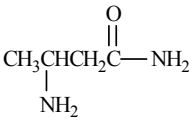
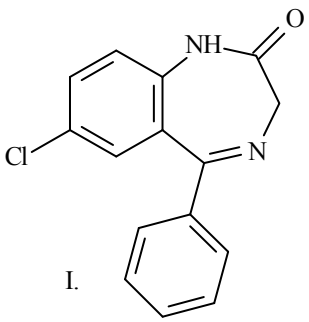


II.

2.



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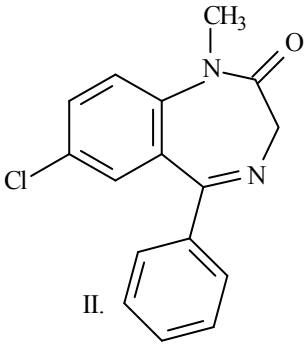
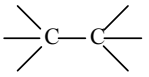
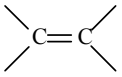


II.

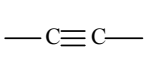
NAMES AND STRUCTURAL FORMULAS OF FUNCTIONAL GROUPS, COMPOUND TYPES AND HETEROCYCLIC SYSTEMS OCCURRING MORE FREQUENTLY



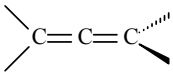
alkane



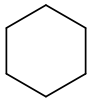
alkene



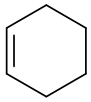
alkyne



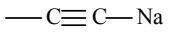
allene



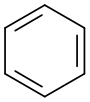
cykloalkane



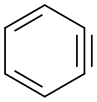
cykloalkene



sodium-acetilide
(metal acetilide)



arene



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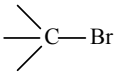
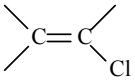
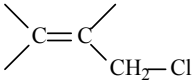


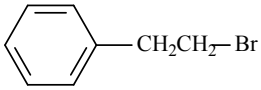
alkyl halide



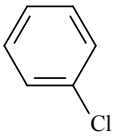
vinyl-halide



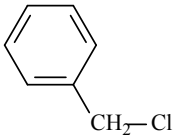
allyl halide



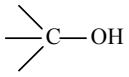
aralkyl halide



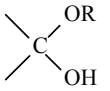
aryl halide



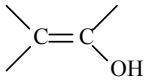
benzyl halide



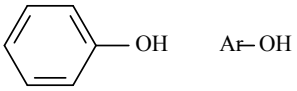
aliphatic alcohol
(alcoholic hydroxy group)



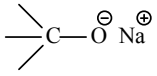
hemiacetal
(hemiacetal hydroxy group)



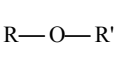
enol
(enolic hydroxy group)



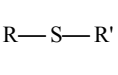
phenol (phenolic hydroxy group)



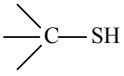
sodium alcoholate



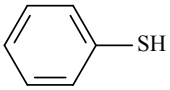
ether



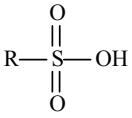
sulfide



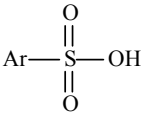
thiol



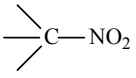
aryl thiol



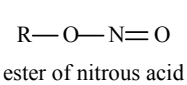
aliphatic sulfonic acid



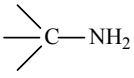
aromatic sulfonic acid



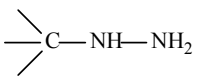
aliphatic nitro compound
(nitroalkane)



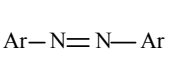
ester of nitrous acid
(alkyl nitrite)



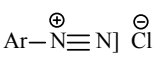
primary amine



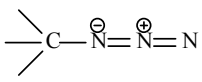
alkyl hydrazine



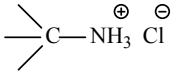
aromatic azo compound



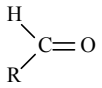
aromatic diazonium salt



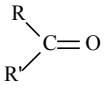
alkyl azide



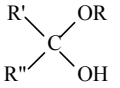
primary ammonium salt



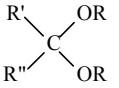
aldehyde



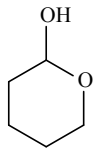
keton



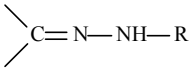
hemiacetal



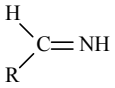
acetal



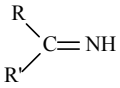
cyclic hemiacetal
(lactol)



hydrazone



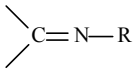
aldimine



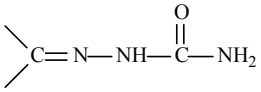
ketimine

carbonyl group

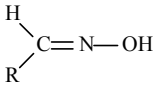
oxo group



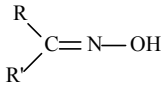
Schiff base



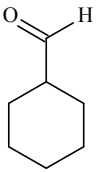
semicarbazone



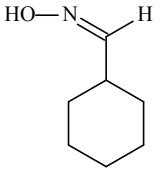
aldoxime



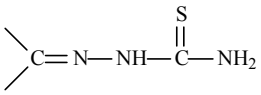
ketoxime



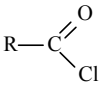
carbaldehyde



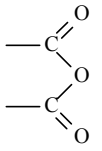
carbaldoxime



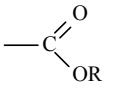
thiosemicarbazone



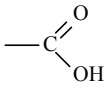
carboxylic acid halide



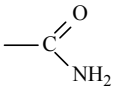
carboxylic
anhydride



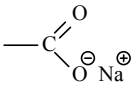
carboxylic acid ester



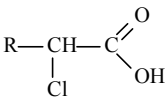
carboxylic acid



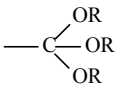
unsubstituted
carboxamide



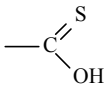
carboxylate salt



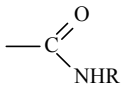
halogenated carboxylic acid



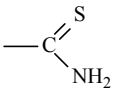
orthocarboxylic
acid ester



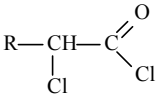
thio-*O*-acid



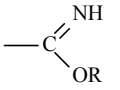
monosubstituted
carboxamide



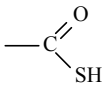
thiocarboxamide



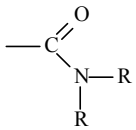
halogenated carboxylic acid halide



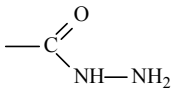
imidoic acid ester



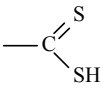
tio-*S*-sav



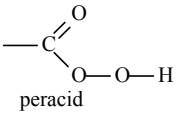
disubstituted
carboxamide



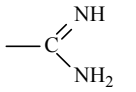
carboxylic acid
hydrazide



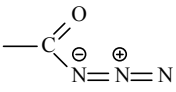
dithioacid



peracid

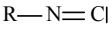


karboxylic acid amidine

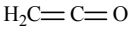


carboxylic acid azide

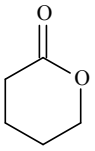
carboxylic acid nitrile



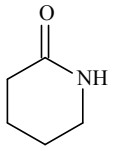
carboxylic acid isonitrile



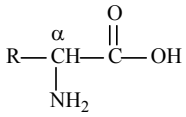
ketene



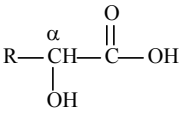
cyclic carboxylic acid (lactone)



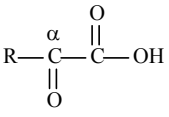
cyclic carboxamide (lactame)



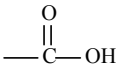
α–aminocarboxylic acid



α–hydroxycarboxylic acid

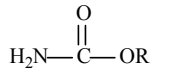


α–oxocarboxylic acid

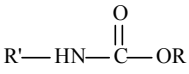


carboxylic group

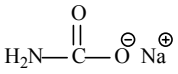
(α carbon atom: where the functional group e.bg., the carboxyl group is attached to)



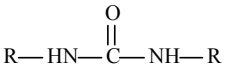
carbamidic acid ester (urethane)



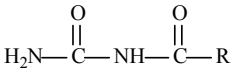
N-alkyl urethane



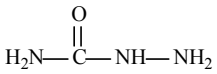
carbamidic acid salt (carbamate)



dialkyl urea



N-acyl urea (ureide)



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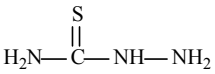

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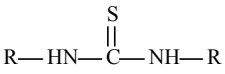

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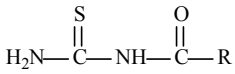

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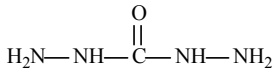

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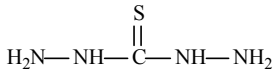

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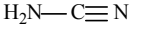

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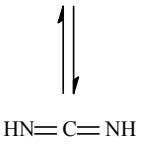

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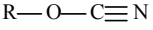

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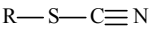

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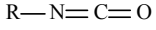

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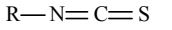


izothiocyanate ester

oxirene

thiirene

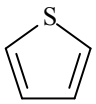
1*H*-azirine

oxet(en)e

thiet(en)e

azete

furan



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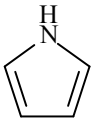

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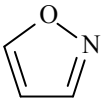

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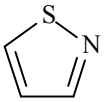

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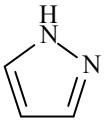

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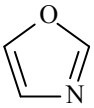

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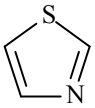

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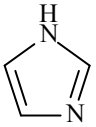

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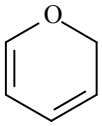

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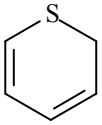

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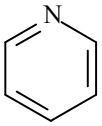

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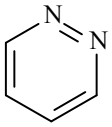

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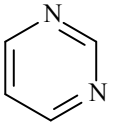

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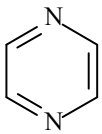

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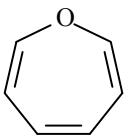

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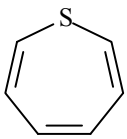

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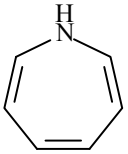

1*H*-azepine

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Chapter I.

1	F/3	
3	Lit. 8.	
4	C-V/429	
6	F/83	
7	F/65	
9	F/77	Sample Problem
10	F/79	Sample Problem
11	F/86	2.21
12	F/88	2.37
	F/90	2.47
13	M/24	

Chapter II.

1/B	F/100	3.5
1/F	F/101	Sample Problem
1/H, I, J	F/102	Sample Problem
2/A, B	F/100	3.6
2/C, D, E	F/102	3.7
2/H, I	F/102	
5/A	F/93	Sample Problem
12	F/245	6.4

Chapter III.

3/E	F/416	Table 10
3/F	F/417	10.3
7	Lit. 9.	

Chapter IV.

3/D, F, G	F/516	
6/A-C	F/803	19.5

Chapter V.

1-3	F/184	
	F/234	5.24/B, C
3	F/234	5.26
8	F/581	13.22
15	F/197	5.6

Chapter VI.

1/A-C	F/277	7.1
2/A-D	F/277	7.2
6/B	M/818	
10/A-D	F/281	7.6
11/A-F	F/277	
11/G-I	F/277	7.

Chapter VII.

1/C	F/208	
1/N	F/329	
2/A-D	F/208	5.12

Chapter VIII.

3	F/762	18.1
9/A	F/523	Sample Problem
9/B	F/523	

Chapter IX.

7/A I-II.	F/564	13.12
7/B I-II.	F/571	13.17
7/C I-III.	F/729	Sample P., 17.10
8/A, B	F/580	13.21

Chapter X.

4/B	F/752	17.26
6/A-D	F/754	17.33
7/A-C	F/657	15.15

Chapter XI.

4/A-D	F/735

Chapter XII.

3	F/958	23.18
9	A-M/524, 525, 527	
11	F/841, 843, 1129	

Chapter XIII.

3/O	N/22	
6	F/149	4.12
7	F/149	4.13

Chapter XV.

6/A	R-K/274
6/B	R-K/251
6/C	R-K/142

Chapter XVI.

2	R-K/325, 326

First column – Number of this collection
Second column - literature

F: Fessenden (2)
C-V: Christen, Vögtle (5)
M: March (1)
N: Nógrádi (7)
R-K: Roth, Kleemann (4)
A-M: Antus-Mátyus (10)