REARRANGEMENT OF ALKYLHALOKETENE-CYCLOPENTADIENE ADDUCTS IN BASIC SOLUTION--A NEW SYNTHESIS OF 2-ALKYLTROPONES

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This research is concerned with determining whether the previously reported synthesis of tropolone by the solvolysis of the dichloroketene-cyclopentadiene adduct in sodium acetate and acetic acid could be used to prepare 2-alkyltropones from the adducts of alkylhaloketenes and cyclopentadiene. The information obtained from these rearrangements could be useful in determining the mechanism of the ring expansion of halogenated ketene-cyclopentadiene adducts to tropone derivatives.

If the cyclopentadiene adducts of alkylhaloketenes were treated with sodium acetate in seventy per cent aqueous acetic acid for a period of several days, the corresponding 2-alkyltropone was obtained in moderate yield. It was observed that the 2-alkyltropone was produced only from the endo-alkyl isomer of ketene-cyclopentadiene adduct, although both isomers were consumed during the reaction. The rearrangement of alkylhaloketene-cyclopentadiene adducts in twenty per cent aqueous sodium carbonate solution resulted in the production of 2-alkyltropones and 6-alkyl-6-carboxybicyclo-(3.1.0) hex-2-enes. The latter product was formed by a stereospecific Favorskii-type ring contraction of the alkylhaloketene cycloadduct. The 2-alkyltropone was produced only from the endo-alkyl isomer of starting material whereas the ring contraction reaction occurred with either isomer, the endo-alkyl ketene cycloadduct producing the endo-alkyl ring contraction product and vice versa.

The ratio of 2-alkyltropone to ring contraction product was highly dependent on the size of the alkyl group and the nature of the halogen on the alkylhaloketene-cyclopentadiene adduct. Large alkyl groups, such as isopropyl, led to almost exclusive production of 2-alkyltropone while small alkyl groups,

such as methyl, produced mainly ring contraction product. The alkylchloroketene adducts produced more 2-alkyltropone than the corresponding alkylbromo or alkyliodoketene adducts.

The cycloadducts of alkylhaloketenes and 1-methylcyclopentadiene underwent the rearrangement reaction in aqueous sodium carbonate to produce 2-alkyl-5-methyltropones; however, these adducts showed a higher tendency to undergo ring contraction than the corresponding cyclopentadiene adducts. The methylchloroketene adduct of indene produced only ring contraction product when treated with aqueous sodium carbonate.

The relative rates of ring contraction of the exo-alkyl isomers of alkylhaloketene cyclopentadiene adducts were measured and were found to be dependent on both halogen and alkyl group. The rate of ring contraction decreases as the steric bulk of the alkyl group is increased; the alkylbromoketene adducts undergo the ring contraction reaction at a considerably faster rate than the corresponding alkylchloroketene adducts. These observations are consistent with the proposed mechanism for ring contraction of α-halocyclobutanones.

By comparing the relative rates of ring contraction and the ratio of 2-alkyltropone to ring contraction product for different alkylhaloketene-cyclopentadiene adducts it is apparent that the rate of 2-alkyltropone formation from the ketene cycloadducts is independent of both the size of the alkyl group and the nature of the halogen of the alkylhaloketene

The experimental observations are explained by assuming that the initial step of the rearrangement is an attack by a hydroxide ion on the carbonyl group of the alkylhaloketene cycloadduct; this intermediate can undergo an internal nucleophilic displacement to produce an epoxide hemiacetal. These two steps can occur with either isomer of cycloadduct, the endo-alkyl isomer leading to an endo-epoxide and the exo-alkyl isomer to the corresponding exo-epoxide. The endo-epoxide can then undergo a disrotatory ring opening to produce a 2-alkyl-2-hydroxy-7-hydrotropone which loses water to yield the

final product. The exo-epoxide would not undergo ring opening since the disrotatory ring opening to displace the exo-epoxide group would introduce a prohibitive amount of strain into the molecule.

This mechanism explains all the experimental observations, namely the independence of tropone formation on alkyl group and halogen and the effect of the methyl group on the five-membered ring on the rate of tropone formation. The indene-methylchloroketene adduct could not form a tropone derivative by this mechanism since the ring opening step would require the destruction of the aromatic system of the benzene ring.

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DISSERTATION

Presented to the Graduate Council of the
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For the Degree of

DOCTOR OF PHILOSOPHY

By

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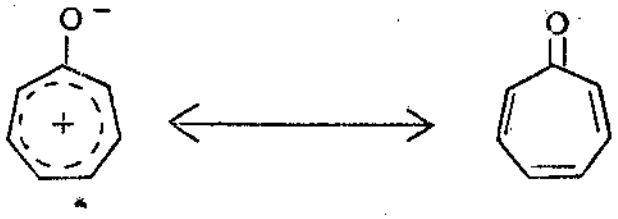
CHAPTER I

INTRODUCTION

The first cycloheptatrienone (tropone) was synthesized in 1909. In recent years, tropones have been of particular interest as an example of the class of compounds designated as pseudoaromatic. This pseudoaromaticity is responsible for the unusual properties of tropones: low energy carbonyl stretch in the infrared spectrum, high water solubility and unusually high boiling point. These properties would indicate that the dipolar form makes a large contribution to the description of the bonding of the tropone molecule (17). The unusually large dipole moment of tropone (4.17 to 4.30 D. (20, 24)) relative to cycloheptanone (3.04 D. (21)) also supports the contribution of the dipolar form.

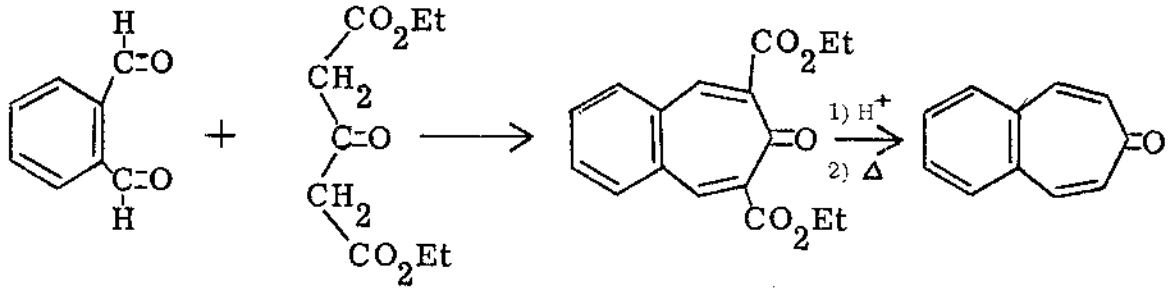


The dipolar form contains the sextet of π-electrons necessary for aromatic delocalization. The existence of this aromaticity explains the fact that tropones are quite stable molecules, whereas cyclopentadienones are unstable except when highly substituted (17). The dipolar resonance form of cyclopentadienones would involve four π-electrons in the ring, a system predicted to be non-aromatic by Huckel calculations.

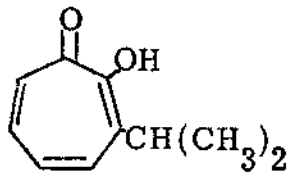
Recent CNDO/2 calculations and nuclear magnetic resonance data have been claimed to show that the dipolar form does not make a significant contribution to tropone (4, 5),but the inclusion of this resonance form seems necessary to explain the physical and chemical properties of tropone.

There has been a vast amount of information on the synthesis and properties of tropone derivatives reported in the literature throughout this century. The vast majority of the compounds described are derivatives of 2-hydroxytropone (tropolone). However, relatively few simple alkyl substituted tropones have been reported, and no general synthesis for this type of compound from inexpensive starting materials has been described.

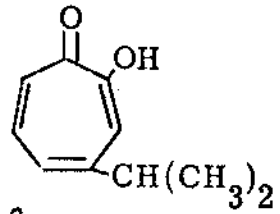
The first tropone prepared was 4,5-benzotropone, synthesized in 1909 by the condensation of o-phthalaldehyde with the diethyl ester of 3-ketoglutaric acid followed by acid hydrolysis and decarboxylation (43, 44).



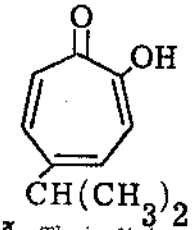
In the period from 1940 to 1950 the terpenoid substances α, β, γ,-Thujaplicin, which had previously been isolated from plant materials, were identified as the three isomeric isopropyl tropolones (32).



α-Thujaplicin

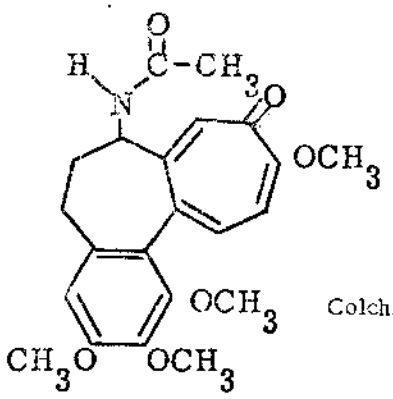


β-Thujaplicin



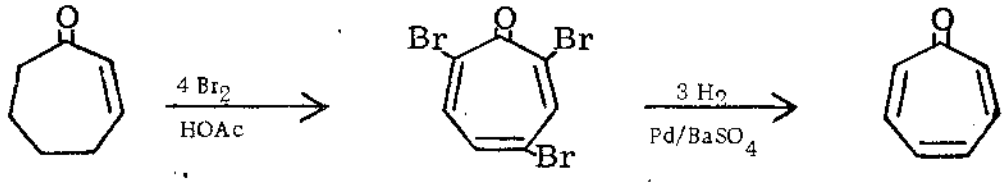
γ-Thujaplicin

Several other naturally occurring tropone derivatives have been isolated including the alkaloid Colchicine (23).

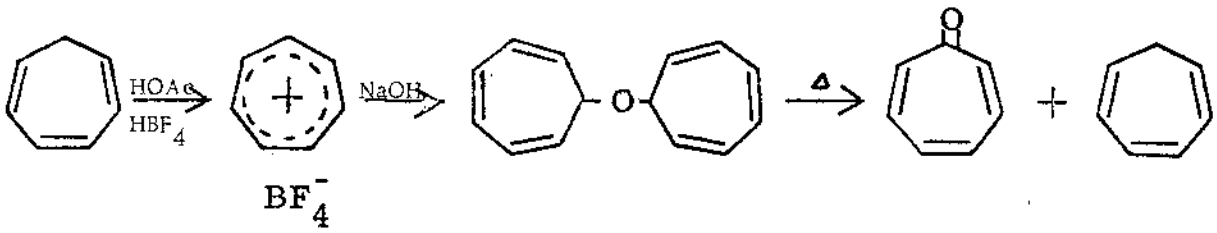


Colchicine

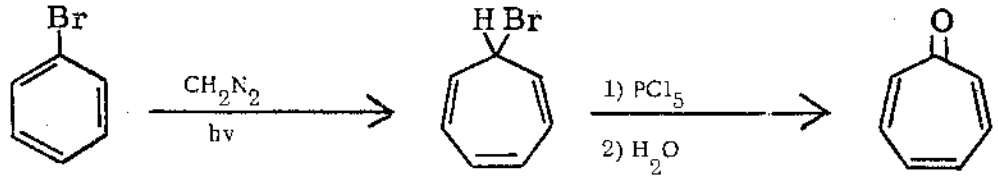
Unsubstituted tropone was first prepared in 1951 when Dauben and Ringold (16) brominated 2-cycloheptenone to produce 2,4,7-tribromotropone and hydrogenated this product on a poisoned palladium catalyst to produce tropone.



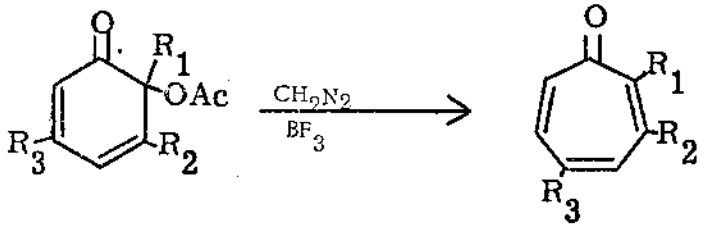
Many preparations of tropone have been reported since the original synthesis. The methods of preparation may be divided into three principal types: 1) The introduction of unsaturation into cycloheptanone derivatives by bromination as in the original preparation (16, 27). 2) Oxidation of cycloheptatriene; this can be done either directly by the use of selenium dioxide (33, 38) or indirectly by the treatment of cycloheptatriene with phosphorus pentachloride followed by hydrolysis (34). Another synthesis in this classification is the formation of dicycloheptatrienyl ether from the hydrolysis of tropylium fluoroborate and disproportionation of this compound by heating with activated silica gel (22, 39, 40, 42).



3) Ring expansion reactions; these reactions generally start with a six-membered ring compound and generate the seven -membered ring by either carbene addition (6, 15, 17, 31, 46) or ring expansion during solvolysis (12, 47). For example, bromobenzene can be treated with diazomethane in the presence of ultraviolet light to produce bromotropylidene which can be converted to tropone by treatment with phosphorus pentachloride and hydrolysis (46).

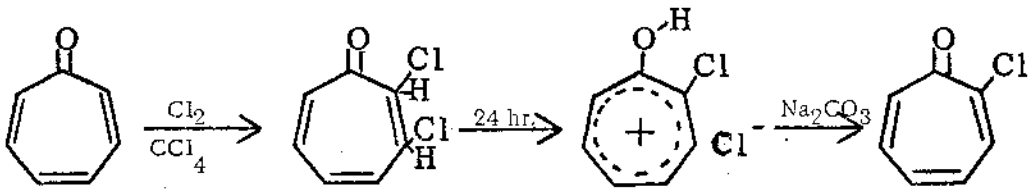


The methods of preparation described are not practical for the preparation of other than unsubstituted tropone due to the extremely limited availability of starting materials. However, 2-methyltropone, 2-ethyltropone and some polyalkylated tropones have been prepared by the addition of diazomethane in the presence of boron trifluoride to benzoquinol acetates (48, 49). The yield of tropone depends on R_1, R_2 and R_3 but is generally very low, ranging from 2 to 42 per cent, and the tropones obtained are contaminated by the starting material.

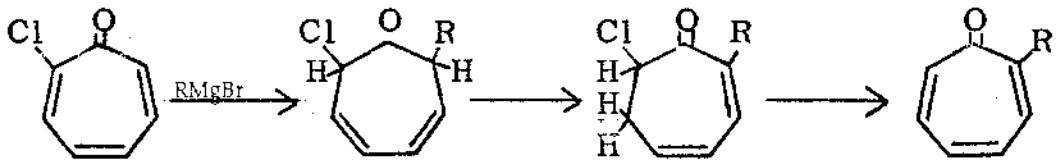


The most commonly used method for the preparation of 2-alkyltropones is the reaction of tropone or a tropone derivative with an organometallic reagent. The reaction of a Grignard reagent with 2-chlorotropone is probably the best method. 2-Chlorotropone is prepared by the direct chlorination

of tropone to produce tropone dichloride which spontaneously rearranges to the hydrochloride of 2-chlorotropone (35, 40). The free tropone can be obtained by the treatment of the hydrochloride with sodium bicarbonate.

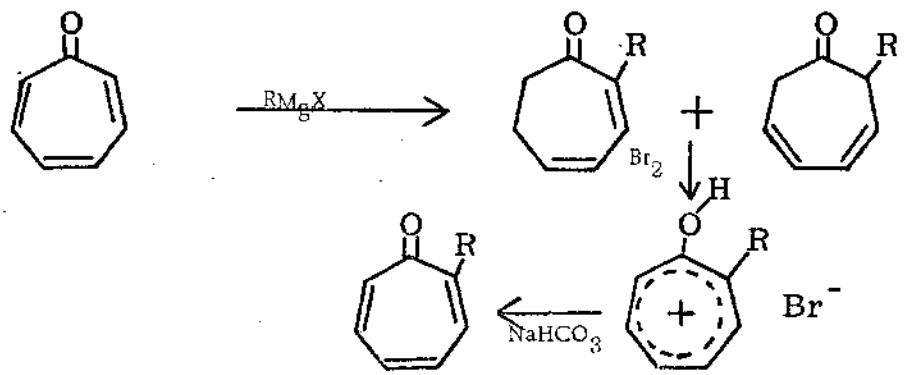


The reaction of 2-chlorotropone with an alkyl magnesium bromide results in the formation of a 7-alkyl-2-chloro-2,7-dihydrotropone. Rearrangement of this compound to the 2,3-dihydro isomer followed by loss of hydrogen chloride produces the 2-alkyltropone (29, 36, 41).



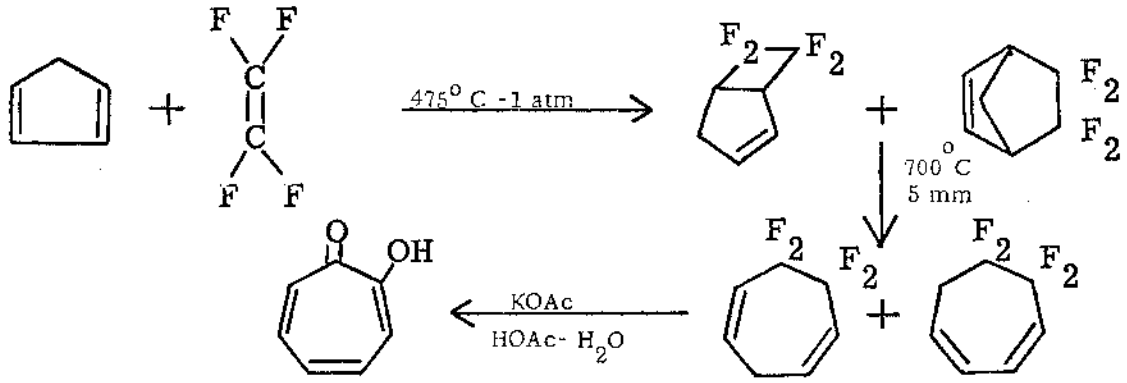
This method has been used to prepare 2-ethyl (36, 41), 2-isopropyl (36, 41) and 2-benzyl (29) tropone.

An organometallic reagent can also be added directly to tropone to form a mixture of alkyldihydrotropones which can be converted to 2-alkyltropones by treatment with bromine and sodium bicarbonate (14, 30).



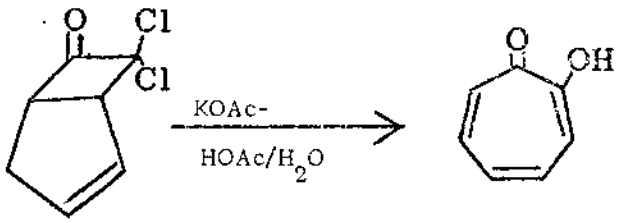
2-Alkyltropones have also been prepared by the reaction of organolithium reagents with tropolone (25) or by the reaction of Grignard reagents with tropolone methyl ether (25, 28). While this reaction can be used to prepare a wide variety of 2-alkyltropones, the necessity of first preparing tropone or a tropone derivative before the alkylation can be accomplished severely limits its utility for the preparation of 2-alkyltropones in reasonable quantities.

The first preparation of a tropone derivative from cyclopentadiene was reported in 1958 (18). Cyclopentadiene was added to tetrafluoroethylene to form a mixture of the 1,2- and 1,4-cycloadducts. This mixture was

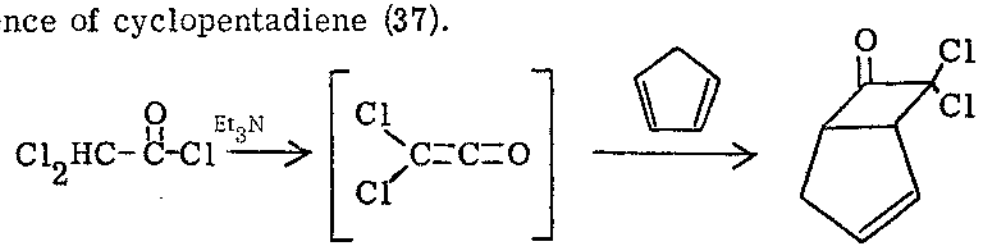


pyrolysed to produce a mixture of two tetrafluorocycloheptadienes. These two compounds were solvolysed in a solution of potassium acetate in acetic acid containing a small amount of water. Tropolone was produced in an overall yield of about twenty per cent. However, special apparatus is necessary to perform the high temperature gas phase reactions involved in this transformation.

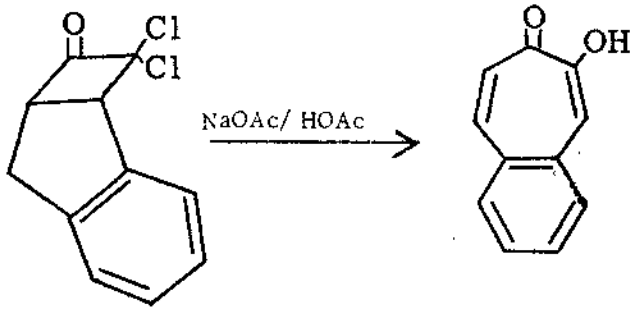
In 1965 Stevens and coworkers (37) prepared tropolone by the solvolysis of the 1,2-cycloadduct of dichloroketene and cyclopentadiene in potassium acetate dissolved in acetic acid. The yield was about fifty per cent; this was the first convenient synthesis of a tropone derivative from inexpensive starting materials-- cyclopentadiene and dichloroacetyl chloride, since the



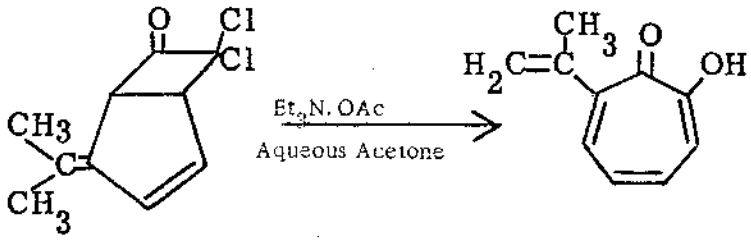
adduct of dichloroketene and cyclopentadiene can easily be prepared in good yield by the dehydrohalogenation of dichloroacetyl chloride in the presence of cyclopentadiene (37).



This synthesis was subsequently used by Turner and Sedan (45) to prepare 4,5-benzotropolone from the cycloadduct of dichloroketene and indene.

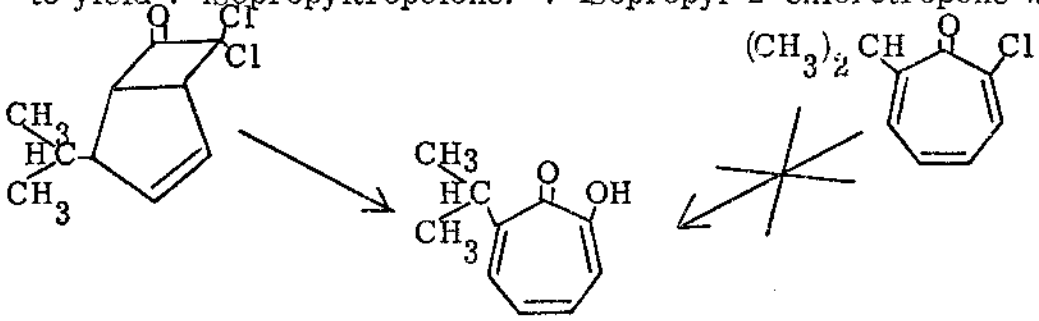


Kitahara and coworkers (2) recently prepared 7-isopropenyltropolone by the solvolysis of the adduct of dichloroketene and 6,6-dimethylfulvene.



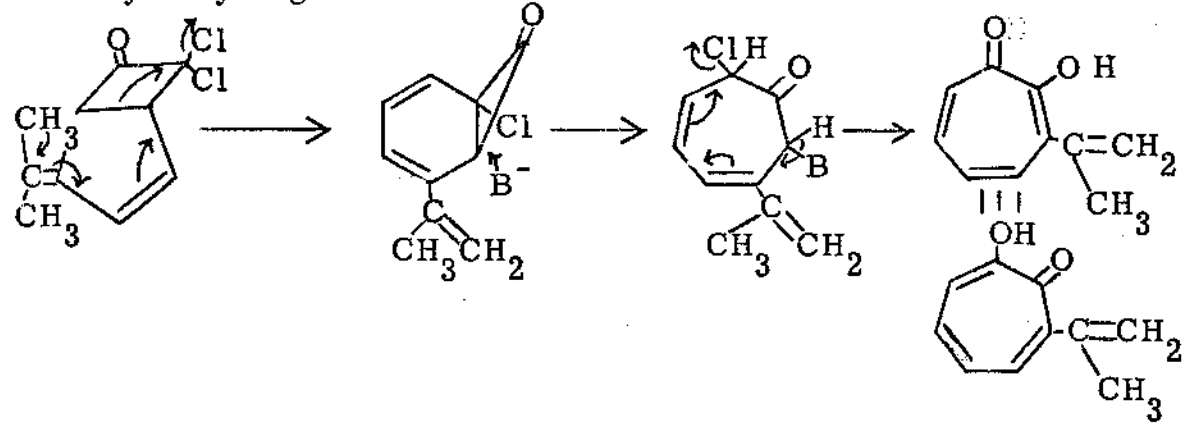
This conversion was accomplished in ninety per cent yield in aqueous

acetone containing triethylammonium acetate. Kitahara proposed a mechanism for the ring expansion of the bicyclo(3.2.0) heptanone system to a seven-membered ring. The observance of 7-isopropenyltropolone rather than the expected 6-isopropenyl isomer eliminates the possibility of a simple ring opening with loss of hydrogen chloride. The 6,6-dimethylfulvene-dichloroketene adduct was hydrogenated to 4-isopropyl-7,7-dichlorobicyclo (3.2.0) hept-2-en-6-one, which was solvolysed under similiar conditions to yield 7-isopropyltropolone. 7-Isopropyl-2-chlorotropone was prepared



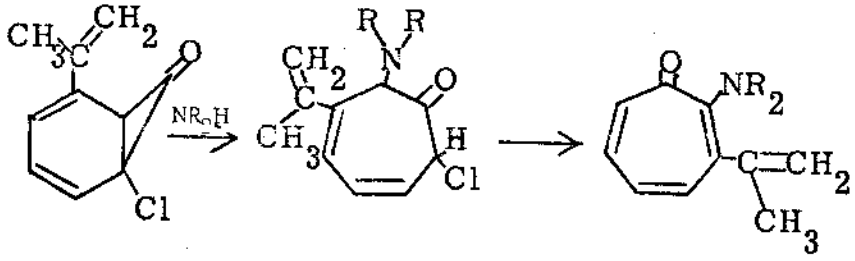
from naturally occurring 7-isopropyltropolone; this compound was not solvolysed to 7-isopropyltropolone at any appreciable rate when subjected to the reaction conditions used to prepare the tropolone from the ketene-cyclopentadiene adduct, revealing that the chlorotropone is not an intermediate in the ring expansion reaction.

Kitahara proposed that the ketene cycloadduct was converted to tropolone through a norcaradienone intermediate, formed by the abstraction of an allylic hydrogen from the adduct. This norcaradienone could then be

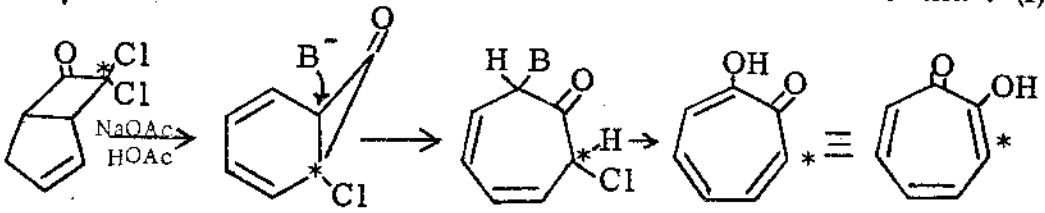


attacked by base, leading to ring opening and loss of a second molecule of hydrogen chloride to yield the final product. The two structures shown for the 7-isopropenyltropolone are equivalent because of the rapid tautomerism between the two forms shown below (26). Reaction of dialkylamines

in ether with the dichloroketene dimethylfulvene adduct yielded 2-dialkylamino-3-isopropenyltropones. This result is explained by the reaction of the amine with the norcaradienone intermediate.

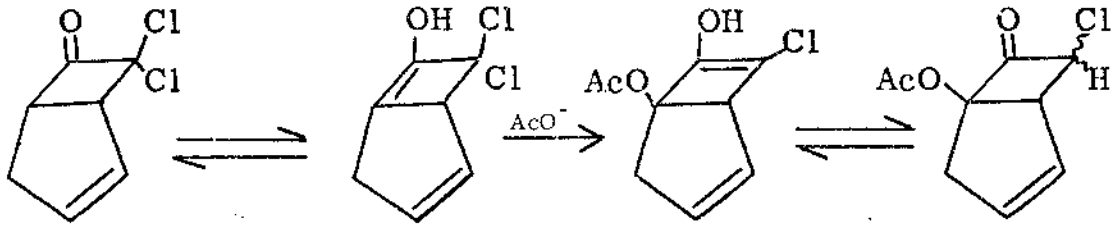


Isotopic labeling has provided further evidence for this mechanism since the dichloroketene-cyclopentadiene adduct labeled with carbon-14 on C_7 solvolysed to yield tropolone labeled on carbons 3 and 7 (1).

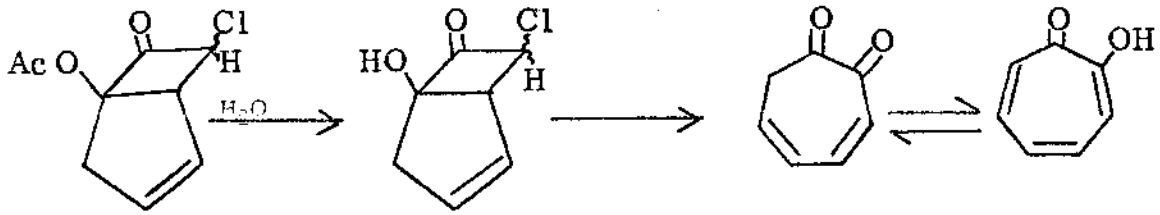


An alternative mechanism has been proposed by Bartlett and Ando (3) in which the first step of the acetate solvolysis is the substitution of acetate on the bridgehead carbon of the adduct adjacent to the carbonyl (C_5). Presumably this substitution occurs through the enol form of the adduct

as was observed by Fletcher and Hassner (19) for the dichloroketene adduct of cyclohexene.

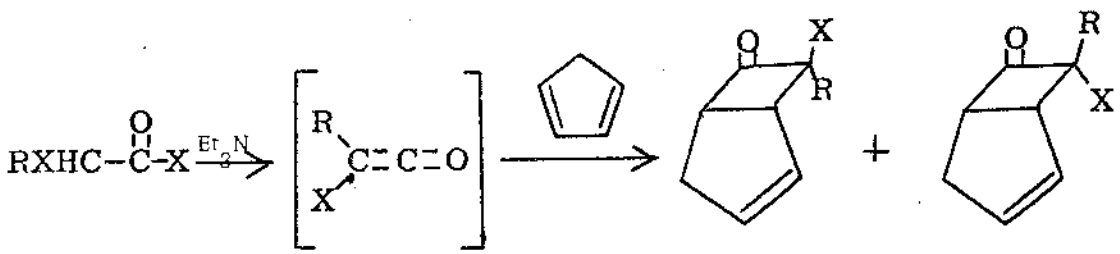


The acetate ester then undergoes hydrolysis followed by rearrangement and loss of hydrogen chloride to produce a cycloheptadienedione which tautomerizes to tropolone. The evidence presented for this mechanism involves



the inhibition of the reaction by the substitution of mesitoate ion for acetate ion. This inhibition results from the resistance of mesitoate esters to hydrolysis which blocks the first step of the above reaction sequence.

The adducts of alkylhaloketenes and cyclopentadiene are readily prepared in up to eighty per cent yield by the dehydrohalogenation of 2-haloacyl halides in the presence of cyclopentadiene (7, 8, 9, 10, 11). The isomer



distribution is dependent upon the size of R, the nature of X, the reaction temperature and the solvent in which the cycloaddition is effected.

If these cycloadducts could be solvolysed to 2-alkyltropones by a reaction analogous to the preparation of tropolone from the cyclopentadiene adduct of dichloroketene, a general synthesis of 2-alkyltropones in two simple steps from inexpensive starting materials would be available.

It was therefore deemed desirable to investigate this rearrangement reaction as a general synthesis of 2-alkyltropones and to determine, if possible, the mechanism of this conversion.

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CHAPTER II

EXPERIMENTAL

Proton nuclear magnetic resonance (nmr)spectra were taken at room temperature on Jeolco-Minimar (60 mHz) and Jeolco PS-100 (100 mHz) spectrometers. Carbon tetrachloride or deuterochloroform were used as solvents, and tetramethylsilane was employed as an internal standard. All nmr spectra were taken at a sample concentration of about twenty-five per cent.

Infrared spectra were taken with a Perkin-Elmer Model 237 Grating Infrared Spectrometer using both neat and solution samples. Sodium chloride disks or fixed thickness sodium chloride cells (path length = 0.1 mm), which were appropriate to sample concentrations, were used.

Analytical vapor phase chromatography (vpc) was done on a F and M Scientific Model 700 instrument employing a thermal conductivity detection system. Separations were achieved using columns ten feet by one-quarter inch packed with ten per cent Silicone Fluid SE-30 on Chromosorb W (AW-DMCS) 80/100 mesh. Small-scale preparative vapor phase chromatography was accomplished,using a Varian-Aerograph 1520 instrument with a column similar to that used for the analytical separations.

Elemental analyses were performed by C. F. Geiger and Associates, of Ontario, California.

Preparation of Reagents

Commercially available hexane of ninety-nine per cent purity was dried by distillation from sodium and was stored over Linde type 4A molecular

sieve. Acetonitrile was distilled from calcium hydride and stored in contact with molecular sieve. Triethylamine was distilled from sodium and stored over molecular sieve.

Commercially available dicyclopentadiene was thermally cracked at about 140°C and slowly fractionated through a twelve-inch Vigreaux column and ice water cooled condenser and collected at 40-41°C in a receiver cooled with ice water. The monomeric cyclopentadiene thus formed was stored at -10°C; at this temperature it could be kept for several days without significant dimerization. However, in most cases the dicyclopentadiene was cracked and distilled immediately before it was to be utilized. Methylcyclopentadiene dimer was cracked in the same manner except that a temperature of about 170°C was required. The monomer was distilled through a Vigreaux column and collected at 70-71°C. A mixture of 1-methylcyclopentadiene and 2-methylcyclopentadiene in approximately equal amounts was formed as evidenced by nmr. This mixture of monomeric methylcyclopentadienes was used directly without separation. Other olefins used for cycloaddition were purified by shaking with molecular sieve followed by fractional distillation immediately before use.

2-Haloacyl chlorides were prepared by the halogenation of the corresponding acid chloride. These acid chlorides were prepared from the carboxylic acids with thionyl chloride according to standard procedures. 2-Chloropropanoyl, 2-bromopropanoyl, 2-chlorobutanoyl, 2-bromobutanoyl, dichloroacetyl and dibromoacetyl chlorides were prepared by the treatment of the commercially available 2-haloacids with thionyl chloride. The structures of these acid chlorides were confirmed by the nmr spectra and agreement of the observed boiling points with those found in the literature. The yields of the acid chlorides were comparable to those cited in the reference indicated in Table I.

TABLE I

ACID CHLORIDES PREPARED FROM COMMERCIALLY AVAILABLE ACIDS

Acid Chloride	Boiling Range (^{O}C)	Reference
2-Chloropropanoyl chloride	110-112	28
2-Bromopropanoyl chloride	131-132	18
2-Chlorobutanoyl chloride	129-131	31
2-Bromobutanoyl chloride	150-152	17
Dichloroacetyl chloride	108-110	11
Dibromoacetyl chloride	60-64/4 mm	32
Pentanoyl chloride	126-128	11
3-Methylbutanoyl chloride	112-113	11
Hexanoyl chloride	151-153	11
Decanoyl chloride	230-233	27
Cyclohexylacetyl chloride	95-96/21 mm	29
3-Cyclohexylpropanoyl chloride	109-111/19mm	29
4-Cyclohexylbutanoyl chloride	123-124/17mm	29

2-Iodopropanoyl chloride

2-Iodopropanoic acid was prepared by the procedure of Abderhalden and Guggenheim (1). A 153 g portion (1.0 mole) of 2-bromopropanoic acid was dissolved in 500 ml. of water containing 332 g. (2.0 mole) of potassium iodide. This solution was heated to 50 ^{O}C with stirring for a period of 4 hours. During this time, the color of the reaction mixture changed from light yellow to black. The solution was allowed to cool and extracted with two 500 ml. portions of ether; the combined ether extracts were dried over $CaCl_2$ and rotary evaporated to yield 200 g. of a dense dark oil which solidified

on standing at 0°C for 3 hours. This solid was used for the preparation of the acid chloride without further purification.

The crude 2-iodopropanoic acid formed in the preceding step was placed in a flask fitted with a reflux condenser, and 150 g. (1.2 mole) of thionyl chloride was cautiously added. This reaction mixture was heated to 60°C (heating above this temperature causes decomposition) for 5 hours and the acid chloride vacuum distilled. A fraction 48-50°at 10 mm. was collected (lit. b. pt. 51-53°C at 13 mm). The overall yield of both steps was 75 per cent. The acid chloride thus formed had a purple color due to free iodine; this color could not be removed but had no detrimental effect of the acid chloride in further cycloaddition reactions.

Fluoroacetyl bromide

Commercially available sodium fluoroacetate (200 g.,2.0 mole) was dissolved in 250 ml. of water; this solution was acidified with concentrated HCl and extracted with ether using a continuous liquid-liquid extractor. After extraction for 24 hours, the ether layer was dried over $CaCl_2$, rotary evaporated and distilled to yield 80 g. (51 per cent) of fluoroacetic acid. This acid was converted to the acid bromide by reaction with PBr_3 using a standard procedure. A 75 per cent yield of fluoroacetyl bromide b.pt. 94-96°C (lit. b. pt. 95-96°C (22)) was obtained.

Chloroacetyl bromide

Chloroacetyl bromide was prepared by the reaction of chloroacetic acid with PBr_3 using a standard procedure. An 80 per cent yield was obtained b.pt 128-130°C (lit. b.pt. 127°C(16)).

Bromochloroacetyl chloride

Bromochloroacetyl chloride was prepared by the procedure of Crompton and coworkers (14, 15). α,β-Dichlorovinyl ethyl ether was prepared by

adding 650 g. (5.0 mole) of trichloroethylene to a previously prepared solution of 175 g. (7.5 mole) of sodium metal in 3 liters of absolute ethanol in a flask fitted with a large reflux condenser. Initially, only a small portion (50 ml.) of trichloroethylene was added, and the reaction was initiated by heating the reaction flask to 95°C with a water bath. After the reaction commenced, the water bath was removed and trichloroethylene added at a sufficient rate to maintain vigorous reflux. After addition was complete, the reaction mixture was allowed to stand at room temperature for 10 hours and then poured into 10 l. of water. The organic layer was separated and dried over $CaCl_2$. Further drying was accomplished by refluxing with 1.5 l. of benzene removing the water by azeotropic distillation. The benzene was evaporated on the rotatory evaporator and the product distilled (b.pt.124-126°C) and stored over molecular sieve (Linde type 4A). The yield was 400 g. (60 per cent).

In a flask fitted with an addition funnel was placed 380 g. (2.68 moles) of α,β-dichlorovinyl ethyl ether. A 430 g. (2.70 mole) portion of bromine was added dropwise over a 3 hour period. The bromine was rapidly absorbed as evidenced by the disappearance of the bromine color. After the bromine addition, the reaction mixture was heated strongly under a stream of nitrogen and the product distilled through a 6 inch Vigreaux column. After about 150 g. of ethyl bromide had been collected at 37-42°C, the temperature rose to 135°C, and 300 g. of bromochloroacetyl chloride were collected from 138-140°C (lit. b. pt. 138-139°C (14)). This corresponds to a 56 per cent yield; careful exclusion of atmospheric moisture is necessary throughout the reaction to prevent the formation of ethyl bromochloroacetate.

General Procedure for the α-Bromination of Acid Chlorides

The acid chloride (1.0 mole) and bromine (1.1 mole) were heated at 75°C until the bromine color had dissipated (usually 12 hours or less). A yield of

at least 90 per cent of the 2-bromoacid chloride was obtained by distillation of the reaction mixture.

2-Bromopentanoyl chloride

B.pt. 78-80°C at 25 mm. (lit. b. pt. 85-90°C at 30 mm. (34))

2-Bromo-3-methylbutanoyl chloride

B. pt. 57-59°C at 15 mm. (lit. b.pt. 59-60°C at 15 mm. (19))

2-Bromohexanoyl chloride

B.pt. 88-90°C at 25 mm. (lit. b. pt. 94-98°C at 30 mm. (34))

2-Bromodecanoyl chloride

B. pt. 82-83°C at 0.2 mm. ;nmr, δ 4.46 (t, 1H), 2.0 (m, 2H), 1.33 (m, 12H), 0.87 (t, 3H).

Bromocyclohexylacetyl chloride

B. pt. 133-136°C at 25 mm. (lit. b. pt. 130-135°C at 24 mm. (39))

2-Bromo-3-cyclohexylpropanoyl chloride

B. pt. 75-76°C at 0.1 mm. ; nmr, δ 4.56 (t, 1H), 2.17-1.00 (broad multiplet, 13H)

2-Bromo-4-cyclohexylbutanoyl chloride

B. pt. 93-95°C at 0.3 mm. ; nmr, δ 4.50 (t, 1H), 2.33-0.95 (broad multiplet, 15H)

2-Chlorohexanoyl chloride

This acid chloride was prepared by a modification of the procedure of Gleason and Harpp (21). A mixture of hexanoyl chloride (1.0 mole) and N-chlorosuccinimide (1.5 mole) in 300 ml. of CCl_4 was refluxed with stirring for 24 hours. The progress of the reaction was followed by periodically withdrawing aliquots, mixing with an equal volume of absolute methanol and assaying by vpc. After 24 hours refluxing, this assay revealed the conversion

to be about 50 per cent complete. Longer reaction times did not increase the amount of chlorinated product. The reaction mixture was filtered, rotary evaporated and fractionally distilled to yield 50 g. (30 per cent) of 2-chlorohexanoyl chloride, b. pt. 175-177°C (lit. b. pt. 174-176°C (23)).

Several attempts to prepare the above acid chloride by direct chlorination of the acid chloride, with or without catalyst, were unsuccessful.

2-Chloro-3-methylbutanoyl chloride

This acid chloride was prepared by the method described above for 2-chlorohexanoyl chloride. A 40 per cent yield was obtained; b. pt. 149-150°C (lit. b.pt. 149-150 °C (28)).

2-Chloropentanoyl chloride

This acid chloride was prepared by the procedure of Kharasch and Brown (25). To a 120g. (1.0 mole) portion of pentanoyl chloride was added 160 g. (1.25 mole) of sulfuryl chloride and 2 g. of iodine. The reaction mixture was refluxed overnight and fractionally distilled to yield 75 g. (50 per cent) of 2-chloropentanoyl chloride; b. pt. 154-155°C (lit. b. pt. 155-157°C (33)).

2,3-Dibromobutanoyl chloride

In 600 ml. of a 50:50 mixture of chloroform and carbon tetrachloride were dissolved 86 g. (1.0 mole) of 2-butenoic acid. To this solution 160 g. (1.0 mole) of bromine was added cautiously; the reaction was refluxed overnight, after which time the bromine color had dissipated. The solvent was removed on the rotatory evaporator, leaving 220 g. of 2,3-dibromobutanoic acid; m. pt. 84-86°C (lit. m. pt. 87°C (26)).

This acid was converted to 2,3-dibromobutanoyl chloride by refluxing with 165 g. (1.2 mole) of thionyl chloride for 10 hours. Vacuum distillation yielded 200 g. (75 per cent overall yield) of 2,3-dibromobutanoyl chloride; b.pt. 62-65°C at 1.0mm. ;nmr, δ 4.50 (m, 2H), 1.93 (d, 3H J=7cps).

General Procedure for in situ Alkylhaloketene Cyclopentadiene Cycloadditions . To a solution of 1.1 mole of triethylamine and 2.0 mole of cyclopentadiene in 1 l. of hexane was added 1.0 mole of acid chloride in 150 ml. of hexane. The addition was made dropwise over a period of 1 hour with vigorous stirring. After the addition was complete, the stirring was continued for 2 hours. The amine salt was removed by filtration and washed with 3x 150 ml. portions of hexane. The filtrate was concentrated on a rotary evaporator and the residue vacuum distilled to yield the alkylhaloketene-cyclopentadiene adduct.

Two isomeric bicyclo(3.2.0) hept-2-en-6-ones were produced in each case. The isomers were separated by fractional distillation at reduced pressure employing either a spinning band column or a 30-plate adiabatic column. Some of the higher boiling cycloadducts could not be fractionated through the above columns without severe decomposition. Consequently, separation was accomplished by repeated vacuum distillation through a short Vigreaux column. This method provided isomeric purity of 75-90 per cent.

7-Chloro-7-methylbicyclo(3.2.0)hept-2-en-6-one

2-Chloropropanoyl chloride was dehydrochlorinated at 0-5^{o}C ; 80 per cent yield. An isomer distribution of 4.5 (endo-methyl/ exo-methyl) was obtained. The physical properties, ir and nmr spectra were identical to those in the literature (6, 9).

7-Bromo-7-methylbicyclo(3.2.0)hept-2-en-6-one

2-Bromopropanoyl chloride was dehydrochlorinated at 0-5^{o}C; 75 per cent yield . An isomer distribution of 0.8 (endo-methyl/ exo-methyl) was obtained. The physical properties, ir and nmr spectra were identical to those in the literature (5, 9).

7-Iodo-7-methylbicyclo(3.2.0)hept-2-en-6-one

2-Iodopropanoyl chloride was dehydrochlorinated at room temperature; 80 per cent yield at 77-80° at 1.6 mm. An isomer distribution of 0.5 (endo-methyl/ exo-methyl was obtained; ir, both isomers, 1790 cm^{-1}; nmr (endo-methyl), δ 5.76 (m, 2H), 4.16 (3d, 1H), 3.92 (m, 1H), 2.48 (m, 2H), 1.70 (s, 3H); (exo-methyl), δ 5.84 (m, 2H), 4.33 (m, 2H), 2.63 (m, 2H), 2.12 (s,3H).

Analysis Calculated for C_8H_9OI: C, 38.75; H, 3.63. Found: C, 39.06 ; H, 3.93.

7-Chloro-7-ethylbicyclo(3.2.0)hept-2-en-6-one

2-Chlorobutanoyl chloride was dehydrochlorinated at 0-5° C; 80 per cent yield. An isomer distribution of 5.5 (endo-ethyl/ exo-ethyl) was obtained. The physical properties, ir and nmr spectra were identical to those in the literature (5).

7-Bromo-7-ethylbicyclo(3.2.0)hept-2-en-6-one

2-Bromobutanoyl chloride was dehydrochlorinated at room temperature; 65 per cent yield. An isomer distribution of 1.4 (endo-ethyl/ exo-ethyl) was obtained. The physical properties, ir and nmr spectra were identical to those in the literature (5).

7-Chloro-7-n-propylbicyclo(3.2.0)hept-2-en-6-one

2-Chloropentanoyl chloride was dehydrochlorinated at room temperature; 70 per cent yield at 50-51°C at 0.05 mm. An isomer distribution of 8 (endo - n-propyl/ exo-n-propyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-n-propyl), δ 5.93 (m, 2H), 4.13 (3d, 1H), 3.50 (m, 1H), 2.45 (m, 2H), 1.56 (m, 4H), 0.90 (def. t, 3H). The exo-n-propyl isomer was not isolated.

Analysis Calculated for $C_{10}H_{13}OCl$: C, 65.01; H, 7.09. Found: C,65.41; H, 7.44.

7-Bromo-7-n-propylbicyclo(3.2.0)hept-2-en-6-one

2-Bromopentanoyl chloride was dehydrochlorinated at room temperature; 70 per cent yield at 73- 75° C at 0.2 mm. An isomer distribution of 1.6 (endo-n-propyl/ exo-n-propyl) was obtained; ir , (both isomers), 1800 cm^{-1}; nmr (endo-n-propyl), δ 5.90 (m, 2H), 4.30 (3d, 1H), 3.82 (m, 1H), 2.56 (m, 2H), 1.66 (m, 4H), 0.96 (def t, 3H) ; (exo-n-propyl), δ 5.88 (m, 2H), 4.01 (3d, 1H), 3.56 (m, 1H), 2.53 (m, 2H), 2.04 (m, 2H), 1.58 (m, 2H), 1.00 (t, 3H).

Analysis Calculated for $C_{10}H_{13}OBr$: C, 52.45; H, 5.68. Found: C, 52.42; H, 5.87.

7-Chloro-7-(2-propyl)-bicyclo(3.2.0)hept-2-en-6-one

2-Chloro-3-methylbutanoyl chloride was dehydrochlorinated at room temperature; 65 per cent yield. An isomer distribution of 10 (endo-2-propyl/ exo-2-propyl) was obtained. The physical properties, ir and nmr spectra were identical to those reported in the literature(8).

7-Bromo-7-(2-propyl)-bicyclo(3.2.0)hept-2-en-6-one

2-Bromo-3-methylbutanoyl chloride was dehydrochlorinated at 70° C; 60 per cent yield. An isomer distribution of 4 (endo-2-propyl/exo-2-propyl) was obtained. The physical properties, ir and nmr spectra were identical to those reported in the literature (8).

7-Chloro-7-n-butylbicyclo(3.2.0)hept-2-en-6-one

2-Chlorohexanoyl chloride was dehydrochlorinated at 0-5°C; 55 per cent yield at 78-80°C at 0.5 mm. An isomer distribution of 10 (endo-n-butyl/ exo-n-butyl) was obtained; ir, (both isomers) , 1800 cm^{-1}; nmr (endo-n-butyl), δ 5.84 (m, 2H), 4.22 (3d, 1H), 3.64 (m, 1H), 2.56 (m, 2H), 1.84-1.12 (broad mult., 6H), 0.92 (t, 3H). The exo-n.butyl isomer was not isolated.

Analysis Calculated for $C_{11}H_{15}OCl$: C, 66.46 H, 7.60. Found: C, 66.81; H, 7.82.

7-Bromo-7-n-butylbicyclo(3 2.0)hept-2-en-6-one

2-Bromohexanoyl chloride was dehydrochlorinated at room temperature; 40 per cent yield at 95-100°C at 0.3 mm. An isomer distribution of 1.75 (endo-n-butyl/ exo-n-butyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-n-butyl), δ 5.95 (m, 2H), 4.33 (3d, 1H), 3.68 (m, 1H), 2.56 (m, 2H), 1.90-1.13 (broad mult., 6H), 0.93 (t, 3H); (exo-n-butyl), δ 5.85 (m, 2H), 3.97 (3d, 1H), 3.52 (m, 1H), 2.53 (m, 2H) , 1.98 (m, 2H), 1.42 (m, 4H), 0.92 (t, 3H).

Analysis Calculated for $C_{11}H_{15}OBr$: C, 54.33; H, 6.17. Found: C, 54.55; H, 5.88.

7-Bromo-7-cyclohexylbicyclo(3.2.0)hept-2-en-6-one

Bromocyclohexylacetyl chloride was dehydrochlorinated in refluxing hexane; 82 per cent yield at 118-120°C at 0.3 mm. An isomer distribution of 3 (endo-cyclohexyl/exo-cyclohexyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-cyclohexyl), δ 5.90 (m, 2H), 4.30 (3d, 1H), 3.89 (m, 1H), 2.60 (m, 2H), 2.0-0.95 (broad mult., 11H). The exo-cyclohexyl isomer was not isolated.

Analysis Calculated for $C_{13}H_{17}OBr$: C, 58.01; H, 6.37. Found C, 58.11; H, 6.33.

7-Bromo-7-cyclohexylmethylbicyclo(3.2.0)hept-2-en-6-one

2-Bromo-3-cyclohexylpropanoyl chloride was dehydrochlorinated in refluxing hexane; 83 per cent yield at 102-104°C at 0.1 mm. An isomer distribution of 2.5 (endo-alkyl/ exo-alkyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-alkyl), δ 5.87 (m, 2H), 4.36 (3d, 1H), 3.85 (m, 1H), 2.58 (m, 2H), 2.0-1.0 (broad mult., 13 H). The exo-alkyl isomer was not isolated.

Analysis Calculated for $C_{14}H_{19}OBr$: C, 59.37; H, 6.76. Found : C, 59.55; H, 6.94.

7-Bromo-7-(2-cyclohexylethyl)bicyclo(3.2.0)hept-2-en-6-one

2-Bromo-4-cyclohexylbutanoyl chloride was dehydrochlorinated in refluxing hexane; 92 per cent yield at 135-136° C at 0.1 mm. An isomer distribution of 2.5 (endo-alkyl/ exo-alkyl) was cbtained ; ir, (both isomers), 1800 cm^{-1}; nmr (endo-alkyl) , δ 5.96 (m, 2H), 4.28 (3d, 1H), 3.87 (m, 1H), 2.73 (m, 2H), 2.0-0.90 (broad mult., 15 H). The exo-alkyl isomer was not isolated.

Analysis Calculated for $C_{15}H_{21}OBr$: C, 60.61; H, 7.12. Found: C, 60.32 ; H, 7.46.

7-Bromo-7-n-octylbicyclo(3.2.0)hept-2-en-6-one

2-Bromodecanoyl chloride was dehydrochlorinated at room temperature; 65 per cent yield at 133-135° C at 0.2 mm. An isomer distribution of 2 (endo-n-octyl/ exo-n-octyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-n-octyl), δ 5.92 (m, 2H), 4.28 (3d, 1H), 3.80 (m, 1H), 2.56 (m, 2H), 1.72 (m, 2H), 1.33 (quasi singlet, 12 H), 0.90 (t, 3H). The exo-n-octyl isomer was not isolated.

Analysis Calculated for $C_{15}H_{23}OBr$: C, 60.20; H, 7.74. Found: C, 59.91; H, 7.72.

7-Bromo-7-vinylbicyclo(3.2.0)hept-2-en-6-one

2,3-Dibromobutanoyl chloride was added at 0-5° C. The initially formed cycloadduct dehydrobrominated readily upon distillation to yield 7-bromo-7-vinylbicyclo(3.2.0)hept-2-en-6-one; 50 per cent yield at 62-63° C at 0.2 mm.; ir, (both isomers), 1800 cm^{-1} and 1650 cm^{-1}; nmr (both isomers), δ 5.68 (m, 5H), 3.87 (m, 2H), 2.64 (m, 2H). The isomer distribution was not determined, since the isomer mixture could not be analysed by vpc without decomposition and the nmr spectra was too complicated for analysis.

Analysis Calculated for C_9H_9OBr: C, 50.73; H, 4.26. Found: C, 50.43; H, 4.61.

General Procedure for in situ Dihaloketene-Cyclopentadiene Cycloadditions. A 0.5 mole portion of dihaloacetyl chloride was added dropwise to a solution of 1.5 moles cyclopentadiene and 0.6 mole of triethylamine in 400 ml. of hexane at 0-5°C. The reaction mixture was allowed to stir at room temperature for 4 hours, and worked up as described for the alkylhaloketene-cyclopentadiene adducts.

7,7-Dichlorobicyclo(3.2.0) hept-2-en-6-one

Dichloroacetyl chloride was dehydrochlorinated to give a 60 per cent yield of cycloadduct. The physical properties, ir and nmr spectra were identical to those in the literature (35).

7,7-Dibromobicyclo(3.2.0)hept-2-en-6-one

Dibromoacetyl chloride was dehydrochlorinated to give a 45 per cent yield of cycloadduct. The physical properties, ir and nmr spectra were identical to those in the literature (2).

7-Bromo-7-chlorobicyclo(3.2.0)hept-2-en-6-one

Bromochloroacetyl chloride was dehydrochlorinated to give a 60 per cent yield of cycloadduct; b. pt. 62-63°C at 0.15 mm. The reaction was apparently stereospecific producing only the endo-bromo isomer This assignment was made by a comparison of the nmr spectra of the cyclopentadiene adducts of bromochloroketene, dichloroketene and dibromoketene. This assignment is consistent with the preference of the larger ketene substituent for the endo-position in the cycloadduct ; ir, 1805 cm^{-1}; nmr, δ 5.70 (m, 2H), 4.18 (3d, 1H), 3.90 (m, 1H), 2.47 (m, 2H).

Analysis Calculated for C_7H_6OClBr: C, 37.81; H, 2.71. Found: C, 37.98; H, 2.93.

General Procedure for in situ Ketene Cycloadditions to 1-Methylcyclopentadiene. The cycloadditions were conducted as described above for

cyclopentadiene except that a mixture of 1-methyl- and 2-methylcyclopentadiene in approximately equal amounts was used instead of cyclopentadiene. A fourfold excess of methylcyclopentadiene to acid chloride was employed. The reaction mixture was worked up as soon as the addition of acid chloride was complete since in this manner the unreacted methylcyclopentadiene could be removed before dimerization had occurred (the dimer was very difficult to separate from the cycloadduct). In all cases the major product obtained was identified as the adduct of the ketene with 1-methylcyclopentadiene; a small amount (less than 10 per cent) of the 2-methylcyclopentadiene adduct was observed in some cases. These results correspond to those obtained by Dreiding and Huber in the cycloaddition of dimethylketene to mixed methylcyclopentadienes (24).

7,7-Dichloro-3-methylbicyclo(3.2.0)hept-2-en-6-one

Dichloroacetyl chloride was dehydrohalogenated at 0-5°C; 55 per cent yield at 75-77°C at 0.3 mm. Vpc revealed the adduct to be a mixture of two components in a ratio of about 10. The major component was identified as the adduct of dichloroketene and 1-methylcyclopentadiene by subsequent solvolysis to the known 4-methyltropolone; ir, 1805 cm^{-1}; nmr, δ 5.34 (m, 1H), 4.00 (m, 2H), 2.57 (m,2H), 1.70 (s, 3H).

Analysis Calculated for $C_8H_8OCl_2$: C, 50.26; H, 4.17. Found: C, 50.11; H, 4.34.

7-Chloro-3,7-dimethylbicyclo(3.2.0)hept-2-en-6-one

2-Chloropropanoyl chloride was dehydrochlorinated at room temperature; 75 per cent yield at 52- 53°C at 0.1 mm. An isomer distribution of 4 (endo-methyl/ exo-methyl) was obtained. No significant amount of the 2-methylcyclopentadiene adduct was produced; ir, (both isomers), 1800 cm^{-1}; nmr (endo -methyl), δ 5.44 (m, 1H), 4.20 (3d, 1H), 3.64 (m, 1H), 2.49 (m, 2H), 1.75 (s, 3H), 1.45 (s, 3H). The exo-methyl isomer was not isolated.

Analysis Calculated for $C_9H_{11}OCl$: 63.53; H, 6.47. Found: C, 63.92;H, 6.41.

7-Bromo-3,7-dimethylbicyclo(3.2.0)hept-2-en-6-one

2-Bromopropanoyl chloride was dehydrochlorinated at 0-5° C in acetonitrile instead of hexane; 50 per cent yield at 75-77° C at 0.2 mm. An isomer distribution of above 20 (exo-methyl/endo-methyl) was obtained; ir, 1800 cm^{-1}; nmr, δ 5.36 (m, 1H), 4.04 (3d, 1H), 3.46 (m, 1H), 2.49 (m, 2H), 1.92 (s, 3H), 1.82 (s, 3H).

Analysis Calculated for $C_9H_{11}OBr$: C, 50.26; H, 5.16. Found : C, 50.44; H, 5.32.

7-Chloro-7-n-propyl-3-methylbicyclo(3.2.0)hept-2-en-6-one

2-Chloropentanoyl chloride was dehydrochlorinated at room temperature; 65 per cent yield at 62-63° C at 0.1 mm. An isomer distribution of 8 (endo-n-propyl/ exo-n-propyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-n-propyl), δ 5.38 (m, 1H), 4.13 (3d, 1H), 3.47 (m, 1H), 2.38 (m, 2H), 1.33 (m, 7H), 0.89 (t, 3H). The exo-n-propyl isomer was not isolated.

Analysis Calculated for $C_{11}H_{15}OCl$: C, 66.46; H, 7.60. Found: C, 66.85; H, 7.97.

7-Chloro-7-(2-propyl)-3-methylbicyclo(3.2.0)hept-2-en-6-one

2-Chloro-3-methylbutanoyl chloride was dehydrochlorinated at room temperature; 60 per cent yield at 71-72° C at 0.1 mm. An isomer distribution of 10 (endo-i-propyl/exo-i-propyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-i-propyl), δ 5.43 (m, 1H), 4.18 (3d, 1H), 3.58 (m, 1H), 2.44 (m, 2H), 2.16 (h, 1H), 1.80 (s, 3H), 1.04 (2d, J= 8 cps, 6H). The exo-i-propyl isomer was not isolated.

Analysis Calculated for $C_{11}H_{15}OCl$: C, 66.46; H, 7.60. Found: C, 66.74; H, 7.84.

General Procedure for in situ Aldohaloketene Cyclopentadiene Cycloadditions. To a solution of 1.25 mole of triethylamine and 4.0 moles of

cyclopentadiene in 1 l. of hexane cooled to -78°C with a Dry Ice-acetone bath, 1.0 mole of haloacetyl bromide in 200 ml. of hexane was added dropwise. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then worked up in the manner previously described.

7-Chlorobicyclo(3.2.0)hept-2-en-6-one

Chloroacetyl bromide was dehydrobrominated to give a 40 per cent yield of cycloadduct. The physical properties, ir and nmr spectra were identical to those in the literature (3, 4). A small amount of the exo-chloro isomer was observed; presumably this isomer arises from an isomerization of the endo-chloro isomer by the excess triethylamine present in the reaction mixture. It was impossible to completely separate the two isomers by fractional distillation.

7- Fluorobicyclo(3.2.0)hept-2-en-6-one

Fluoroacetyl bromide was dehydrobrominated to give a 30 per cent yield of cycloadduct. The physical properties, ir and nmr spectra were identical to those in the literature (3, 4). Only the endo-fluoro isomer was observed, even after prolonged standing in the presence of excess amine.

7-Chloro-7-methylbicyclo(3.2.0)heptan-6-one

To a solution of 60 g. (0.6 mole) of triethylamine and 136 g. (2.0 mole) of cyclopentene in 400 ml. of hexane heated to reflux , 65 g. (0.5 mole) of 2-chloropropanoyl chloride in 150 ml. of hexane was added dropwise over a period of 3 hours. It was essential to add the acid chloride very slowly to prevent the formation of α-halovinyl ester. After the acid chloride had been added, the reaction mixture was allowed to stir at room temperature for 3 hours and worked up by the previously described procedure. A 35 per cent yield was obtained; the isomer distribution was 4.5 (endo-methyl/exo-methyl).

The physical properties, ir and nmr spectra were identical to those in the literature (9).

8-Chloro-8-methylbicyclo(4.2.0)octan-7-one

The adduct was prepared by the same procedure as that described for 7-chloro-7-methylbicyclo(3.2.0)heptan-6-one, except that cyclohexene was substituted for cyclopentene. A 60 per cent yield was obtained ; the isomer distribution was 4 (endo-methyl/ exo-methyl). The physical properties, ir and nmr spectra were identical to those in the literature (7).

8-Chloro-8-methylbicyclo(4.2.0)octa-2-en-7-one

The adduct was prepared by the same procedure as that described for 7-chloro-7-methylbicyclo(3.2.0)heptan-6-one , except that 1,3-cyclohexadiene was substituted for cyclopentene. A 50 per cent yield was obtained ; the isomer distribution was 4.5 (endo-methyl/ exo-methyl) . The physical properties, ir and nmr spectra were identical to those in the literature (7).

2-Bromo-2,3,4-trimethylcyclobutanone

A 20 g. (0.12 mole) portion of 2-bromopropanoyl chloride was added dropwise with vigorous stirring to a solution of 20 g. (0.2 mole) of triethylamine and 80 ml. (1.0 mole) of cis-2-butene in 200 ml. of dry hexane at 0°C. The reaction flask was fitted with a cold-finger condenser filled with Dry Ice - acetone to prevent loss of cis-2-butene. The reaction mixture was allowed to stand for 3 hours and then the amine salt was removed by filtration. Concentration on a rotary evaporator and distillation afforded 5 g. (22 per cent); b.pt. 40-42°C at 0.1 mm . An isomer distribution of 0.9 (cis-methyl/trans-methyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (both isomers), δ 3.45 (m, 1H), 2.48 (m, 1H), 1.87 and 1.68 (2 s, 3H), 1.1 (d, J = 8 cps, 6H).

Analysis Calculated for $C_7H_{11}OBr$: C, 44.00; H , 5.76. Found: C, 43.83; H, 5.50.

11,11-Dichlorotricyclo (7.2.0.$0^{2,7}$)undeca-2.4.6-trien-10-one

To 116 g. (1.0 mole) of indene and 60 g. (0.6 mole) of triethylamine in 400 ml. of hexane at reflux was added 75 g. (0.5 mole) of dichloroacetyl chloride in 150 ml. hexane. The acid halide was added dropwise over a period of 1 hour with vigorous stirring; after the addition was complete, the reaction mixture was allowed to stir at room temperature for 2 hours. The triethylamine salt was removed by filtration and the solvent removed by rotary evaporation. The excess indene was removed by distillation at 0.5 mm and the residue , which solidified on standing, was purified by sublimation at reduced pressure. The yield of purified adduct was 50 g. (44 per cent). The melting point and nmr spectrum were identical to those reported in the literature (20, 38).

11-Chloro-11-methyltricyclo(7.2.0.$0^{2,7}$)undeca-2.4.6-trien-10-one

A solution of 1.0 mole indene, 0.75 mole of triethylamine in dry hexane was refluxed with stirring while 0.5 mole of 2-chloropropanoyl chloride was added dropwise over a period of 1 hour. Workup in the usual manner yielded 80 g. (78 per cent) of the cycloadduct at 105-108^{o}C at 0.1 mm which solidified on standing, m. pt. 45-46^{o}C. An isomer distribution of 5 (endo-methyl/ exo-methyl) was obtained; ir, (both isomers), 1800 cm^{-1}; nmr (endo-methyl), δ 7.21 (s, 4H), 4.42 (3d, 1H), 4.04 (m, 1H), 3.15 (m, 2H), 1.28 (s, 3H). The exo-methyl isomer was not isolated.

Analysis Calculated for $C_{12}H_{11}OCl$: C, 69.74; H, 5.36. Found: C, 69.79; H, 5.52.

General Procedure for the Sodium Carbonate Solvolysis of endo-Alkyl-exo-haloketene Cyclopentadiene Adducts. The endo-alkyl isomer of the alkylhaloketene-cyclopentadiene adduct, 0.15 mole, and 250 ml. of 20 per cent aqueous Na_2C0_3 solution was refluxed with vigorous stirring. Periodically 1 ml. aliquots were withdrawn by syringe and mixed with an equal volume

of $CHCl_3$. The organic layer was assayed by vpc to determine the extent of reaction. It was necessary to assay the solvolysis mixtures of the alkylbromoketenes by ir analysis of the $CHCl_3$ extracts, observing the disappearance of the cyclobutanone carbonyl absorption at 1800 cm^{-1} and the appearance of the strong tropone carbonyl absorption at 1575 cm^{-1}. When all the cycloadduct had been consumed, the reaction mixture was extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried over $CaCl_2$, rotary evaporated and distilled to yield the 2-alkyltropone. The aqueous layer was acidified with 6 N HCl solution. The 6-alkyl-6-carboxybicyclo(3.1.0)hex-2-ene would separate as either a solid precipitate or an oil. The solid was collected by filtration and purified by vacuum sublimation at 0.1 mm. If the product was an oil, the acidified reaction mixture was extracted with $CHCl_3$. This extract was dried over $CaCl_2$, rotary evaporated and distilled. The distillate generally solidified on standing and no further purification was necessary. For the yields of 2-alkyltropone and 6-alkyl-6-carboxybicyclo(3.1.0)hex-2-ene, see Table III in the discussion section.

2-Methyltropone

B.pt. 70-72°C at 1.0 mm; ir, 1630 cm^{-1}(s), 1575 cm^{-1}(vs) and 1525 cm^{-1}(s). (The ir spectrum was identical to that reported in the literature for this ccmpound (12).) Nmr, δ 6.95 (m, 5H), 2.19 (s, 3H).

2-Ethyltropone

B.pt. 78°C at 1.5 mm (lit. 63-64°C at 0.05 mm (37)); ir, 1630 cm^{-1}(s), 1575 cm^{-1}(vs) and 1525 cm^{-1}(s); nmr, δ 7.04 (m, 5H), 2.80 (q, 2H), 1.27 (t, 3H).

2-n-Propyltropone

B. pt. 78-80°C at 0.5 mm; ir, 1640 cm^{-1}(s), 1580 cm^{-1}(vs) and 1530 cm^{-1}(s); nmr, δ 7.04 (m, 5H), 2.63 (t, 2H), 1.58 (sextet, 2H), 0.93 (t, 3H).

Analysis Calculated for $C_{10}H_{12}O$: C, 81.08 ; H, 8.10. Found: C, 81.48; H, 8.20.

2-(2-Propyl)tropone

B. pt. 75-76°C at 0.1 mm (lit. 59-60°C at 0.01 mm (37)); ir, 1630 cm^{-1} (s), 1575 cm^{-1} (vs) and 1525 cm^{-1} (s); nmr, δ 7.13 (m, 5H), 3.44 (h, 1H), 1.13 (d, J=7cps, 6H).

2-n-Butyltropone

B. pt. 115-117°C at 2.0 mm; ir, 1640 cm^{-1} (s), 1580 cm^{-1} (vs) and 1525 cm^{-1} (s); nmr, δ 6.94 (m, 5H), 2.50 (t, 2H),1.37 (m, 4H), 0.90 (t, 3H); mass spectrum m/e = 162, theory 162.

Analysis Calculated for $C_{11}H_{14}O$: C, 81.44; H, 8.65. Found: C, 81.47; H, 8.82.

2-Cyclohexyltropone

An isomeric mixture containing 80 per cent of the endo-cyclohexyl isomer was used as starting material; b. pt. 120-125°C at 1.0 mm; ir, 1640 cm^{-1} (s), 1575 cm^{-1} (vs) and 1530 cm^{-1} (s) ; nmr, δ 7.16 (m, 5H), 2.57 (m, 1H), 2.05-0.95 (broad mult., 10H); mass spectrum, m/e = 188 (theory 188). An acceptable elemental analysis could not be obtained due to residual starting material (exo-cyclohexyl isomer) which could not be removed.

2-Cyclohexylmethyltropone

An isomeric mixture containing 85 per cent of the endo-alkyl isomer was used as starting material; b. pt. 112-115°C at 0.3 mm; ir, 1640 cm^{-1} (s), 1580 cm^{-1} (vs) and 1530 cm^{-1} (s) ; nmr, δ 6.84 (m, 5H), 2.48 (d, J= 5 cps, 2H), 1.95-0.80 (broad mult., 11H); mass spectrum m/e= 202 (theory 202). An acceptable elemental analysis could not be obtained due to residual starting material (exo-alkyl isomer) which could not be removed.

2-(2-Cyclohexylethyl)tropone

An isomeric mixture containing 85 per cent of the endo-alkyl isomer was used as starting material; b. pt. 140-145°C at 0.4 mm; ir, 1635 cm^{-1} (s),

1575 cm^{-1}(vs), 1530 cm^{-1}(s); nmr, δ 6.90 (m, 5H), 2.36 (t, 2H), 1.88-0.76 (broad multiplet, 13 H); mass spectrum, m/e = 216 (theory 216). An acceptable elemental analysis could not be obtained due to residual starting material (exo-alkyl isomer)which could not be removed.

2-n-Octyltropone

An isomer mixture containing 90 per cent of the endo-n-octyl isomer was used as starting material; b. pt. 125- 127° at 0.1 mm; ir, 1640 cm^{-1}(s), 1580 cm^{-1}(vs), 1520 cm^{-1}(s); nmr, δ 7.00 (m, 5H), 2.62 (t, 2H), 1.32 (m, 12 H), 0.95 (t, 3H); mass spectrum, m/e = 218 (theory 218). An acceptable elemental analysis could not be obtained due to residual starting material (exo-n-octyl isomer) which could not be removed.

2,5-Dimethyltropone

This tropone was obtained from the cycloadduct of methylchloroketene and 1-methylcyclopentadiene by the procedure described above; b. pt. 72-74°C at 0.5 mm; ir, 1640 cm^{-1}(s), 1570 cm^{-1}(vs), 1540 cm^{-1}(s); nmr, δ 7.27 (m, 4H), 2.22 (s, 3H), 2.15 (s, 3H).

Analysis Calculated for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.53; H, 7.68.

2-n-Propyl-5-methyltropone

This tropone was obtained from the cycloadduct of n-propylchloroketene and 1-methylcyclopentadiene by the procedure described above; b. pt. 85-87°C at 0.1 mm; ir, 1640 cm^{-1}(s), 1575 cm^{-1}(vs), 1535 cm^{-1}(s); nmr, δ 7.02 (m, 4H), 2.42 (t, 2H), 2.17 (s, 3H), 1.45 (sextet, 2H), 0.88 (t, 3H).

Analysis Calculated for $C_{11}H_{14}O$: C, 81.44; H, 8.65. Found: C, 81.13; H, 8.67.

2-(2-Propyl)-5-methyltropone

This tropone was obtained from the cycloadduct of isopropylchloroketene and 1-methylcyclopentadiene by the procedure described above;

b. pt. 89-90°C at 0.1 mm; ir, 1640 cm^{-1}(s), 1575 cm^{-1}(vs), 1540 cm^{-1}(s); nmr, δ 7.00 (m, 4H), 3.40 (h, 1H), 2.23 (s, 3H), 1.17 (d, J = 7 cps, 6H).

Analysis Calculated for $C_{11}H_{14}O$: C, 81.44; H, 8.65. Found: C, 81.07; H, 8.93.

Exo-6-carboxy-endo-6-methylbicyclo(3.1.0)hex-2-ene

M. pt. 82-84°C; nmr, δ 11.96 (s, 1H), 5.76 (s, 2H), 2.68 (m, 2H), 2.26 (m, 2H), 1.00 (s, 3H).

Analysis Calculated for $C_8H_{10}O_2$: C, 69.54; H, 7.25. Found; C, 69.81; H, 7.50.

Exo-6-carboxy-endo-6-ethylbicyclo(3.1.0)hex-2-ene

M, pt. 55-60°C; nmr, δ 12.12 (s, 1H), 5.58 (s, 2H), 2.56 (m, 2H), 2.18 (m, 2H), 1.68 (m, 1H), 0.96 (m, 4H).

Analysis Calculated for $C_9H_{12}O_2$: C, 71.02; C, 7.89. Found: C, 71.19; H, 8.02.

Exo-6-carboxy-endo-6-n-propylbicyclo(3.1.0)hex-2-ene

B. pt. 110-112°C at 0.1 mm; m. pt. 48-50°C; nmr, δ 12.70 (s, 1H), 5.70 (s, 2H), 2.60 (m, 2H), 2.20 (m, 2H), 1.28 (m, 4H), 0.84 (t, 3H).

Analysis Calculated for $C_{10}H_{14}O_2$: C, 72.26; H, 8.48. Found: C, 71.93; H, 8.40.

Exo-6-carboxy-endo-6-n-butylbicyclo(3.1.0)hex-2-ene

B. pt. 125-127°C at 0.1 mm (this acid did not solidify after distillation); nmr, δ 12.23 (s, 1H), 5.74 (s, 2H), 2.61 (m, 2H), 2.20 (m, 2H), 1.33 (m, 6H), 0.92 (t, 3H).

Analysis Calculated for $C_{11}H_{16}O_2$: C, 73.29; H, 8.96. Found: C, 73.21; H, 8.85.

Exo-6-carboxy-endo-6-methyl-3-methylbicyclo(3.1.0)hex-2-ene

M. pt. 106-108°C; nmr, δ 11.53 (s, 1H), 5.54 (m, 1H), 2.44 (m, 2H), 2.12 (m, 1H), 1.90 (m, 1H), 1.64 (s, 3H), 0.93 (s, 3H).

Analysis Calculated for $C_9H_{12}O_2$: C,71.02; H, 7.89. Found: C, 70.91; H, 7.68.

Exo-6-carboxy-endo-6-n-propyl-3-methylbicyclo(3.1.0)hex-2-ene

M. pt. 122-125°C; nmr, δ 11.42 (s, 1H), 5.34 (m, 1H), 2.33 (m, 2H). 2.03 (m, 2H), 1.64 (s, 3H), 1.22 (m, 4H), 0.84 (t, 3H).

Analysis Calculated for $C_{11}H_{16}O_2$: C, 73.29; H, 8.96. Found: C, 73.16; H, 8.70.

General Procedure for the Acetic Acid/ Sodium Acetate Solvolysis of endo-Alkyl-exo-haloketene Cyclopentadiene Adducts. The solvolysis medium was prepared by dissolving 200 g. of NaOAc·3 H_2O in a mixture of 800 ml. of glacial acetic acid and 300 ml. of water. To 300 ml. of this solution was added 0.15 mole of cycloadduct (endo-alkyl isomer) and the mixture refluxed. The progress of the reaction was followed by withdrawing aliquots periodically, neutralizing with 30 per cent aqueous NaOH, extracting with an equal volume of $CHCl_3$ and assaying by vpc or ir as described for the sodium carbonate solvolysis. Upon completion of the reaction, neutralization was effected with a 30 per cent aqueous NaOH solution to a pH of about 10 and the mixture extracted with 2 x 500 ml. portions of $CHCl_3$. The combined $CHCl_3$ extracts were dried over $CaCl_2$, rotary evaporated and distilled to yield the 2-alkyl-tropone. This procedure was used to prepare 2-methyl-, 2-ethyl and 2-n-butyl-tropones. The yields are recorded in Table II in the discussion section.

Exo-10-carboxy-endo-10-methyltricyclo ($7.1.0.0^{2,7}$) deca-2,4,6-triene

A mixture of 10 g (0.1 mole) of the endo-methyl isomer of the cycloadduct of methylchloroketene and indene in 200 ml. of 20 per cent aqueous Na_2CO_3

solution was refluxed with stirring until solution was accomplished (about 5 hours). The reaction solution was neutralized while still hot with 6 N HCl solution and the precipitated product (5 g. (60 per cent)) collected by filtration; m. pt. 118-120° C; nmr, δ 9.36 (s, 1H), 6.96 (m, 4H), 2.16 (m, 2H), 2.72 (d, J= 9 cps, 1H), 2.40 (m, 1H), 0.76 (s, 3H).

Analysis Calculated for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.26; H, 6.42.

General Procedure for Determining the Relative Rates of Ring Contraction of exo-Alkyl-endo-haloketene-Cyclopentadiene Adducts. A mixture of 0.03 mole of the exo-alkyl-endo-haloketene-cyclopentadiene adduct and 100 ml. of 20 per cent aqueous Na_2CO_3 solution was refluxed with stirring. Periodically, 2 ml aliquots were withdrawn from the aqueous layer, diluted with 50 ml. of water and titrated with 0.1 N standardized HCl solution using thymol blue as an indicator. The relative rates of reaction were obtained by comparing the amounts of acid required to neutralize the reaction mixture versus time. These plots were essentially linear until about 50 per cent of the cycloadduct had been consumed. The reactions were allowed to go to completion and then worked up in the usual manner. The yield of product and the relative rate of ring contraction for different alkyl groups and halogens are shown in Table IV .

Endo-6-carboxy-exo-6-methylbicyclo(3.1.0)hex-2-ene

M. pt. 93-95°C (lit. m. pt. 95.5° C (10)); nmr, δ 10.84 (s, 1H), 5.68 (m, 2H), 2.68 (m, 2H), 2.14 (m, 1H), 1.72 (m, 1H), 1.38 (s, 3H).

Endo-6-carboxy-exo-6-ethylbicyclo(3.1.0)hex-2-ene

M. pt. 52-54°C (lit. m. pt. 55° C (10)); nmr, δ 11.64 (s, 1H), 5.48 (m, 2H), 2.56 (m, 2H), 1.96 (m, 2H), 1.56 (m, 1H), 1.16 (m, 1H), 1.00 (t, 3H).

Endo-6-carboxy-exo-6-n-propylbicyclo(3.1.0) hex-2-ene

B. pt. 105-106 °C at 0.1 mm; m. pt. 37-40°C; nmr, δ 11.80 (s, 1H), 5.48 (m, 2H), 2.68 (m, 2H), 2.20-1.08 (complex mult., 6H), 0.94 (t, 3H).

Analysis Calculated for $C_{10}H_{14}O_2$: C, 72.26; H, 8.48. Found: C, 71.93; H, 8.40.

Endo-6-carboxy-exo-6-(2-propyl)bicyclo(3.1.0) hex-2-ene

B. pt. 103-105°C at 0.1 mm; n. pt. 66-69°C (lit. m. pt. 70°C (10)); nmr, δ 9.38 (s, 1H), 5.64 (m, 2H), 2.12 (m, 1H), 1.48 (m, 1H), 1.28 (h, 1H) overlapping 1.08 (2d, J = 7 cps, 6H).

Endo-6-carboxy-exo-6-n-butylbicyclo(3.1.0)hex-2-ene

B. pt. 117-119°C at 0.1 mm (This acid did not solidify after distillation); nmr, δ 11.24 (s, 1H), 5.60 (m, 2H), 2.60 (m, 2H), 2.02 (m, 1H), 1.66 (m, 1H), 1.36 (m, 6H), 0.90 (t, 3H).

Analysis Calculated for $C_{11}H_{16}O_2$: C,73.29; H, 8.96. Found: C, 73.21; H, 8.85.

Endo-6-carboxy-exo-6-methyl-3-methylbicyclo(3.1.0)hex-2-ene

M. pt. 46-48°C ; nmr, δ 10.68 (s, 1H), 5.32 (m, 1H), 2.60 (m, 2H), 2.04 (m, 1H), 1.72 (m, 1H) overlapping 1.65 (s, 3H), 1.32 (s, 3H).

Analysis Calculated for $C_9H_{12}O_2$: C, 71.02 ; H, 7.89. Found: C, 70.91; H, 7.68.

6-Carboxybicyclo(3.1.0)hex-2-ene

This compound was obtained from the endo-chloro isomer of the adduct of chloroketene and cyclopentadiene. A mixture of endo-carboxy and exo.-carboxy isomers was produced; b. pt. 94-96°C at 0.4 mm; m. pt. 75- 80°C; nmr, δ 10.64 (s, 1H), 5.72 (m, 2H), 2.56 (m, 3H), 1.88 (m, 2H).

Analysis Calculated for $C_7H_8O_2$: C, 67.60; H, 6.45. Found: C, 67.67; H, 6.59.

General Procedure for the Sodium Methoxide Treatment of Ketene-Olefin Cycloadducts. A 150 ml. portion of methanol to which 4 g. of sodium had been added was vigorously refluxed while a solution of 10 g. of the ketene-olefin cycloadduct in 25 ml. of methanol was added. There was an immediate precipitate of the sodium halide with all of the halogenated ketene adducts. Refluxing was continued for 15 minutes and then the mixture was added to 150 ml. of water. This aqueous mixture was extracted with chloroform . The organic layer was dried over $CaCl_2$, the solvent was removed on a rotatory evaporator and the residue was distilled to yield the product.

Endo -6-carbomethoxy-exo-6-methylbicyclo(3.1.0)hex-2-ene

About a 60 per cent yield was obtained from either the methylchloroketene- or methylbromoketene-cyclopentadiene adduct (exo-methyl isomer): b. pt. 60-62°C at 2.0 mm; ir, 1740 cm^{-1}; nmr, δ 5.52 (m, 2H), 3.55 (s, 3H), 2.64 (m, 2H), 2.00 (m, 1H), 1.58 (m, 1H), 1.28 (s, 3H); mass spectrum, parent peak at m/e = 152 (theory 152), major peak at m/e=93 corresponding to the loss of carbomethoxy group.

Analysis Calculated for $C_9H_{12}O_2$: C, 71.02; H, 7.89. Found: C, 70.97; H, 8.26.

Exo-6-carbomethoxy-endo-6-methylbicyclo(3.1.0)hex-2-ene

A 60 per cent yield was obtained from the rearrangement of the adduct of methylchloroketene and cyclopentadiene (endo-methyl isomer); b. pt. 60-62°C at 2.0 mm ; ir, 1740 cm^{-1}; nmr,δ5.54 (s, 2H), 3.58 (s, 3H), 2.48 (m, 2H), 2.07 (m, 2H), 0.92 (s, 3H).

Analysis Calculated for $C_9H_{12}O_2$: C, 71.02; H, 7.89. Found: C, 70.97; H, 8.26.

6-Carbomethoxy-6-vinylbicyclo(3.1.0)hex-2-ene

A 15 per cent yield was obtained from the rearrangement of the adduct of vinylbromoketene and cyclopentadiene (mixture of isomers); b. pt. 70-72°C

at 2.5 mm; ir, (both isomers), 1730 cm^{-1} and 1630 cm^{-1}; nmr (both isomers), δ 5.40 (m, 5H), 3.64 and 3.58 (2s, 3H), 2.4 (complex mult., 4H).

Analysis Calculated for $C_{10}H_{12}O_2$: C, 73.10; H, 7.31. Found: C, 72.68; H, 7.89.

6-Carbomethoxybicyclo(3.1.0)hex-2-ene

A 15 per cent yield was obtained from the chloroketene-cyclopentadiene adduct (endo-chloro isomer) and a 10 per cent yield was obtained from the corresponding fluoroketene adduct (endo-fluoro isomer); a mixture of isomers was obtained; b. pt. 55°C at 2.5 mm; ir (both isomers), 1730 cm^{-1}; nmr (both isomers), δ 5.7 (m, 2H), 3.70 and 3.58 (2 s, 3H), 2.32 (complex mult., 5H).

Analysis Calculated for $C_8H_{10}O_2$: C, 69.54; H, 7.25. Found: C, 69.49; H, 7.52.

8-Methyl-6-methoxybicyclo(4.2.0)octan-7-one

A 60 per cent yield was obtained from the adduct of methylchloroketene and cyclohexene (endo-methyl isomer); b. pt. 56-58° at 1.8 mm; ir, 1780 cm^{-1}; nmr, δ 3.45 (s, 3H), 1.80 (m, 10H), 1.15 (d, J = 8 cps, 3H); mass spectrum, m/e = 168 (theory 168).

Analysis Calculated for $C_{10}H_{16}O_2$: C, 71.30; H, 9.52. Found: C, 70.55; H, 9.17.

2-Methoxy-2,3,4-trimethylcyclobutanone

A 70 per cent yield was obtained from the adduct of methylbromoketene and cis-2-butene (mixture of isomers); b. pt. 98-100°C at 60 mm; ir, 1780 cm^{-1}; nmr, δ 3.2 (s, 3H), 2.1 (m, 2H), 1.2 (m, 9H).

Analysis Calculated for $C_8H_{14}O_2$: C, 67.50; H, 9.85. Found: C, 67.14; H, 9.78.

7-Methyl-5-methoxybicyclo(3.2.0) hept-2-en-6-one

A solution of sodium methoxide in methanol was prepared by dissolving

2g. (0.1 mole) of sodium in 50 ml. of absolute methanol. This solution was cooled to -78°C with a Dry Ice-acetone bath and 5 gm (0.03 mole) of the methylchloroketene-cyclopentadiene adduct (endo-methyl isomer) in 25 ml. methanol was added. There was no immediate reaction; the reaction mixture was allowed to warm to room temperature ; when the temperature of the solution reached about 0-5°C there was a sudden precipitate of sodium chloride. The reaction mixture was allowed to stand at room temperature for 1 hour and then was poured into 150 ml. of water; this solution was extracted with 2x 100 ml. portions of chloroform. The combined chloroform extracts were dried over $CaCl_2$, rotary evaporated and the residue vacuum distilled to yield the substitution product; b. pt. 70-71°C at 4.0 mm. A yield of 4 g. (80 per cent) was obtained; ir (both isomers), 1780 cm^{-1}; nmr (both isomers)δ5.68 (m, 2H), 3.28 (s, 3H), 2.88 (m, 1H), 2.69 (m, 1H), 2.44 (m, 2H), 1.20 and 0.92 (2 d, J = 7 cps, 3H). A mixture of isomers was obtained from either the endo-methyl or exo-methyl isomer of cycloadduct.

Analysis Calculated for $C_9H_{12}O_2$: C, 71.02; H,7.89. Found: C, 70.81; H, 8.01.

7-Ethyl-5-methoxybicyclo(3.2.0)hept-2-en-6-one

The adduct of ethylchloroketene and cyclopentadiene (endo-ethyl isomer) was treated with sodium methoxide in methanol as described above for the methylchloroketene-cyclopentadiene adduct. A 70 per cent yield of substitution product was obtained; b. pt. 85-86°C at 5.0 mm; ir (both isomers), 1785 cm^{-1}; nmr (both isomers), δ 5.68 (m, 2H), 3.28 and 3.26 (2 s, 3H), 2.68 (m, 1H), 2.48 (m, 3H), 1.58 (m, 2H), 1.01 (t, 3H).

Analysis Calculated for $C_{10}H_{14}O_2$: C, 72.26; H, 8.48. Found: C, 71.98; H, 8.38.

Several aldoalkyl-and ketoalkylketene-cyclopentadiene adducts were reacted with refluxing sodium methoxide in methanol. There was no evidence of any

reaction, and the cycloadducts were recovered unchanged in all cases. There was some isomerization of the aldoalkylketene cycloadducts.

General Procedure for the Sodium Hydroxide Treatment of Alkylhaloketene Cyclopentadiene Adducts. The reaction was carried out in the manner described for the sodium carbonate rearrangements except that a 20 per cent aqueous sodium hydroxide solution was used instead of sodium carbonate. The rearrangement of exo-7-alkyl-endo-7-halobicyclo-(3.2.0)hept-2-en-6-ones produced the corresponding exo-6-alkyl-endo-6-carboxybicyclo(3.1.0) hex-2-enes as in the case of sodium carbonate rearrangement. If the endo-alkyl isomer was treated with sodium hydroxide, the endo-6-alkyl-exo-6-carboxybicyclo(3.1.0)hex-2-ene was produced; there was no evidence of the formation of 2-alkyltropone from the endo-alkyl isomer in this medium. If a mixture of endo-alkyl and exo-alkyl isomers were reacted with aqueous sodium hydroxide, a mixture of endo-and exo-alkyl rearrangement products were observed in the same isomer ratio as in the starting material.

This rearrangement was performed on both isomers and isomer mixtures of the adducts of methylchloroketene, methylbromoketene and ethylbromoketene with cyclopentadiene. The products obtained were the same as described above in the sodium carbonate solvolyses; the yields were comparable.

8-Methylbicyclo(4.2.0)oct-2-en-6-ol-7-one

To 200 ml. of 20 per cent aqueous sodium carbonate solution was added 10 g. (0.08 mole) of the adduct of methylchloroketene and 1,3-cyclohexadiene (endo-methyl isomer). The solution was refluxed with vigorous stirring for 24 hours. The reaction mixture was allowed to cool, then extracted with 2x 200 ml. portions of chloroform. The combined chloroform extracts were dried over $CaCl_2$, rotary evaporated and the residue distilled to yield 2.5 g. (30 per cent) of the substitution product; b. pt. 77-79^{o}C at

0.5 mm; m. pt. 67-69°C; ir, 1780 cm^{-1} ; nmr, δ 5.80 (m, 2H), 3.44 (broad s , 1H), 2.74 (m, 1H), 2.08 (m, 3H), 1.73 (m, 2H), 1.21 (d, J = 7 cps, 3H).

Analysis Calculated for $C_9H_{12}O_2$: C, 71.02; H, 7.89. Found: C, 70.96; H, 7.80.

General Procedure for the Triethylammonium Acetate Solvolysis of Dihaloketene Olefin Cycloadducts . The solvolysis medium was prepared by mixing 50 g. of glacial acetic acid, 60 g. of water and 100 g. of triethylamine and adding acetone (about 300 ml.) to form a homogeneous solution. To 300 ml. of this solution, 0.08 mole of cycloadduct was added and the solution refluxed. The progress of the reaction was followed by periodically withdrawing samples and assaying by vpc. Indene was added to provide a reference peak. The area of the cycloadduct peak was measured as a function of time. After the cycloadduct had been consumed, the reaction mixture was extracted with 2 x 500 ml. portions of ether. The combined ether extracts were rotary evaporated and the residue added to 300 ml. of benzene. The residual water was removed by azeotropic distillation. The benzene was evaporated on a rotatory evaporator and the residue vacuum distilled. The yields of product and relative rates of formation are shown in Table VII in the discussion section.

Tropolone

Tropolone was obtained from the solvolysis of the cyclopentadiene adducts of dichloroketene, dibromoketene and bromochloroketene ; b. pt. 80-84°C at 0.1 mm; m. pt. 49-50° C (lit. 51° C (13)).

4-Methyltropolone

4-Methyltropolone was obtained from the solvolysis of the adduct of dichloroketene and 1-methylcyclopentadiene; b. pt. 95-100° C at 0.1 mm; m. pt. 74-75°C (lit. m. pt. 75°C (30)); nmr, δ 8.95 (s, 1H), 7.10 (m, 4H), 2.43 (s, 3H).

4,5-Benzotropolone

4,5-Benzotropolone was obtained from the solvolysis of the adduct of dichloroketene and indene; the tropolone precipitated from the residue of the initial ether extraction of the reaction mixture after rotary evaporation; m. pt. 157-159°C (lit. 159-160°C (36)).

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CHAPTER III

RESULTS AND DISCUSSION

The synthesis of 2-alkyltropones was initially attempted by the solvolysis of alkylhaloketene-cyclopentadiene adducts employing the conditions used by Stevens (14) in the preparation of tropolone from the cyclopentadiene adduct of dichloroketene. The adduct was refluxed in a solution of sodium acetate in glacial acetic acid containing a small amount (ten per cent) of water. The adduct of methylchloroketene and cyclopentadiene was converted to 2-methyltropone under these conditions in thirty per cent yield after refluxing for 48 hours.

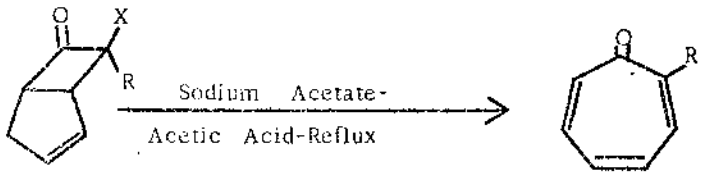
This reaction was repeated with the cyclopentadiene adducts of ethylbromo and n-butylbromoketenes. The corresponding 2-alkyltropones were produced after reflux for 48 hours in the case of the ethylbromoketene adduct and 120 hours for the n-butylbromoketene adduct. However, the yields of 2-alkyltropone were considerably lower than in the case of the methylchloroketene adduct.

The cycloadducts employed in the above reactions consisted of both the endo- and exo-alkyl isomers. The isomer ratio was approximately the ratio of these isomers as produced in the cycloaddition of the alkylhaloketene to cyclopentadiene; that is, endo-methyl/exo-methyl of 4.5 for the methylchloroketene adduct and 1.4-1.6 endo-alkyl/exo-alkyl for the ethylbromo- and n-butylbromoketene adducts. The lower yield for the latter two adducts suggested that only the endo-alkyl adduct was producing 2-alkyltropone. This was confirmed by separating the endo and exo isomers of the cycloadducts by fractional distillation through a spinning band column and subjecting each isomer to the solvolysis individually.

The results of these solvolyses are shown in Table II. In each case the starting material was of at least ninety-five per cent isomeric purity.

TABLE II

SOLVOLYSIS OF ALKYLHALOKETENE-CYCLOPENTADIENE ADDUCTS IN SODIUM ACETATE-ACETIC ACID

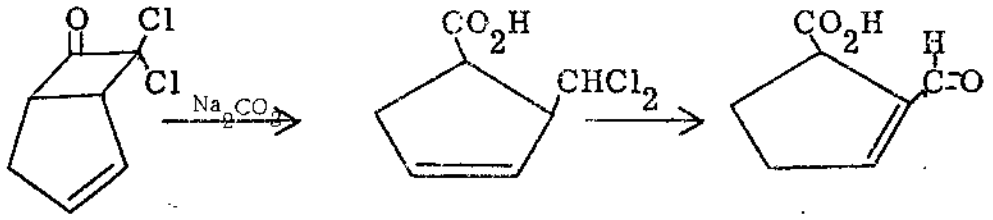


R	X	Reaction Time	Yield of Tropone
endo-CH_3	exo-Cl	48 hr	45
exo-CH_3	endo-Cl	48 hr	0
endo-CH_3	exo-Br	36 hr	22
endo-C_2H_5	exo-Br	72 hr	45
endo-n-C_4H_9	exo-Br	120 hr	40
exo-n-C_4H_9	endo-Br	72 hr	0

The exo-alkyl isomer of the cycloadduct was consumed during the sodium acetate/acetic acid solvolysis, but no product could be isolated from the reaction mixture following completion of the reaction.

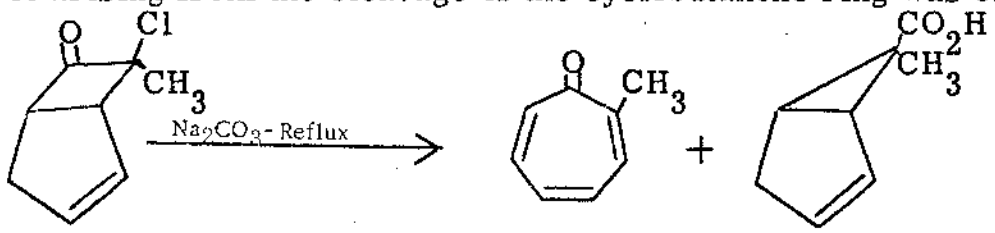
The treatment of the dichloroketene-cyclopentadiene adduct with base generally leads to cleavage of the cyclobutanone ring. This has been observed by Ghosez and coworkers (10) in the reaction of the dichloroketene-cyclopentadiene adduct with sodium methoxide to produce 3-dichloromethyl-4-carbomethoxycyclopentene. A similar ring opening reaction was observed by Stevens (14) when the dichloroketene-cyclopentadiene adduct was

solvolysed in aqueous sodium carbonate or bicarbonate solution. The initially formed product underwent hydrolysis and a shift of the double bond to produce 2-formyl-3-carboxycyclopentene. The formation of these



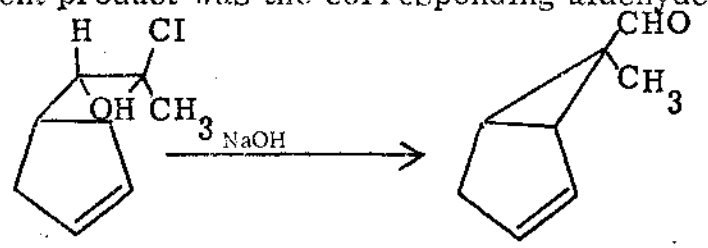
ring opening products during the solvolysis of the dichloroketene-cyclopentadiene adduct in basic media is explained by the stability of the dichloromethyl carbanion which is formed by the cleavage of the cyclobutanone ring. The analogous carbanion formed from the alkylhaloketene-cyclopentadiene adducts would not be expected to be as stable; therefore, the cyclobutanone ring cleavage reactions would not be expected to occur as readily during the treatment of these cycloadducts with basic solutions.

When the endo-methyl isomer of the cyclopentadiene adduct of methylchloroketene was treated with twenty per cent aqueous sodium carbonate, no product arising from the cleavage of the cyclobutanone ring was observed.

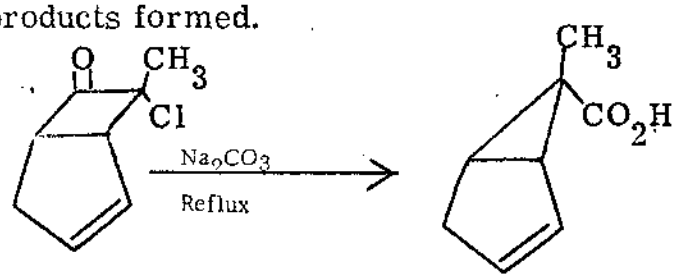


Instead, two products were isolated: 2-methyltropone, formed in thirty-two per cent yield, and endo-6-methyl-exo-6-carboxybicyclo(3.1.0)hex-2-ene, formed in fifty per cent yield. The latter is the result of a stereospecific Favorskii-type ring contraction reaction. This type of ring contraction has been previously observed by Brook and coworkers upon treatment of alkylhaloketene-cyclopentadiene adducts with strong aqueous potassium hydroxide (5) . A similar rearrangement was also observed when the

alcohols obtained by the reduction of the methylchloroketene-cyclopentadiene adduct was treated with potassium hydroxide. In this case the rearrangement product was the corresponding aldehyde (4).



The exo-methyl isomer of the methylchloroketene-cyclopentadiene adduct yielded only the ring contraction product, exo-6-methyl-endo-6-carboxybicyclo(3.1.0)hex-2-ene, in seventy-five per cent yield upon treatment with aqueous sodium carbonate. There were small amounts of polymeric decomposition products formed.



The ring contraction product was also formed from the exo-alkyl cycloadduct during the sodium acetate/acetic acid solvolysis. However, this product was initially overlooked because of its solubility in the large amounts of acetic acid. Isolation can be effected by partial neutralization of the acetic acid followed by fractional distillation under reduced pressure to separate the rearrangement product from the remaining acetic acid.

The solvolysis of the cyclopentadiene adducts of methylbromo and ethylbromoketenes was attempted under the same conditions used for the sodium carbonate solvolysis of the methylchloroketene cycloadduct. The ethylbromoketene adduct yielded 2-ethyltropone along with the corresponding ring contraction product, but the methylbromoketene adduct produced almost entirely ring contraction product, with only a small amount (five per cent) of 2-methyltropone being produced.

To determine the effect of the alkyl group and the halogen on the yield of 2-alkyltropone and ring contraction product, a large number of cycloadducts were treated with sodium carbonate, and the yields of the two resulting products were measured. The results are presented in Table III.

TABLE III

RING CONTRACTION VERSUS 2-ALKYLTROPONE FORMATION FROM EXO-HALO-ENDO-ALKYL ISOMERS

X	R	Overall Yield	Yield 2-Alkyltropone	Yield Ring Con.	Ratio
Cl	Me	82	32	50	0.64
Br	Me	98	5	93	0.06
I	Me	29[a]	1	28	0.03
Cl	Et	80	65	15	4.35
Br	Et	97	27	70	0.39
Cl	n-Pr	75	68	7	9.75
Br	n-Pr	63	39	24	1.60
Cl	i-Pr	88	88	0	-
Br	i-Pr	71	71	trace	20.
Cl	n-Bu	71	66	5	13.
Br	n-Bu	50	32	18	1.75
Br	C_6H_{11}	40	40	*	
Br	C_6H_{11}-CH_2-	35	35	*	
Br	C_6H_{11}-CH_2-CH_2-	30	30	*	
Br	n-Octyl	40	40	*	

* Not measured

[a] Decomposition of starting cycloadduct under reaction conditions

The rearrangements in aqueous sodium carbonate were complete after refluxing for a period of from two to sixteen hours whereas the rearrangements

in sodium acetate/acetic acid required up to a week for completion. The isolation of 2-alkyltropone from the carbonate reaction mixture requires only extraction followed by distillation while isolation from the acetate media requires a time consuming neutralization of large amounts of acetic acid before the 2-alkyltropone can be extracted. The sodium acetate formed during the neutralization usually precipitates, further complicating the workup procedure. The ring contraction product is easily isolated from the carbonate reaction solution by acidification of the aqueous solution after the extraction of the 2-alkyltropone. The ring contraction product often would precipitate and could be collected by filtration.

The only advantage of the sodium acetate/acetic acid media is that ring contraction occurs to a lesser degree than in the sodium carbonate reaction. This is significant for the smaller alkyl groups where ring contraction is a serious competing reaction with 2-alkyltropone formation. For example, a moderate yield of 2-methyltropone can be obtained from the sodium acetate/acetic acid rearrangement of the methylbromoketene-cyclopentadiene adduct whereas the sodium carbonate rearrangement of this adduct produces only a trace of 2-methyltropone.

The generation of alkylhaloketenes in the presence of a mixture of 1- and 2-methylcyclopentadiene yields only the adduct of the alkylhaloketene and 1-methylcyclopentadiene. These adducts can be rearranged in aqueous sodium carbonate under the same conditions used for the formation of 2-alkyltropones to produce 2-alkyl-5-methyltropones. The results of several such rearrangements are shown in Table IV.

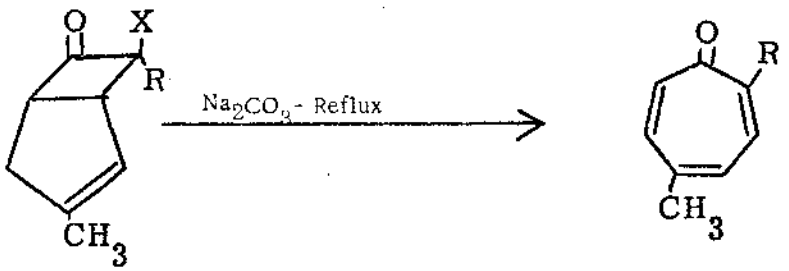


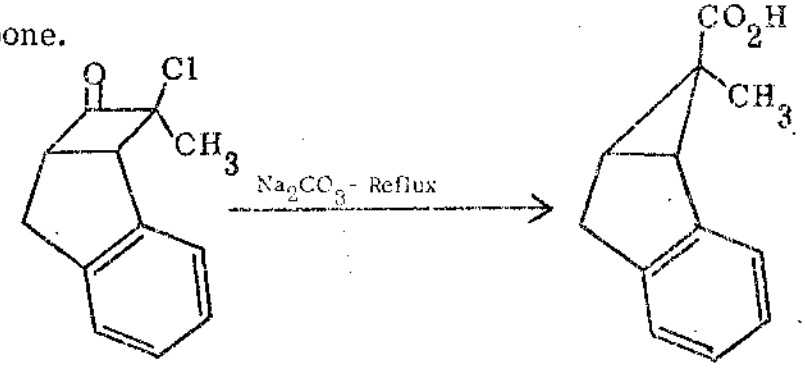
TABLE IV

REARRANGEMENT OF ALKYLHALOKETENE-1-METHYLCYCLOPENTADIENE ADDUCTS-ENDO-ALKYL-EXO-HALO ISOMER

R	X	Overall Yield	Yield 2-Alkyltropone	Yield Ring Con.	Ratio
Me	Cl	92	13	79	0.17
n-Pr	Cl	90	74	16	4.61
i-Pr	Cl	92	92	0	-

It is evident from the data presented in Table IV that ring contraction occurs to a greater extent in the methylcyclopentadiene adducts than in the corresponding cyclopentadiene adducts. However, when the alkyl group was large, such as isopropyl, no ring contraction occurred in the solvolysis of either the cyclopentadiene of 1-methylcyclopentadiene adduct.

When the endo-methyl isomer of the cycloadduct of methylchloroketene and indene was treated with aqueous carbonate, only the ring contraction product was formed. There was no evidence of the formation of any 2-methyl-4,5-benzotropone.



The preparation of unsubstituted tropone by rearrangement of the adduct of cyclopentadiene and chloroketene was attempted many times with no success. The preparation of tropone in this manner has been mentioned (11, 13)

in unpublished work, but the yields are low and no experimental details have been given. The results obtained for the alkylhaloketene adducts would indicate that the exo-chloro isomer is required for the rearrangement to proceed. This isomer is not formed in the normal cycloaddition of chloroketene to cyclopentadiene since the addition is stereoselective, producing only the endo-chloro isomer. The isomerization of the endo-chloro isomer to the exo- isomer by treatment of the cycloadduct with triethylamine has been reported (7). This method of isomerization was attempted without success. However, if the dehydrohalogenation of chloroacetyl bromide was conducted in the presence of a fifty per cent excess of triethylamine, and the reaction mixture allowed to stand overnight before workup, the resulting cycloadduct contained about thirty per cent of the exo-chloro isomer.

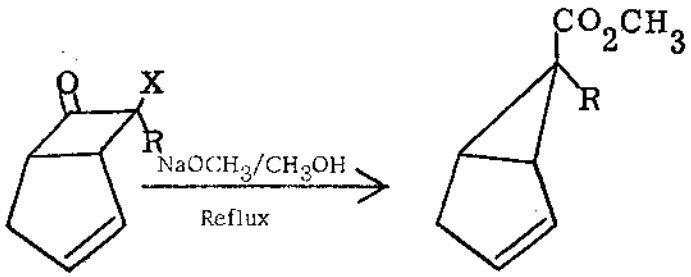
A small quantity of the above exo-chloro adduct was obtained in sixty per cent isomeric purity by fractional distillation through a spinning band column of the isomeric mixture obtained from the cycloaddition. The separation was complicated by the fact that the two isomers had almost identical boiling points and that the desired exo-isomer was the higher boiling component. However, treatment of the exo- cycloadduct with aqueous sodium carbonate produced only ring contraction. This was to be expected since the ratio of tropone formation to ring contraction decreases as the steric bulk of the alkyl group is decreased.

No tropone could be isolated from the solvolysis of the chloroketene-cyclopentadiene adduct in sodium acetate/acetic acid. It is possible that a small amount of tropone is formed but cannot be isolated, due to the infinite solubility of tropone in water.

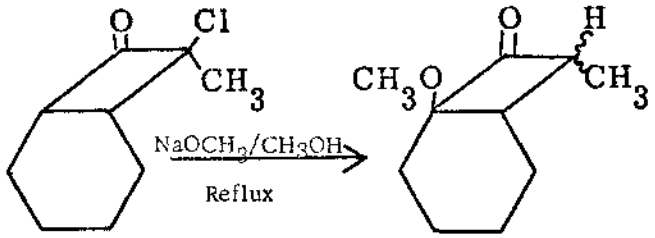
If the cyclopentadiene adducts of alkylhaloketenes were treated with twenty per cent aqueous sodium hydroxide, ring contraction occurred exclusively. This is consistent with the results observed by Brook (5). The

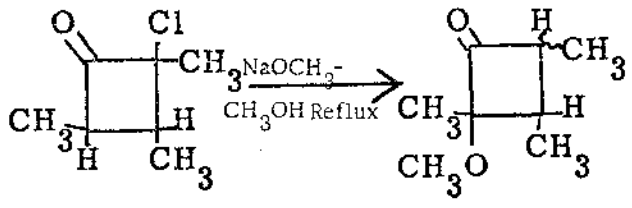
endo- and exo-alkyl isomers both underwent ring contraction stereospecifically to produce the 6-alkyl-6-carboxybicyclo(3.1.0)hex-2-enes. The ring contraction proceeded smoothly and in good yield.

The solvolysis of alkylhaloketene-cyclopentadiene adducts in refluxing sodium methoxide in methanol resulted in the same type of ring contraction reaction, producing 6-alkyl-6-carbomethoxybicyclo(3.1.0)hex-2-enes. The reaction was almost instantaneous, the conversion being complete within one minute after the cycloadduct was added to the refluxing methoxide solution.



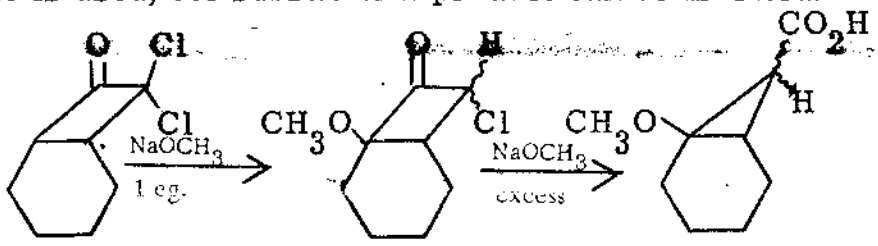
The ring contraction to produce cyclopropanecarboxylic acid derivatives is unique to the cycloadducts of cyclopentadiene. When a similar ring contraction was attempted on the adducts of cyclohexene and cis-2-butene with methylchloroketene using sodium methoxide in methanol, substitution at the bridgehead carbon adjacent to the carbonyl occurs. This substitution



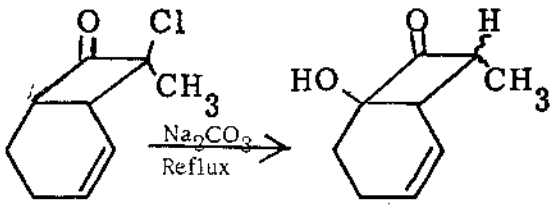


undoubtedly occurs through the enol form of the cycloadduct. This enol form would be expected to be less stable for the cyclopentadiene adduct than the other two adducts above, since the bridgehead double bond would introduce a considerable amount of strain to the bicyclo(3.2.0)heptane ring system.

A similar type of bridgehead substitution has been observed by Fletcher and Hassner (8) in the sodium methoxide solvolysis of the dichloroketene adducts of cyclohexene and cholestene. With an excess of methoxide, the initially formed substitution product can undergo ring contraction since this product still contains one chlorine atom. However, if one equivalent of methoxide is used, the substitution product can be isolated.



If the adduct of methylchloroketene and 1,3-cyclohexadiene is treated with aqueous sodium carbonate, a similar type of substitution is observed. There is no evidence of ring contraction or any type of ring opening reaction.



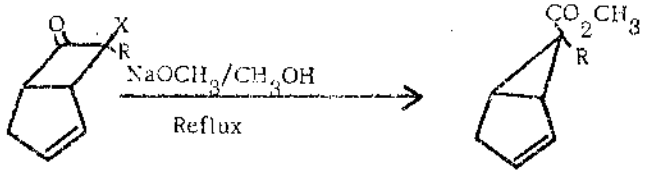
The methylchloroketene adduct of cyclopentene undergoes ring contraction in the same manner as the cyclopentadiene adduct when treated with sodium carbonate or hydroxide; when treated with sodium methoxide in refluxing methanol this adduct undergoes ring contraction predominantly with some substitution. This provides further evidence that the substitution reaction proceeds through the enol form of the cycloadduct since the enol formed from

the cyclopentene adduct would be expected to be highly strained, as in the case of the cyclopentadiene adduct.

The ring contraction in sodium methoxide was conducted with several haloketene-cyclopentadiene adducts. The results are shown in Table V.

TABLE V

REACTION OF KETENE-CYCLOPENTADIENE ADDUCTS WITH SODIUM METHOXIDE IN METHANOL

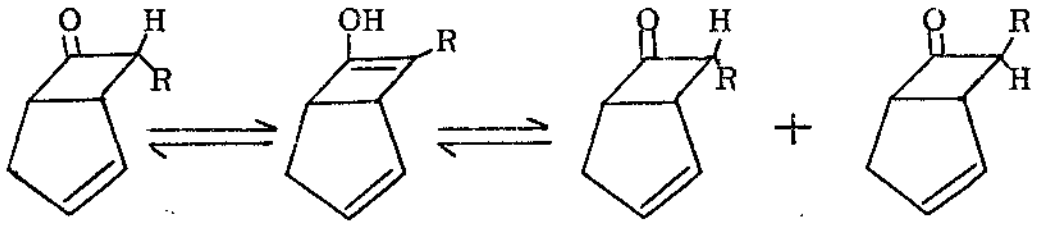


R	X	Yield of Ring Contraction Product
H	Cl	15
H	F	10
Me	Cl	60
Me	Br	60
Vinyl	Br	15

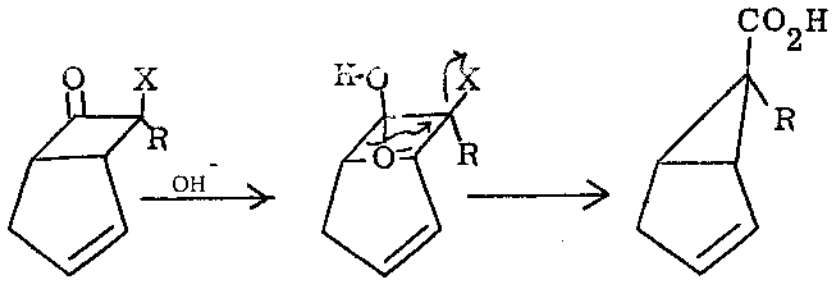
The yields of ring contraction are good for the alkylhaloketene cycloadducts. The low yields obtained for the aldoketene cycloadducts are a result of the polymerixation of the adducts under the reaction conditions.

The cycloadducts of cyclopentadiene and several nonhalogenated ketenes were subjected to sodium methoxide in refluxing methanol. As would be expected, no ring contraction occurred, and the adducts were recovered unchanged. However, some isomerization of the aldoalkylketene cycloadducts was observed. This is logical since the strong base would be expected to cause enolization of the cycloadducts by the loss of the hydrogen on C_7;

tautomerism of this enol to the original keto form would cause isomerization at C_7.



A mechanism for the ring contraction of alkylhaloketene-cyclopentadiene adducts to 6-alkyl-6-carboxybicyclo(3.1.0)hex-2-enes has been proposed by Brook (5). This mechanism involves the initial attack of base on the carbonyl group, followed by an intramolecular nucleophilic displacement to form the ring contraction product.

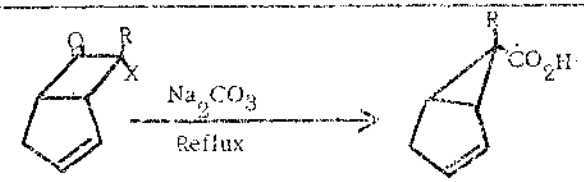


If the nucleophilic displacement is the rate determining step of the ring contraction reaction, the rate of ring contraction should be strongly dependent on the steric bulk of the alkyl group on C_7. The rate of reaction should also be dependent on halogen, with iodine and bromine adducts undergoing the reaction faster than the corresponding chlorine adducts.

The relative rates of ring contraction of several alkylhaloketene adducts were measured in twenty per cent aqueous sodium carbonate solution. In each case the exo- alkyl isomer was used, since this isomer can only undergo ring contraction with no possibility of 2-alkyltropone formation. The results obtained are shown in Table VI.

TABLE VI

RING CONTRACTIONS OF EXO-ALKYL-ENDO-HALO ISOMERS IN AQUEOUS SODIUM CARBONATE



R	X	Yield	Relative Rate[a]
Me	Cl	75	6.4
Me	Br	87	25.
Me	I	30	28.[b]
Et	Br	62	9.5
n-Pr	Br	70	3.9
i-Pr	Br	75	1.0
H	Cl	65	50.

[a] Average of two determinations, average variance, 10 per cent

[b] Relative rate undoubtedly low due to decomposition of starting material during reaction

It is obvious that, as the size of the alkyl group is increased, the rate of ring contraction decreases. The isopropylbromoketene adduct, in which the steric bulk is concentrated near the site of displacement, undergoes the ring contraction at one-fourth the rate of the n-propylbromoketene adduct.

As expected, the alkylbromoketene adducts undergo ring contraction faster than the corresponding alkylchloroketene adducts. The relative rate for the methyliodoketene- cyclopentadiene adduct is difficult to measure accurately due to a large amount of decomposition, but this adduct definitely undergoes the ring contraction faster than the methylbromoketene adduct.

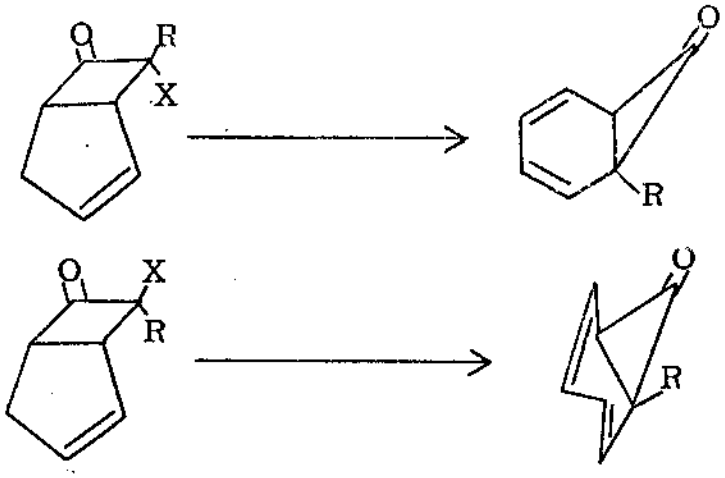
The exo-methyl isomer of the cycloadduct of methylbromoketene and 1-methylcyclopentadiene underwent the ring contraction at almost the same rate as the corresponding cyclopentadiene adduct. This is expected since the methyl group is far removed from the reaction site.

The chloroketene-cyclopentadiene adduct produced a mixture of endo- and exo- 6-carboxybicyclo(3,1,0)hex-2-enes. This occurs through isomerization of the chloroketene adduct through the enol form before ring contraction can occur.

From a comparison of the data in Table III and Table VIit can be shown that the rate of formation of 2-alkyltropone is independent of both the size of the alkyl group and the nature of halogen on the alkylhaloketene cyclopentadiene adduct. This is evidenced by the fact that the ratio of 2-alkyltropone formation to ring contraction is directly proportional to the relative rate of ring contraction as measured on the exo-alkyl isomer.

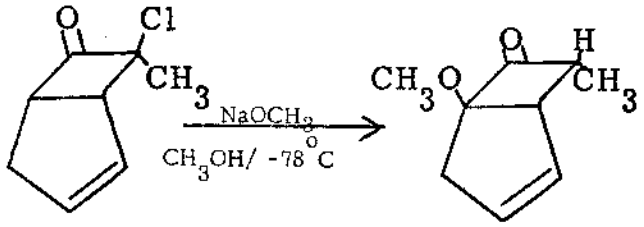
Any mechanism proposed for the conversion of alkylhaloketene-cyclopentadiene adducts to 2-alkyltropones must therefore explain the two experimentally observed facts; 1) only the endo-alkyl isomer of cycloadduct can form 2-alkyltropone and 2) the rate of 2-alkyltropone formation is independent of both the size of the alkyl group and the nature of the halogen on the alkylhaloketene cycloadduct.

An examination of the two proposed mechanisms for the formation of tropolones from dichloroketene-cyclopentadiene adducts shows that neither mechanism can explain the formation of 2-alkyltropones from alkylhaloketene-cyclopentadiene adducts. In the mechanism proposed by Asao and coworkers (1,2), a norcaradienone intermediate is proposed. If this type of intermediate was present in the alkylhaloketene cyclopentadiene adduct rearrangements, the exo-alkyl isomer of the cycloadduct would be expected to form tropone, since this isomer would lead to a cis fusion between the six- and three-membered rings in the intermediate. The endo-alkyl isomer



would be expected to lead to the very highly strained trans - fused norcaradienone.

In the mechanism proposed by Bartlett and Ando (3) the initial step in the solvolysis is the substitution of acetate on C_5 of the dichloroketene-cyclopentadiene adduct. This is followed by hydrolysis of the acetate ester and ring opening to form a cycloheptadiendione, which subsequently undergoes tautomerism to produce tropolone. Substitution at C_5 can occur in the alkylhaloketene-cyclopentadiene system as was found when the adduct of methylchloroketene and cyclopentadiene was treated with sodium methoxide in methanol at low temperature. However, this substitution proceeds



equally rapidly with either the exo- or endo-methyl isomer with isomerization at C_7 in either case. Therefore, this type of mechanism could not explain why only the endo-alkyl cycloadduct forms 2-alkyltropone. Even if it is assumed that there is a preference for C_5 substitution on the endo-alkyl isomer, the substitution product formed has no readily available pathway to yield the final product since after the initial substitution no leaving group is present.

A comparison of the rearrangements of the methylchloroketene and dihaloketene adducts of cyclopentadiene, 1-methylcyclopentadiene and indene provides proof that the formation of tropolones and 2-alkyltropones does not take place by the same mechanism. The dichloroketene adducts of cyclopentadiene, 1-methylcyclopentadiene and indene as well as the dibromoketene and bromochloroketene adducts of cyclopentadiene were solvolysed to tropoloen or tropolone derivatives using triethylammonium acetate in aqueous acetone as the solvolysis medium. The results of these rearrangements are presented in Table VII.

TABLE VII

SOLVOLYSIS OF SOME DIHALOKETENE ADDUCTS TO TROPOLONES

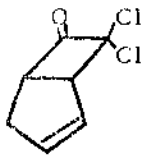
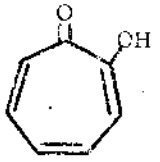
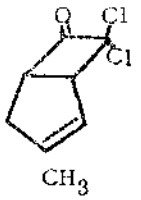
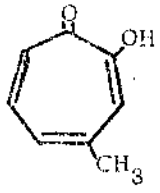
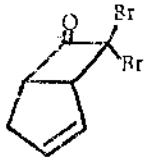
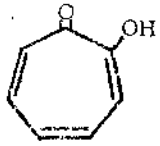
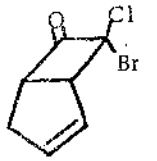
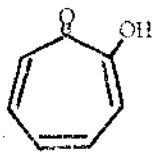
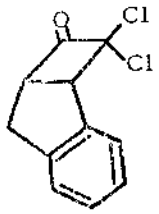
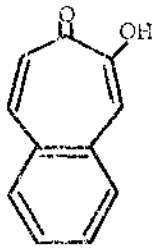
Cycloadduct	Tropolone	Yield	Relative Rate
		60	1
		70	1
		45	2

TABLE VII- Continued

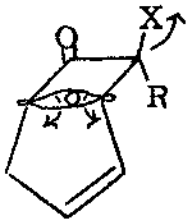
Cycloadduct	Tropolone	Yield	Relative Rate
		55	2
		79	2

[a]The production of 4-methyltropolone is consistent with the observations of Kitahara and Bartlett (1,2,3) concerning the position of substituents on the cycloadduct with respect to substituent position on the rearrangement product.

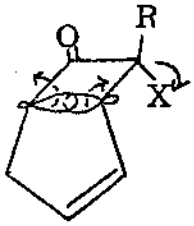
All of these reactions proceed at approximately the same rate. Upon rearranging the methylchloroketene adducts of the above three olefins, it was found that the 1-methylcyclopentadiene adduct underwent rearrangement at one-third the rate of the corresponding cyclopentadiene adduct and that the indene adduct did not undergo any tropone formation whatsoever. The n-propyl and isopropylchloroketene adducts of 1-methylcyclopentadiene also revealed a rearrangement rate of about one-third that of the corresponding cyclopentadiene adducts.

The formation of 2-alkyltropones does not occur by a simple ring opening with loss of hydrogen halide. If the reaction proceeded in this manner, the

exo-alkyl isomer should undergo rearrangement preferentially, since experiments have shown (15) that an endo- leaving group leaves much more readily than the leaving group in an exo position. This is due to the participation of the orbitals formed by the disrotatory opening of the bicyclic ring system. The ring opening can occur in only one direction since the opening in the other direction would increase , rather than decrease ring strain, as shown below. In the solvolysis of endo- and exo-6-tosylbicyclo-



Strain Increased

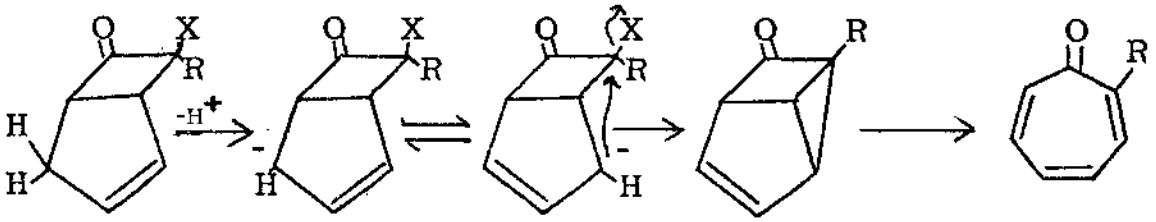


Strain Decreased

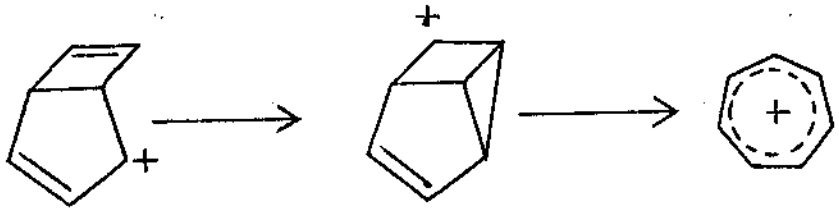
(3.2.0) heptanes, the endo-tosylate was found to leave approximately 500 times faster then the exo-tosylate (15).

A ring opening reaction occurring by this mechanism would also be expected to occur at a slower rate as the size of the alkyl group was increased, due to steric hindrance at the reaction site. The alkylbromoketene adducts would be expected to form 2-alkyltropones at a higher rate than the alkylchloroketene adducts. This is not consistent with the experimentally observed results.

A possible mechanism which explains the experimental observations involves the initial abstraction of one of the allylic hydrogens of the adduct



to form an allylic carbanion. This carbanion could undergo an allylic rearrangement, followed by an internal nucleophilic displacement of halogen to form the tricyclic intermediate. This intermediate could undergo an intramolecular rearrangement to form the 2-alkyltropone. A similar type of rearrangement from the bicyclo(3.2.0) heptane system to a seven-membered ring has been observed by Winstein and coworkers (6, 12).



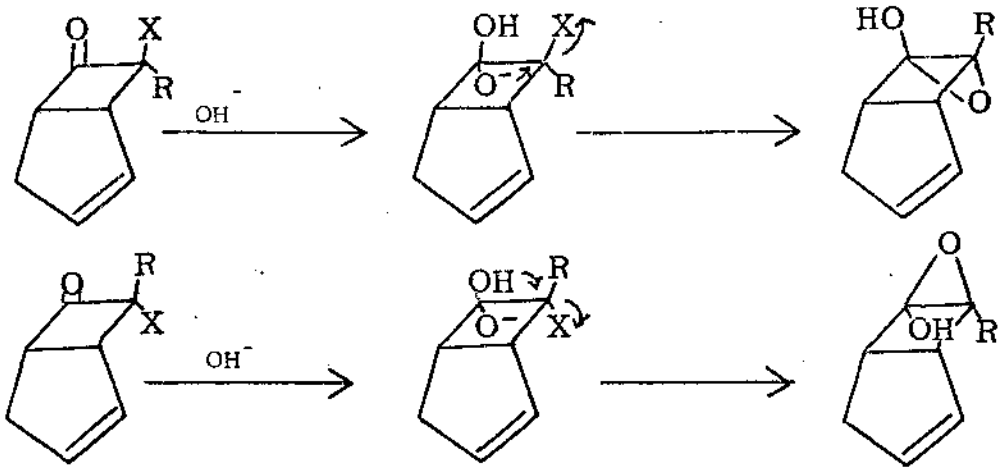
If the rate determining step is assumed to be the initial proton abstraction, the rate of tropone formation would be independent of alkyl group size and nature of halogen. The effect of a methyl group on the five-membered ring in slowing the rearrangement could be attributed to the electron donating effect of the methyl group destabilizing the allylic carbanion. This mechanism also explains the failure of the methylchloroketene-indene cycloadduct to undergo tropone formation since the initially formed carbanion could not undergo allylic rearrangement in this adduct.

The failure of the exo-alkyl isomer to undergo rearrangement is also explained since the leaving group must be in the exo-position for a back-side displacement to be possible.

The principal disadvantage of this proposed mechanism is the requirement for the abstraction of a proton by relatively weak bases such as carbonate or acetate. If the rearrangement was proceeding by this route, stronger bases such as hydroxide or methoxide would be expected to lead to the production of 2-alkyltropones.

A more likely mechanism involves the initial attack of base on the most nucleophilic site in the molecule--the carbon atom of the carbonyl (C_6).

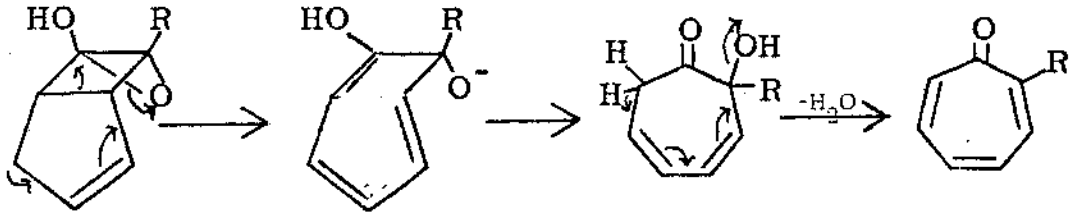
The initially formed species can undergo an internal displacement of halogen to produce an intermediate hemiacetal.



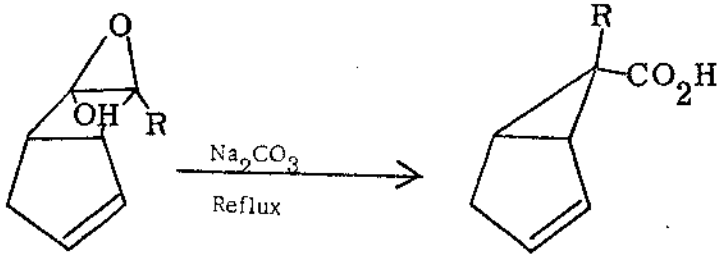
These initial two steps can occur with either the endo or exo-alkyl isomer of cycloadduct. The endo-alkyl isomer will lead to the endo-epoxide and the exo-alkyl to the exo-epoxide regardless of whether the initial attack of base occurs from the endo or exo side of the cyclobutanone ring.

The endo -epoxide could then undergo a ring opening reaction to produce a 2-alkyl-2-hydroxy-7-hydrotropone. The endo-epoxide would be expected to undergo this ring opening at a much higher rate than the exo-epoxide for the same reasons involved in the solvolyses of the bicyclic tosylates described earlier since the ring strain is decreased only by a disrotatory ring opening in the direction favoring the displacement of an endo-leaving group.

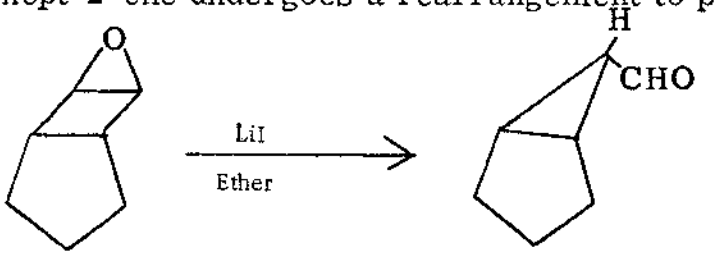
The product formed from the ring opening of the epoxide could abstract a proton to form the 2-alkyl-2-hydroxy-7-hydrotropone which would be expected to undergo an elimination of water to form the 2-alkyltropone. This elimination occurs readily due to the formation of the delocalized tropone system.



The hemiacetal formed from the exo-alkyl isomer can undergo the ring contraction reaction to produce the 6-alkyl-6-carboxybicyclo(3.1.0)hex-2-ene.



Recent work by Garin (9) has shown that the bicyclic epoxide derived from bicyclo(3.2.0)hept-2-ene undergoes a rearrangement to produce the same

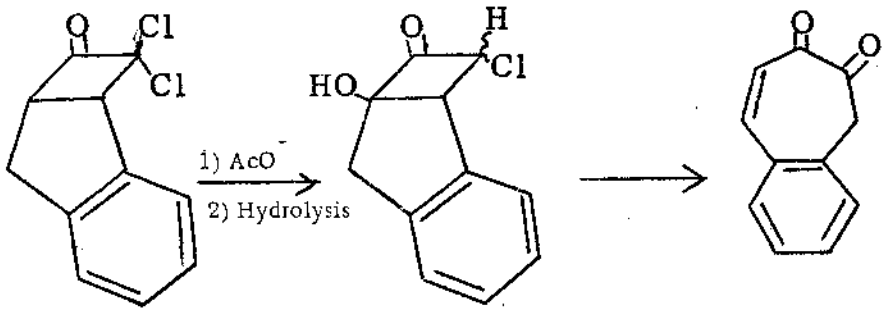


type of bicyclic aldehyde system observed by Brook (4) in the rearrangement of the carbinols derived from the reduction of the alkylhaloketene-cyclopentadiene adducts. The intermediacy of an epoxide in these ring contractions explains the formation of an exo-alkyl ring contraction product from the exo-alkyl cycloadduct since the configuration of C_7 undergoes two inversions leading to a net retention of configuration.

This mechanism involving an internal epoxide explains the experimentally observed data concerning the relationship of the 2-alkyltropone to ring contraction ratio to the nature of halogen and size of the alkyl group of the cycloadduct. The ring opening of the hemiacetal does not involve C_7 ; therefore, if this is the rate-determining step in the reaction sequence, the rate of 2-alkyltropone formation would be expected to be independent of alkyl group. The halogen has been lost before the ring opening occurs. Therefore,the nature of the halogen would not effect the rate of 2-alkyltropone formation .

The effect of the methyl group on the rearrangement of the alkylhaloketene adducts of 1-methylcyclopentadiene is not as obvious. However, since the ring opening step involves the loss of one of the allylic hydrogens of the cycloadduct, the methyl group on C_3 would be expected to have an effect on the ease of removal of these hydrogens.

In order for the cycloadduct of methylchloroketene and indene to undergo rearrangement to 2-methyl-4,5-benzotropone by this reaction sequence, the aromaticity of the benzene ring would have to be destroyed during the ring opening step. This would involve a great amount of energy and would not be expected to occur. The ease of solvolysis of the dichloroketene-indene adduct to 4,5-benzotropolone indicates that the mechanism involved does not require a shift of a double bond out of the aromatic system of the benzene ring. This is consistent with Bartlett's proposed mechanism involving C_5 substitution followed by ring opening to produce a cycloheptadiendione.



The rearrangement of alkylhaloketene-cyclopentadiene adducts has proved to be extremely useful as a general synthesis of 2-alkyltropones. The rearrangement proceeds quickly and in good yield, and the 2-alkyltropones are easily isolated in a high degree of purity since the only other product formed is easily separated due to its solubility in the basic reaction mixture.

This synthesis is far superior to any previously used method of tropone synthesis. The principal advantage is that readily available and inexpensive starting materials are used: cyclopentadiene and an α-haloacid chloride.

This allows the preparation of almost any conceivable 2-alkyltropone. The side reaction producing the 6-alkyl-6-carboxybicyclo(3.1.0) hex-2-ene represents a simple method of preparing this ring system. Since the ring contraction is stereospecific, either the endo- or exo-alkyl carboxylic acid can be prepared.

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