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PROMOTOR:

PROF.DR. R.J.F. NIVARD

ERRATA

Page 2. Third line from the bottom read: might become greater
Page 16. Tenth line add: eq. 6
Page 111. Equation 1 read: $-d[I_2]/dt = k[A][I_2]^2$

Pagina 142. Laatste regel: niet-dissymmetrisch in plaats van a-symmetrisch

IODINE CATALYZED ISOMERIZATION OF CIS α,ω-DIARYLPOLYENES AND ELECTROPHILIC IODINATION OF 1,3-DIARYLALLENES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
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ANTONIUS JOHANNES GERARDUS VAN ROSSUM
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Voor Tineke, Milou
en Joris

CONTENTS

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CHAPTER I

INTRODUCTION

I-1 IODINE CATALYZED ISOMERIZATION OF CIS α,ω-DIARYLPOLYENES

Geometrical isomerization of olefins has already been the subject of many investigations. The isomerization can be achieved thermally, photochemically or catalytically[1].

In the catalytic process iodine has long been recognized as an extremely effective catalyst. In the cases in which rate studies have been made, the rate law generally follows the form:

$$v = k\,[\text{olefin}]\,[I_2]^{\frac{1}{2}}$$

The half-order rate dependence of iodine has been interpreted as involving iodine atom addition to the olefin as part of the mechanism. The iodine atoms required can be produced from iodine molecules either photochemically ($h\nu$) by irradiation of the reaction mixture with visible light or thermally (T) by heating the reaction mixture at an appropiate temperature.

Addition of an iodine atom to an olefin generates an intermediate radical capable of internal rotation. Since the addition reaction is reversible, the rate determining step along this pathway can be either the rate of internal rotation in the intermediate or the addition of the iodine atom.

Rate studies on simple olefins have revealed that generally the internal rotation of the intermediate is the rate determining step in iodine catalyzed cis-trans isomerizations. This was found in isomerizations of butene-2[2], 1,2-diiodoethylene[3,4] cis-stilbene derivatives[5,6], cis-cinnamic esters[7,8,9] and ring substituted cis-methylcinnamates[10].

The high rate of isomerization of pentadiene-1,3[11] was regarded as an indication that in this case the addition of iodine atoms to the double bond is rate determining, but owing to side-reactions the reproducibility of the kinetic measurements was too poor to get conclusive evidence of this supposition.

A change in the rate determining step might be expected in going to olefins which add iodine atoms in a rather exothermic reaction and at the same time give easily rotating intermediate radicals. This being the case, it is possible that the free energy level of the transition state of the rotation step becomes lower than that of the addition step. In this study it has been anticipated that both conditions might be fulfilled by extension of the conjugation in cis-stilbene. The difference between the resonance stabilization energy of the intermediates expected in the iodine catalyzed isomerizations, and that of the corresponding parent compounds become greater in the series cis-stilbene, cis-trans 1,4-diphenylbutadiene-1,3, cis-trans-trans 1,6-diphenylhexatriene-

1,3,5 etc. The steric relations, however, in none of the intermediates seem te be less suitable for internal rotation than those in the intermediate from cis-stilbene.

By variation of the position of the cis double bond in e.g. 1,6- diphenylhexatriene the balance between the relevant factors, *viz.* the stability and the ease of rotation of the intermediate, can be varied. The cis-trans-trans isomer may be expected to give the stabler intermediate; in the trans-cis-trans isomer, however, coplanarity in the intermediate radical during the internal rotation is most easily maintained.

On account on these considerations and the work previously done in this department, the iodine catalyzed isomerization of several types of α, ω-diphenylpolyenes has now been studied.

The experimental methods used in this study will be described in chapter II. Chapter III deals with the isomerization of substituted cis-trans diphenylbutadienes-1,3. The reaction has been studied over a large temperature interval; its Arrhenius parameters have been determined, and substituent influences have been analyzed.

Kinetic investigations on the isomerization of cis-trans-trans and trans-cis-trans 1,6-diphenylhexatriene -1,3,5, and of trans-cis-trans-trans 1,8-diphenyloctatraene-1,3,5,7 will be described in chapter IV. The syntheses of the compounds investigated will be reported in chapter V.

I-2 ELECTROPHILIC IODINATION OF 1,3-DIPHENYLALLENES

The mechanism of additions to allenic compounds is very interesting owing to the variation in the character of the reaction intermediate that can be involved. Caserio[12,13,14] studied the halogenation and methoxymercuration of levorotatory 1,3-dimethylallene, and the bromination of dextrorotatory 1,2-cyclononadiene. The results reveal that these additions are stereospecific trans additions, and dissymmetric brigded carbonium ions have been suggested as intermediates to explain the stereoselectivity observed. Bach[15] studied the ethoxymercuration of levorotatory 1,2-cyclononadiene with a series of mercury salts. He found that the optical purity of the reaction product depends on the electrophile used. This result has been explained by supposing that in these reactions also symmetric allylic carbonium ions are involved.

So far, all knowledge about the mechanism involved in addition reactions to allenes has been based mainly on structures and configurations of the additions products. We thought it worthwhile to examine the addition from a kinetic point of view, because in this approach the study of substituent effects on the addition rate might give additional information about the mechanism and the transition state involved. We chose the iodine addition to 1,3-diphenylallenes as subject for this study because of the experience gained in our department with reactions involving iodine.

Preliminary experiments revealed that the iodination of 1,3-diphenylallene in 1,2-dichloroethane as a solvent is second order in iodine and first order in diphenylallene, and that the reaction leads to an equilibrium state. The reaction can then be formulated as follows:

$$A + 2I_2 \rightleftarrows AI_2 + I_2$$

The second order rate dependence of iodine indicates that the iodination of diphenylallene is a heterolytic process under these circumstances. It was noticed, however, that the decrease of the iodine concentration in consequence of the addition is followed by an increase of the iodine concentration This release of iodine is caused by an iodine catalyzed dimerization of diphenylallene. This side-reaction appeared to be especially important for diphenylallenes with electron donating substituents; this reaction is still being studied.

In carbon tetrachloride or in n-hexane as solvent the addition rate of iodine to diphenylallene appeared to be much slower than in dichloroethane as solvent, but the reaction could be accelerated a hundredfold by degassing the reaction mixture. It is probable that in apolar solvents the iodination proceeds *via* a homolytic chain process. A kinetic study of this radical addition appeared very difficult and disappointing. In spite of the high purity of reactants and solvents used and careful degassing of the reaction mixture no reproducible results could be obtained.

Fortunately, both side-reactions become gradually unimportant at lower temperatures in dichloroethane. Hence the electrophilic addition of iodine could be studied at temperatures between 10° and -30°.

The iodination of twelve substituted 1,3-diphenylallenes has been investigated, the results of which will be reported in chapter VI. In chapter VII the conclusion about the nature of the transition state involved in this reaction is verified by experiments in which the variation of optical rotation during the addition to optical active 1,3-diphenylallene was followed. Finally, the syntheses of the 1,3-diphenylallenes will be described in chapter VIII.

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CHAPTER II

EXPERIMENTAL METHODS

II-1 MATERIALS

Isomerizations were carried out by using n-hexane (Merck, distilled over sodium wire) and carbon tetrachloride (Merck p.a. distilled over phosphorus pentoxide) as solvents.
Iodine (Merck p.a.) was used without any further purification. 3,3',5,5' -Tetramethyl-cis-stilbene as prepared by Dr. W.J. Muizebelt[1] was made use of. The synthesis and purification of the α,ω-diphenyl-polyenes will be described in chapter V.

II-2 APPARATUS AND MEASURING PROCEDURE

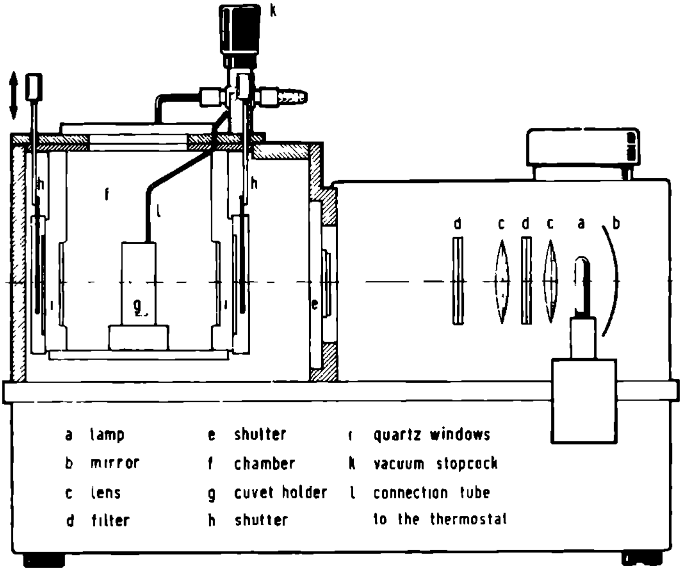

fig.1 Irradiation apparatus

The arrangement of the equipment used in the isomerization experiments is illustrated in figure 1. Illumination was supplied by a Philips HPK-125 high pressure mercury lamp, operating from the 220 V output of a Philips constant volt transformer.

The optical part (mirror and lenses) of a Leitz Pradovite slide-projector was built into the apparatus in order to concentrate the beam of light. This beam was further led through a filter, absorbing all light below 370 mμ to minimize photochemical side-reactions, and an IR filter to prevent rise of temperature of the reaction mixture during illumination.

The position of the lamp was adjusted in such a way that the variation in light intensity incident on various parts of the reaction-cell was only a few percent.

The maximum iodine concentration used in the experiments was 10^{-4} moles/litre, so that only a fairly small fraction of the incident light was absorbed by the solution and the absorption was assumably uniform throughout the cell.

A Prontor Press central-shutter with 3 cm diameter was used for regulating the exposure times.

The isomerization reactions were carried out in a quartz photometer cuvet (1 cm) fitted with a high vacuum stopcock. During an experiment the cuvet was placed in a fixed cell holder mounted in a double-walled chamber with optically flat quartz windows on opposite sides. The cuvet could be secluded from light by means of shutters. The reaction temperature was adjustable by pumping thermostated water or ethanol through the cell holder.

In the absence of light two ml of an iodine solution and two ml of a solution of a cis derivative were pipetted into the cuvet. The cell with closed stopcock was placed in the chamber fitting in a Cary-15 spectrophotometer, and was brought to the temperature desired. After the spectrum of the mixture had been recorded the chamber with closed shutters was placed in the exposure apparatus, and the cell was illuminated for a given time interval . Subsequently the spectrum was recorded again. This procedure was repeated five or six times, after which the solution was being illuminated until the isomerization was completed, and an infinity reading could be made.

Some measurements were carried out under nitrogen. In these experiments the cell was cooled down to -80° with a dry ice-ethanol mixture and evacuated three times with an Edwards Speedivac oil diffusion pump to a pressure of 10^{-3} mm Hg. Between pumpings the stopcock was closed, and the cell warmed up to room temperature. Finally nitrogen, purified by passing through a column of BTS catalyst heated to 180° and a KOH drying tube, was led into the cell.

The isomerizations of the cis derivatives have been studied at temperatures between -45° and $+65^{\circ}$. At low temperatures a vacuum was set up between the walls of the chamber, and dry nitrogen was passed through the chamber. In spite of these precautions measurements were impossible below -45° due to fogging of the cuvet and windows.

II-3 SPECTROPHOTOMETRIC ANALYSES

From the change of the spectrum during an isomerization the reaction rate constant (k_i) can be calculated from the formula:

$$k_i = \frac{1}{t} \ln \frac{D_\infty - D_o}{D_\infty - D_t} \left[I_2\right]^{-\frac{1}{2}} \quad \text{litre}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$$

in which D_o, D_t and D_∞ are the optical densities at a particular wave-length at times $t = 0$, $t = t$ and $t = \infty$.

This method is only properly applicable at wave-lengths at which the extinction coefficients for cis-trans isomers differ sufficiently. Such a wave-length could , however , readily be found for all compounds investigated .

From the presence of an isosbestic point in all measurements it can be concluded that no side-reactions are involved, in which diphenylpolyenes are consumed.

II-4 THE INFLUENCE OF PHOTOCHEMICAL ISOMERIZATION AND OF THERMALLY GENERATED IODINE ATOMS

In order to estimate the influence of photochemical isomerization, a solution of trans, trans

1 phenyl, 4 para-nitrophenyl butadiene in n-hexane, absorbing at a relative high wave-length (λ_{max}= 371 mμ), was illuminated for a few minutes. After the irradiation the spectrum of the solution was unchanged, which indicates that photochemical isomerization is unimportant under the experimental circumstances used.

Isomerization in unexposed solutions, caused by thermally produced iodine atoms, was noticeable in experiments with cis-trans dienes as well as with trans-cis-trans-trans tetraene at temperatures above 60°. However, by using a low iodine concentration and a short measuring method in which only the change in extinction at one wave-length was determinated, the contribution of the dark reaction was lower than one percent and hence negligible. The isomerization of cis-trans-trans triene by thermally generated iodine atoms was much more important; even with the fast technique mentioned above, only measurements below 40° were possible.

II-5 EFFECT OF OXYGEN

In preliminary experiments we measured the isomerization of some cis-trans dienes catalyzed by thermally generated iodine atoms according to the procedure applied by Muizebelt[1,2]. Because of the very high reaction rate and the necessity for reaction times which are not too short, iodine atom concentrations of about 10^{-12}moles/litre were used. Under these circumstances oxygen revealed an enormous retarding effect on the reaction rate. Even with careful degassing of the reaction mixtures no satisfactory results were obtained. Apparently this must be due to the very low catalyst concentration, because in experiments with photochemically produced iodine atoms inhibitation by oxygen was not observed (see further).

Table 1 summarizes the effect of oxygen on the iodine catalyzed isomerization of olefins.

TABLE 1

Effect of oxygen on the isomerization rate constants

olefin	method	$[I^{\cdot}]\ \frac{\text{moles}}{\text{litre}}$	$\frac{k_{\text{uninhibited}}}{k\ O_2}$
cis-trans diphenylbutadiene	T	10^{-12}[c]	large
cis stilbene[a]	T	$10^{-9.8}$[c]	2.3
methyl cis-cinnamate[b]	T	$10^{-9.4}$[c]	1.1
3,3',5,5'-tetramethyl-cis-stilbene	hν	10^{-8}[d]	1.0
cis-trans diphenylbutadiene	hν	10^{-8}[d]	1.0

a) ref.1 b) ref.3 c) calculated with eq.5 d) calculated with eq.1

The data illustrate that the influence of oxygen on the isomerization reaction becomes important at iodine atom concentrations lower than 10^{-9} moles/litre.

II-6 SOURCES OF ERRORS

The reaction mixtures were prepared at room temperature. A systematic error is introduced by neglecting the temperature dependence of the solvent density, which causes a change in the iodine concentration on varying the temperature. Since the isomerization rate is proportional to the square root of the iodine concentration and the temperature interval is not very large, the effect will be small, however.

The accuracy of the determination of the reaction temperature can be estimated at about 0.5^o. A variation of 0.5^o in temperature causes a 1% change in the rate constant at the most.

The shutter times were checked electronically; corrected values have been used for the calculation of the rate constants (Appendix 1).

The error in the individual k values (k_i) is almost constant within the range of 20-70% conversion, assuming that the error in the determination of $D_t(i)$ is the most important one and independent of the conversion percentage[1]. Therefore the isomerization reactions were followed within this range. The isomerization rate constants were calculated by taking the mean value of a series of measured k_i values. 95% Confidence limits of the rate constants were determined according to standard procedures.

I-7 DETERMINATION OF THE STEADY STATE CONCENTRATION OF IODINE ATOMS

II-7-1 THEORY

When a solution of iodine is illuminated with visible light, dissociation of iodine occurs according to the following equations:

$$I_2 + h\nu \rightarrow 2\ I^{\bullet}$$

$$I^{\bullet} + I^{\bullet} \xrightarrow[k_r]{} I_2$$

The photostationary concentration of iodine atoms is given by the expression

$$[I^{\bullet}] = \sqrt{\frac{\alpha I_o}{k_r}}\ [I_2]^{\frac{1}{2}} \qquad \text{eq.1}$$

in which α is equal to ϕ.a.l, ϕ, a and l denoting the quantum yield of the photodissociation of iodine, its molar absorption coefficient and the light path, respectively. I_o represents the intensity of the incident light, and k_r is the rate constant for the recombination of iodine atoms.

The rate law for the irreversible cis-trans isomerization of olefins catalyzed by iodine atoms is:

$$v = k\ [\text{cis}][I^{\bullet}] \qquad \text{eq.2}$$

From equations 1 and 2 and using f for the quantity $(\alpha I_o/k_r)^{\frac{1}{2}}$ it follows that

$$v = f.k\ [cis][I_2]^{\frac{1}{2}} \qquad \text{eq.3}$$

and hence $k_{obs.h\nu} = f.k$ eq.4

The steady state concentration of thermally generated iodine atoms is given by

$$[I\cdot] = K_I^{\frac{1}{2}}\ [I_2]^{\frac{1}{2}} \qquad \text{eq.5}$$

in which K_I is the dissociation constant of iodine. Substitution of eq.5 in eq.2 yields an expression for the observed rate constant of isomerizations with thermally produced iodine atoms

$$k_{obs.T} = K_I^{\frac{1}{2}} \cdot k$$

Muizebelt[1,2] measured isomerization rate constants of symmetrically substituted cis-stilbenes at temperatures of 70° - 120° in carbon tetrachloride as a solvent. Avoiding the laborious and difficult estimation of α, I_o and k_r, we have used his kinetic data of 3,3',5,5'-tetramethyl-cis-stilbene to determine the value of f.

From eq.4 and 6 follows

$$k_{obs.\ h\nu} = f.\frac{k_{obs.T}}{K_I^{\frac{1}{2}}} \qquad \text{eq.7}$$

The value of K_I is given by Benson[4],

$$K_I = 10^{3.4} 10^{-35.4/2.303RT} \text{ mole/litre}$$

The observed rate constant of the isomerization of 3,3',5,5'-tetramethyl-cis-stilbene as given by Muizebelt is

$$k_{obs.T} = 10^{9.46}10^{-21.39/2.303RT}\ \text{litre}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$$

By substituting these values in eq.7 and expressing the rate constants in terms of the Arrhenius equation the result reads

$$\log A_{obs.h\nu} - \frac{E_{a\ obs.h\nu}}{2.303\ RT} = \log f + 7.76 - \frac{3.69}{2.303\ RT} \quad \text{eq.8}$$

Assuming that f is temperature independent, the activation energy of the isomerization of 3,3',5,5'-tetramethyl-cis-stilbene catalyzed by photochemically generated iodine atoms will be about 3.7 kcal/mole and

$$\log f = \log A_{obs.h\nu} - 7.76 \qquad \text{eq.9}$$

The use of the isomerization of the cis-stilbene derivative as a standard reaction also offers us a possibility to check the intensity of incident light. For this reason these measurements were repeated regularly during the isomerization experiments with the α, ω-diphenylpolyenes investigated. When the rate of isomerization of tetramethyl-cis-stilbene slightly diminished, the lamp was replaced. The four lamps used in this study are represented by the figures 1, 2, 3, and 4.

II-7-2 RESULTS

The observed rate constants of the isomerization of 3,3',5,5'-tetramethyl-cis-stilbene have been listed in table II. The headings are:

T = temperature (degrees centigrade)

$[I_2]$ = iodine concentration in the reaction mixture

k_{min}, k, k_{max} = isomerization rate constants expressed in $\text{litre}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$ with 95% confidence limits.

n-Hexane was used as a solvent unless stated otherwise.

TABLE II

Isomerization rate constants

Lamp	T	$[I_2].10^6$	$k_{min}10^2$	$k\ 10^2$	$k_{max}10^2$	remarks
1	-24.4	113	7.22	7.53	7.84	under N_2
1	40.4	104	30.1	30.6	30.9	
1	56.3	104	41.4	41.8	42.1	
1	-23.7	104	7.23	7.48	7.73	
1	-11.8	113	9.84	10.30	10.76	under N_2
1	11.3	104	17.9	18.0	18.1	
1	39.5	104	29.7	30.3	30.8	
1	23.4	104	22.5	22.8	23.1	
2	58.6	113	25.5	25.8	26.1	
2	36.2	113	17.2	17.4	17.6	
2	23.1	113	13.3	13.7	14.0	

table II (continued)

Lamp	T	$[I_2].10^6$	$k_{min}10^2$	$k\ 10^2$	$k_{max}10^2$	remarks
2	-17.0	113	4.33	4.65	4.98	
2	-45.0	113	1.84	1.91	1.97	
3	23.8	113	12.3	12.6	13.0	
3	37.1	113	16.3	16.8	17.3	
3	50.7	113	20.6	20.8	21.1	
3	62.3	113	24.7	25.0	25.2	
3	-22.8	113	3.71	3.77	3.83	
3	25.4	152	12.3	12.9	13.5	in CCl_4
3	56.4	101	22.1	22.5	23.0	in CCl_4
3	62.3	28.2	24.0	24.5	24.9	
3	- 3.7	113	6.45	6.61	6.77	
4	61.7	84.2	23.2	23.6	24.0	
4	44.3	84.2	16.8	17.0	17.2	
4	22.6	84.2	11.4	11.7	12.0	
4	- 9.5	84.2	5.37	5.38	5.39	
4	-29.4	84.2	2.88	2.96	3.03	

II-7-3 ARRHENIUS ACTIVATION PARAMETERS

For all four lamps used log k values measured with the same light source have been plotted against the reciprocal of the temperature (see e.g. figure 2). From these plots Arrhenius activation parameters have been derived together with their 95% confidence limits. They are listed in table III. The values of log f (expressed in mole$^{\frac{1}{2}}$litre$^{-\frac{1}{2}}$) have been calculated from equation 9.

TABLE III

Arrhenius activation parameters

Lamp	log A_{min}	log A	log A_{max}	$E_{a\ min}$	E_a	$E_{a\ max}$	r	log f
1	1.83	1.89	1.96	3.35	3.43	3.51	1.000	-5.87
2	1.81	1.94	2.07	3.64	3.81	3.98	1.000	-5.82
3	1.72	1.80	1.88	3.55	3.66	3.78	0.999	-5.96
4	1.65	1.77	1.90	3.50	3.66	3.82	1.000	-5.99

Log A and E_a are expressed in $\text{litre}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$ and kcal/mole, respectively.

r = correlation coefficient

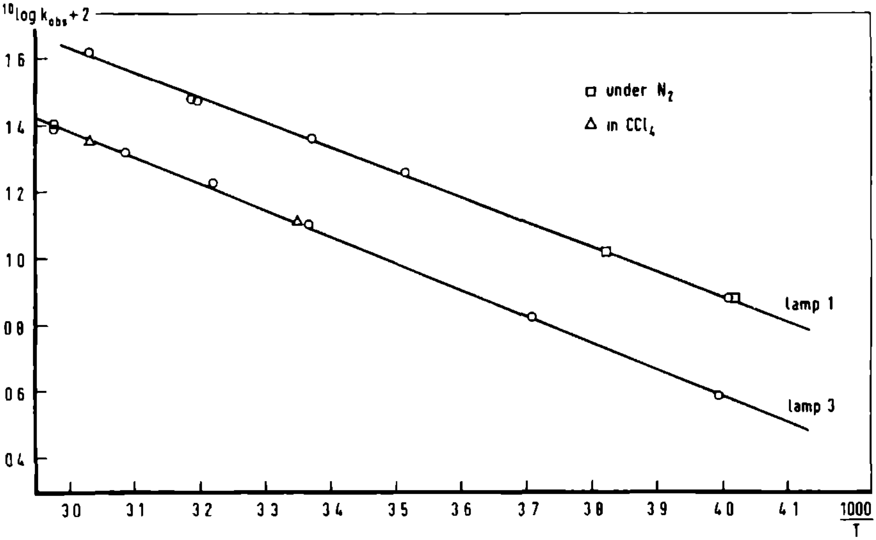

fig.2 Arrhenius plots for the isomerization of 3,3',5,5'-tetramethyl-cis-stilbene.

II-7-4 DISCUSSION

The accuracy of the measurements is excellent, as appears from the 95% confidence limits in table II and III and from the very high correlation coefficients of the straight lines in figure 2. It is comparable with that obtained by Muizebelt[1,2]. The mean value of the activation energy is 3.64 kcal/mole, in close agreement with the value found with thermally generated iodine atoms, $E_{a\ T}$= 3.69 kcal/mole. From this equality it may be concluded that the temperature dependence of f is small indeed, as assumed in equation 9. This can be understood as follows: Of the factors, on which f is dependent ϕ, a and k_r are temperature dependent. The variation of the molar absorption (a) of iodine with the temperature is small, however, and hence negligible. The recombination reaction of iodine atoms itself has presumably no activation energy[5]; the process is diffusion controlled and depends perceptibly on the temperature[6] and solvent viscosity[6,7]. The same quantities also influence the quantum yield (ϕ) of the iodine dissociation[8,9], but the effects on ϕ and k_r may be cancelled for the greater part in the fraction ϕ/k_r. In that case f will be almost temperature independent[6].

In order to estimate the influence of the solvent on the rate of isomerization some experiments have been carried out in carbon tetrachloride.

As can be seen from figure 2 the values of the rate constants of these measurements fit into the log k-1/T plot obtained from measurements in n-hexane. Since apparently the isomerization rate constant itself is hardly solvent dependent, the value of f must be almost the same for n-hexane and carbon tetrachloride solutions. This observation is contradictory to values of f_{hexane}/f_{CCl_4} (1.6 and 1.7) reported by Rabinowitch[10] and Noyes[6,8], respectively. The reason for this disagreement is not clear.

The value of the activation energy found for the isomerization of 3,3',5,5'-tetramethyl-cis-stilbene* (3.7 kcal/mole) is also in agreement with the value of 3.6 kcal/mole reported by Cauzzo *et al.*[11] for the isomerization of cis-stilbene in n-hexane catalyzed by iodine atoms generated with light of 520 mμ.

Yamashita[12] studied the iodine catalyzed isomerization of cis-stilbene with light from different wave-length intervals. In the spectral range of 530-600 mμ an activation energy of 7.6 kcal/mole was found, whereas the isomerization experiments with light of 360-430 mμ yielded an activation energy of 4.1 kcal/mole. This discrepancy and the quantum yields observed suggested that the mode of

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*The methyl substituents reduce the activation energy by about 0.2 kcal/mole with respect to the value of the activation energy of unsubstituted cis-stilbene[1.2].

initiation was different. The primary process in the range of 360 - 430 mμ was assumed to be:

$$C.I_2 \xrightarrow{h\nu} C.I_2^*$$

$$C.I_2^* + C \rightarrow 2\ CI^{\bullet}$$

where $C.I_2$ represents a charge-transfer complex of iodine and cis-stilbene. The over-all rate equation is identical to that proposed for the isomerization reaction catalyzed by iodine atoms. However, the value of 4.1 kcal/mole obtained in the range of 360 -430 mμ corresponds with the values reported by Muizebelt en Cauzzo for the activation energy of the iodine atom catalyzed isomerization. On the other hand the activation energy of 7.6 kcal/mole obtained in the other wavelength interval seems to be too large for an iodine atom catalyzed isomerization.

An explanation of the inconsistent data of Yamashita may be that the temperature ranges of the measurements were very small and the iodine atom concentration used, as appears from his observed rate constants, was extremely low. So, there is little reason to consider an alternative isomerization mechanism.

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CHAPTER III

ISOMERIZATION OF CIS-TRANS-1,4-DIARYLBUTADIENES-1,3

III-1 GENERAL REMARKS

The experimental methods were described in chapter II. The measurements were carried out with lamps 1 and 2. In order to get comparable rate constants, those estimated with lamp 2 were multiplied by 1.8, the ratio of the isomerization rate constants of 3,3',5,5'-tetramethyl-cis-stilbene at 12.5° (midpoint of the temperature range) obtained from the Arrhenius plots with lamps 1 and 2, respectively.

Due to the very poor solubility of the all-trans isomers of bis-(para-nitrophenyl)- and bis-(meta-nitrophenyl)-butadienes, measurements with these derivatives were impossible below -25°.

The isomerization experiments with 1-para-dimethylaminophenyl-4-phenyl-butadiene were interfered by side-reactions. These reactions, presumably an iodine catalyzed isomerization *via* an ionic mechanism[1,2] and a photo-oxidation of the dimethylamino substituent by iodine[3], became dominant below room temperature.

III-2 RESULTS

The observed isomerization rate constants of 1,4-diarylbutadienes (expressed in litre$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$sec^{-1}) together with their 95% confidence limits have been listed in table 1.

$k_{corr.}$ are converted rate constants.

TABLE 1

compound	lamp	T(^{o}C)	$[I_2] .10^6$ moles/l	k_{min}	k	k_{max}	$k_{corr.}$
unsubst. cis-trans	1	-22.3	104	106.9	111.5	116.0	
	2	-43.0	113	48.1	49.0	49.9	88.2
	2	-39.0	113	49.9	53.1	56.4	95.8
	2	-28.3	113	64.3	65.1	65.9	117.1
	1	-26.8	104	109.2	111.5	113.9	
	1	-11.3	104	124.0	127.2	130.4	
	1	2.2	104	126.0	127.3	128.6	
	1	10.9	104	131.6	138.0	144.3	
	1	22.0	104	154.9	156.9	158.9	
	1	35.8	104	137.7	141.2	144.8	
	1	48.8	104	145.1	149.2	153.4	
	1	57.5	104	142.4	145.9	149.4	
	1	67.0	25	130.8	140.9	150.9	
	1	-24.1	113	96.1	100.9	105.8	under N_2
	1	44.9	113	136.4	140.3	144.3	under N_2
meta-nitro cis-trans	2	-34.5	113	18.4	18.7	19.1	33.7
	1	-27.6	104	33.1	33.6	34.1	
	1	-25.7	104	34.9	35.2	35.5	
	2	-12.0	113	21.9	22.1	22.2	39.7

table 1 (continued)

compound	lamp	T(^{o}C)	$[I_2]\cdot10^6$ moles/l	k_{min}	k	k_{max}	$k_{corr.}$
(meta-nitro cis-trans)	1	-11.9	104	34.9	35.2	35.5	
	2	0.0	113	25.1	25.4	25.6	45.6
	1	10.9	104	39.8	41.0	42.3	
	2	11.0	113	24.6	25.0	25.3	45.0
	1	21.9	104	50.0	51.9	53.9	
	1	31.2	104	48.4	49.5	50.5	
	1	40.1	104	49.1	50.0	50.9	
	1	49.5	104	52.2	53.2	54.2	
	1	57.0	104	49.5	50.9	52.3	
	1	67.1	25	53.2	55.6	57.9	
para-nitro cis-trans	2	-40.0	113	14.1	14.8	15.4	26.6
	1	-27.4	104	30.1	30.6	31.1	
	1	-23.2	104	31.1	32.4	33.9	
	1	-11.3	104	34.9	35.9	36.9	
	2	-9.0	113	19.1	19.6	20.2	35.3
	2	0.0	113	20.2	21.0	21.9	37.8
	1	2.2	104	37.6	38.2	38.8	
	2	8.2	113	21.9	22.2	22.6	40.0
	1	10.8	104	38.5	40.0	41.5	
	1	22.0	104	45.8	46.9	48.0	
	1	35.8	104	45.8	46.6	47.4	
	1	48.9	104	45.2	45.6	46.0	
	1	57.4	104	48.3	49.6	50.9	
	1	67.1	25	48.8	51.8	54.8	

table 1 (continued)

compound	lamp	T(^{o}C)	$[I_2].10^6$ moles/l	k_{min}	k	k_{max}	$k_{corr.}$
para-chloro cis-trans	2	-47.0	113	31.5	31.9	32.3	57.5
	2	-36.0	113	35.2	35.9	36.6	64.6
	1	-27.3	104	67.8	70.4	73.0	
	1	-25.7	104	65.5	67.7	69.9	
	2	-13.0	113	41.7	41.9	42.2	75.5
	1	-11.9	104	70.5	72.4	74.3	
	1	3.0	104	78.9	79.4	79.8	
	1	10.9	104	79.2	80.1	81.1	
	1	21.2	104	90.0	93.8	97.7	
	1	31.3	104	86.8	88.2	89.7	
	1	40.1	104	83.3	86.7	90.2	
	1	48.8	104	93.4	95.4	97.5	
	1	57.9	104	91.4	95.9	100.3	
	1	67.1	25	88.8	94.6	100.5	
β-naphtyl cis-trans	2	-36.0	113	55.9	58.1	60.2	104.5
	2	-35.0	113	45.0	59.6	74.3	107.3
	1	-15.4	113	111.9	118.2	124.5	
	2	-11.0	113	73.4	74.8	76.1	134.6
	1	-11.2	104	130.5	132.1	133.8	
	1	- 0.9	104	120.3	122.6	124.8	
	1	10.9	104	128.3	133.7	139.0	
	1	21.9	104	144.2	147.0	149.8	
	1	31.8	104	132.3	139.8	147.3	
	1	40.5	104	138.0	147.5	156.9	
	1	53.5	104	133.5	140.4	147.3	
	1	67.1	25	140.5	143.6	146.8	

table 1 (continued)

compound	lamp	T(^{o}C)	$[I_2].10^6$ moles/l	k_{min}	k	k_{max}	$k_{corr.}$
para-methyl cis-trans	2	-37.0	113	57.9	60.1	62.2	108.1
	1	-23.6	104	124.0	129.7	135.6	
	1	-12.7	104	122.6	129.6	136.5	
	1	3.4	104	140.2	142.4	144.7	
	1	10.6	104	146.5	152.5	158.5	
	1	21.1	104	157.8	165.0	172.1	
	1	22.7	104	159.6	160.7	171.8	
	1	35.1	104	156.0	160.1	164.2	
	1	44.7	104	149.3	154.8	160.3	
	1	53.4	104	139.0	146.5	153.9	
	1	67.1	25	135.7	142.8	149.8	
para-methoxy cis-trans	2	-37.0	113	59.6	62.4	65.2	112.3
	2	-36.0	113	56.5	57.1	57.8	99.6
	1	-26.5	104	120.3	122.8	125.4	
	1	-18.1	104	125.6	127.0	128.3	
	1	-11.3	104	140.7	143.8	147.0	
	1	2.2	104	134.9	140.0	145.2	
	1	23.2	104	154.4	161.5	168.6	
	1	35.5	104	144.9	150.9	156.8	
	1	44.1	104	143.0	145.9	148.7	
	1	53.9	104	149.5	155.2	161.0	
	1	67.1	25	145.9	157.1	168.3	
	1	10.8	104	138.7	143.9	149.1	

table 1 (continued)

compound	lamp	T(^{o}C)	$[I_2].10^6$ moles/l	k_{min}	k	k_{max}	$k_{corr.}$
para $-N(CH_3)_2$ cis-trans	1	34.0	28	207.1	226.7	246.4	
	1	36.9	104	204.6	219.4	243.2	
	1	49.5	104	202.0	215.3	228.6	
	1	58.3	104	191.9	205.5	219.1	
	1	66.6	104	182.8	193.4	204.0	
bis meta-nitro cis-trans	2	-24.1	113	11.9	12.5	13.2	22.6
	2	-14.2	113	12.4	13.2	13.9	23.7
	2	-12.0	113	12.4	12.8	13.3	23.1
	2	3.7	113	18.7	19.2	19.6	34.5
	2	11.8	113	16.7	17.4	18.0	31.3
	2	23.7	113	19.9	20.7	21.5	37.2
	2	34.4	113	19.3	19.6	20.0	35.4
	2	44.7	113	18.3	19.1	19.8	34.3
	2	53.9	113	19.0	19.9	20.7	35.7
	2	64.4	113	20.9	21.5	22.1	38.7
bis para-nitro cis-trans	2	-24.3	113	25.1	25.8	26.4	46.4
	2	-9.0	113	29.2	30.0	30.9	54.1
	2	0.9	113	30.2	30.5	30.8	54.9
	2	11.1	113	33.6	36.1	38.7	65.1
	2	24.0	113	35.2	37.4	39.6	67.3
	2	34.9	113	31.9	34.6	37.4	62.3
	2	44.4	113	33.1	35.2	37.2	63.3
	2	53.9	113	37.3	38.9	40.6	70.1
	2	64.9	113	30.9	34.9	38.9	62.8

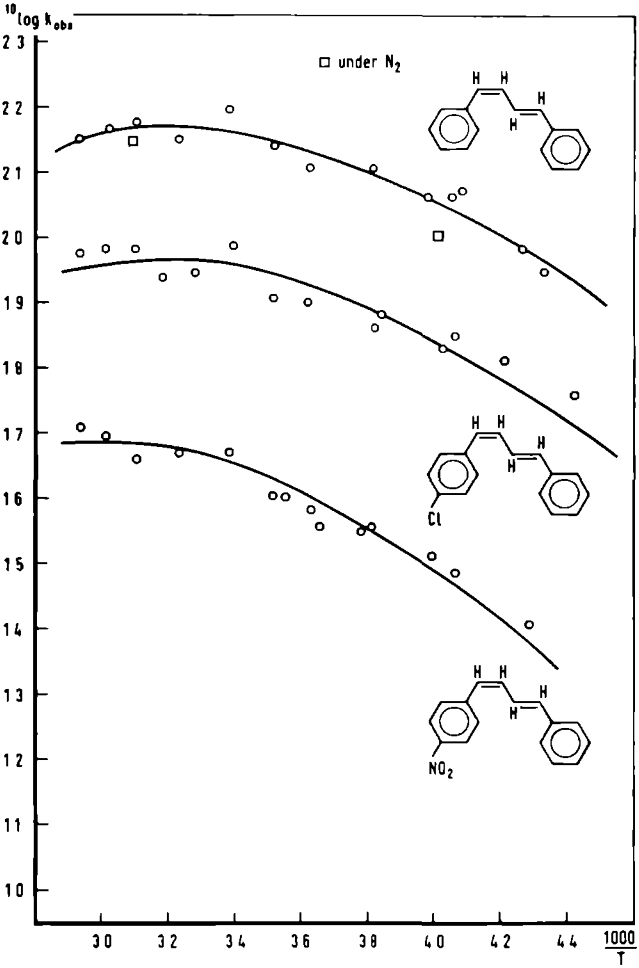


Fig.1[a] Arrhenius plots for the iodine catalyzed isomerization of cis-trans diphenylbutadiene derivatives.

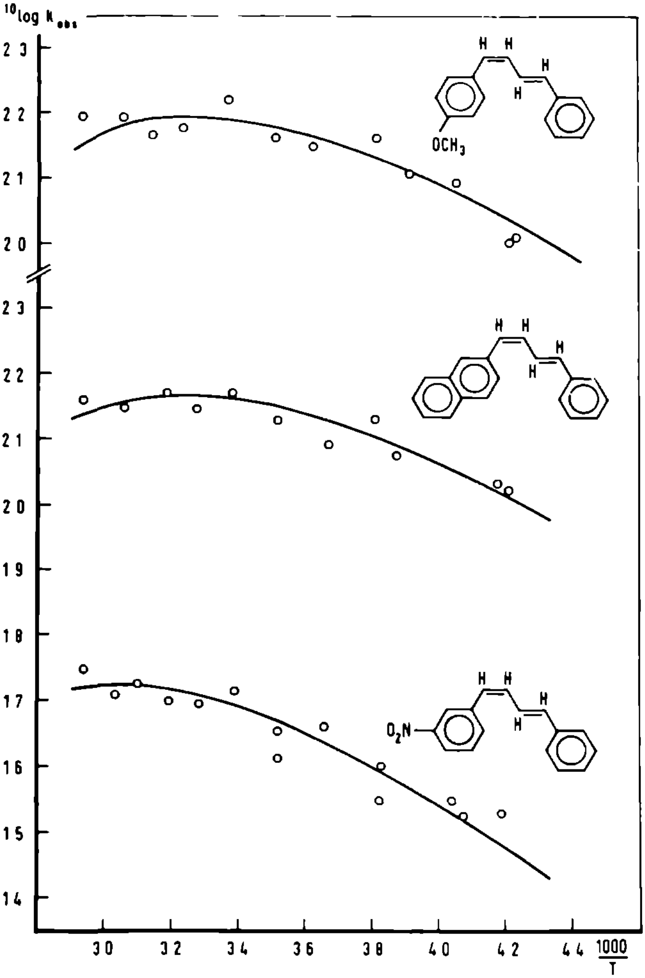


Fig.1^{b} Arrhenius plots for the iodine catalyzed isomerization of cis-trans diphenylbutadiene derivatives.

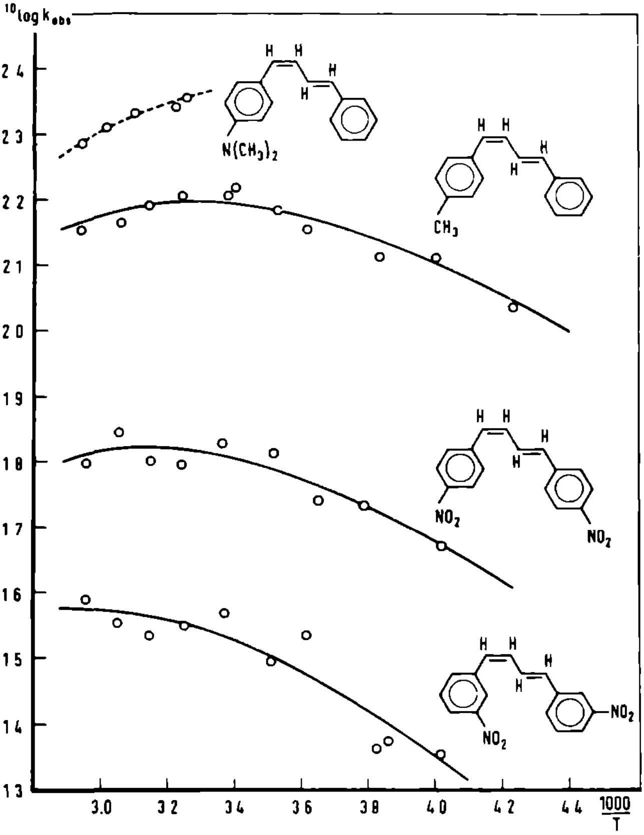


Fig.1^c Arrhenius plots for the iodine catalyzed isomerization of cis-trans diphenylbutadiene derivatives.

III-3 ARRHENIUS PLOTS

In figures 1 a, b, c the logarithms of the observed rate constants have been plotted against the reciprocal of the absolute temperature for the whole series of cis-trans butadienes investigated. As can be seen from these graphs no linear relationships are obtained. All plots show the same kind of curvation. At higher temperatures the values of the activation energies seem to diminish. It is unlikely that this behaviour is caused by a systematic error in the estimation of the rate constants, because Arrhenius plots of other cis compounds found by the same method afford good linear correlations (chapters II and IV) .

The dependence of rate constants on temperature is generally expressed in the empirical Arrhenius equation

$$k = A\ e^{-E_a/RT} \qquad \text{eq.1}$$

in which A and E_a are supposed to be independent of temperature. However, a more accurate relationship based on the transition state theory, is given in equation 2

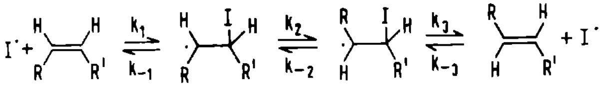
$$k = A'T^m\ e^{-E_o/RT} \qquad \text{eq.2}$$

in which E_o represents the theoretical activation energy[4a]. Differentiation of equations 1 and 2 with respect to the temperature gives then

$$E_a = E_o + mRT \qquad \text{eq.3}$$

This expression shows that the Arrhenius activation energy (E_a) is in fact temperature dependent. The value of m predicted by Frost and Pearson[4b] for the reaction between an atom and a non-linear molecule is: $-\frac{1}{2} \leqslant m \leqslant \frac{1}{2}$. This means that the variation in the Arrhenius activation energy may be only 0.1 kcal/mole over a temperature range of 100°. This value is much too small to account for the curvation of the Arrhenius plots observed.

It is generally accepted, as was originally proposed by Berthoud and Urech[5], that the first step in the iodine atom catalyzed isomerization of an olefin is the addition of an atom to the double bond. In this way the double bond becomes a single bond and rotation around this bond becomes much easier. Dissociation of the iodine atom from the intermediate radical after the rotation step results in the formation of the trans compound.



Because the isomerization is irreversible, on account of the (much) lower energy content of the trans isomers, the rate law can be formulated as follows:

$$v = f.\frac{k_1 k_2}{k_{-1} + k_2}[\text{cis}][\text{I}^{\bullet}] \qquad \text{eq.4}$$

(The meaning of the factor f was explained in chapter II).

This expression can be simplified if $k_{-1} << k_2$ or $k_{-1} >> k_2$. In the first case the rotation rate constant (k_2) of the intermediate radical (cis-I$^\bullet$) is very great in comparison with its dissociation rate constant (k_{-1}) and the attack of iodine atoms on the double bond is rate determining, since each attack effects isomerization ($k_{obs.} = f.k_1$).

The reverse situation arises in the other case. Only relatively few iodine atom additions to the double bond result in isomerization and the rotation step is rate determining ($k_{obs.} = f.\frac{k_1.k_2}{k_{-1}}$).

When k_{-1} and k_2 are of comparable size, however, equation 4 cannot be simplified. If at the same time the activation energies E_{-1} and E_2 differ substantially, no linear relationship between log $k_{obs.}$ and the reciprocal of the absolute temperature will be observed. In order to investigate if the curvation of the Arrhenius plots has to be ascribed to such a multiple rate determining process, we examined the consistence of the data of unsubstituted cis-trans diphenylbutadiene with expression 5 by a curve-fit program based on the method of least squares.

$$k_{obs.} = f.\ \frac{k_1.k_2}{k_{-1} + k_2} \qquad \text{eq.5}$$

Equation 5 was reduced and expressed in terms of the Arrhenius equation.

$$k_{obs.} = f.\ \frac{A_1\ e^{-E_1/RT}}{A_{-1}/A_2\ e^{-(E_{-1}\ -E_2)/RT} + 1}$$

The results are listed in table II.

TABLE II

Results of the curve-fit program applied on the data of unsubstituted cis-trans diphenylbutadiene.

Parameter	found
E_1	1.52
$E_{-1}-E_2$	4.22
A_{-1}/A_2	520
$f.A_1$	2700

The activation energies are expressed in kcal/mole. The unit of $f.A_1$ is $\text{litre}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$.

From the standard errors of the parameters, of the same magnitude as the parameters themselves, it appeared that no unambiguous least square solution was possible. The curve-fitting, however, is very satisfactory (drawn line in figure 1a) and the values of A_1 and A_{-1}/A_2 are in agreement with expected values (see further).

Muizebelt[1,6] found that the influence of substituents on the rate constants of iodine atom catalyzed isomerizations of substituted cis-stilbenes must be ascribed only to a variation of the relevant activation energies; substituents do not alter the entropy of activation. This turns out to hold generally in side-chain radical reactions of benzene derivatives[7]. Assuming that this is also true in the iodine catalyzed isomerization of substituted cis-trans diphenylbutadienes, the values of A_1 and A_{-1}/A_2, obtained by using the curve-fit program applied to the kinetic data of the unsubstituted cis-trans diene can be used for curve-fittings of the kinetic data of substituted derivatives. This restriction of the number of variable parameters is important, because by doing so the standard errors of the calculated activation energies become smaller and hence the values of these parameters will be more reliable.

The calculated curves have been drawn in figs. 1 a, b, c. It appears that the experimental rate constants coincide very well with the calculated curves. The deviations, mostly within the range of the confidence limits of the rate constants, seldom exceed 10% of the value of the relevant rate constant. The values of E_1 and $E_{-1}-E_2$ thus obtained for the isomerizations of the cis-trans dienes have been listed in table III. The values of E_r (the energy difference between the initial state (cis-trans + $I^{\bullet}$) and the transition state for the rotation step) have been obtained by subtracting the values of $E_{-1}-E_2$ from the relevant values of E_1. All the energies are expressed in kcal/mole.

TABLE III

Activation energies of the isomerization of cis-trans dienes.

compound	E_1	standard error	$E_{-1}-E_2$	standard error	E_r
H	1.52	0.01	4.22	0.05	-2.70
para-CH_3	1.46	0.02	4.15	0.05	-2.69
para-OCH_3	1.48	0.02	4.20	0.06	-2.72
β-naphtyl	1.50	0.02	4.14	0.06	-2.64
para-Cl	1.75	0.02	4.07	0.06	-2.32
meta-NO_2	2.08	0.02	4.00	0.07	-1.92
para-NO_2	2.15	0.02	4.04	0.05	-1.89
bis meta-NO_2	2.29	0.04	3.99	0.10	-1.70
bis para-NO_2	1.93	0.03	3.99	0.08	-2.06

The values of E_1 and E_r of the monosubstituted dienes have been plotted against the σ^o values of the substituents (figs.2 and 3). Good linear relationships were obtained with slopes of 0.78 and 0.98, and correlation coefficients of 0.993 and 0.991, respectively.

III-4 HAMMETT PLOTS

In recent years several investigators have proposed an extended Hammett equation of the form

$$\log k/k_o = \rho\sigma^o + \beta$$

for the correlation of substituent effects in radical reactions. Here, ρ and σ^o are the usual reaction and

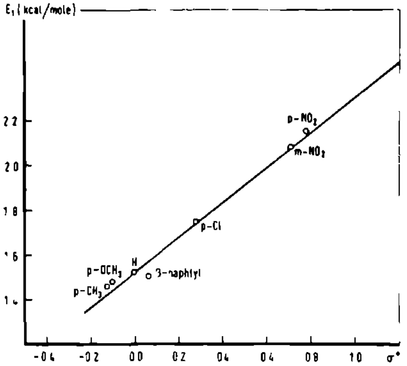


Fig.2 The calculated activation energies of iodine atom addition to mono-substituted cis-trans diphenylbutadienes as function of the σ^o values.

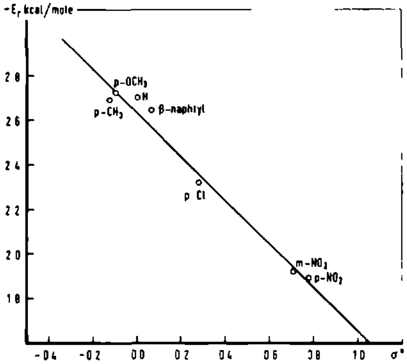
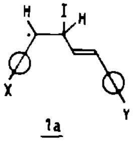
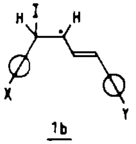


Fig.3 The calculated energy differences between TS_2 and the initial state of mono-substituted cis-trans diphenylbutadienes as function of the σ^o values.

substituent constants whereas β accounts for the extra stabilisation of the transition state due to resonance interactions of the para substituents with the reaction centre. The σ^{o} values differ from the original Hammett σ values in so far as they exclusively account for the polar effects of the substituents. We have used the σ^{o} values listed by Kieboom[8]. The value of the β-naphtylgroup, not given by Kieboom, has been taken from Yukawa and coworkers[9].

The isomerizations of cis-trans dienes may proceed *via* two different intermediates, 1a or 1b.


1a


1b

The additional resonance interaction is to be expected for substituents in the X position if the isomerization proceeds *via* an intermediate like 1a but for substituents in the Y position if 1b is the intermediate in the isomerization reaction.

In figs. 4 and 5 the logarithms of the isomerization rate constants at two temperatures for the monosubstituted dienes and similarly in figs. 6 and 7 log k-values of the symmetrically disubstituted dienes have been plotted against the relevant σ^{o} values. Only the isomerization rate constants of bis-(para-nitrophenyl) butadiene are larger than expected; all the rate constants of the monosubstituted derivates fit into a Hammett plot based on σ^{o} values. Although only two compounds substituted in both phenylrings have been investigated, it seems quite certain that only substituents in the Y position cause para interaction, which indicates that the isomerization always proceeds *via* an intermediate like 1b. The ρ values calculated from the Hammett lines have been listed in table IV.

TABLE IV

ρ-Values calculated from the Hammett lines

T($^{\circ}$C)	plot	ρ_{min}	ρ	ρ_{max}	r
49.5	4	-0.52	-0.59	-0.65	-0.994
-35.0	5	-0.64	-0.73	-0.83	-0.994
49.5	6		-0.84		
-23.0	7		-0.99		

$\rho\,{}^{max}_{min}$ = 95% confidence limits of ρ

r = correlation coefficient.

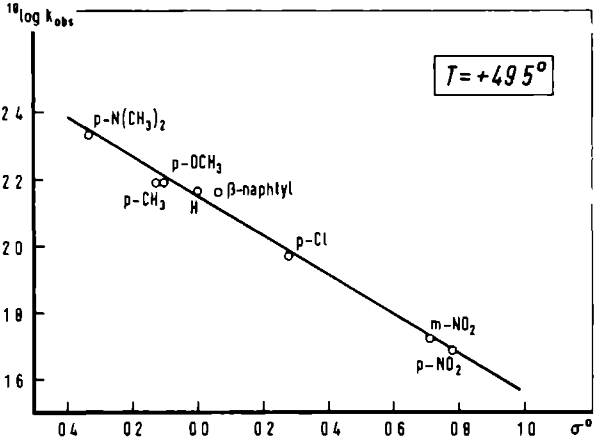


Fig.4 Hammett plot for the isomerization of mono-substituted cis-trans diphenylbutadienes at 49.5^{O}.

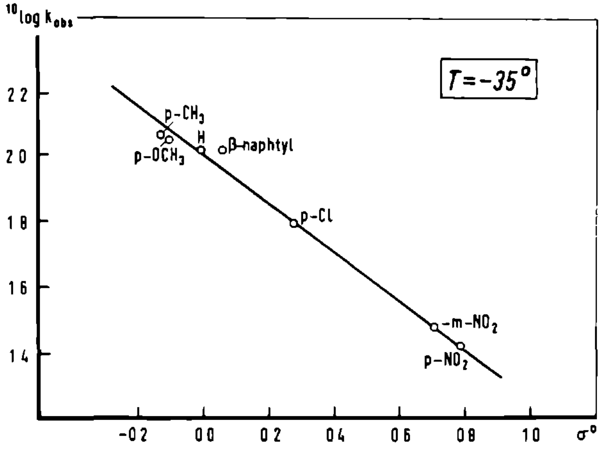


Fig.5 Hammett plot for the isomerization of mono-substituted cis-trans diphenylbutadienes at -35^{O}.

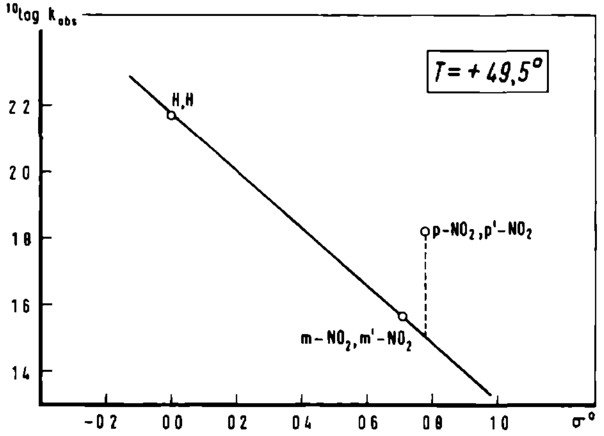


Fig.6 Hammett plot for the isomerization of symmetrically substituted cis-trans diphenylbutadienes at 49.5°

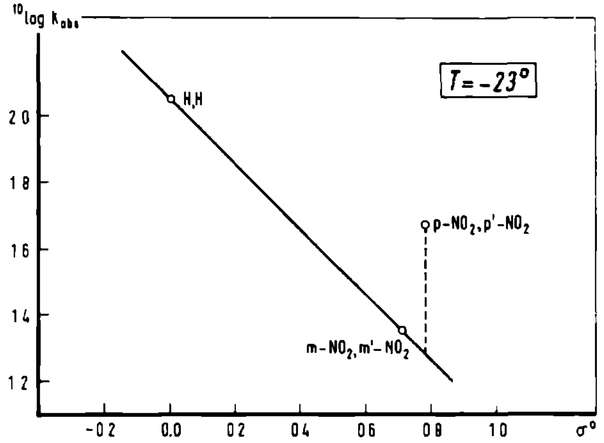


Fig.7 Hammett plot for the isomerization of symmetrically substituted cis-trans diphenylbutadienes at -23°.

III-5 DISCUSSION

III-5-1 THE FREQUENCY FACTORS OF THE REACTION

It may be concluded from the discussions in III-3 that the curvation in the Arrhenius plots of all cis-trans diphenylbutadienes must be ascribed to the correspondence in size of the rotation rate constants (k_2) of the intermediate radicals with their dissociation rate constants (k_{-1}). A similar observation was made by Steinmetz and Noyes[10] in their study of the bromine catalyzed isomerization of 1,2-dibromoethylene. These authors measured the exchange rate of cis-1,2-dibromoethylene with radioactive bromine and the rate of cis-trans isomerization. At 35° the exchange rate was about twice the rate of isomerization, which indicates that k_{-1} and k_2 are of comparable size in the latter reaction.

The values of A_1 and A_{-1}/A_2 calculated from the kinetic data of diphenylbutadiene (table II) and with $f = -5.87$ (section II-7-3) are remarkably consistent with comparable data. The value of log A_1 (9.3) agrees well with the value calculated for a reaction between an atom and a non-linear molecule (log A = 9 -10)[4b] and with the log A values found for the iodine exchange of cis- and trans-diiodoethylene[11] (9.4 and 9.6, respectively), in which the attack of iodine atoms on the double bond is rate-determining. The value of the frequency factor for these reactions was also calculated by Benson and coworkers[12]; they found log A = 9.8, which is in agreement with the experimental data. k_{-1} Concerns the dissociation of the intermediate radical. The value of the frequency factor of such an unimolecular bond-breaking calculated from the transition state theory is 10^{13} in the absence of entropy effects[4c]. Considering the fact that TS_1 for the isomerization of cis-trans diphenylbutadiene may be a rather loose complex (see further), a value of 14 for log A_{-1} seems to be a reasonable estimate[25]. In that case the value of log A_2 should be about 11.3 (14 - log 520). This value is in agreement with the log A factors of 11.3 and 11.8 calculated by Benson[12,26] for the rotation in the intermediates of the iodine catalyzed isomerization of butene-2 and 1,2-diiodoethylene, respectively.

Finally, the rate constant for isomerizations in which the rotation step is rate determining is equal to $k_1.k_2/k_{-1}$. Hence,

$$\log A_r = \log A_1 - \log A_{-1}/A_2$$

Filling in the values from table II gives

$$\log A_r = 6.6.$$

This value is lower than the log A factor (7.76) found for the isomerization of 3,3',5,5'-tetramethyl-cis-stilbene, in which the rotation is the rate controlling, slow step. The difference may be caused (at least partly) by the extra loss of entropy due to the increased rigidity of the central C-C bond of diphenylbutadiene in the cinnamyl radical as a consequence of resonance (see further).

From this discussion it is obvious that, in spite of their inaccurate estimation, the values of A_1 and A_{-1}/A_2 are consistent with those expected for this reaction. Therefore, the values of the activation energies obtained by the curve-fitting procedure can certainly be considered as reliable.

III-5-2 ENERGY SCHEME OF THE REACTION

Figure 8 represents an energy diagram for the iodine catalyzed isomerization of cis-trans diphenylbutadiene.

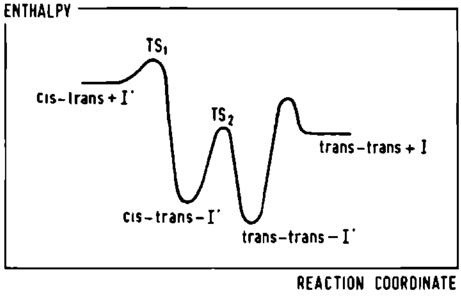


Fig.8 Energy diagram for the isomerization of cis-trans diphenylbutadiene.

cis-trans = cis-trans diphenylbutadiene

TS_1 = transition state for the iodine atom addition to cis-trans

cis-trans-I$^{\bullet}$ = intermediate radical

TS_2 = transition state for the rotation of cis-trans-I$^{\bullet}$ to trans-trans-I$^{\bullet}$

trans-trans = trans-trans diphenylbutadiene.

The energy difference between the initial state (cis-trans+I$^{\bullet}$) and TS_2 is -2.7 kcal/mole (table III). The value of the energy of activation observed for the isomerization of cis-stilbene is 3.6 kcal/mole. Thus the energy level of TS_2 is lowered by about 6 kcal/mole in the case of cis-trans diphenylbutadiene in comparison with cis-stilbene. At room temperature the isomerization rate constant of the cis-trans diene is about 700 times that of cis-stilbene; this is caused by the lowering of the energy level of TS_2.

The energy difference between cis + I$^{\bullet}$ and cis-I$^{\bullet}$ (ΔH_1) is influenced by the following factors: The bond breaking of the Π bond in an ethylene and the simultaneous formation of a C-I bond is endothermic (about 6 kcal/mole) according to bond energies. With cis-stilbene such a transformation should be even more endothermic due to the resulting loss of resonance energy of the compound (2.3 kcal/mole)[13]. However, in this case the product is a benzyl radical which itself is strongly stabilized by resonance (13 kcal/mole)[14]. So the addition of an iodine atom to cis-stilbene is ultimately an exothermic reaction (about 5 kcal/mole). The resonance energy of the radical is lost for the greater part during the rotation step, in which the benzyl residue cannot remain planar, and reaches a minimum in TS_2.

The resonance energy of cis-trans diphenylbutadiene is not known but can roughly be estimated as follows: The resonance energies given by Wheland[13] for cis-stilbene, trans-stilbene and all-trans diphenylbutadiene are 2.3, 7.0 and 10.7 kcal/mole, respectively. The difference between the last two values is mainly due to the extension of the conjugation with an additional double bond in diphenylbutadiene (the resonance energy of butadiene-1,3 is 3.5 kcal/mole). The resonance energy of cis-trans diphenylbutadiene may then be estimated at about 6 kcal/mole. The actual value can even be larger because cis-trans diphenylbutadiene is more coplanar than cis-stilbene. In the addition of an iodine atom to cis-trans diphenylbutadiene a cinnamyl radical is formed. Its resonance energy is not known either but is certainly larger than 13 kcal/mole, because the resonance energy of an allyl radical is already comparable with that of a benzyl radical[15,16]. Hence, the loss of bond energy (about 6 kcal/mole) and resonance energy of the starting compound (6-8 kcal/mole) is certainly compensated by the resonance stabilization of the radical formed in this case as well.

I II

Fig.9 Probable way of internal rotation in the intermediates involved in the isomerization of cis-trans diphenylbutadiene and cis-stilbene .

Figure 9 visualizes the rotation step of the intermediates in the cis-stilbene and cis-trans diphenylbutadiene isomerizations. Because of the greater steric requirements of the phenyl group in comparison with the iodine atom it may be accepted that the rotation occurs as indicated. These drawings show that the rotation is less sterically hindered in intermediate I than it is in intermediate II. Hence, the radical part of the intermediate of cis-trans diphenylbutadiene remains more planar during the rotation step than the corresponding intermediate of cis-stilbene, which results in a smaller value of the activation energy in the former case.

The energy difference (E_r) between the initial state (cis + $I^\bullet$) and the transition state for the rotation step (TS_2) equals $\Delta H_1 + E_2$. Assuming a minimum value of 5 kcal/mole for the activation energy of the rotation in the intermediate radical of the isomerization of cis-trans diphenylbutadiene (the rotation in ethane has already a barrier of 3 kcal/mole)[17], the addition of iodine atoms to the double bond is at least 8 kcal/mole exothermic. So it is likely that the observed lowering of E_r for the isomerization of cis-trans diphenylbutadiene in comparison with cis-stilbene must be attributed both to a more exothermic addition and to a smaller value of the activation energy for the rotation (E_2).

It has already been argued that it depends on the ratio k_{-1}/k_2 if there is an unambiguous rate-determining step or not. With the values of table II the ratio is found to be:

$$k_{-1}/k_2 = 10^{2.72}10^{-4.22/2.303RT}$$

Values of k_{-1}/k_2 calculated from this expression at several temperatures have been listed in table V.

TABLE V

Values of k_{-1}/k_2 for the isomerization reaction of cis-trans diphenylbutadiene.

T(^{o}C)	k_{-1}/k_2	rate determining step
260	10	rotation of the intermediate
66	1	
-27	0.1	addition of iodine atoms to the double bond

Assuming that k_{-1} and k_2 have to differ at least a factor ten to obtain an unambiguous rate determining step, it appears from table V that at temperatures above 260° the rotation step is rate determining, whereas at temperatures below -27° the addition is the slow step.

In our experiments performed between +65° and -40°, the values of k_{-1} and k_2 are about equal in the upper part of the temperature range, while in the lower part the addition reaction becomes gradually rate controlling.

III-5-3 EFFECTS OF SUBSTITUENTS

As referred to before, Muizebelt found that the influences of substituents on the isomerization rate constant of symmetrically substituted stilbenes must be ascribed only to a variation in the activation energy. The plot of activation energies against σ-values yielded a linear relationship for meta- and para-substituted stilbenes with a slope of 2.04 (kcal/σ). The activation energies of some para-substituted stilbenes, however, were lower than was expected from the polar effect of the substituents only, which was caused by resonance stabilization of the transition state due to conjugation of the para substituents with the odd electron of the intermediate[6, 18]. Since the rotation step is rate controlling in this case, the substituents can influence the reaction rate via the equilibrium constant (K_1) for the transformation from cis + $I^{\cdot}$ to cis-$I^{\cdot}$, via the rate of rotation (k_2) of the intermediate radical, or *via* both of these. It was argued, however, that the influence of the substituents could be attributed mainly to charge separation due to the formation of the polar C-I bond and that therefore the influence of the substituents on the rate of rotation should be small.

Tinnemans[18] studied the iodine catalyzed isomerization of ring-substituted cis methyl cinnamates at 120°. The logarithms of the rate constants correlated well with the σ-values of the substituents affording a ρ-value of -0.51. In this case some para-substituted cinnamates also showed positive deviations from the regression line. So it was concluded that the isomerization proceeds again via a benzyl radical. The ρ-value (-0.51) is about half the value obtained for the isomerization of symmetrically substituted cis-stilbenes at the same temperature ($\rho = -1.12$). The ρ-value for the isomerization of the stilbene derivatives can be split up into two parts:

$$\rho = \rho_\alpha + \rho_\beta$$

ρ_α concerns the influence of the substituents attached to the phenyl ring at the saturated carbon atom (CHI group), whereas ρ_β concerns the influence of substituents present in the benzyl radical moiety (fig.9). In the case of the cis-cinnamates, we can consider the ρ-value found (-0.51) as equal to ρ_β.

This implies that the transmission coefficient of the methylene group involved $(-\dot{C}-)$ for polar influences must be close to unity. The same result is obtained by comparing the ρ-value (presumably ρ_β) for the iodine catalyzed isomerization of 4-substituted-3'-styrylpyridines ($\rho = -0.70$)* at 25° with the ρ value of the reaction of the symmetrically substituted cis-stilbene derivatives extrapolated to the same temperature ($\rho = -1.60$).

Since the ρ-value involved in our isomerization is a ρ_α value, the expected influence of substituents in mono-substituted cis-trans diphenylbutadienes on the energy level of TS_2 will be slightly more than half the corresponding influence of substituents in the symmetrically substituted cis-stilbenes. In fig.3 the values of E_r (the energy difference between cis-trans + $I^\cdot$ and TS_2) have been plotted against the σ^o of the substituents. The slope of this regression line (0.98 kcal/σ^o) accords reasonable well with the expected value of 1.1-1.2.

In fig.2 the values of the activation energies for the addition of an iodine atom to substituted cis-trans diphenylbutadienes have been plotted against the σ^o values of the substituents, which results in a linear relationship with a slope of

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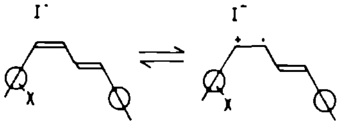
* The logarithms of these rate constants were originally correlated with σ^+ values of the substituents[19], giving $\rho = -0.3$. A correlation with σ, however, is more satisfactory[1].

0.78 (kcal/σ^{o}). This value is smaller than that obtained from the linear relation between E_r and σ^{o} (0.98 kcal/σ^{o}). So substituents exert somewhat more influence on TS_2 than on TS_1. In section III-5-2 we have argued that the heat of the addition of an iodine atom to cis-trans diphenylbutadiene is at least -8 kcal/mole. Since the activation energy for the addition reaction is only 1.5 kcal/mole, we may conclude on the basis of Hammond's postulate[20], that TS_1 very much ressembles the initial state (cis-trans + $I^{\bullet}$). Hence, it can be concluded that the influence of substituents on the stability of the intermediate radical is not the determining factor for the substituent effect on the rate of attack of iodine atoms on the double bond.

The precise origin of polar substituent effects on the rate of radical additions to olefins is still a matter of current interest. Two explanations have been advanced[21]. One of them is based on the assumption that substituents alter the electron density at the double bond; the other explanation says that the energy of the transition state may be lowered by the participation of substituent dependent charge-transfer interactions. Charge-transfer interaction of the type proposed by Walling[21] in which electron transfer occurs between the olefin and the iodine atom, generates a resonance structure in which a benzyl carbonium ion participates:



In this case a $\rho\sigma^+$ relation instead of the observed $\rho\sigma^o$ correlation may be expected to govern the addition reaction. However, charge-transfer complexes, in which the iodine atom is complexed by an aromatic ring in an equilibrium step *prior* to the addition to the double bond can not be excluded *a priori* . Similar complexes were proposed by Martin and Gleicher[22] in the trichloromethyl radical additions to substituted allylbenzenes, 3-butenylbenzenes and other 1-olefins .

Charge-transfer interactions were also suggested in the trichloromethyl radical addition to substituted styrenes[23].

Effects of substituents on the electron density at the double bond have been assumed by Cadogan and Sadler[24] to be involved in the radical additions to substituted styrenes and trans-stilbenes.
Our results do not permit of making a definite choice between the two explanations for the polar effects of substituents.

The value of ρ at -35° for the isomerization of monosubstituted cis-trans dienes is -0.73 (table IV). The negative sign of the value is consistent with the view that the iodine atom is an electrophilic species. At -35° the ratio of k_{-1}/k_2 is smaller than 0.1 throughout the series of mono-substituted dienes, which indicates that the addition reaction is rate determining at this temperature. So the value of ρ only expresses the influence of the substituents on the addition rate of iodine atoms at the double bond. The value of -0.73 is comparable with the ρ-values of -0.43 and -0.7 for the trichloromethyl radical additions to styrenes at 80°[23] and mono-substituted trans-stilbenes at 105°[24] respectively, and the ρ-value of -0.4 for the addition of thiyl radicals derived from thioglycolic acid to mono-substituted trans-stilbenes at 105°[24].

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CHAPTER IV

ISOMERIZATION OF CIS-TRANS-TRANS- AND TRANS-CIS-TRANS-1,6-DIPHENYLHEXATRIENE-1,3,5 AND OF TRANS-CIS-TRANS-TRANS-1,8-DIPHENYLOCTATETRAENE-1,3,5,7

IV-1 GENERAL REMARKS

The measuring procedure has been described in chapter II. The kinetic measurements with the trans-cis-trans triene have been carried out in two seperate series with lamps 3 and 4. In all the experiments with the cis-trans-trans triene and the trans-cis-trans-trans tetraene lamp 4 has been used as a light source.

Due to the very high rate of isomerization of the cis-trans-trans triene only exposure times of 1/100 sec have been used in experiments with this compound. With such short exposure times, continuation of the isomerization after interruption of exposure becomes important. In appendix 1 an estimation of the magnitude of this effect has been made, and the very short exposure times have been corrected by conversion into effective exposure times.

Finally, from the calculations of the rate constants of the cis-trans-trans triene it appeared that the value of k_i increased with increasing conversion percentage. This systematic error was eliminated by multiplying the estimated value of D_∞ with 1.02. The reason why the kinetic expression used does not fully satisfy in this case, is not known. The disagreement, however, is small.

IV-2 RESULTS

The observed isomerization rate constants of the α, ω-diphenylpolyenes together with their 95% confidence limits have been listed in table I. The rate constants are expressed in litre$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$sec^{-1}. n-Hexane was used as solvent unless stated otherwise.

TABLE I

Isomerization rate constants

compound	lamp	T(^{o}C)	$[I_2].10^6$ moles/l	k_{min}	k	k_{max}
trans-cis-trans triene	4	22.6	84.2	1.78	1.81	1.84
	4	37.3	84.2	2.35	2.40	2.44
	4	51.5	84.2	3.19	3.27	3.35
	4	64.2	84.2	4.09	4.18	4.27
	4	6.7	84.2	1.24	1.30	1.36
	4	- 9.7	84.2	0.82	0.86	0.91
	4	-22.8	84.2	0.62	0.63	0.65
	4	-39.2	84.2	0.37	0.40	0.42
	3	24.7	113	2.09	2.16	2.22
	3	37.4	113	2.90	3.10	3.31
	3	52.2	113	3.24	3.37	3.49
	3	63.2	113	4.40	4.57	4.73
	3	52.2	113	3.64	3.70	3.76
	3	37.3	113	2.71	2.84	2.79
	3	3.8	113	1.24	1.31	1.38
	3	-32.8	113	0.44	0.47	0.51
	3	-44.1	113	0.28	0.30	0.31

table I (continued)

compound	lamp	T(°C)	$[I_2].10^6$ moles/l	k_{min}	k	k_{max}
trans-cis-trans-trans tetraene	4	22.3	84.2	100	105	111
	4	37.3	84.2	114	117	120
	4	51.4	84.2	131	134	138
	4	6.5	84.2	75	78	81
	4	-10.4	84.2	67	69	71
	4	-25.3	84.2	50	54	59
	4	-38.5	84.2	40	42	44
	4	64.6	21.0	145	157	169
cis-trans-trans triene	4	- 2.4	21.0	4090	4280	4470
	4	-10.3	21.0	4530	4610	4690
	4	- 6.6	21.0	4420	4610	4810
	4	-17.3	21.0	3820	4250	4680
	4	-17.1	21.0	3920	4100	4270
	4	-25.8	21.0	2820	2910	3000
	4	-25.6	21.0	2820	2930	3050
	4	15.8	21.0	4020	4180	4340
	4	- 3.2	21.0	4120	4290	4460
	4	- 9.7	21.0	3940	4220	4500
	4	-16.2	21.0	3790	3980	4370
	4	-24.4	21.0	3100	3300	3510
	4	-23.6	42.1	3270	3580	3890
	4	-32.8	42.1	2830	2940	3060
	4	-34.4	21.0	2340	2450	2560
	4	-37.4	84.2	2420	2570	2720
	4	-37.8	42.1	2460	2590	2710
	4	-37.5	84.2	2600	2690	2790

table I (continued)

compound	lamp	T(^{o}C)	$[I_2]$ .10^6 moles/l	k_{min}	k	k_{max}	remarks
cis-trans-trans triene	4	17.3	21.0	4090	4200	4300	
	4	23.3	10.5	4890	5040	5180	
	4	25.8	10.5	4700	5010	5320	
	4	29.0	10.5	4460	4680	4890	
	4	32.4	10.5	4290	4620	4950	
	4	38.3	10.5	4700	4920	5130	
	4	9.2	21.0	1560	1650	1740	in CCl_4
	4	0.3	21.0	1510	1570	1620	"
	4	- 6.8	21.0	843	871	900	"
	4	-23.1	21.0	440	460	481	"
	4	- 5.0	21.0	1230	1340	1450	"
	4	10.5	21.0	1457	1463	1468	"
	4	- 5.5	21.0	946	974	1006	"
	4	-13.5	21.0	732	790	850	"
	4	-20.3	21.0	464	537	610	"

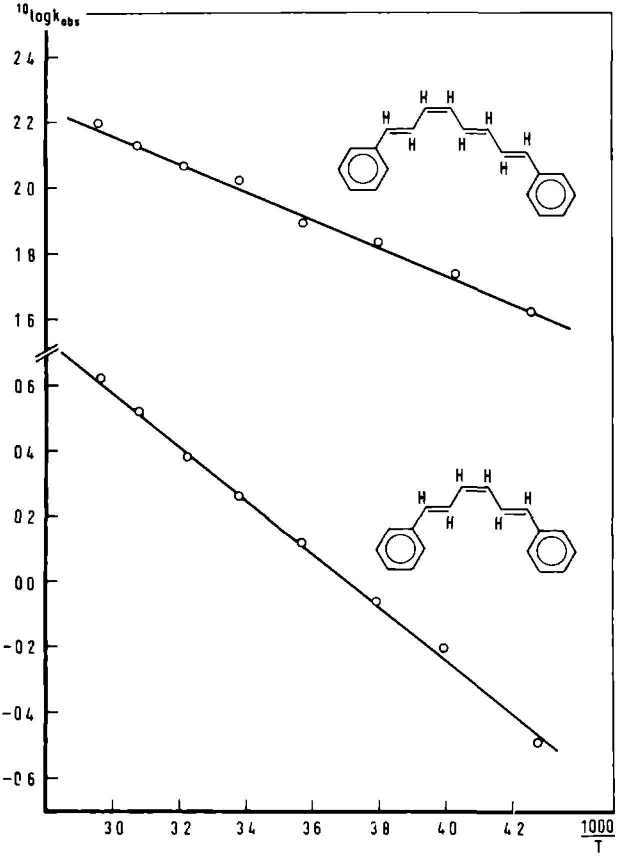


Fig.1 Arrhenius plot for the isomerization of trans-cis-trans-trans diphenyloctatraene and trans-cis-trans diphenylhexatriene. All rate constants plotted in this graph have been estimated using lamp 4 as light source.

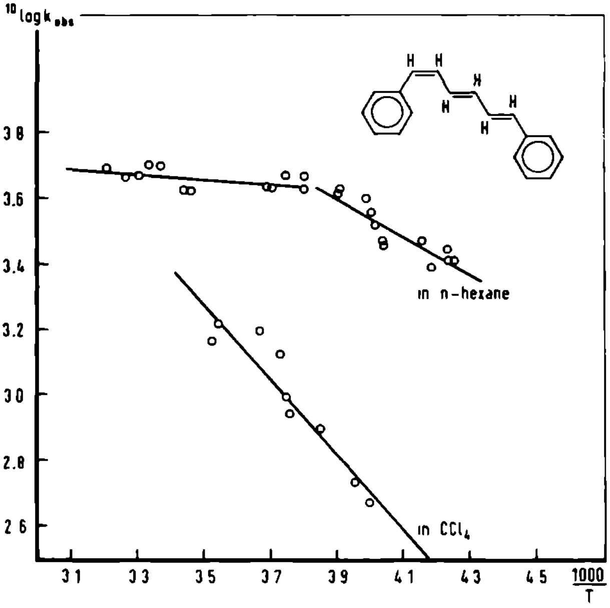


Fig.2 Plot of the logarithms of the isomerization rate constants of cis-trans-trans diphenylhexatriene against 1000/T (°K).

TABLE II

Arrhenius activation parameters

compound	lamp	$E_{a\ min}$	E_a	$E_{a\ max}$	log f A_{min}	log f A	log f A_{max}	log A	r
trans-cis-trans triene	4	3.36	3.53	3.70	2.76	2.89	3.02	8.9	0.999
trans-cis-trans triene	3	3.63	3.82	4.00	3.01	3.15	3.29	9.1	0.999
trans-cis-trans-trans-tetraene	4	1.81	1.96	2.11	3.34	3.46	3.57	9.5	0.997
cis-trans-trans triene n-hexane above -15°	4	-0.05	0.33	0.70	3.62	3.91	4.20	9.9	0.527
cis-trans-trans triene n-hexane below -15°	4	1.89	2.62	3.35	5.18	5.83	6.49	11.8	0.930
cis-trans-trans triene in CCl_4	4	3.69	5.32	6.94	6.03	7.37	8.70	13.4	0.946

The values of log f.A and E_a are expressed in litre^{½}mole$^{-½}$sec^{-1} and kcal/mole, respectively. The values of log A (calculated from equation 9 and data of table III of chapter II) are expressed in litre mole^{-1}sec^{-1}.

IV-3 ARRHENIUS ACTIVATION PARAMETERS

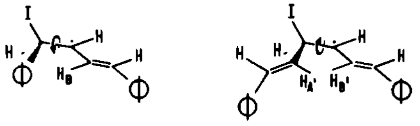
The log k values have been plotted against 1000/T (see figures 1 and 2). From these plots the Arrhenius activation parameters have been calculated together with their 95% confidence limits. As can seen from figure 2,the Arrhenius plot of the rate constants of the cis-trans-trans triene estimated in n-hexane as solvent is not a straight line. Between -10^{o} and -15^{o} there seems to be a kink in the relationship. Therefore separate Arrhenius parameters have been estimated for measurements above and below -15^{o}.

All parameters have been listed in table II.

IV-4 DISCUSSION

IV-4-1 ISOMERIZATION OF TRANS-CIS-TRANS-1,6-DIPHENYLHEXATRIENE-1,3,5

Examination of the data listed in table II reveals that the reproducibility of the measurements is satisfactory; the values of the collision factors and activation energies obtained from both series of measurements agree very well. The mean values for the activation energy and log A factor are 3.7 kcal/mole and 9.0 litre $mole^{-1}sec^{-1}$, respectively. The value of log A suggests that the addition of an iodine atom to the double bond is the rate determining step (see section III-5-1). In that case the activation energy for the addition reaction is about 2 kcal/mole larger than the corresponding value of the cis-trans diene (1.5 kcal/mole). This result can be accounted for as follows: The difference in heat of additions for the two isomerizations is caused by differences in resonance energy in the initial states and intermediate radicals.



I

II

fig.3 Intermediate radicals of the iodine atom catalyzed isomerization of cis-trans diene (I) and trans-cis-trans triene (II).

As can be seen from figure 3 both intermediates are cinnamyl type radicals; intermediate II, however, contains an additional resonance energy of about 2 kcal/mole[1a] from the styrene moiety of the intermediate. In section III-5-2 we estimated the resonance energy of the cis-trans diene at 6-8 kcal/mole. The unknown resonance energy of the trans-cis-trans triene can be estimated in the same manner. The resonance energies of trans-stilbene and trans-trans diphenylbutadiene are 7.0 and 10.7 kcal/mole, respectively. The difference is about equal to the resonance energy of 1,3- butadiene. Since the resonance energy of cycloheptatriene is 6.7 kcal/mole[1b], we can estimate the resonance energy of (coplanar) trans-cis-trans diphenylhexatriene at about 14 kcal/mole. The addition of an iodine atom to the trans-cis-trans compound should then be 4-6 kcal/mol less endothermic than that to the cis-trans diene, and the transition-state may then be expected to be reached at a later stage of the reaction. Its activation energy may be higher then , as is found.

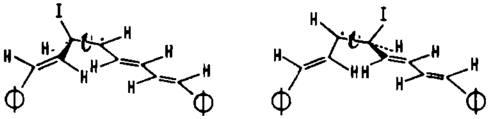
From these figures it can also be calculated that the energy difference between the intermediate radical and TS_1 (E_{a-1}) in the isomerization reaction of the cis-trans diene is 2-4 kcal/mole greater than the corresponding value of the trans-cis-trans triene. If we assume that the pertinent values of frequency factors are about equal, it can be concluded that k_{-1} (cis-trans diene) $<k_{-1}$(trans-cis-trans triene).

The fact that the isomerization of the trans-cis-trans triene is addition controlled implies that $k_{-1}<k_2$ (section III-3). In the case of the cis-trans diene we found that $k_{-1}\simeq k_2$. So it must be true that k_2 (cis-trans diene)$<<k_2$(trans-cis-trans triene).

The arrows drawn in figure 3 indicate the most favourable way of the rotation in intermediates I and II. With I iodine and H_B will be opposed in TS_2; in II, however, the atoms $H_{A'}$ and $H_{B'}$. So in the latter case steric strain in TS_2 will be lower (the trans-cis-trans triene itself is coplanar), which results in a lower value for the activation energy of the rotation step.

IV-4-2 ISOMERIZATION OF TRANS-CIS-TRANS-TRANS-1,8-DIPHENYLOCTATETRAENE-1,3,5,7

The values of the frequency factor (log A= 9.5) and activation energy (2.0 kcal/mole) for the isomerization of the trans-cis-trans-trans tetraene strongly indicate that also in this case the attack of an iodine atom on the double bond is rate determining. The value of the activation energy for this reaction is about 1.5 kcal/mole smaller than that for the isomerization of the trans-cis-trans triene. Apparently the addition reaction is more exothermic in the former case. This might be explained by the supposition that the intermediate involved in the isomerization reaction of the trans-cis-trans-trans tetraene is a phenylpentadienyl type radical (III) and not a cinnamyl type radical (IV)



III IV

fig.4 Possible intermediates for the isomerization of the trans-cis-trans-trans tetraene.

The greater heat of reaction in the addition to the trans-cis-trans-trans tetraene in comparison with the trans-cis-trans triene implies that the extension of conjugation leads to a higher increase in the resonance energy of the intermediate radical than in the parent compound. This has also been noticed in cis-stilbene going to cis-trans diphenylbutadiene. A quantitative evaluation of the increase in the heat of addition, however, cannot be given in the former case, because not all relevant data are available.[*]

The internal rotation of the intermediate involved in the isomerization of the trans-cis-trans-trans tetraene (III) occurs as indicated in the figure. Very little resonance energy is lost during the rotation, which results in a low value of the relevant activation energy.

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[*] The resonance stabilization of a pentadienyl radical is estimated by Benson *et al.*[2] The observed value, 15.4 kcal/mol, is regarded as a lower limit.

IV-4-3 ISOMERIZATION OF CIS-TRANS-TRANS-1,6-DIPHENYLHEXATRIENE-1,3,5

Considering the facts that the cis-trans-trans triene is not planar (crowding here is similar to that in cis-trans diphenylbutadiene) and that the isomerization certainly proceeds *via* a strongly resonance stabilized phenylpentadienyl radical,a very fast isomerization rate for this compound may be expected (see discussions in the sections IV-4-1,2 and III-5-2).

As can be seen from table I the rate constant observed for the isomerization of the cis-trans-trans triene is about 5000 (litre$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$sec^{-1}) at room temperature, by far the greatest value found in our series of compounds. As appears from table I and figure II the accuracy and reproducibility of the measurements with this compound are still quite statisfactory. The value of the activation energy calculated from measurements in hexane above -15° (0.3 kcal/mole) is as expected for a strongly exothermic addition reaction.

The temperature dependence of the rate constants estimated in n-hexane below -15° and in carbon tetrachloride is larger (table II). Moreover, rate constants in the solvent carbon tetrachloride are much smaller than those estimated in hexane at the same temperatures (fig.2); this result is quite distinct from that with 3,3',5,5'-tetramethyl-cis-stilbene where no influence of the solvent on the reaction rate was found (chapter II). These observations suggest that, at least in part, the isomerization is diffusion controlled under these circumstances. Table III summarizes kinetic data of some diffusion controlled reactions.

TABLE III

Kinetic data for some diffusion controlled reactions

Reaction	solvent	$k.10^{-9}(25^{o})$	E_a	log A	ref.
$I^{\cdot} + I^{\cdot} \rightarrow I_2$	CCl_4	10	5.6	14.1	3
$I^{\cdot} + I^{\cdot} \rightarrow I_2$	n-hexane	14	2.4	11.9	3
β-naphtylamine + CCl_4	cyclohexane	8	2.5	11.7	4
(fluorescence quenching)	iso-octane	13	1.6	11.3	4
cis-trans-trans triene + $I^{\cdot}$ (isomerization)	CCl_4	3	5.3	13.4	this work

Rate constants and frequency factors are expressed in litre/mole.sec, activation energies in kcal/mole.

It appears that the activation energies for these reactions are in the range of 2-6 kcal/mole. Since the activation energy calculated from measurements in n-hexane above -15^{o} is only 0.3 kcal/mole, this value and the belonging value of the frequency factor (9.9) may be considered as kinetic data for the addition step. It is noted that the reaction is not entirely diffusion controlled until $k_{diff.} << k_{add.}$

This condition is only fulfilled in carbon tetrachloride at low temperature.

IV-4-4 INFLUENCE OF TRANS-CIS ISOMERIZATION

When a solution of iodine with trans-stilbene or trans-trans diphenylbutadiene is irradiated with visible light no changes in the absorption spectrum are observed. Apparently the equilibrium cis $\rightleftarrows$ trans for these compounds lies far to the right. This is, however, not the case with the more extended α, ω-diphenylpolyenes. Zechmeister and coworkers[5,6] estimated the compositions of mixtures of the stereoisomeric 1,6-diphenylhexatrienes and 1,8-diphenyloctatetraenes obtained by iodine catalyzed isomerizations of the all-trans derivatives. The percentages of all-trans triene and all-trans tetraene in the mixtures were only 94% and 86%, respectively. The ratios of the amounts of cis isomers in the mixtures suggest that not only thermodynamic but also kinetic factors are involved in the composition of the mixtures[6,7].

The equation used for the calculation of rate constants (section II-3) is also valid for reversible isomerization reactions[8]. In these cases, however, the meaning of k-values found is given by: $k = k_{c \to t} + k_{t \to c}$. Considering the high percentages of the all-trans isomers in the final composition of the reaction mixtures, the contribution of the trans-cis isomerization to the rate constants observed will probably be small and therefore no corrections have been made.

IV-5 CONCLUDING REMARKS

Table IV summarizes the Arrhenius activation parameters and the relative rate constants at 25° for the iodine atom catalyzed cis-trans isomerization of the α,ω-diphenylpolyenes investigated and some other olefins.

So far, differences in rate constants have only been discussed in terms of activation energies. An examination of the data listed in table IV reveals, however, that the log A factors of the addition steps in the isomerizations of α,ω-diphenylpolyenes are not fully equal either. To be sure, the differences are rather small and do not always exceed the confidence limits of the frequency factors. As a general trend in the whole series, however, the log A values seem to increase on decreasing activation energies.

In the addition of an iodine atom to a conjugated olefine the entropy is reduced by the reduction of the number of species and by the stiffening of bonds as a consequence of resonance in the radical formed. The lowering of entropy in the transition state of the addition step is stronger when the transition state is reached at a later stage (differs more from the initial state). On the other hand, on the basis of Hammond's postulate, the transition state ressembles

TABLE IV

Arrhenius activation parameters and relative rate constants for the iodine catalyzed isomerization of olefins .

compound	method	solvent	log A	E_a	rate determining step	k(rel.)	ref.
cis-2-butene	T	-	8.5	9.4	rotation	$3.6\ 10^{-4}$	9
trans-1,2-diiodo ethylene[a]	T	-	8.85	11.0	rotation	$5.2\ 10^{-5}$	10
methyl cis-cinnamate	T	CCl_4	7.5[b]	5.0	rotation	$6\ 10^{-2}$	11
3,3'5,5'-tetramethyl-cis-stilbene	hν	n-hexane	7.76[c]	3.7	rotation	1	this work
cis-trans diphenyl-butadiene	hν	n-hexane	6.6 9.3	-2.7 1.5	rotation + addition	$6.8\ 10^{2}$	"
cis-trans-trans diphenylhexatriene	hν	n-hexane	9.9	0.3	addition	$4.4\ 10^{4}$	"
trans-cis-trans diphenylhexatriene	hν	n-hexane	9.0	3.7	addition	$1.7\ 10^{1}$	"

table IV (continued)

compound	method	solvent	log A	E_a	rate determining step	k(rel.)	ref.
trans-cis-trans-trans diphenyloctatetraene	hν	n-hexane	9.5	2.0	addition	$9.8\ 10^2$	this work

Values of log A and E_a are expressed in litre/mole.sec and kcal/mole, respectively.

a) Trans-cis isomerization. The value of the rate constant at 417°K calculated with the listed parameters is in agreement with the value of the rate constant obtained by Noyes[12] for this reaction in decaline as solvent at the same temperature.

b) Estimated value.

c) An error in this value will only cause a constant error in the log A values for the isomerization of the α, ω-diphenylpolyenes (equation 9, chapter II).

more the initial state in strongly exothermic additions (with low activation energies, e.g. with cis-trans-trans diphenylhexatriene), and more the final state in less exothermic additions (with higher actitivation energies, e.g. with the trans-cis-trans hexatriene). So a negative correlation between log A and E_a values in the series should be comprehensible.

The log A factors of the other compounds in table IV concern rotation controlled isomerizations; their mutual differences are much larger. The highest values are to be expected when the relevant radical is not stabilized by resonance; this is found with cis-butene and trans-diiodoethylene. The difference between the log A_r factors found for the isomerization of the cis-stilbene derivative and cis-trans diphenylbutadiene has been ascribed for the same reason to the more rigid structure of the cinnamyl radical intermediate in the latter reaction, in comparison with the benzyl radical in the former (see section III-5-1).

Finally, it is noted that the ratios $k_{c\text{-}t\text{-}t \text{ triene}}/k_{c\text{-}t \text{ diene}}$ (not planar compounds) and $k_{t\text{-}c\text{-}t\text{-}t \text{ tetraene}}/k_{t\text{-}c\text{-}t \text{ triene}}$ (planar compounds) are about equal (ca. 60 at 25°). Both ratios concern pairs of compounds, which differ only in the presence of an additional trans substituted double bond in one of them. In each pair one compound isomerizes *via* a phenylpentadienyl radical and the other in a completely similar way *via* a phenylallyl radical.

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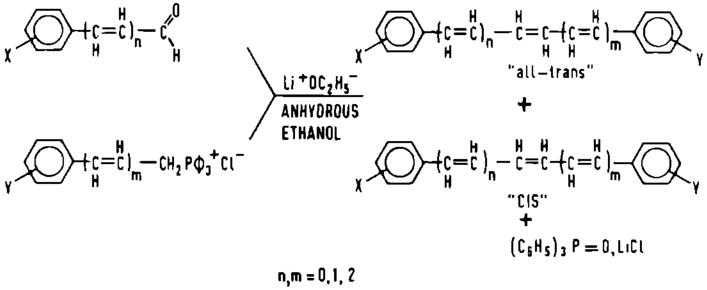
CHAPTER V

SYNTHESES OF THE α,ω-DIPHENYLPOLYENES

This chapter describes the syntheses and purification of the α, ω-diphenylpolyenes and other starting compounds; also their physical constants are given. U.V. absorption spectra were recorded on a Beckman DK-2A and a Cary-15 spectrophotometer by using n-hexane as a solvent. Melting points are uncorrected. Micro-analyses were carried out by Mr.J.Diersmann.

The syntheses of α, ω-diphenylpolyenes could be carried out easily using the Wittig synthesis, which allowed the introduction of cis and trans ethylenic linkages at a definite position in the molecule.



The procedure given by Mc.Donald and Campbell[1,2] was modified in order to make possible the isolation of the cis product. To a solution of 0.048 mol of a triphenylposphonium chloride and 0.052 mol of an aldehyde in 65 ml of anhydrous ethanol was added a solution of a twofold excess of lithium ethoxide in 285 ml of anhydrous ethanol. After the mixture had been left at room temperature in the dark overnight, 230 ml of water were added, and the precipitate was filtered and washed with 60% ethanol. After being dried under vacuum the crude product was treated with boiling hexane for a few minutes, cooled down to -80° and filtered. The solid was crystallized from ethanol or toluene, which yielded the all-trans diphenylpolyene. The hexane solution was concentrated and chromatographed on alumina. The solid cis products were crystallized from n-hexane. The combined yield was 50-70%, the cis-all trans ratio was mostly about 1:5.

Monosubstituted 1,4-diphenylbutadienes-1,3.

$Y = H$, $n = 0$, $m = 1$.

The substituted benzaldehydes used were all commercially available.

Triphenylcinnamylphosphonium chloride.

Trans cinnamaldehyde was reduced with $NaBH_4$[3], and the resulting cinnamyl alcohol was treated with HCl in CCl_4 at 0° giving cinnamyl chloride[4]. The reaction between cinnamyl chloride and triphenylphosphine in boiling xylene produced triphenylcinnamylphosphonium chloride.

Disubstituted 1,4-diphenylbutadienes-1,3.

$X = Y$, $n = 1$, $m = 0$.

Para and meta nitrocinnamaldehyde were prepared by condensation of the corresponding benzaldehyde with acetaldehyde[5,6]. 4- and 3-nitrobenzyltriphenylphosphonium bromide were synthesized by the reaction of the corresponding benzyl bromides with triphenylphosphine in boiling xylene.

1,6-diphenylhexatrienes-1,3,5.

$X = Y = H$, $n = 1$, $m = 1$.

The reaction of triphenylcinnamylphosphonium chloride with cinnamaldehyde afforded the all-trans and the trans-cis-trans isomer[7].

$X = Y = H$, $m = 2$, $n = 0$.

The third isomer, trans-trans-cis 1,6-diphenylhexatriene-1,3,5 was obtained from the reaction of trans-trans triphenyl 5-phenyl-2,4-pentadienylphosphonium chloride with benzaldehyde[7]. The synthesis of the phosphonium salt was carried out according to the following procedure. Ethynylstyrylcarbinol was prepared from trans cinnamaldehyde with ethynylmagnesiumbromide[8]. Partial hydrogenation of the carbinol in pyridine over 5% Pd-$BaSO_4$ yielded 1-phenyl-1,4-pentadienol-3, which was treated with HCl in CCl_4 at 0° to give trans-trans 5-phenyl-2,4-pentadienyl chloride. Refluxing triphenylphosphine with the crude 5-phenyl-2,4-pentadienyl chloride in xylene produced triphenyl 5-phenyl-2,4-pentadienylphosphonium chloride.

1,8-diphenyloctatetraenes-1,3,5,7.

$X = Y = H$, $n = 1$, $m = 2$.

The reaction of triphenyl 5-phenyl-2,4-pentadienylphosphonium chloride with trans cinnamaldehyde gave two isomers of 1,8-diphenyloctatetraene: The all-

TABLE

U.V. absorption data, physical constants and microanalysis of α,ω-diphenylpolyenes.

Compound	λmax	εmax.	melting point	C analysis Found Calc.	H analysis Found. Calc.	N analysis Found Calc.
cis-trans diene	312(312)[9,10]	34200(30200)[9,10]	oil	92.4(93.16)	7.0(6.84)	
trans-trans diene	328(328)[9,10]	57700(56200)[9,10]	153.5-155.5(154-156)[2]	92.8(93.16)	6.9(6.84)	
m-NO$_2$ cis-trans diene	314	34900	42.8-44.0	76.2(76.48)	5.1(5.21)	5.8(5.57)
m-NO$_2$ trans-trans diene	330	49900	145.6-146.9	76.4(76.48)	5.0(5.21)	5.9(5.57)
p-NO$_2$ cis-trans diene	352	46000	80.2-81.0	76.8(76.48)	5.1(5.21)	5.8(5.57)
p-NO$_2$ trans-trans diene	371	87600	176.5-178(181.5-182)[2]	76.2(76.48)	5.0(5.21)	5.8(5.57)
p-Cl cis-trans diene	315	37800	oil	79.8(79.83)	5.3(5.28)	
p-Cl trans-trans diene	332.5	63800	165.0-166.2(166-167)[11]	79.5(79.83)	5.3(5.28)	
βnapht.cis-trans diene	325	30000	77.4-78.9	93.3(93.71)	6.4(6.29)	
βnapht.trans-trans diene	339.5	67400	187.0-187.5	93.7(93.71)	6.3(6.29)	
p-OCH$_3$ cis-trans diene	322	31600	oil	86.5(86.41)	6.9(6.82)	
p-OCH$_3$ trans-trans diene	336	56800	163.2-164.2(163-164)[11]	86.2(86.41)	7.0(6.82)	
p-CH$_3$ cis-trans diene	315	34000	33.9-34.9	92.6(92.68)	7.2(7.32)	
p-CH$_3$ trans-trans diene	331	63000	156-158(155-156)[11]	92.8(92.68)	7.6(7.32)	
p-N(CH$_3$)$_2$ cis-trans diene	357	30400	55.0-57.0	86.4(86.70)	7.9(7.68)	5.6(5.62)
p-N(CH$_3$)$_2$ trans-trans diene	364	52500	180.2-183.2(177-180)[2]	86.5(86.70)	7.7(7.68)	5.6(5.62)
bis m-NO$_2$ cis-trans diene	309	29600	a)	64.6(64.86)	4.3(4.08)	9.3(9.46)
bis m-NO$_2$ trans-trans diene	326	41600	210.5-213.2	64.7(64.86)	4.0(4.08)	9.3(9.46)
bis p-NO$_2$ cis-trans diene	350	32700	a)	65.0(64.86)	4.1(4.08)	9.5(9.46)
bis p-NO$_2$ trans-trans diene	369	58900	276.5-279(269-271)[5]	64.5(64.86)	4.2(4.08)	9.5(9.46)
trans-cis-trans triene	350(351)[7]	63000(54000)[7]	107 -109(109-110)[7]	92.9(93.06)	7.0(6.94)	
cis-trans-trans triene	337(338)[7]	51000(46000)[12]	oil	91.9(93.06)	6.8(6.94)	
trans-trans-trans triene	350.5(351.5)[7]	85000(85000)[7]	203 -204(198-199)[7]	93.0(93.06)	7.1(6.94)	
trans-cis-trans-trans tetraene	370.5(371)[7]	80000(77000)[13]	134.5-135.5(132.5-133.5)[7]	92.7(92.98)	7.0(7.02)	
trans-trans-trans-trans-tetraene	371(372.5)[7]	118000(110000)[7]	236 -237(235-236.5)[7]	93.1(92.98)	7.1(7.02)	

a) Long melting ranges have been obtained, probably due to cis→trans rearrangement during the melt.

trans and the trans-cis-trans-trans configuration[7].

Most of the cis compounds mentioned in this section are unstable at room temperature even in darkness. They slowly transform into the all-trans configuration. Therefore these compounds, the oily produc dissolved in n-hexane, were stored in a refrigerator at -25°. Under these circumstances they remained pure for more than a year.

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APPENDIX 1

ISOMERIZATION BY PHOTOCHEMICALLY GENERATED IODINE ATOMS AFTER TERMINATION OF IRRADIATION

The concentration of iodine atoms in the reaction mixtures after termination of the irradiation decreases according to the expression

$$-d[I^{\cdot}]/dt = 2\ k_r\ [I^{\cdot}]^2 \qquad \text{eq. 1}$$

in which k_r is the recombination rate constant of iodine atoms. Since k_r is very large (about 10^{10}litre mole^{-1}sec^{-1}) the iodine catalyzed isomerization proceeds only a very short time after the end of the exposure. However, if the exposure time itself is very short, the influence of this "dark reaction" may become noticeable. On the other hand, it is probable that the time needed for building up the steady-state concentration of iodine atoms is not very small in comparison with short irradiation times. This factor diminishes the effectiveness of the exposure times.

In order to estimate the influence of these effects under our experimental circumstances, we measured the isomerisation rate constant of cis-trans diphenylbutadiene at 25^{o} with different exposure times using n-hexane as a solvent. The results have been listed in table I.

TABLE I

Isomerization rate constant of cis-trans diphenylbutadiene measured with different exposure times. $[I_2] = 84.2\ 10^{-6}$, lamp 4.

shutter times	corrected times	k_{min}	k	k_{max}	effective times
1/2	1/2	69.6	72.7	75.8	
1/4	1/4	74.6	78.3	82.1	
1/8	1/8	70.5	75.6	80.8	
1/15	1/15.6	74.0	79.1	84.1	
1/30	1/26.7	78.4	81.9	85.5	
1/60	1/50	116	119	122	1/33
1/125	1/100	138	146	153	1/50

Shutter times are given in seconds; the rate constants are expressed in $\text{litre}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$.

Inspection of table I reveals that the rate constant estimated with exposure times of 1/50 and 1/100 sec is 50 and 100% higher, respectively, than the mean value at longer exposure times. This means that the effective exposure time is about 1/100 sec longer than the corrected time measured.

Obviously, out of the two factors influencing the effectiveness of the exposure time mentioned above, the effect of the isomerization after termination of irradiation is the more important one.

PART II

CHAPTER VI

ELECTROPHILIC IODINATION OF SUBSTITUTED 1,3-DIPHENYLALLENES

VI-1 MATERIALS

The synthesis and purification of the substituted 1,3-diphenylallenes will be described in chapter VIII. 1,2-Dicloroethane (Baker) was dried over calcium chloride and distilled with a vigreux column of 100 x 1.4 cm. Iodine (Merck p.a.) was used without further purification.

VI-2 KINETIC AND THERMODYNAMIC EXPRESSIONS

As stated in chapter I the addition reaction proves to be first order in diphenylallene and second order in iodine and gives rise to an equilibrium situation.

$$A + 2\,I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AI_2 + I_2$$

The reaction rate may then be represented by the following equation:

$$-d[I_2]/dt = k_1[A][I_2]^2 - k_{-1}[AI_2][I_2]$$

Substitutions of $K_e = k_1/k_{-1}$, $[A] = [A]_o - [I_2]_o + [I_2]$, and $[AI_2] = [I_2]_o - [I_2]$ yield

$$-d[I_2]/dt = k_1[I_2]\{[I_2]^2+[I_2]([A]_o-[I_2]_o + 1/K_e)-[I_2]_o/K_e\}$$

or, with $b = [A]_o - [I_2]_o + 1/K_e$, and $c = -[I_2]_o/K_e$

$$-d[I_2]/dt = k_1 [I_2]([I_2]^2 + b[I_2]+ c)$$

or, $$-d[I_2]/[I_2]([I_2]^2 + b[I_2]+ c) = k_1\,dt$$

Integration of this equation and substitution of q for the quantity $\sqrt{b^2 - 4c}$ result in

$$-\frac{1}{2c}\ln\frac{[I_2]^2}{[I_2]^2 + b[I_2]+c} + \frac{b}{2cq}\ln\frac{2[I_2] + b - q}{2[I_2] + b + q}$$
$$+\frac{1}{2c}\ln\frac{[I_2]_o^2}{[I_2]_o^2 + b[I_2]_o + c} - \frac{b}{2cq}\ln\frac{2[I_2]_o + b - q}{2[I_2]_o + b + q} = k_1\,t$$

or, in an abbreviated form $y = k_1\,t$.

The equilibrium constants (K_e) were estimated with the formula:

$$K_e = \frac{([I_2]_o - [I_2]_e)}{([A]_o - [I_2]_o + [I_2]_e)\,[I_2]_e}$$

VI-3 MEASURING PROCEDURE

The addition reactions were studied spectrophotometrically in 1,2-dichloroethane as solvent The photometer cuvet (1 cm), equiped with a side arm, was used as a reaction vessel. The cuvet was placed in a chamber with optical flat windows * fitting into a Cary-15 spectrophotometer. Two ml of an allene solution were placed in the cuvet and one ml of an iodine solution in the side arm. The reaction vessel was brought on the temperature desired by means of a cryoson installation for variable temperatures. After measuring the extinction of the allene solution, the reactants were mixed in the dark and the extinction of the reaction mixture at 500 mμ was then determined at various times. The number of measuring points was usually 10-20. The equilibrium constants were estimated by following the reaction until the optical density of the reaction mixture reached a constant value. This value was used in the calculation of K_e.

VI-4 THE INFLUENCE OF CHARGE-TRANSFER COMPLEX FORMATION

The first stage in the addition reaction is the formation of a charge-transfer complex between iodine as acceptor and a diphenylallene as donor.

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* A sketch and a description of the chamber have been given in chapter II.

$$I_2 + A \overset{K_c}{\rightleftarrows} A.I_2$$

The presence of the charge-transfer complex has been demonstrated by extrapolation of the optical density of the reaction mixture to zero time. The optical density is always lower than the extinction of the same iodine concentration in the absence of a diphenylallene. In consequence of this complex formation the concentration of free iodine is different from the total iodine concentration.

$$[I_2]_{free} = [I_2] - K_c[A][I_2]_{free} \quad \text{(for [A] in excess)}$$

or, $$[I_2]_{free} = \frac{[I_2]}{1 + K_c[A]}$$

This effect is important for high values of $K_c[A]$.

The value of K_c is not known in this case, but can roughly be estimated as follows: The complex constant for styrene and iodine at 25° in CCl_4 is 0.31 litre/mole[1]. Assuming a complex constant for the iodine diphenylallene charge-transfer complex under these circumstances of 0.6 litre/mole, this value has to be corrected for solvent and temperature influences. In general charge-transfer complex constants are lowered by increasing solvent polarity[2]. The dielectric constants of carbon tetrachloride and dichloroethane at 25° are 2.23 and 10.36, respectively[3]. Thus K_c is likely to be smaller in the latter solvent.

Complex constants are also temperature dependent; ΔH is about -2 kcal/mole[4]. This enlarges the values of the complex constants under our circumstances. Finally, complex constants are substituent dependent but the influence of substituents is rather small[5].

From this discussion it may be assumed that 1.0 litre/mole is the upper limit of the complex constants under our conditions. However, even with this value, no more than 10% of the iodine should be bound at the relative high diphenylallene concentration of 0.1 mole/litre. This rough calculation is in agreement with the small difference (a few percent) in optical densities of a reaction mixture at zero time and a comparable iodine solution. Therefore no corrections were made for the presence of the charge-transfer complex. It is clear that in the calculations of the addition rate constants it could not be exacted that $y = 0$ at zero time.

VI-5 SOURCES OF ERRORS

Temperatures were measured at the end of a series of extinction measurements with a thermo-couple. The accuracy was about 0.5°. With long reaction times the temperature of the reaction mixture slightly dropped; in these cases the measurements were less accurate.

All solutions were prepared at 25°. No corrections were made for the increase of the diphenylallene concentration at lower temperatures. A plot of the optical density of an iodine solution against temperature was used for the determination of the molar density of iodine at various temperatures. In this determination the increase of the iodine concentration with temperature was neglected.

The addition reactions were mostly followed within the range of 15-80% conversion. The very fast additions, however, could only be measured from about 50% conversion. The addition rate constants were calculated from the y-t plots by the method of least squares. 95% Confidence limits of the rate constants were determined according to standard procedures.

For diphenylallenes with electron donating substituents accurate determinations of the equilibrium iodine concentrations were impossible on account of the iodine liberating side-reaction (chapter 1). For this reason the equilibrium constants for these diphenylallenes are less exact.

VI-6 RESULTS

VI-6-1 EQUILIBRIUM CONSTANTS

The values of the equilibrium constants (K_e) have been listed in table 1.

The headings are:

X, Y = The position and character of the substituent in each phenyl ring

T = Temperature in degrees centigrade

$[A]_o$ = Diphenylallene concentration at zero-time in moles/litre

$[I_2]_o$ = Initial iodine concentration in moles/litre

$[I_2]_e$ = Iodine equilibrium concentration in moles/litre

K_e = Equilibrium constant in litres/mole.

TABLE 1

X	Y	T	$[A]_o\ 10^3$	$[I_2]_o\ 10^3$	$[I_2]_e\ 10^3$	K_e
H	H	20.0	9.08	3.89	1.155	375
		8.8	4.40	4.13	1.515	964
		8.7	10.09	1.55	0.162	982
		1.2	10.09	4.13	0.443	1300
		- 1.1	4.40	4.13	1.188	1695
		-14.9	5.05	4.13	0.588	4005
β-naphtyl	H	11.2	5.53	4.28	1.456	718
		- 0.8	4.14	4.13	1.250	1830

Table 1 (continued)

X,Y		T	$[A]_o 10^3$	$[I_2]_o 10^3$	$[I_2]_e 10^3$	K_e
β-naphtyl	H	-11.8	4.14	4.13	1.070	2634
		-22.2	4.14	4.13	0.822	4829
p-F	H	20.1	5.96	4.28	1.737	429
		9.9	4.22	4.13	1.669	840
		0.3	4.22	4.13	1.315	1525
		-10.8	4.22	4.13	0.951	3216
p-Cl	H	31.1	4.92	2.57	1.453	202
		20.5	5.47	4.28	2.057	334
		- 0.3	3.21	4.13	1.936	1120
H	p-CH_3	10.3	5.27	4.13	1.317	896
		- 0.8	11.17	4.13	0.273	1932
		-11.9	11.17	4.13	0.145	3826
		-21.6	5.58	4.13	0.324	6605
p-CH_3	p-CH_3	- 8.9	5.34	4.13	0.433	5200
		-15.9	5.34	4.13	0.239	11200
		-18.1	4.39	4.28	0.543	10700
		-20.0	4.39	4.28	0.481	13600
		-28.1	4.39	4.28	0.380	21360
p-Br	p-CH_3	8.3	4.31	4.28	1.596	1035
		- 0.5	4.31	4.28	1.349	1580
		-10.1	4.31	4.28	1.126	2430
		-22.2	4.44	4.13	0.596	6530
p-CF_3	p-CH_3	10.5	6.13	4.28	1.623	473
		- 1.1	6.13	4.28	1.132	938
		-12.2	3.06	4.28	1.864	2020
		-19.1	3.06	4.28	1.748	2750

By using the van 't Hoff equation for the variation of the equilibrium constant with temperature: $2.303 \log K_e = -\Delta H/RT + \Delta S/R$, ΔH (in kcal/mole) and ΔS (in cal/mole-degr.) have been calculated together with their 95% confidence limits (table II).

TABLE II

X,Y		$-\Delta S_{min}$	$-\Delta S$	$-\Delta S_{max}$	$-\Delta H_{min}$	$-\Delta H$	$-\Delta H_{max}$	r
H	H	13.91	21.27	28.63	7.73	9.77	11.80	0.989
β-naphtyl	H	-2.16	13.90	29.96	3.45	7.73	12.01	0.984
p-F	H	18.30	21.65	24.99	8.96	9.89	10.81	1.000
p-Cl	H		19.90			9.03		
p-CH_3	p-CH_3	1.67	17.55	33.43	5.14	9.18	13.23	0.972
H	p-CH_3	8.82	18.00	27.19	6.50	8.94	11.39	0.996
p-Br	p-CH_3	4.15	16.05	27.95	5.19	8.36	11.53	0.992
p-CF_3	p-CH_3	10.64	18.39	26.14	6.62	8.69	10.76	0.997

In figure 1 the logarithms of the equilibrium constants at 5° have been plotted against $\Sigma\sigma^+$ of the substituents. A rather good linear relationship has been found with $\rho = -0.58$ ($r = -0.976$); the linear correlation ($\rho = -0.71$) with $\Sigma\sigma$ is less good ($r = -0.955$).

As can been seen from figure 1 electron donating substituents enlarge the value of the equilibrium constant whereas electron attracting substituents lower it. The values of ΔH and ΔS are too inaccurate (table II) to decide if the differences in K_e have to be ascribed mainly to the differences in ΔH or in ΔS, although the former is more probable . The equilibrium constants of diphenylallenes with strongly electron attracting substituents have not been determinated because the equilibria are reached very slowly. For the calculations of the addition rate constants of these allenes (table III) K_e values have been obtained by extrapolation from Hammett plots (see figure 1).

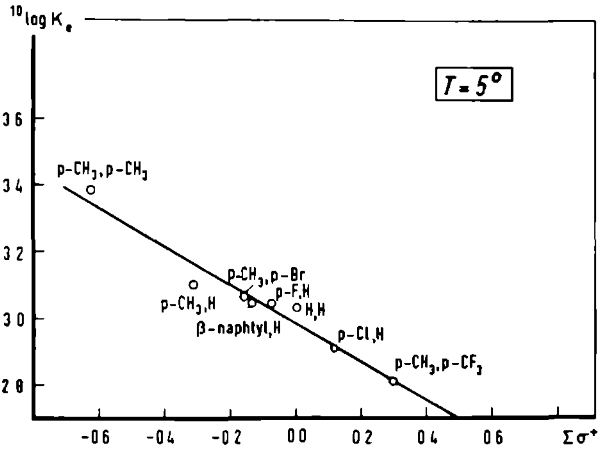

Fig.1 The logarithms of the equilibrium constants of the iodine addition to diphenylallenes at 5° as a function of $\Sigma\sigma^+$ of the substituents.

VI-6-2 ADDITION RATE CONSTANTS

The rate constants of the additions of iodine to substituted 1,3-diphenylallenes have been listed in table III. The headings are:

X,Y = the substituents in the different rings
T = temperature in degrees centigrade
$[I_2]_o$, $[A]_o$ = iodine and diphenylallene concentrations at zero time in moles/litre
k_{min}, k, k_{max} = addition rate constants expressed in $litre^2 mole^{-2} min^{-1}$ with 95% confidence limits.

TABLE III

X, Y	T	$[I_2]_o 10^3$	$[A]_o 10^3$	k_{min}	k	k_{max}
H H	1.6	1.56	31.1	$1.07\ 10^4$	$1.11\ 10^4$	$1.13\ 10^4$
	- 6.7	1.56	31.1	$1.00\ 10^4$	$1.02\ 10^4$	$1.03\ 10^4$
	-18.7	1.56	31.1	$7.65\ 10^3$	$7.80\ 10^3$	$7.95\ 10^3$
	-28.7	1.56	31.1	$5.85\ 10^3$	$6.03\ 10^3$	$6.22\ 10^3$
m,m-Cl_2, H						
	- 1.8	1.56	194	$2.55\ 10^1$	$2.81\ 10^1$	$3.08\ 10^1$
	- 6.4	6.23	48.6	$2.19\ 10^1$	$2.60\ 10^1$	$3.00\ 10^1$
	-13.0	1.56	194	$1.48\ 10^1$	$1.61\ 10^1$	$1.75\ 10^1$
	-23.3	1.54	48.6	$1.07\ 10^1$	$1.52\ 10^1$	$1.98\ 10^1$
	-25.1	6.23	48.6	6.09	8.06	$1.00\ 10^1$

table III (continued)

X, Y	T	$[I_2]_o 10^3$	$[A]_o 10^3$	k_{min}	k	k_{max}
β-naphtyl, H						
	7.6	1.49	16.3	$3.70\ 10^4$	$4.20\ 10^4$	$4.70\ 10^4$
	6.3	1.54	23.1	$3.70\ 10^4$	$3.96\ 10^4$	$4.22\ 10^4$
	0.0	1.49	16.3	$3.45\ 10^4$	$4.00\ 10^4$	$4.50\ 10^4$
	- 0.5	1.54	11.6	$4.11\ 10^4$	$4.32\ 10^4$	$4.53\ 10^4$
	- 8.4	1.49	15.1	$4.05\ 10^4$	$4.30\ 10^4$	$4.55\ 10^4$
	-21.4	1.49	15.1	$3.60\ 10^4$	$3.95\ 10^4$	$4.30\ 10^4$
p-F ,H	- 1.0	1.49	34.9	$9.78\ 10^3$	$9.94\ 10^3$	$1.10\ 10^4$
	11.5	1.54	34.4	$1.21\ 10^4$	$1.28\ 10^4$	$1.34\ 10^4$
	-10.7	1.49	34.9	$7.66\ 10^3$	$8.08\ 10^3$	$8.50\ 10^3$
	-17.1	1.49	34.9	$7.36\ 10^3$	$7.61\ 10^3$	$7.86\ 10^3$
	-25.8	1.49	34.9	$5.49\ 10^3$	$5.84\ 10^3$	$6.18\ 10^3$
p-Cl,H	19.9	1.59	52.1	$4.27\ 10^3$	$4.53\ 10^3$	$4.80\ 10^3$
	10.3	1.59	44.3	$3.77\ 10^3$	$3.83\ 10^3$	$3.89\ 10^3$
	0.0	1.59	50.0	$3.36\ 10^3$	$3.59\ 10^3$	$3.81\ 10^3$
	- 9.8	1.59	44.8	$2.97\ 10^3$	$3.17\ 10^3$	$3.38\ 10^3$
$p-CH_3$, $p-CH_3$						
	- 0.3	1.49	7.44	$4.42\ 10^5$	$6.12\ 10^5$	$7.82\ 10^5$
	- 7.4	1.49	7.44	$8.02\ 10^5$	$8.76\ 10^5$	$9.51\ 10^5$
	- 8.4	1.54	7.99	$1.09\ 10^6$	$1.18\ 10^6$	$1.28\ 10^6$
	-12.1	1.49	7.44	$8.90\ 10^5$	$9.50\ 10^5$	$1.11\ 10^6$
	-12.7	1.54	7.99	$6.35\ 10^5$	$7.01\ 10^5$	$7.66\ 10^5$
	-14.1	1.54	7.99	$5.72\ 10^5$	$6.69\ 10^5$	$7.66\ 10^5$
	-18.1	1.49	7.44	$7.60\ 10^5$	$8.19\ 10^5$	$8.78\ 10^5$
H, $p-CH_3$	8.4	1.49	17.7	$1.51\ 10^5$	$1.58\ 10^5$	$1.65\ 10^5$
	0.9	1.49	17.8	$1.59\ 10^5$	$1.62\ 10^5$	$1.65\ 10^5$
	- 7.6	1.49	17.8	$1.45\ 10^5$	$1.53\ 10^5$	$1.61\ 10^5$

table III (continued)

X , Y	T	$[I_2]_o 10^3$	$[A]_o 10^3$	k_{min}	k	k_{max}
H,p-CH_3	-20.6	1.49	17.7	$1.38\ 10^5$	$1.56\ 10^5$	$1.74\ 10^5$
	-22.2	1.54	4.07	$1.31\ 10^5$	$1.64\ 10^5$	$1.97\ 10^5$
p-Br , p-CH_3						
	12.7	1.49	17.3	$6.71\ 10^4$	$6.86\ 10^4$	$7.01\ 10^4$
	4.7	1.49	17.3	$7.03\ 10^4$	$6.98\ 10^4$	$7.23\ 10^4$
	- 5.4	1.49	17.3	$6.44\ 10^4$	$6.55\ 10^4$	$6.69\ 10^4$
	-12.9	1.49	17.3	$6.08\ 10^4$	$6.26\ 10^4$	$6.43\ 10^4$
p-CF_3 , p-CH_3						
	11.3	1.54	59.8	$8.20\ 10^3$	$8.47\ 10^3$	$8.75\ 10^3$
	- 1.7	1.54	59.8	$8.13\ 10^3$	$8.37\ 10^3$	$8.60\ 10^3$
	- 9.5	1.54	59.8	$7.70\ 10^3$	$7.90\ 10^3$	$8.10\ 10^3$
	-19.9	1.54	59.8	$7.17\ 10^3$	$7.40\ 10^3$	$7.62\ 10^3$
m,m-Cl_2 , p-CH_3						
	- 3.2	1.56	97.2	$1.70\ 10^3$	$1.77\ 10^3$	$1.83\ 10^3$
	- 6.6	1.56	194.4	$1.62\ 10^3$	$1.67\ 10^3$	$1.72\ 10^3$
	-13.2	1.56	97.2	$1.39\ 10^3$	$1.47\ 10^3$	$1.56\ 10^3$
	-26.4	1.56	97.2	$1.25\ 10^3$	$1.32\ 10^3$	$1.40\ 10^3$
	-35.8	1.56	97.2	$1.06\ 10^3$	$1.10\ 10^3$	$1.15\ 10^3$
m-Cl, H	4.1	1.54	73.1	$6.64\ 10^2$	$7.08\ 10^2$	$7.51\ 10^2$
	- 5.1	1.49	79.8	$5.05\ 10^2$	$5.49\ 10^2$	$5.92\ 10^2$
	-24.1	1.49	79.8	$3.45\ 10^2$	$3.55\ 10^2$	$3.64\ 10^2$
	-19.7	1.49	79.8	$3.90\ 10^2$	$4.02\ 10^2$	$4.13\ 10^2$
p-CF_3, H	-0.7	1.54	105	$1.44\ 10^2$	$1.64\ 10^2$	$1.84\ 10^2$
	-12.1	1.54	105	$1.05\ 10^2$	$1.08\ 10^2$	$1.11\ 10^2$
	-18.8	3.09	105	$1.00\ 10^2$	$1.03\ 10^2$	$1.06\ 10^2$
	-29.0	2.16	105	$7.54\ 10^1$	$8.25\ 10^1$	$8.96\ 10^1$

Good linear y-t relationships were obtained for the greater range of the measurements. However, a small systematic error was often observed. The addition rate at the beginning of the reactions was somewhat slower than expected. This systematic error, not due to the neglect of charge-transfer complex formation (section VI-4), might be caused by a small participation of second order kinetics.

The accuracy of the measurements apparent from the confidence limits is less for the very fast and slow reactions, which is in agreement with the comment given in section VI-5.

VI-6-3 ARRHENIUS ACTIVATION PARAMETERS

From the Arrhenius expression $\log k = \log A - E_a/2.303\ RT$, the frequency factors in $\text{litre}^2\text{mole}^{-2}\ \text{min}^{-1}$ and the activation energies in kcal/mole for the diphenylallene derivatives have been calculated by the method of least squares. The values of these quantities together with their 95% confidence limits have been listed in table IV.

TABLE IV

Arrhenius activation parameters

X ,	Y	log A_{min}	log A	log A_{max}	$E_{a\ min}$	E_a	$E_{a\ max}$
H	H	5,39	6.12	6.84	1.72	2.58	3.44
β-naphtyl,	H	4.09	4.70	5.30	-0.64	0.11	0.85
p-F	H	5.82	6.28	6.73	2.28	2.82	3.38
p-Cl	H	4.06	4.93	5.80	0.61	1.72	2.28
m-Cl	H	4.83	5.42	6.00	2.57	3.26	3.96
p-CF_3	H	2.54	4.66	6.80	0.58	3.08	5.58
m,m-Cl_2	H	2.05	6.25	10.45	0.97	5.93	10.88
H	p-CH_3	4.72	5.17	5.62	-0.57	-0.04	0.50
p-Br	p-CH_3	4.62	5.29	5.96	-0.25	0.58	1.41
p-CF_3	p-CH_3	3.91	4.43	4.94	0.01	0.64	1.27
p-CH_3	p-CH_3	0.07	5.28	10.50	-6.99	-0.75	5.50
m,m-Cl_2,	p-CH_3	4.23	4.63	5.04	1.25	1.72	2.19

The log A factors and the activation energies have been plotted against the values of the relevant addition rate constants at 5°, calculated by means of the Arrhenius expression (figs. 2 and 3). From these graphs it appears that the influence of the substituents on the k-values must only be ascribed to a variation of the activation energies. The equality of the frequency factors means that the kinetics of the addition reaction remain constant through the whole series of diphenylallene derivatives investigated.

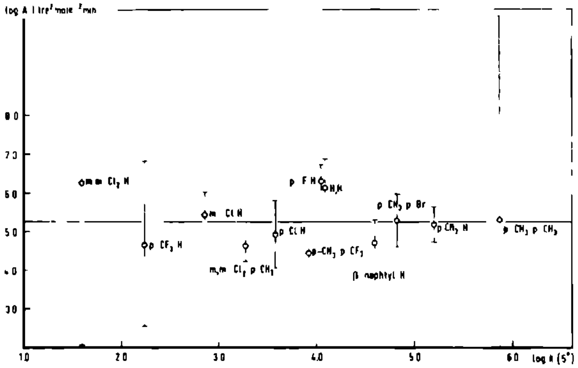

Fig.2 Log A factors of the iodination of substituted diphenylallenes plotted against the relevant addition rate constants at 5°.

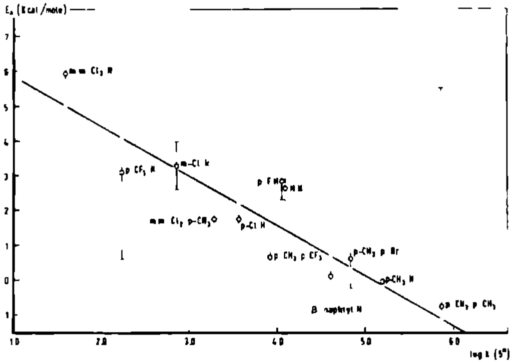

Fig.3 Activation energies of the iodination of substituted diphenylallenes plotted against the relevant addition rate constants at 5°.

VI-6-4 HAMMETT PLOTS

As can be seen from table III electron donating substituents accelerate the addition reaction whereas electron attracting substituents retard it. The addition rate constants of the whole series of compounds cannot be correlated satisfactorily with the sum of σ^+ or σ values of the substituents. However, graphs of log k against σ^+ for compounds, in which the substitution pattern has only been varied in one of the aromatic rings afford good linear correlations (figs. 4,5,6 and 7, table V).

TABLE V

ρ-Values calculated from the Hammett lines in figs. 4, 5, 6 and 7.

fixed substituent	T(°C)	ρ_{min}	ρ	ρ_{max}	r
H	5.0	-2.93	-3.18	-3.44	-0.998
H	-20.0	-3.19	-3.54	-3.89	-0.996
p-CH_3	5.0	-1.95	-2.26	-2.57	-0.997
p-CH_3	-20.0	-1.98	-2.39	-2.79	-0.996

r = correlation coefficient.

ρ_{min}^{max} = 95% confidence limits of ρ.

The addition rate constants of p-fluorophenyl,phenylallene are lower than expected; for this reason they have not been used in the calculation of the ρ values (see further).

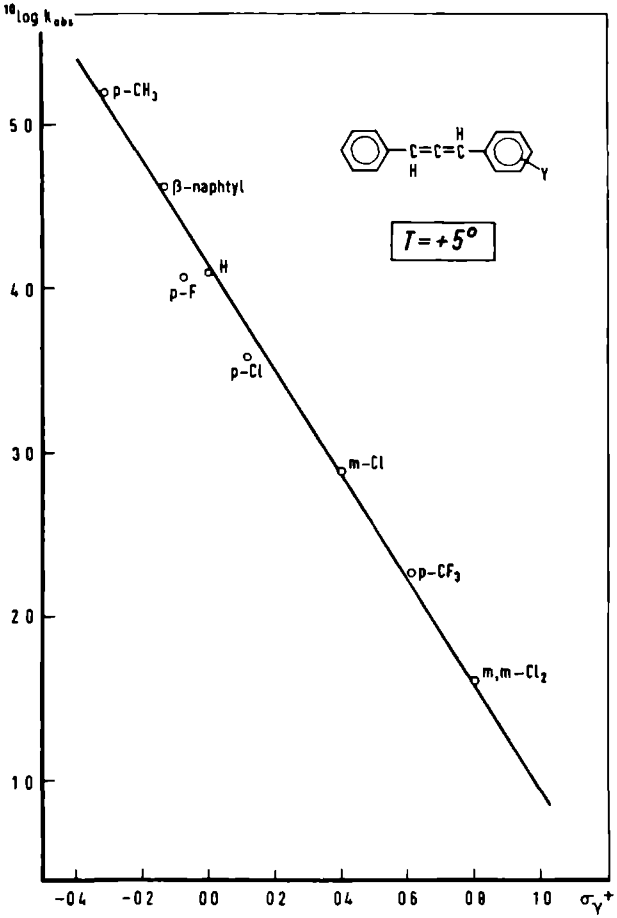

Fig.4 Hammett plot for the iodination of mono-substituted diphenylallenes at 5°.

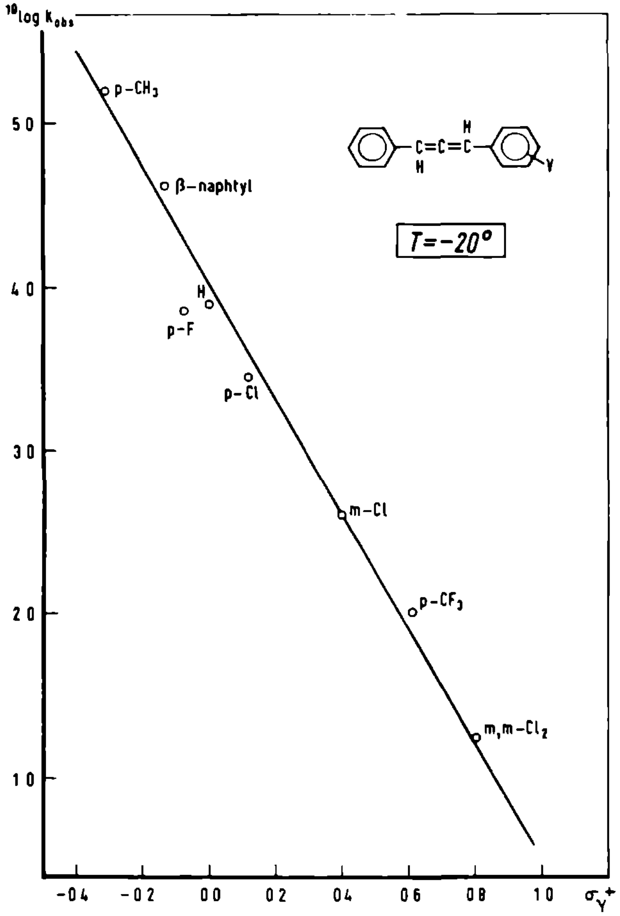

Fig.5 Hammett plot for iodination of mono-substituted diphenylallenes at -20^{O}.

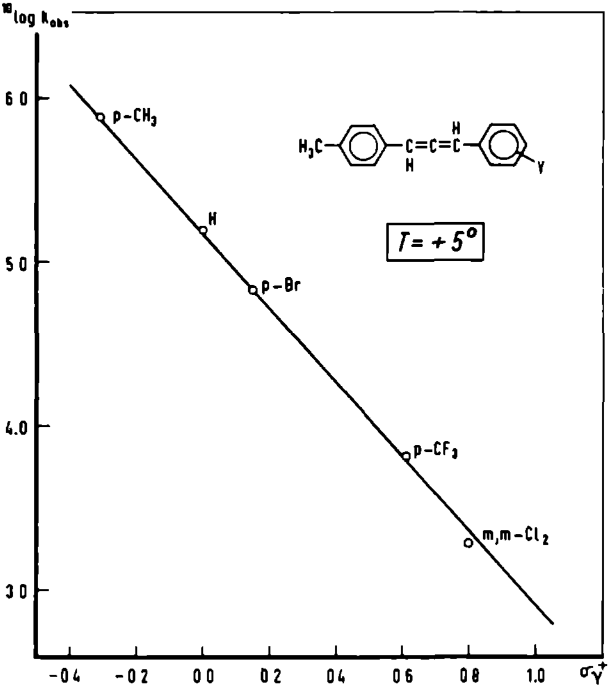

Fig.6 Hammett plot for the iodination of substituted-phenyl, para-tolyl allenes at 5°.

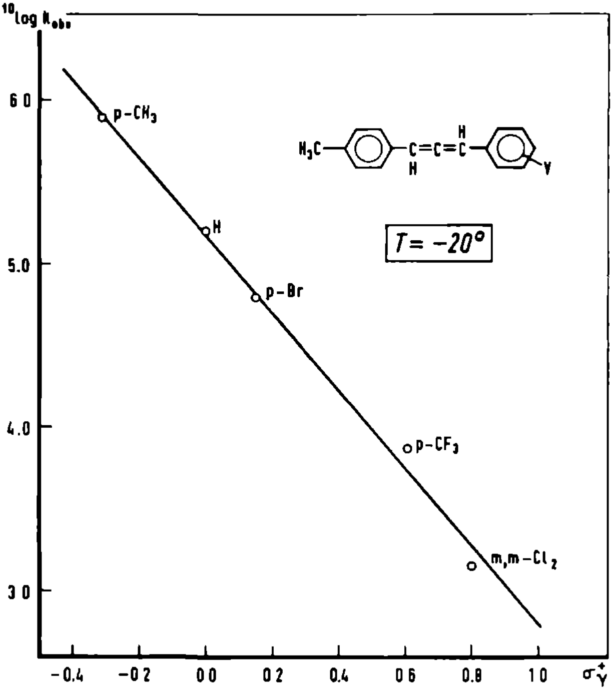

Fig.7 Hammett plot for the iodination of substituted-phenyl, para-tolyl allenes at -20°.

VI-7 DISCUSSION

VI-7-1 THE MECHANISM OF THE ADDITION REACTION

The third order kinetic form for the addition of iodine to diphenylallene

$$-d\ I_2\ /\ dt = k\ A\ I_2{}^{2} \qquad \text{eq.1}$$

is quite common for bromine and iodine additions to unsaturated systems in solvents of moderate polarity. So the bromination of styrene derivatives in dry acetic acid[6] and of cis and trans stilbene in 1,2-dichloroethane[7], and the iodination of olefins in acetic acid or nitrobenzene[8] are second order with respect to the halogen. Such kinetic results are consistent with a polar mechanism as outlined in the equations 2-5

$$A + I_2 \rightleftarrows A.I_2 \qquad \text{eq.2}$$

$$A.I_2 + I_2 \rightleftarrows AI^{+}.I_3{}^{-} \qquad \text{eq.3}$$

$$A.I^{+}.I_3{}^{-} \rightleftarrows AI^{+} + I_3{}^{-} \qquad \text{eq.4}$$

$$AI^{+} + I_3{}^{-} \rightleftarrows AI_2 + I_2 \qquad \text{eq.5}$$

Since the formation of the complex $A.I_2$ (eq.2) is diffusion controlled, a rate expression as formulated in eq.1 can be expected. It is generally accepted that neither the dissociation of the ion-pair (eq.4) nor the nucleophlic attack of the $I_3{}^{-}$ ion (eq.5) but the formation of the ion-pair (eq.3) is the slow step[9]. In that case the observed rate constants (k) equal $K_c \cdot k'$; K_c and k' represent the complex constants and the rate constants of the formation of the ion-pair, respectively.

The second iodine molecule is involved in the dispersion of negative charge by formation of the large triiodine ion. The value of the activation entropy, calculated from the mean value of the frequency factor (table IV), is about -46 cal/mole-degree. Such a high negative value reflects the unfavourable nature of the termolecular transition state.

VI-7-2 ENERGY DIAGRAM OF THE ADDITION REACTION

In fig.8 an energy scheme for the iodination of the 1,3-diphenylallenes has been presented.

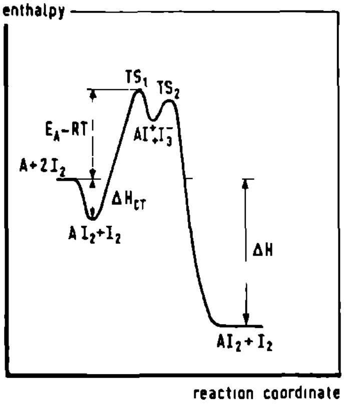

Fig.8 Energy diagram for the iodination of substituted 1,3-diphenylallenes.

ΔH_{ct} = enthalpy of the formation of the iodine-diphenylallene charge-transfer complex ($A.I_2$)

TS_1 = transition state for the heterolytic fission of the iodine molecule (rate-determining)

TS_2 = transition state for the nucleophilic attack by the triiodide ion

ΔH = enthalpy of formation of diiodo addition product (AI_2).

A separate transition state for the dissociation of the contact ion-pair into a solvent-separated ion-pair has been omitted.

VI-7-3 EFFECTS OF SUBSTITUENTS

Substituent effects in electrophilic reactions in aromatic side-chains are often studied to acquire knowledge about the structure of the transition state. Thus for the bromination of substituted styrenes linear free-energy relationships, $\log k/k_o = \rho\sigma^+$, were reported by Dubois *et al.*[10] and Yates *et al.*[11]. The value* of ρ, -4.3 in methanol and -4.2 in acetic acid is comparable with that of the solvolysis of tert-cumylchlorides[12] ($\rho = -4.8$). This was used as an indication that the benzylic carbon atom bears a positive charge in the transition state in these reactions. Similar observations were made in the

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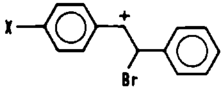
*All ρ-values reported were estimated at 25° or thereabouts.

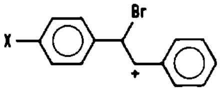
bromination of ring-substituted phenylacetylenes in acetic acid[13], where the addition rate constants are linearly correlated with σ^+-values ($\rho = -5.2$). The fact that in this reaction an open, not (only) a brigded, ion is an intermediate is also apparent from the observation that this addition is not stereospecific.

In contrast, the addition of 2,4-dinitrobenzenesulfenyl chloride to styrene derivatives in acetic acid[14] gives only a linear Hammett plot when σ-values instead of σ^+-values are used. The value of ρ (-2.4) is substantially smaller and the intermediate is supposed to be an episulfonium ion. The addition of 2,4-dinitrobenzenesulfenyl chloride to cis and trans 1-phenylpropene[15] was found to be a stereospecific trans addition.

In principle, the transition state of the bromination of a mono-substituted trans stilbene can ressemble one of three structures (1,2 or 3),



1



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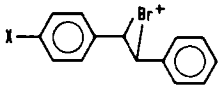


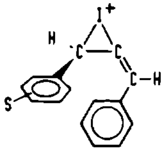
3

in which the charge is located on the α-carbon, the β-carbon, or the bromine atom, respectively. For trans stilbenes with electron-donating substituents a free-energy relationship, $\log k/k_o = \rho\sigma^+$ with $\rho = -5.0$ has been obtained; for trans stilbenes with electron-attracting substituents a relationship $\log k/k_o = \rho\sigma$ with $\rho = -1.5$ has been found [16,17]. Apparently, with the former substituents bromination proceeds mainly *via* a transition-state ressembling structure 1, whereas the transition-state with the latter ressembles structure 2, in which case some bromonium ion character of the transition state, structure 3, cannot fully be excluded.

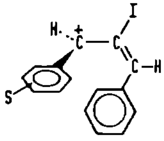
Another reaction type with a fluctuating transition state is the acid catalyzed isomerization of cis stilbene derivatives[18]. Its rate constants satisfy the equation $\log k/k_o = -3.3\sigma_x^+ -1.0\sigma_y$ (x = the strongest electron donating substituent, y = substituent in the other ring).

The iodination of a mono-substituted 1,3-diphenylallene might proceed *via* five different transition states as formulated in the structures $4^{a,b}$ $5^{a,\ b}$ and 6.

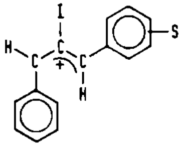
Structures $4^{a,b}$ are brigded iodoniums ions; $5^{a,b}$ are open, benzyl cations in which the Π-orbitals of the ethylenic bond and the Π-orbital of the benzylic C-atom are mutually perpendicular. Bond rotation of structures 5 gives the planar allylic ion 6.



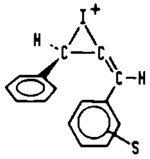
4^a



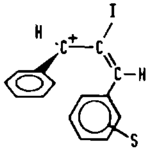
5^a



6



4^b



5^b

When the transition state of the iodination of mono-substituted 1,3-diphenylallenes is always like one of the a-symmetric structures 4 or 5, then 4^a or 5^a may be expected for diphenylallenes with electron-donating substituents, and the iodination of diphenylallenes with electron-attracting substituents should proceed practically only *via* 4^b or 5^b. Free-energy relationships similar to those found for the bromination and isomerization of unsymmetrically substituted stilbenes are to be found then. The influence of the electron-attracting substituents in structures 4^b or 5^b should be comparable with that in the corresponding cases of the bromination and isomerization of stilbenes (e.g. structure 2), because the transmission factor for polar effects of an ethylenic moiety is about equal to that of a methylene group[19].

With derivatives containing electron donating substituents (reaction *via* 4^a or 5^a) the ρ-value should be higher as the transition state is more like 5^a than 4^a.

If, however, the iodination proceeds *via* the symmetric transition-state (6), the same free-energy relationship ($\log k/k_o = \rho\sigma^+$) should be obtained for all monosubstituted diphenylallenes. In figs.4 and 5 the logarithms of the addition rate constants of the mono-substituted diphenylallenes at two temperatures have been plotted against σ^+-values[20]. The relationships are linear in a wide range of σ^+-values. *This indicates that the transition state for the iodination of diphenylallenes ressembles the diphenylallyl cation 6.* The slight, negative deviations of some p-substituted derivatives will be discussed later.

As stated before (section VI-6-4) rather poor correlations have been obtained by plotting the addition rate constants of mono-substituted diphenylallenes together with those of substituted phenyl, p-tolylallenes against $\Sigma\sigma^+$, but the latter type of compounds gives excellent linear plots (figs. 6 and 7 table V). Obviously the substituent effects are not simply additive. The only way to explain these results is to suppose that the presence of a substituent in one of the aryl residues changes the sensitiveness (ρ -value) for substituent variation in the second ring.

An analogous case of non-additivity of substituent effects has recently been investigated more fully by Dubois *et al.*[21] in the bromination of a great number of manifoldly substituted 1,1-diphenylethylenes. Dubois posits that the presence of a substituent (Y) in one aromatic ring alters the charge distribution in the transition state, so that substituents (X) introduced into the other ring interact with a different effective charge if the former substituent is varied. The effective charge is lower if this substituent has electron-donating properties. If so, the influence of the variable substituent diminishes. The reverse is true if the fixed substituent has electron-withdrawing properties. So, ρ-values increase in proportion to the σ^+ values of the fixed substituent. This multiple ρ treatment also appeared applicable to data of the solvolysis of substituted benzhydryl chlorides (table VI).

TABLE VI

ρ-Values calculated for the variation of substituent X with substituent Y held constant.

fixed substituent (Y)	σ^+(Y)	ρ^a	ρ^b	ρ^c
p-OCH_3	-0.78	-2.27	-2.63	
p-CH_3	-0.31	-3.03		-2.26
H	0	-3.57	-4.31	-3.18
m-Cl	0.40	-4.08		

table VI continued

fixed substituent (Y)	$\sigma^+(Y)$	ρ^a	ρ^b	ρ^c
p-NO_2	0.79		-5.26	
	$\Delta\rho/\Delta\sigma^+$	-1.54	-1.68	-2.95

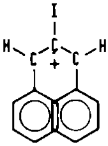
a) bromination of substituted 1,1-diphenylethylenes[20], b) solvolysis of substituted benzhydryl chlorides [20] and c) iodination of 1,3-diphenylallenes at 5°.

From table VI it appears that the value of $\Delta\rho/\Delta\sigma^+$ for the iodination of diphenylallenes is larger than those for the bromination of 1,1-diphenylethylenes and the solvolysis of benzhydryl chlorides, which are almost equal. This result can be interpreted as follows. Consider the unsubstituted 1,3-diphenylallylcation (6, S=H). The positive charges on the terminal allylic carbon atoms will be about equal. The introduction of a substituent into one of the aromatic rings does not only affect the amount of charge, but also generates an unsymmetrical distribution of charge on the allylic part of the cation. On the other hand, in the bromination of 1,1-diphenylethylenes and in the solvolysis of benzhydryl chlorides, substituents only alter the amount of charge in the reaction centre. If an electron donating substituent is present in one of the aromatic rings of the intermediate diphenylallyl cation the charge on the allylic carbon bearing the other ring is lower than in the absence of this substituent, and the sensitiveness of the addition reaction for substituents in the second ring is less than that for substituents in mono-substituted diphenylallenes.

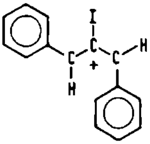
A similar situation was observed in the solvolysis of para-nitrobenzoates of unsymmetrically substituted chalcols[22]. The rate-controlled solvolysis of these compounds proceeds *via* 1,3-diphenylallyl cations. The product ratios obtained in these reactions indicate that also in this case the unsymmetrical charge-distribution over the terminal allylic carbon atoms in the transition state varies with the substitution pattern.

The ρ-value of the iodination of monosubstituted diphenylallenes is about -3.0 at 25°. This value is lower than the ρ-values obtained for reactions involving open benzylic carbonium ions in solvents of moderate polarity at this temperature (ρ = -4 to -5). In the transition state of the iodine addition reaction, however, the charge is dispersed over a 1,3-diphenylallyl system. For the same reason ρ-values of reactions *via* carbonium ions decrease gradually as the carbonium ion is successively conjugated with one, two and three phenyl rings[23].

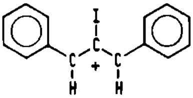
Even with the conclusion that the transition state of the iodination of diphenylallenes ressembles a diphenylallyl carbonium ion there remain three possible structures for this cation ($6^{a,b,c}$)



$\underline{6}^{a}$



$\underline{6}^{b}$



$\underline{6}^{c}$

From Stuart molecular models it is apparent that structure 6^{a} is unlikely; the two opposing phenyl rings prevent each other from coming in plane with the allylic part of the structure, which results in an important loss of resonance energy. The same conclusion can be drawn from an application of Yukawa and Tsuno's modified form[24] of the Hammett relation proposed for electrophilic reactions in which the use of σ^{+}-values introduces too high or too low corrections for the resonance contributions of the substituents. In this equation:

$$\log k/k_{o} = \rho_{meta}(\sigma^{o} + R\Delta\sigma^{+})$$

the parameter R is introduced as a resonance transmission coefficient and $\Delta\sigma^{+}$ $(\sigma^{+} - \sigma^{o})$ is a measure of the resonance contribution of the substituent. From examination of our Hammett plots it appears that the log k-values of para-fluorophenyl,phenylallene (with the greatest value of $\Delta\sigma^{+}$[24])and in a less degree also for para-chlorophenyl,phenylallene are only slightly lower than expected from the linear Hammett plots, whereas the data of all other diphenylallenes containing substituents with mesomeric properties do not deviate. In terms of the Yukawa-Tsuno relation this means that R will be close to unity. The magnitude of R has been shown to decrease when the torsion angle between the phenyl ring and the plane of the cation increases[21,23]. Assuming that R = 1 (the value observed for most electrophilic side-chain reactions) when both aryl rings are coplanar with the allyl carbonium ion, it may be concluded that the structure of the transition state is nearly flat, ruling out 6^a.

Although Stuart models indicate that steric hindrance in planar 6^b is somewhat less than in 6^c, no definite choice can be made on the basis of only kinetic data *.

VI-8 CONCLUDING REMARKS

The presumed dependence of $\Delta G^{\neq}$ of a-symmetric transition states on variation of the substituents (σ^+) and the observed relationship between $\Delta G^{\neq}$ of the symmetrical transition state and σ^+ have schematically been drawn in figure 9.

The conclusion that the iodination of the diphenylallenes investigated proceeds exclusively

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*NMR and visible spectroscopic data suggest that the conformations of the 2-methyl and 2-tert-butyl-1,3-diphenylallyl carbanions are like structure 6^b,while the conformation of the 1,3-diphenylallyl carbanion is analogous to structure 6^c [25].

via the symmetric transition-state implies that $\Delta G^{\neq}$ - values of the other potential transition-states must always be larger. However, as can be seen from figure 9, it might be that for diphenylallenes with very strongly electron-attracting or withdrawing substituents an a-symmetric transition state becomes important.

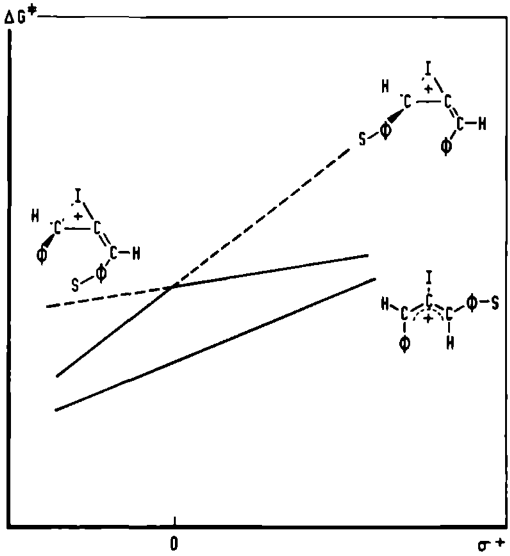

Fig.9 Possible relationships between the free energy of activation and the σ^+ values of the substituents in the iodination of diphenylallenes.

The polar addition of halogens to alkyl substituted alkenes and alkynes generally proceeds stereospecifically as a trans addition. Brigded halogenium ions of the type orginally proposed by Roberts and Kimball[26], have been suggested e.g. for the chlorination of cis- and trans-2-butenes[27], di-tert-butylethylenes[28], and for the bromination of cis- and trans-2-butenes[11], and 1- and 3-hexynes[13]. On the other hand, chlorination of 1-phenylpropenes[27], bromination of styrene derivatives[11] and substituted phenylacetylenes[13] are non-stereospecific, and the transition states in these reactions ressemble open α-phenyl carbonium ions.

Halogenation of allenes seems to follow the same trend. Bromination and iodination of 1,3-dimethylallene[29,30] involve bridged intermediates because they proceed stereospecifically as trans additions, but this study shows that the iodine addition to diphenylallenes proceeds *via* a symmetric transition state.

The preference of arylolefins for addition reactions *via* open carbonium ions may be ascribed to the ability of phenyl rings to disperse charge.

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CHAPTER VII

THE STEREOSPECIFICITY OF THE IODINATION OF 1,3-DIPHENYLALLENE

In chapter VI we found that the transition state of the iodination of substituted 1,3-diphenylallene ressembles a diphenylallylic cation. Consequently the addition reactions are non-stereospecific and lead to optical inactive products and, since the additions are reversible, to racemized diphenylallenes as well. The occurrence of racemization in the addition of iodine to an optically active diphenylallene was investigated by following the optical rotation of the reaction mixture during the reaction.

The optical rotations were measured with a Jasco spectropolarimeter model ORD/CD/UV-5, equiped with a 450 W Xenon lamp. A photometer cell with a pathlength of 1 cm was used as a reaction vessel. The change in the optical rotation (α) was followed at 355 mμ. At this wave-length the absorption of iodine is very low.

In section VI-7-1 we argued that the rate determining step in the iodination of diphenyallene is probably the formation of the ion-pair $AI^+.I_3^-$. Since at that stage of the reaction the optical activity has already been lost, the addition rate constant must be equal to the racemization rate constant. In order to avoid a complex kinetic expression, we followed the change in the optical rotation after the iodine concentration had reached the equilibrium concentration. In that case the integrated rate equation for the racemization is

$$\ln\alpha_o - \ln\alpha = k_{rac}[I_2]_e^2\, t$$

$[I_2]_e$ is the equilibrium iodine concentration. This quantity can be calculated from the expression of the equilibrium constant given in section VI-2. For that purpose the equilibrium constant was calculated from the van 't Hoff expression with data listed in table II of chapter VI. All measurements were carried out at 11°. The times needed for reaching the equilibrium iodine concentrations were estimated by following the reaction under the same circumstances spectrophotometrically. The results have been listed in table I.

TABLE I

Racemization rate constants at 11°.

$[A]_o 10^3$	$[I_2]_o 10^3$	$[I_2]_e 10^4$	$k_{rac} 10^4$
16.48	4.28	4.35	1.78
14.13	5.51	7.30	1.34
11.83	5.51	9.09	1.56

$[A]_o$ and $[I_2]_o$ are the diphenylallene and iodine concentrations at zero time, respectively.
$[I_2]_e$ is the equilibrium iodine concentration. The racemization rate constants are expressed in litre^{2}mole^{-2}min^{-1}.

The value of the addition rate constant at 11° is 1.41 10^{4} litre^{2}mole^{-2}min^{-1} (calculated from the Arrhenius equation by using the parameters listed in table IV of chapter VI). This value is in full agreement with the mean value of the racemization rate constants obtained (1.56 10^{4}). This experiment proves not only that the iodination of diphenylallene proceeds *via* a diphenylallyl cation, but also that the formation of this cation is rate-determining.

CHAPTER VIII

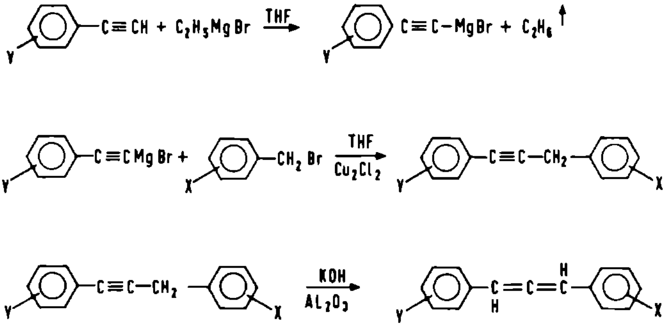
SYNTHESES OF SUBSTITUTED 1,3-DIPHENYLALLENES

This chapter describes the syntheses of the 1,3-diphenylallenes, the 1,3-diphenylpropynes and other starting compounds. U.V. absorption spectra were recorded on a Beckman Dk-2A or a Cary-15 spectrophotometer by using 95%-ethanol as solvent. Microanalyses were performed by Mr.J.Diersmann. The melting points are uncorrected.

There are several synthetic routes known for preparing (substituted) 1,3-diphenylallenes. Craig and Moyle[1] synthesized 1,3-diphenylallene in 77% yield from the reaction of diethyl cis-α-benzylstyryl phosphate with $NaNH_2$ in liquid NH_3. Caserio[2], however, reported yields under 20% for this reaction. Optically active 1,3-diphenylallene was prepared[3] from ethyl N-nitroso-N-(trans-2,3-diphenylcyclopropyl) carbamates through the corresponding diazocyclopropane. The nitrosocarbamate was prepared from trans-2,3-diphenylcyclopropane carboxylic acid which was resolved with quinine as base.

A convenient method has been given by Jacobs[4,5] who prepared (substituted)1,3-diphenylallenes *via* a prototropic rearrangement of the corresponding 1,3-diphenylpropynes by absorption on basic alumina. The 1,3-diphenylpropynes were prepared from phenylethynylmagnesium bromide with substituted benzyl-p-toluenesulfonates[4,5,6]. However, the p-toluenesulfonates are unstable (in particular those with electron-donating substituents[7]), and must be used in twofold excess.

Coupling of phenylethynylmagnesium bromide with benzyl bromide in dry ether in the presence of cuprous chloride afforded 35% 1,3-diphenylpropyne, but p-biphenylethynylmagnesium bromide used in stead of phenylethynylmagnesium bromide did not react with benzylbromide in this way[4]. By using THF, however, as solvent the cuprous chloride promoted couplings of (para-methyl) phenylethynylmagnesium bromide with substituted benzyl bromides were more successful and gave the corresponding 1,3-diphenylpropynes in good yield. The procedure is quite similar to the reaction between phenylethynylmagnesium bromide and propargyl bromide[8] and is given for the synthesis of 1,3-diphenylpropyne.



Reaction scheme for the syntheses of substituted 1,3-diphenylallenes.

Procedure:

0.1 Mole of magnesium is placed in a 250 ml three-necked flask fitted with a reflux condensor carrying a calcium chloride tube, an inlet for nitrogen gas, a dropping funnel and magnetic stirrer. After flushing the flask with dry nitrogen 0.12 mole of ethyl bromide in 50 ml of anhydrous THF is added. After the magnesium has dissolved, nitrogen is led through the boiling solution in order to expel the excess of ethyl bromide. Then the solution is cooled and 0.1 mole of freshly distilled phenylacetylene in 25 ml of THF is added dropwise at room temperature. After 30 minutes 0.5 gr of cuprous chloride and 0.1 mole of freshly distilled benzyl bromide in 50 ml of THF are added and the reaction mixture is refluxed overnight under an atmosphere of nitrogen. The reaction mixture, containing a heavy yellow precipitate, is decomposed with cold aqueous hydrochloric acid solution, stirred thoroughly and extracted three times with 50 ml portions of ether. The ethereal extracts are combined and washed with cold water, neutralized with cold aqueous sodium bicarbonate solution and finally washed with cold water. The ether layer is dried with anhydrous magnesium sulfate. On destillation some unreacted phenylacetylene and benzylbromide are recovered. 1,3-Diphenylpropyne (73%) distilled at 116-118^{o}/0.1 mm (litt.140-145^{o}/3 mm[4]); n_d^{22} = 1.6016 (litt. $n_d^{19.8}$ = 1.5995[4]).

Benzyl bromide and p-methylbenzyl bromide were commercial samples. p-Chloro-, m-chloro-, p-bromo- and p-fluorobenzyl bromide were obtained by bromination

of the corresponding toluenes[9].
2-Bromomethylnaphtalene was prepared from 2-methylnaphtalene with N-bromosuccinimide[10].
Deamination of 3,5-dichloroanthranilic acid, obtained by chlorination of anthranilic acid[12], yielded 3,5-dichlorobenzoic acid[11]. Reduction of the acid with $LiAlH_4$ gave the corresponding alcohol, which reacted with PBr_3 giving 3,5-dichlorobenzyl bromide[13].
The reaction of p-trifluoromethylphenylmagnesium bromide, from p-trifluoromethylphenyl bromide (E.G.A.) and magnesium in ether, with CO_2 afforded p-trifluoromethylbenzoic acid. The reduction of the acid and the reaction of the corresponding alcohol with PBr_3 was carried out in the same way as in the synthesis of 3,5-dichlorobenzyl bromide[13].
p-Methylphenylacetylene was prepared by chlorination of p-methylacetophenone followed by dehydrochlorination with alkali[14].

The substituted 1,3-diphenylpropynes were obtained as oils or low melting solids. They got coloured at room temperature on exposure to air, probably due to autoxidation[6]. Therefore the propynes were stored in tightly stoppered flasks at -25°.

TABLE 1

Physical constants of 1,3-diphenylpropynes.

X^a	Y^a	b.p.°C	mm Hg	m.p.°C	yield
H	H	116-118	0.1	oil	73%
p-CH_3	H	134-138	0.5	oil	55%
p-Cl	H	140-142	0.7	oil	55%
p-F	H	125-132	0.4-0.6	oil	60%
βnapht.	H	160-166	0.3	64-65°C	27%
p-CF_3	H	134-136	1.0	oil	55%
m-Cl	H	132-136	0.3	oil	46%
m,m-Cl_2	H	162-164	1.0	oil	35%
p-CH_3	p-CH_3	140-143	0.7	42-45	56%
p-Br	p-CH_3	160-163	0.4	51-54	48%
p-CF_3	p-CH_3	138	0.6	48-50	56%
m,m-Cl_2	p-CH_3	170-172	0.4-0.5	oil	45%

a) The positions of the substituents have been indicated in the reaction scheme.

The rearrangement of 1,3-diphenylpropynes into 1,3-diphenylallenes[15] was carried out on basic alumina. A solution of 2 gr of a 1,3-diphenylpropyne in a few ml of benzene was brought on a column (3 cm diameter) filled at the bottom with normal alumina over 10 cm and on top of this with basic alumina over 7 cm, and eluted with petroleum-ether (40-60°). A deep red band formed at the top as soon as the propyne was added. The allene left the column with the first 200 ml of eluate and was isolated by evaporating the solvent at room temperature under vacuum. The remaining light-coloured oil could in general be crystallized from hexane in the cold. Yield 50-60%. The allenic products are unstable; dimers and oxidation products are readily formed[2,4]. The instability seems to be correlated with the melting points. Thus 1-(p-bromophenyl)-3-(p-methylphenyl) allene (m.p. 89-90°) remained pure for several weeks at room temperature, whereas 1-(p-fluorophenyl)-3-phenyl allene (m.p. 43-44°) softened in a few hours under these circumstances. Therefore all the operations were carried out as quickly as possible and the allenes, the oily products dissolved in n-hexane, were stored in a freezer at -25° in tightly stoppered flasks. They remained pure for months under these circumstances.

The basic alumina was prepared from alumina and potassium hydroxide by the method of Jacobs[4]. It was pulverized and dried at 200° at 1mm for several hours before use.

Partial resolution of racemic 1,3-diphenylallene.

A convenient method for partial resolution of racemic allenes, through hydroboration of an excess of allene with (+)-sym-tetraisopinocamphenyldiborane is described by Caserio[2,16]. This procedure applied to 836 mg of racemic 1,3-diphenylallene yielded 350 mg of levorotatory 1,3-diphenylallene, $[\alpha]^{26.8}_{D} = -50^{\circ}$ (c 0.5, $CHCl_3$), litt. $[\alpha]^{26}_{D} = -180^{\circ}$ (c 0.4, $CHCl_3$)[2].

TABLE II

U.V. ABSORPTION DATA, MELTING POINTS AND ELEMENTAL ANALYSES OF SUBSTITUTED 1,3-DIPHENYLALLENES.

					C analysis		H analysis	
X	Y	λ_{max}	$\varepsilon_{max} 10^{-3}$	m.p. °C	found.	calc.	found.	calc.
H	H	255[c]	43.0[a]	53.5-55[b]	93.3	93.71	6.3	6.29
p-CH_3	H	256	41.3	51.0-52.5	93.0	93.12	6.9	6.88
p-Cl	H	259	47.6	54.0-55.5	79.4	79.47	4.9	4.89
p-F	H	253	41.6	43.0-44.0	85.6	85.69	5.3	5.27
βnapht.	H	258	81.5	91.5-92.5	93.4	94.18	5.7	5.82
p-CF_3	H	258	40.4	54 -55	73.6	73.84	4.1	4.26
m-Cl	H	256	36.0	oil	76.8	79.47	4.8	4.89
m,m-Cl_2	H	258	32.6	oil	66.1	68.46	4.2	4.60
p-CH_3	p-CH_3	259	45.5	75.5-77.5	92.3	92.68	7.4	7.32
p-Br	p-CH_3	265	48.3	89 -90	67.5	67.39	4.8	4.59
p-CF_3	p-CH_3	261	43.8	60 -61	74.1	74.44	4.7	4.78
m,m-Cl_2	p-CH_3	261	35.3	oil	69.3	69.84	4.7	4.40

litt. a) 38.10^{3}[3], $52.2.10^{3}$[4]

b) 53-54[3], 49-51[4]

c) 255[3], 255[4].

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SAMENVATTING

Geometrische isomerisaties kunnen gekatalyseerd worden door jodium. Uit de gevonden snelheidsvergelijking voor de reaktie

$$v = k[\text{olefine}][I_2]^{\frac{1}{2}} \qquad (1)$$

blijkt dat jodium atomen participeren in het mechanisme van de isomerisatie. Een jodium atoom addeert aan de dubbele band waarbij een intermediair radikaal ontstaat (cis-I$^\cdot$). Na interne rotatie van dit radikaal wordt de trans verbinding gevormd door afsplitsing van het jodium atoom.
Voor irreversibele isomerisaties geldt:

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (2)$$

k_1 en k_{-1} zijn de reaktiesnelheidskonstanten voor de vorming en dissociatie, k_2 is de reaktiesnelheidskonstante voor de interne rotatie van het intermediaire radikaal. Vergelijking 2 kan vereenvoudigd worden indien $k_{-1} << k_2$ of $k_{-1} >> k_2$. In het eerste geval is de additie van jodium atomen, in het tweede geval de interne rotatie van het intermediair de snelheidsbepalende stap. Bij de door jodium gekatalyseerde isomerisatie van de tot nu toe onderzochte olefinen bleek in alle gevallen de interne rotatie snelheidsbepalend te zijn.

Dit proefschrift behandelt de isomerisatie van een aantal cis α, ω-diphenylpolyenen. Om reproduceerbare metingen te verkrijgen bleek het noodzakelijk deze isomerisaties bij een relatief hoge jodium atomen konsentratie te bestuderen. Daar deze verbindingen zeer snel isomeriseren konden dan slechts zeer korte reaktietijden gebruikt worden. Aan deze voorwaarden werd voldaan door reaktiemengsels van de te onderzoeken cis verbinding en jodium in n-hexaan gedurende zeer korte tijden intens te belichten.

De 'steady-state' konsentratie van jodium atomen in de reaktiemengsels werd berekend door op deze wijze bepaalde isomerisatiesnelheidskonstanten van 3,3',5,5'-tetramethyl-cis-stilbeen te vergelijken met uit de literatuur bekende waarden. In de gekozen opstelling bleek de konsentratie van jodium atomen ongeveer 10^{-8} mol/liter te zijn. Bij deze konsentratie heeft de aanwezigheid van zuurstof in het reaktiemengsel geen remmende invloed op de isomerisatiesnelheid.

Met behulp van substituent effekten kon aangetoond worden dat de isomerisatie van cis-trans 1,4-diphenylbutadienen-1,3 via intermediaire phenylallyl radikalen verloopt. De Arrhenius grafieken voor alle onderzochte cis-trans diphenylbutadienen zijn in het gebruikte temperatuur trajekt ($+65^{o}$ tot -45^{o}) kromme lijnen. Dit bleek het gevolg te zijn van het feit dat voor deze verbindingen de dissociatiesnelheidskonstante van het intermediaire radikaal (k_{-1}) van dezelfde orde van grootte is als de snelheidskonstante van de interne rotatie van dit radikaal (k_2). Met de gevonden Arrhenius relatie van ongesubstitueerd cis-trans diphenylbutadieen werden met behulp van een 'curve-fit' programma de onafhankelijke parameters van vergelijking 2, te weten A_1, A_{-1}/A_2, E_1 en $E_{-1}-E_2$, berekend. De verkregen waarden voor A_1 en A_{-1}/A_2 bleken in overeenstemming te zijn met waarden die op grond van theoretische overwegingen verwacht kunnen worden of bij vergelijkbare reakties experimenteel gevonden zijn.

De gevonden waarden van A_1 en A_{-1}/A_2 zijn gebruikt voor de berekening van de parameters E_1 en $E_{-1}-E_2$ voor de isomerisatie van gesubstitueerde cis-trans diphenylbutadienen. Voor monogesubstitueerde verbindingen zijn de volgende relaties gevonden.

$$E_1 = 1,54 + 0,78\sigma^o \quad \text{(kcal/mol)} \qquad (3)$$

$$E_r = -2,63 + 0,98\sigma^o \quad \text{(kcal/mol)} \qquad (4)$$

E_r is het energieverschil tussen de uitgangstoestand (cis-trans + $I^{\bullet}$) en de overgangstoestand voor de interne rotatie van het intermediair.
σ^o is de substituent konstante.

De waarde van E_r voor de isomerisatie van cis-trans diphenylbutadieen is ongeveer 6 kcal/mol lager dan de overeenkomstige waarde voor cis-stilbeen. Deze verlaging is waarschijnlijk het gevolg van een sterker exotherme additie van jodium atomen, alsmede van een lagere waarde voor de aktiveringsenergie van de interne rotatie in het intermediaire radikaal tijdens de isomerisatie van cis-trans diphenylbutadieen. Het effekt van substituenten op E_r en op de additiesnelheid van jodium atomen is vergelijkbaar met de substituentsinvloeden bij soortgelijke reakties.

Bij de isomerisaties van trans-cis-trans en cis-trans-trans 1,6-diphenylhexatrieen-1,3,5, en van trans-cis-trans-trans 1,8-diphenyloctatetraeen-1,3,5,7 bleek de additie van jodium atomen over het gehele onderzochte temperatuur interval de snelheidsbepalende stap te zijn. De isomerisatiesnelheid van cis-trans-trans diphenylhexatrieen is zo groot, dat in tetrachloorkoolstof, en bij lagere temperaturen ook in n-hexaan, de diffusie mede de snelheid bepaalt.

De grote onderlinge verschillen in de isomerisatie snelheidskonstantes bij deze drie verbindingen worden voornamelijk veroorzaakt door verschillen in de akteriveringsenergie voor de additie reaktie. Deze verschillen duiden erop dat de reaktiewarmten van de jodium addities aan de α, ω-diphenylpolyenen niet gelijk zijn, hetgeen veroorzaakt blijkt te worden door de variatie in de resonantie energieën van de diphenylpolyenen enerzijds en de intermediaire radikalen anderzijds. De verschillen in de botsingsfaktoren voor de additiereakties zijn klein. Niettemin neemt in de reeks onderzochte verbindingen

log A enigszins af als de aktiveringsenergie toeneemt. De verklaring voor deze relatie kan gevonden worden in het Hammond postulaat. Bij een sterk exotherme additie zal de 'transition-state' sterk lijken op de uitgangstoestand en hierdoor zal het verlies aan entropie beperkt blijven. Dit leidt tot een relatief hoge waarde voor de botsingsfaktor.
Een sterk exotherme additie impliceert echter ook dat de aktiveringsenergie voor deze reaktie juist klein zal zijn.

Het tweede gedeelte van dit proefschrift handelt over de electrofiele jodering van gesubstitueerde 1,3-diphenylallenen. Deze additiereakties zijn uitgevoerd in 1,2-dichloroethaan tussen $+10^{o}$ en -30^{o}. De jodering van diphenylallenen blijkt een tweede orde reaktie in jodium en een eerste orde reaktie in diphenylalleen te zijn. De zeer grote invloed van substituenten op de additiesnelheid bleek het gevolg te zijn van variaties in de aktiveringsenergie. De gemiddelde waarde voor de log A faktor voor de reaktie is 5,3 liter^{2}mol^{-2}min^{-1}, de aktiveringsenergie in de onderzochte reeks derivaten varieert van -1 tot +6 kcal/mol. Voor alle monogesubstitueerde diphenylallenen, zowel die met electronenzuigende als die met electronenstuwende groepen, vertoont log k een linear verband met de σ^{+} waarden van de substituenten. Hieruit is de konklusie getrokken dat de overgangstoestand voor de jodering op een a-symmetrisch 1,3-diphenylallyl-carbonium ion lijkt. Deze konklusie wordt gesteund door het feit dat de jodering van optisch aktief diphenylalleen geracemiseerde produkten geeft. De racemisatiesnelheidskonstante bij 11° is vrijwel gelijk aan de additiesnelheidskonstante bij dezelfde temperatuur. Dit bewijst dat de vorming van het diphenylallyl cation de snelheidsbepalende stap is in de additie reaktie.

De ρ waarde voor de Hammett-Brown relatie voor de in de phenylgroep gesubstitueerde 1-para-tolyl-3-phenylallenen (-2,26 bij 5°) blijkt kleiner te zijn dan de ρ waarde voor de monogesubstitueerde diphenylallenen (-3,18 bij 5°). De sterk verminderde invloed van de substituenten in het eerste geval is verklaard door aan te nemen dat de aanwezigheid van de vaste para-methyl groep de grootte van de lading op het allyl gedeelte van het cation verkleint en dat bovendien hierdoor een a-symmetrische ladingsverdeling over het allylgedeelte geïnduceerd wordt.

CURRICULUM VITAE

Na het doorlopen van de middelbare school en het vervullen van de militaire dienstplicht ben ik in 1963 begonnen met de studie scheikunde aan de Nijmeegse Universiteit.

Het doctoraal examen, met als hoofdvak organische chemie en als bijvak anorganische chemie, heb ik in juni 1969 cum laude behaald.

Na mijn doctoraal heeft de Hoofddirectie van N.V.Staatsmijnen/DSM door het verstrekken van een promotietoelage mij gedurende twee jaar in de gelegenheid gesteld een promotie onderzoek te beginnen.
Sinds juni 1971 ben ik als wetenschappelijk medewerker verbonden aan de afdeling Organische Chemie van de Katholieke Universiteit Nijmegen .

STELLINGEN

I

In het gepostuleerde reaktieschema voor de katalytische ontleding van waterstofperoxyde onder invloed van koper(II)-ethyleendiamine komplexen dient het vrije ethyleendiamine vervangen te worden door koper(II)-bis-(ethyleendiamine).

Th. Kaden und H. Sigel, Helv. Chim. Acta 51, 947 (1968)

II

De door Craig, Dinner en Mulligan beschreven omleggingen van 1-acetyl-1-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphtaleen en 3-phenyl-3-hydroxy-2-butanon met natriumhydride in diethylcarbonaat worden door hen ten onrechte beschouwd als Favorsky omleggingen van α-hydroxyketonen.

J C. Craig, A. Dinner and P.J. Mulligan, J Org Chem. 37, 3539 (1972)

III

De vorming van methyl α,α-dimethoxy-β,β,β-trichloropropionaat uit tetramethoxyethyleen en tetra, door Hoffmann toegeschreven aan thermische ontleding van tetramethoxyethyleen, zou ook verklaard kunnen worden door overdracht van lading tussen de reaktanten.

R W Hoffmann, J. Schneider und H Hauser, Ber. 99, 1892 (1966)

IV

De bewering van Yamashita dat de door jodium gekatalyseerde isomerisatie van cis-stilbeen met behulp van kortgolvig licht verloopt via een aangeslagen charge-transfer komplex is onjuist.

S Yamashita, Bull. Chem. Soc Japan 34, 972 (1961)

V

De aanwezigheid van homoserine in de reaktieprodukten van cytochroom-C met broomcyaan, kan ook worden verklaard door rekombinatie van de fragmenten

G Corradin and H A Harbury, Biochim. Biophys Acta **221**, 489 (1970)

VI

De door Kobayashi, Fujii en Minato gegeven korrelatie tussen de partial-rate-factors voor de para posities bij de homolytische phenylering van benzeenderivaten en de Hammett σ waarden is weinig zinvol.

M Kobayashi, S Fujii and H. Minato, Bull. Chem Soc Japan **45**, 2039 (1972)

VII

Uit stralingshygienisch oogpunt is de beperking van stralenbelasting veroorzaakt door medische rontgenapparatuur van nog meer belang dan het 'lekvrij' maken van kerncentrales

Nijmegen, 29 juni 1973

A.J G. van Rossum