Iodine Atom-catalysed Isomerisation of Substituted *cis,trans*-1,4-Diphenylbutadienes

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Rate constants have been measured for the iodine-catalysed *cis–trans*-isomerisation of several substituted *cis,-trans*-diphenylbutadienes in hexane between −40 and 65°. To obtain reproducible results the measurements were carried out at relatively high iodine atom concentrations, generated by short, intense illumination of the reaction mixtures. The non-linearity of the Arrhenius plots in the temperature range investigated revealed that the isomerisation is a multiple rate-determining process: the rate constants for dissociation and internal rotation of the intermediate radical are about equal. By the appliance of a curve-fit program the independent parameters of the Arrhenius equation could, however, be determined. The isomerisations proceed *via* cinnamyl, not *via* benzyl radicals. The activation energy is *ca.* 6 kcal mol^{-1} lower than in the isomerisation of *cis*-stilbenes. This reduction can be ascribed to the larger gain of stabilisation energy in the formation of a cinnamyl radical in comparison with a benzyl radical, and to the lower activation energy of the rotation step. The influence of substituents on the isomerisation is discussed briefly.

KINETIC studies of the iodine-atom catalysed *cis–trans*-isomerisation of various olefins have revealed that these reactions generally proceed *via* the reversible addition of an iodine atom to the olefin, followed by internal rotation in the adduct radical.[1] For all the simple olefins investigated to date, but-2-ene,[2] 1,2-di-iodoethylene,[3,4] *cis*-stilbenes,[5] and *cis*-cinnamic esters,[6,7] internal rotation in the intermediate has appeared to be the rate-determining step.

A rate-determining addition step might be expected in going to olefins which add the iodine atom in a more exothermic reaction, and give at the same time easily rotating intermediate radicals. These conditions may be fulfilled in olefins with conjugated double bonds, because extension of the conjugation will enlarge the difference between the resonance stabilisation energy of the intermediate radical and the parent compound, whereas the steric relations in the intermediate will certainly not be less suitable for internal rotation than in the case of a simple olefin. For the isomerisation of *cis*-penta-1,3-diene, the only 1,3-diene investigated,[8] it has indeed been suggested that the addition of the iodine atom is rate-determining, but due to side-reactions the reproducibility of the kinetic measurements was too poor to provide conclusive evidence.

We have now studied [9] the iodine-catalysed isomerisations of several types of αω-diarylpolyenes. The results for several ring-substituted 1,4-diarylbutadienes will be discussed in this and those for 1,6-diphenylhexatrienes and a 1,8-diaryloctatetraene in the following paper.

EXPERIMENTAL

Apparatus and Procedure.—For the determination of rate constants an iodine solution (2 ml, *ca.* 10^{-4}M) and a solution of a *cis*-compound (2 ml, *ca.* 10^{-5}M), both in n-hexane, were pipetted into a photometer cuvette with exclusion of light. The cuvette was closed with a stopcock and placed in a fixed cell holder, mounted in a double-walled chamber with optically flat quartz windows at opposite sides and shutters to prevent unwanted illumination (Figure 1). Measurements were carried out between −45 and +65°. The temperature was adjusted by pumping thermostatted water or ethanol through the cell holder. To prevent fogging of the cuvette and windows a vacuum was set up between the walls of the chamber in experiments at low temperatures.

For the light-induced generation of iodine atoms the chamber was placed in an irradiation apparatus containing a Philips HPK125 mercury lamp, the optical section (mirror and lenses) of a Leitz Pradovite slide-projector to concentrate the light beam, a filter absorbing below 370 nm to minimize photochemical side-reactions, an IR filter to prevent rise of temperature, and a Prontor Press central-shutter (3 cm diameter) for the regulation of exposure times.† The

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† Because a significant time may be needed to build up the steady-state concentration of iodine atoms and since iodine-catalysed isomerisations will continue for a short time after the end of exposure, effective reaction times may be slightly different from the exposure times. Measurements of the rate constant of the isomerisation of *cis*-1,4-diphenylbutadiene revealed that reaction times were generally 0.01 s longer than shutter times. Very short shutter times were therefore corrected.

[1] R. G. Dickinson and H. Lotzkar, *J. Amer. Chem. Soc.*, 1937, **59**, 472.

[2] S. W. Benson, K. W. Egger, and D. M. Golden, *J. Amer. Chem. Soc.*, 1965, **87**, 468.

[3] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, 1952, **74**, 4141.

[4] D. M. Golden, S. Furuyama, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 57.

[5] W. J. Muizebelt and R. J. F. Nivard, *J. Chem. Soc. (B)*, 1968, 913.

[6] E. A. R. Visscher and E. C. Kooyman, *J. Catalysis*, 1963, **2**, 421.

[7] A. J. G. van Rossum, W. J. Muizebelt, and R. J. F. Nivard, *J. Chem. Soc. (B)*, 1970, 733.

[8] K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87**, 3314.

[9] See also A. J. G. van Rossum, Thesis, Nijmegen, 1973.

position of the lamp was adjusted so that the variation of light intensity incident on various parts of the cell was only a few percent. At the iodine concentrations used only a small fraction of the incident light was absorbed by the solution, and the absorption was presumably uniform throughout the cell.

The optical density of the mixtures was measured at wavelengths at which the extinction coefficients of *cis*- and *trans*-isomers were sufficiently different. Measurements were made before exposure (D_0), 5 or 6 times after gradually increasing exposure times covering 20—70% conversion (D_t), and after complete isomerisation (D_∞) by placing the chamber in a Cary-15 spectrophotometer and recording the spectrum. Rate constants (k_i) were calculated from equation (1) where t is the exposure time. From the

$$k_i/l^{\frac{1}{2}}\ \mathrm{mol}^{-\frac{1}{2}}\ \mathrm{s}^{-1} = \frac{1}{t} \ln \frac{D_\infty - D_0}{D_\infty - D_t} [\mathrm{I}_2]^{-\frac{1}{2}} \qquad (1)$$

presence of an isosbestic point it could be concluded that no side-reactions were involved in which diphenylbutadienes were consumed.

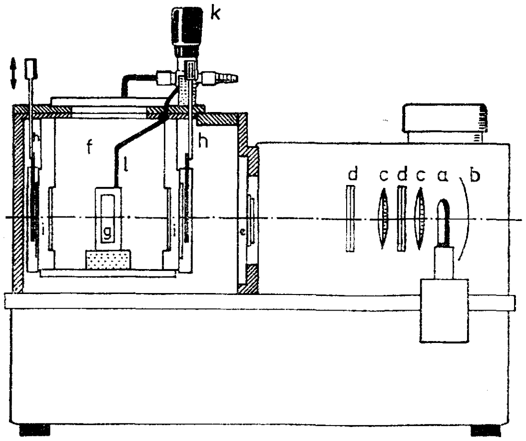

FIGURE 1 Irradiation apparatus: a, lamp; b, mirror; c, lens; d, filter; e shutter; f, chamber; g, cuvette holder; h, shutter; i, quartz windows; k, vacuum stopcock; l, connection tube to thermostat

Isomerisation by thermally generated iodine atoms in unexposed solutions was only found above 60°, but the contribution of this reaction was always <1% under the experimental conditions. The occurrence of photoisomerisation in our experiments could be excluded by measuring the spectrum of *trans,trans*-1-phenyl-4-*p*-nitrophenylbutadiene in hexane ($\lambda_{\mathrm{max.}}$ 371 nm) before and after illumination for a few minutes (much longer than the exposure times). It was unchanged.

The k_i values found from equation (1) depend, amongst other parameters, on the lamp used and the light path. According to equation (2) the photostationary concentration of iodine atoms is given by equation (3), in which ϕ is the

$$\mathrm{I}_2 \xrightarrow{h\nu} 2\mathrm{I}\cdot \qquad (2a)$$

$$2\mathrm{I}\cdot \xrightarrow{k_r} \mathrm{I}_2 \qquad (2b)$$

$$[\mathrm{I}\cdot] = (\phi a l I_0/k_r)^{\frac{1}{2}}[\mathrm{I}_2]^{\frac{1}{2}} \qquad (3)$$

quantum yield of the photodissociation, a the molar absorption coefficient, l the light path, I_0 the intensity of incident light, and k_r the rate constant of the recombination of iodine atoms. If the substitution (4) is used the rate law of the

$$(\phi a l I_0/k_r)^{\frac{1}{2}} = f \qquad (4)$$

irreversible *cis–trans*-isomerisation catalysed by photolytically generated iodine atoms is (5) and the rate constant k

$$v = fk[cis][\mathrm{I}_2]^{\frac{1}{2}} \qquad (5)$$

is found from (6).

$$k = k_i/f \qquad (6)$$

The value of f, which varies for different lamps, was calculated from kinetic measurements on 3,3′,5,5′-tetramethyl-*cis*-stilbene. The rate constant of its isomerisation with thermally generated iodine atoms (k_t) is given [5] by equation (7). The steady state concentration of iodine

$$k_t/l^{\frac{1}{2}}\ \mathrm{mol}^{-\frac{1}{2}}\ \mathrm{s}^{-1} = 10^{9.46}10^{-21.39/2.303RT} \qquad (7)$$

atoms in this case is given by (8) in which K_I is the dissociation constant of iodine.

$$[\mathrm{I}\cdot] = K_I^{\frac{1}{2}}[\mathrm{I}_2]^{\frac{1}{2}} \qquad (8)$$

From (6) and (9) it follows that

$$k_t = K_I^{\frac{1}{2}}k \qquad (9)$$

equation (10) applies. The value of K_I given by Benson [2]

$$k_i = fk_tK_I^{-\frac{1}{2}} \qquad (10)$$

is obtained from equation (11). Substituting (7) and (11)

$$K_I/\mathrm{mol\ l}^{-1} = 10^{3.4},10^{-35.4/2.303RT} \qquad (11)$$

in (10), and expressing the rate constants in terms of the Arrhenius equation gives (12). Assuming that f is indepen-

$$\log k_i = \log A_i - (E_a)_i/2.303RT = \log f + 7.8 - 3.7/2.303RT \qquad (12)$$

dent of temperature, $(E_a)_i$ should be 3.7 kcal mol^{-1}, and $\log f = \log A_i - 7.8$. The assumption is only correct if the influences of T on ϕ and k_r are cancelled [10] (the influence on a will be small). Arrhenius plots for the isomerisation of the *cis*-stilbene derivative between −45 and +65° in experiments with four different lamps yielded in each case a straight line with a very high correlation coefficient (0.999—1.000), and a mean value of E_a, 3.64 kcal mol^{-1}, in close agreement with the value found for thermally generated iodine atoms (3.7 kcal mol^{-1}). The dependence of f on temperature must therefore be regarded as negligible.

The determination of the rate constant (k_i) for the isomerisation of the *cis*-stilbene derivative was frequently repeated during the kinetic measurements to check the constancy of the light intensity. As soon as a lower k_i value was found the lamp was replaced. The $\log f$ values of the lamps used varied from −5.8 to 6.0 mol$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$. From (3) and (4) it follows that [I·] is *ca.* 10^{-8}M. In preliminary experiments it was found that a retarding effect of oxygen became apparent only if [I·] $<10^{-9}$M; therefore the measurements were done without exclusion of oxygen.

Materials.—Hexane (Merck p.a.) was distilled over sodium. Iodine (Merck p.a.) was used without purification. The monosubstituted 1,4-diphenylbutadienes were prepared *via* Wittig reactions. A twofold excess of lithium ethoxide in anhydrous ethanol (285 ml) was added to a solution of an appropriately substituted benzaldehyde (0.048 mol) and triphenylcinnamylphosphonium chloride

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[10] H. Rosman and R. M. Noyes, *J. Amer. Chem. Soc.*, 1958, **80**, 2410.

(0.052 mol; obtained from cinnamyl chloride[11] and triphenylphosphine in boiling xylene) in the same solvent (65 ml). After 16 h in the dark at room temperature water (230 ml) was added, and the precipitate was filtered and washed with 60% ethanol. The product was dried, treated with boiling hexane, cooled to −80°, and filtered again. The solid *trans–trans*-product was crystallized from ethanol or toluene. The hexane solution was concentrated and chromatographed over alumina. Solid *cis*-products eluted from the column were crystallized from hexane; oily derivatives were used without further purification. The combined yield was 50—70%; the *cis–trans* : *trans–trans*-ratio was usually *ca.* 1/5. Disubstituted 1,4-diphenylbutadienes were prepared in a similar way from a substituted triphenylbenzylphosphonium bromide, obtained from the appropriate benzyl bromide and triphenylphosphine, and the appropriately substituted cinnamaldehyde.[12]

TABLE 1

U.v. data, m.p.s, and elemental analyses of substituted 1,4-diphenylbutadienes

				C		H		N	
cis–trans-Dienes	λ_{max}/nm	ε_{max} 10^{-4}	M.p. (°C)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)
Unsubstituted	312	3.42	Oil	92.4	93.15	7.0	6.85		
	(312) [b]	(3.02) [b]							
m-NO_2	314	3.49	43—44	76.2	76.5	5.1	5.2	5.8	5.55
p-NO_2	352	4.60	80—81	76.8	76.5	5.1	5.2	5.8	5.55
p-Cl	315	3.78	Oil	79.8	79.85	5.3	5.3		
p-MeO	322	3.16	Oil	86.5	86.4	6.9	6.8		
p-Me	315	3.40	34—35	92.6	92.7	7.2	7.3		
p-Me_2N	357	3.04	55—57	86.4	86.7	7.9	7.7	5.6	5.6
1-(β-$C_{10}H_7$)	325	3.00	77.5—79	93.3	93.7	6.4	6.3		
m,m'-$(NO_2)_2$	309	2.96	*a*	64.6	64.85	4.3	4.1	9.3	9.45
p,p'-$(NO_2)_2$	350	3.27	*a*	65.0	64.85	4.1	4.1	9.5	9.45
trans–trans-Dienes									
Unsubstituted	328	5.77	154—155	92.8	93.15	6.9	6.85		
	(328) [b]	(5.62) [b]	(154—156) [c]						
m-NO_2	330	4.99	146—147	76.4	76.5	5.0	5.2	5.9	5.55
p-NO_2	371	8.76	177—178	76.2	76.5	5.0	5.2	5.8	5.55
			(181.5—182) [c]						
p-Cl	332.5	6.38	165—166	79.5	79.85	5.3	5.3		
			(166—167) [d]						
p-MeO	336	5.68	163—164	86.2	86.4	7.0	6.8		
			(163—164) [d]						
p-Me	331	6.30	156—158	92.8	92.7	7.6	7.3		
			(156—156) [d]						
p-Me_2N	364	5.25	180—183	86.5	86.7	7.7	7.7	5.6	5.6
			(177—180) [c]						
1-(β-$C_{10}H_7$)	339.5	6.74	187—187.5	93.7	93.7	6.3	6.3		
m,m'-$(NO_2)_2$	326	4.16	211—213	64.7	64.85	4.0	4.1	9.3	9.45
p,p'-$(NO_2)_2$	369	5.89	276—279	64.5	64.85	4.2	4.1	9.5	9.45
			(296—271) [e]						

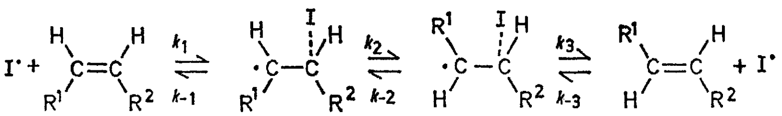
[a] Long melting ranges, probably due to *cis–trans*-isomerisation during melting. [b] J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Amer. Chem. Soc.*, 1948, **70**, 1938. [c] R. N. MacDonald and T. W. Campbell, *J. Org. Chem.*, 1959, **24**, 1969. [d] C. C. Leznoff and R. J. Hayward, *Canad. J. Chem.*, 1970, **48**, 1842. [e] D. J. Lyman, J. Heller, and M. Barlow, *Macromol. Chem.*, 1965, **84**, 64.

All compounds were characterised by m.p., u.v. spectra, and elemental analyses (Table 1). Most of the *cis*-compounds transform slowly into their all-*trans*-isomers at room temperature, even in darkness. Stored at −25° (oily products dissolved in hexane) they remained pure, however, for more than a year.

RESULTS AND DISCUSSION

For all compounds investigated, the observed isomerisation rate constants (k_i),* expressed in $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ s^{-1} and plotted against the reciprocal temperature, are given in Figure 2. All values were obtained using a lamp with log $f = -5.87$. (The Arrhenius plots of the other compounds show similar curvatures.) It appears that the activation energies for all compounds decrease at higher temperatures.

According to the generally accepted reaction scheme (14),[12] the rate law of irreversible *cis–trans*-isomerisation can be formulated as (15). If k_{-1} and k_2 are of comparable magnitude equation (15) cannot be simplified.



(14)

$$v = fk_1k_2[cis][I\cdot]/(k_{-1} + k_2) \qquad (15)$$

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* The numerical data together with 95% confidence limits are presented in Supplementary Publication No. SUP 21362 (5 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full-size copies.

[11] A. Klages and K. Klenk, *Ber.*, 1906, **39**, 2552.

[12] A. Berthoud and C. Urech, *J. Chim. Phys.*, 1930, **27**, 291.

The observed rate constant $[k_i = fk_1k_2/(k_{-1} + k_2)]$ can be expressed in terms of the Arrhenius equation (16). If

$$k_i = f\frac{A_1e^{-E_1/RT}}{A_{-1}/A_2e^{-(E_{-1}-E_2)/RT} + 1} \qquad (16)$$

E_{-1} and E_2 differ substantially no linear relationship between $\log k_i$ and $1/T$ is found; the isomerisation is a multiple rate-determining process.

With a curve-fit program based on the method of least squares and applied to the data of unsubstituted *cis,-trans*-diphenylbutadiene the independent parameters of equation (16) were determined for this compound. Values obtained were as follows: $E_1 = 1.52$; $E_{-1} - E_2 = 4.22$ kcal mol^{-1}; $fA_1 = 2700$ l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ s^{-1}; $A_{-1}/A_2 = 520$. The standard errors are of the same order of magnitude as the parameters themselves, but the curve-fitting is very satisfactory (see drawn line in Figure 2), and the Arrhenius parameters agree very well with expected values.

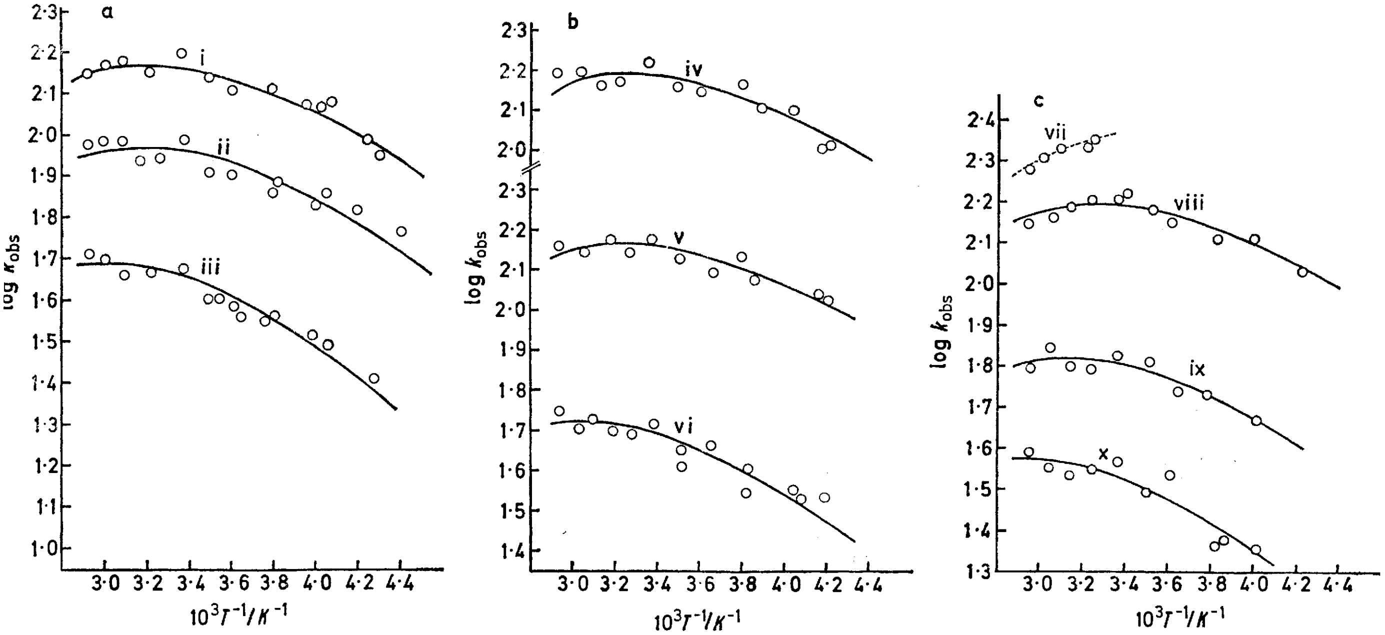

FIGURE 2 Arrhenius plots for the iodine catalysed isomerisation of some *cis,trans*-diphenylbutadienes. The full lines were drawn with a curve-fit program: i, 1,4-diphenylbutadiene; ii, 1-(4-chlorophenyl)-4-phenyl-; iii, 1-(4-nitrophenyl)-4-phenyl-; iv, 1-(4-methoxyphenyl)-4-phenyl-; v, 1-β-naphthyl-4-phenyl-; vi, 1-(3-nitrophenyl)-4-phenyl-; vii, 1-(4-dimethylaminophenyl)-4-phenyl-; viii, 1-(4-methylphenyl)-4-phenyl-; ix, 1,4-bis-(4-nitrophenyl)-; x, 1,4-bis-(3-nitrophenyl)-butadiene

Our value of $\log A_1$ (9.3 l^{-1} mol^{-1} s^{-1}) is in accordance with that calculated [13] for reactions between an atom and a non-linear molecule (9—10) and with those found [14] for the iodine exchange of *cis*- and *trans*-di-iodoethylene (9.4 and 9.6, respectively) in which the attack of an iodine atom is rate determining.

In the absence of entropy effects the frequency factor of a unimolecular bond-breaking, as in the dissociation of the intermediate radical ($\log A_{-1}$), is 13 s^{-1} according to transition state theory.[15] If the transition state is a rather loose complex $\log A_{-1} = 14$ may be a better estimate.[8] Accepting this value $\log A_2$ is 11.3 s^{-1} (14 − log 520), which is in good agreement with values found for the rotations in the intermediates of the iodine-catalysed isomerisations of but-2-ene [2] and 1,2-di-iodoethylene [4] (11.3 and 11.8, respectively).

The frequency factor for isomerisations in which the rotation step is rate determining ($\log A_r$) is $\log A_1 - \log A_{-1}/A_2$, equal to 6.6. This value is lower than the corresponding value for the isomerisation of 3,3′,5,5′-tetramethyl-*cis*-stilbene [7.76; see equations (7), (10), (11), and (13)]. The difference may be due to additional loss of entropy in the intermediate of the isomerisation of diphenylbutadiene, caused by increased rigidity of the central carbon–carbon bond.

Assuming that the influence of substituents on the isomerisation rate constants need only be ascribed to variations of the relevant activation energies, as was found with *cis*-stilbenes [5] and other radical side-chain reactions of benzene derivatives,[16] the values of A_1 and A_{-1}/A_2 could be applied to the curve-fit program on the kinetic data of substituted diphenylbutadienes. In this way the standard errors of the calculated activation energies (Table 2) were reduced, and the values themselves were more reliable. The observed rate constants for all compounds appeared to coincide very well with curves calculated in this way (see *e.g.* full lines in Figure 2). Deviations are mostly within the 95% confidence limits.

The values of E_1 as well as E_r are linearly related to the σ^0 values of the substituents (Figures 3 and 4); the

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[13] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, p. 94.

[14] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, 1945, **67**, 1319.

[15] Ref. 13, pp. 110—111.

[16] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

TABLE 2

Activation energies of the isomerisation of *cis,trans*-diphenylbutadienes

Substituents in phenyl groups	E_1/ kcal mol^{-1}	Standard error	$E_1 - E_2$/ kcal mol^{-1}	Standard error	E_r */ kcal mol^{-1}
None	1.52	0.01	4.22	0.05	−2.70
p-Me	1.46	0.02	4.15	0.05	−2.69
p-MeO	1.48	0.02	4.20	0.06	−2.72
1-(β-$C_{10}H_7$) instead of 1-Ph	1.50	0.02	4.14	0.06	−2.64
p-Cl	1.75	0.02	4.07	0.06	−2.32
m-NO_2	2.08	0.02	4.00	0.07	−1.92
p-NO_2	2.15	0.02	4.04	0.05	−1.89
m,m'-$(NO_2)_2$	2.29	0.04	3.99	0.10	−1.70
p,p'-$(NO_2)_2$	1.93	0.03	3.99	0.08	−2.06

* E_r is the energy difference between the initial state and the transition state (TS_2) of the rotation step.

slopes are 0.78 and 0.98, the correlation coefficients 0.993 and 0.991, respectively.

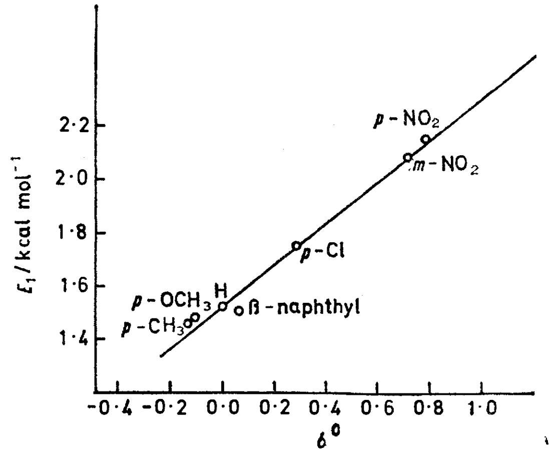


FIGURE 3 Plot of calculated activation energies of iodine atom addition to monosubstituted *cis,trans*-diphenylbutadienes against σ^0 values

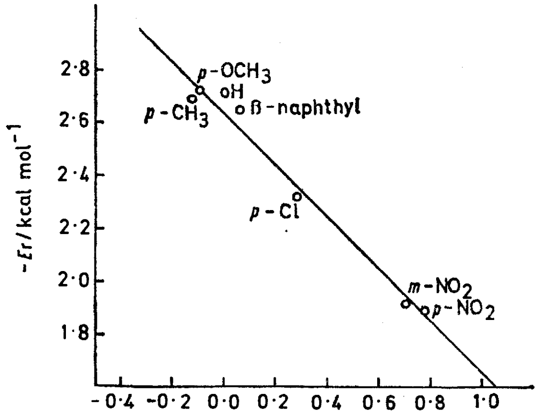
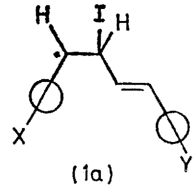
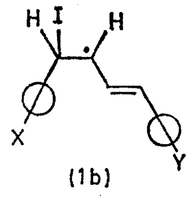


FIGURE 4 Plot of calculated energy differences between the initial state and TS_2 for *cis,trans*-isomerisations of diphenylbutadienes against σ^0 values

Hammett Plots.—The isomerisations of *cis,trans*-diphenylbutadienes might proceed *via* two different intermediates (1a and b). Substituents in the 1-phenyl residue (X) will have only polar effects if (1b) is the intermediate; in isomerisations *via* (1a) some additional resonance interaction of the substituent may be expected. With substituents in the 4-phenyl residue (Y) the reverse should be the case, since then conjugation occurs in (1b), not in (1a).



(1a)



(1b)

It appeared that the rate constants of all monosubstituted diphenylbutadienes containing an X substituent fit excellently into a linear Hammett plot based on σ^0 values, which account only for polar effects.[17] With *k* values measured at 49.5°, $\rho = -0.59$ (Figure 5; correlation coefficient 0.994); a similar plot with values at −35° gave $\rho = -0.73$ (correlation coefficient 0.994). log *k* Values of symmetrically disubstituted diphenylbutadienes are not linearly related to the relevant σ^0 values (Figure 6). The isomerisation of the *p,p'*-bis-(nitrophenyl) derivative is much faster than expected. This deviation may be ascribed to resonance interaction of one of the nitro-groups.

Both plots (Figures 5 and 6) point to (1b) as the intermediate in all isomerisations investigated.

Energy Scheme of the Reaction.—The activation energy for the iodine-catalysed isomerisation of *cis*-stilbene is 3.7 kcal mol^{-1}.[5] The corresponding energy difference (E_r) between the initial and the transition state (TS_2)

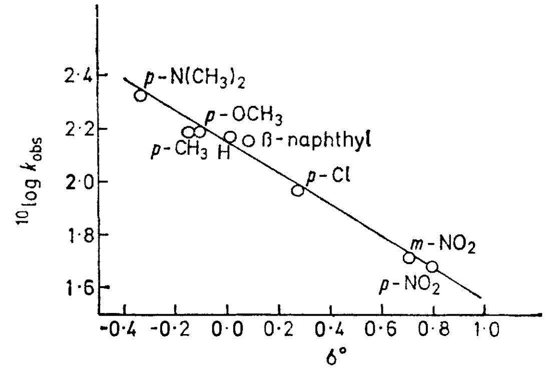


FIGURE 5 Hammett plot for the isomerisation of monosubstituted *cis,trans*-diphenylbutadienes at 49·5°

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[17] A. P. G. Kieboom, *Tetrahedron*, 1972, **28**, 1325: σ^0 of β-naphthyl is taken from Y. Yukawa, F. Tsuno, and M. Sawada, *Bull. Chem. Soc. Japan*, 1966, **39**, 2274.

(see Figure 7) in the isomerisation of *cis,trans*-1,4-diphenylbutadiene is —2.7 kcal mol^{-1}. The reduction of TS_2 by >6 kcal mol^{-1} in the latter case causes a 700-fold increase in the isomerisation rate constant at room temperature.

E_r Equals $\Delta H_1 + E_2$ in which ΔH_1 is the reaction enthalpy of the addition step and E_2 the activation enthalpy of the rotation step. It can be argued that the lowering of TS_2 may be attributed to a decrease of ΔH_1 as well as of E_2.

ΔH_1 For the addition of an iodine atom to *cis*-stilbene, calculated from the bond energies of the broken π-bond and the new C–I bond (together 6 kcal mol^{-1}), and from the lost resonance energy of the stilbene[18] (2.3 kcal mol^{-1}) and the gained resonance energy of a benzyl radical[19] (—13 kcal mol^{-1}), is *ca.* 5 kcal mol^{-1}. Even with the assumption that E_2 for the rotation in the intermediate of the isomerisation of *cis,trans*-diphenylbutadiene has the very low value of 5 kcal mol^{-1}, only slightly larger than the energy barrier for rotation in ethane, ΔH for the addition of an iodine atom to diphenylbutadiene should be *ca.* —8 kcal mol^{-1}. The larger exothermicity of this addition is presumably due to the larger stabilisation energy of a cinnamyl radical (1b) in comparison with a benzyl radical, since bond breaking and making are similar in both reactions and the resonance energy of *cis,trans*-diphenylbutadiene will even be larger than that of *cis*-stilbene. It is known that the resonance energy of an allyl radical[20] is already about the same as that of a benzyl radical. Radicals (2) and (3) depict the probable ways of internal rotation in the intermediates involved in the isomerisation of *cis,trans*-diphenylbutadiene and *cis*-stilbene, respectively. During the rotation shown in (3) coplanarity of the benzylic radical part cannot be maintained and the stabilisation energy of the radical is for the larger part lost. Rotation in (2) suffers less steric hindrance, and the radical part will remain more planar, resulting in a lower value of the activation enthalpy.

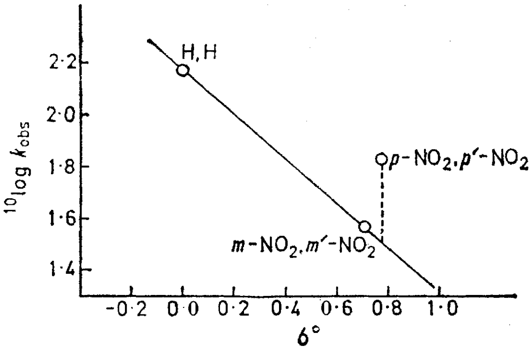


FIGURE 6 Hammett plot for the isomerisation of symmetrically substituted *cis,trans*-diphenylbutadienes at 49.5°

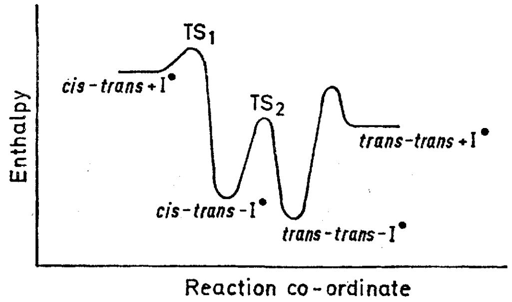
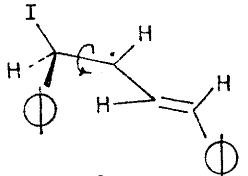
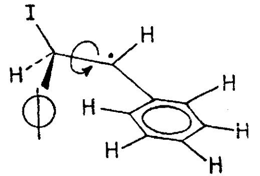


FIGURE 7 Energy diagram for the isomerisation of *cis,trans*-diphenylbutadiene



(2)



(3)

Rate-determining Step.—Using the results of the curve-fit program mentioned previously, the ratio $k_{-1} : k_2$ for the unsubstituted diphenylbutadiene can be formulated as $k_{-1} : k_2 = 10^{2.72}10^{-4.22/2.303RT}$. At 66° this ratio is unity. Assuming that the rate constants should differ by a factor of ten to get an unambiguous rate-determining step, the iodine-atom addition is rate determining below —27°, the rotation step above 260°. In the greater part of the temperature interval used in our measurements the difference between k_{-1} and k_2 is rather small, the addition step becoming gradually rate controlling in the lower part of the temperature range.

Effects of Substituents.—For the isomerisation of symmetrically disubstituted *cis*-stilbenes[5] ρ is —1.12 at 120°. Substituents might influence the reaction rate *via* the equilibrium constant of the addition step and/or *via* the rate constant of the rotation step because the latter is rate determining. It has been argued,[5] however, that the substituent effects can be attributed mainly to charge separation in the formation of the polar C–I bond, and that their influence on the rate of rotation should therefore be small.

The ρ value can be split up into two parts: $\rho = \rho_\alpha + \rho_\beta$. The value ρ_α concerns the influence of substituents attached to the phenyl ring at the saturated CHI group [left side of (3)], ρ_β the effect of substituents in the benzyl radical [right side of (3)].

For the similar isomerisation of ring-substituted methyl *cis*-cinnamates[21] ρ is —0.51 at 120°. This isomerisation proceeds *via* a benzyl radical because *para*-substituted compounds show positive deviations from the linear Hammett plot, as in the case of *cis*-stilbenes. ρ Can therefore be considered as equal to ρ_β. This implies that ρ_α is only slightly more than half the ρ value, and that the transmission coefficient of the CHI group for polar substituent influences is close to unity.

The ρ value involved in the isomerisation of *cis,trans*-diphenylbutadienes is a ρ_α value. Thus it could be

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[18] G. W. Wheland, ' Resonance in Organic Chemistry,' Wiley, New York, 1955, p. 80.

[19] R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1966, **88**, 650.

[20] A. B. Trenwith, *Trans. Faraday Soc.*, 1970, **66**, 2805.

[21] A. H. A. Tinnemans, unpublished results.

expected that the substituent influence on E_r should be slightly more than half the corresponding influence on the activation energy of the isomerisation of *cis*-stilbenes (slope 2.04).[5] The value found (0.98, see Figure 3) accords reasonably well with this expectation.

It may be noted that the substituent influence on the activation energy of the addition step (E_1) is significantly lower (0.78, see Figure 3). It follows that substituents exert somewhat more influence on TS_2 than on TS_1. Their influence in the addition step cannot be related to the stability of the intermediate radical, because the transition state of this rather exothermic reaction (ΔH_1 >8 kcal mol^{-1}) with a low activation energy (1.51 kcal mol^{-1}; Table 2) is a somewhat loose complex which according to Hammond's postulate[22] much resembles the initial state. The origin of polar substituent effects on the rate of radical additions to olefins is not yet fully understood.[23]

We are indebted to Dr. W. J. Muizebelt for valuable discussions.

[4/2303 *Received*, 6*th November*, 1974]

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[22] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[23] C. Walling, ' Free Radicals in Solution,' Wiley, New York, 1957, p. 132.