Iodine Atom-catalysed Isomerisations of *cis,trans,trans*- and *trans,cis,-trans*-1,6-Diphenylhexa-1,3,5-trienes and of *trans,cis,trans,trans*-1,8-Diphenylocta-1,3,5,7-tetraene

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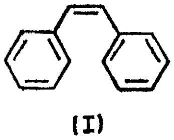
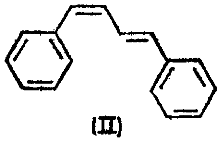
Rate constants have been measured for iodine atom-catalysed isomerisations of *cis,trans,trans*- (III) and *trans,cis,-trans*-diphenylhexatriene (IV), and of *trans,cis,trans,trans*-diphenyloctatetraene (V). The results have been compared with those of *cis,trans*-diphenylbutadiene (II) and simple olefins. Addition of an iodine atom is rate determining in all three cases, but at lower temperatures (<−15°) the isomerisation of the *cis,trans,trans*-hexatriene gradually becomes a diffusion controlled reaction. Differences in the rate constants are due mainly to differences in the activation energy of the addition reaction. It appeared that extension of conjugation in the starting olefin, which is accompanied by a similar change in the intermediate radical of the isomerisation [*e.g.* (II) $\longrightarrow$ (III) or (IV) $\longrightarrow$ (V)], leads to a 60-fold increase in the rate constant. Introduction of an additional double bond which does not change the type of intermediate [(II) $\longrightarrow$ (IV) or (III) $\longrightarrow$ (V)] lowers the isomerisation rate *ca.* 40-fold.

In the preceding paper [1] we reported kinetic data on the iodine-catalysed isomerisations of substituted *cis,trans*-diphenylbutadienes, and compared these results with similar data on isomerisations of *cis*-stilbenes.[2] It appeared that the insertion of a *trans*-ethylenic bond in *cis*-stilbene (I) leads to a substantial increase in the isomerisation rate constant. As opposed to the isomerisation of *cis*-stilbene, where internal rotation in a primarily formed, intermediate radical is rate determining, the isomerisation of *cis,trans*-diphenylbutadiene (II) is a multiple rate-determining process over a wide temperature range around 66°. Both effects could ultimately be ascribed to a difference in the type of the intermediate radical: *cis*-stilbenes isomerise *via* benzylic, diphenylbutadienes *via* phenylallylic radicals.

Further extension of conjugation in (II) is possible with or without a further change in the type of radical formed during isomerisation. Such a change may be expected in going from (II) to *cis,trans,trans*-diphenylhexatriene (III), but cannot occur in going from (II) to *trans,cis,trans*-diphenylhexatriene (IV). Similarly, a change in the type of intermediate is probable in going from (IV) to *trans,cis,trans,trans*-diphenyloctatetraene (V), but not from (III) to (V). In order to evaluate the effects of the introduction of additional olefinic bonds in one or the other way into (II), the isomerisation rate constants of (III)—(V) have been measured; the Arrhenius parameters of these isomerisations have been calculated and compared with those of (I), (II), and some other simple olefins.


(I)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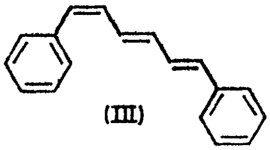
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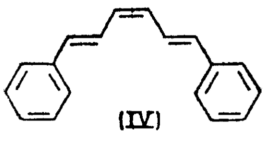
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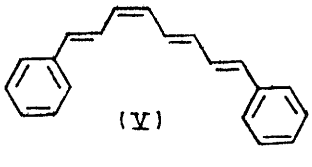
(V)

EXPERIMENTAL

Apparatus and experimental procedures were described in the previous paper.[1] With all three compounds irradi-

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[1] A. J. G. van Rossum, A. H. M. de Bruin, and R. J. F. Nivard, preceding paper.

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

ation was carried out with the same light source (log $f = -5.99$) to avoid differences in the photostationary concentration of iodine atoms under otherwise equal conditions. With (IV) a second series of measurements was done on irradiation with another lamp (log $f = -5.96$). The collision factors and activation energies derived from both series agreed very well, indicating satisfactory reproducibility of the measurements (see Table 2). All compounds were investigated in hexane solution and also (III) in carbon tetrachloride (Merck p.a., distilled over P_2O_5).

As opposed to (I) and (II) *cis–trans*-isomerisations of (III)—(V) are not completely irreversible. The k values derived from spectral changes represent the sum of the rate constants for *cis–trans* and *trans–cis*-isomerisations [3] under such circumstances. In view of the high percentages of the all-*trans*-isomers found by Zechmeister [4,5] in the equilibrium mixtures of (III)—(V), $k_{t\rightarrow c}$ will nevertheless be very low in comparison with $k_{c\rightarrow t}$. The measured rate constants have therefore been used for $k_{c\rightarrow t}$.

From calculations of the k values of (III) it appeared that k increased slightly with increasing conversion percentage. It is not known why the kinetic expression was not wholly adequate in this case. This disagreement was small, however, and the systematic error was eliminated by multiplying the estimated D_∞ value by 1.02.

TABLE 1

Analytical data for the αω-diphenylpolyenes

Compound	$\lambda_{max.}$/nm	log $\varepsilon_{max.}$	M.p. (°C)	C Found (%)	C Calc. (%)	H Found (%)	H Calc. (%)
(IV)	350 (351) [a]	4.80 (4.73) [a]	107—109 (109—110) [a]	92.9	93.05	7.0	6.95
(III)	337 (338) [a]	4.71 (4.66) [b]	Oil	91.9	93.05	6.8	6.95
all-*trans*-1,6-Diphenylhexatriene	350.5 (351.5) [a]	4.93 (4.93) [a]	203—204 (198—199) [a]	93.0	93.05	7.1	6.95
(V)	370.5 (371) [a]	4.90 (4.89) [c]	134.5—135.5 (132.5—133.5) [a]	92.7	93.0	7.0	7.0
all-*trans*-1,8-Diphenyloctatetraene	371 (372.5) [a]	5.07 (5.04) [c]	236—237 (235—236.5)	93.1	93.0	7.1	7.0

[a] S. Misumi and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1963, **36**, 399. [b] Ref. 4. [c] Ref. 5.

The compounds investigated were prepared *via* Wittig reactions from triphenylcinnamylphosphonium chloride [1] (0.048 mol) [for (IV)] or *trans,trans*-5-phenylpenta-2,4-dienyltriphenylphosphonium chloride (0.048 mol) [for (III) and (V)] and the appropriate aldehyde (0.052 mol) (benzaldehyde or cinnamaldehyde). The reagents were dissolved in absolute ethanol (65 ml), and treated with a twofold excess of lithium ethoxide in absolute alcohol (285 ml). The mixture was then left at room temperature for 16 h in the dark. After addition of water (230 ml) the precipitate formed was filtered off and washed with 60% ethanol. In all cases the desired product was accompanied by its all-*trans*-isomer. After drying this crude product *in vacuo* it was treated with boiling hexane for a few minutes, cooled to −80°, and filtered again. Crystallisation from ethanol or toluene yielded the pure all-*trans*-isomer. The desired *cis*-isomer was obtained by concentration of the filtrate, followed by column chromatography and crystallisation from hexane. The products were identified and characterised by spectral data, m.p.s, and elemental analyses (Table 1).

For the synthesis of 5-phenylpenta-2,4-dienyltriphenylphosphonium chloride ethynylstyrylmethanol was prepared from cinnamaldehyde and ethynylmagnesium bromide.[6] Partial hydrogenation of the methanol over 5% $Pd-BaSO_4$ in pyridine yielded 1-phenylpenta-1,4-dien-3-ol which was treated with hydrochloric acid in carbon tetrachloride at 0° to give 5-phenylpenta-2,4-dienyl chloride. The crude product was then treated with triphenylphosphine in xylene.

RESULTS AND DISCUSSION

The measured isomerisation rate constants (k), expressed in $l^{\frac{1}{2}}\ mol^{-\frac{1}{2}}\ s^{-1}$ have been listed in Table 2, together with their 95% confidence limits. Plots of log k values against the reciprocal temperature for compounds (IV) and (V) showed linear relationships with high correlation coefficients (0.997 and 0.999, respectively). Arrhenius parameters calculated from these plots are given in Table 3. The 95% confidence limits are shown in parentheses. As appears from Table 3, the results from two independent series of measurements with (IV) agree very well.

The Arrhenius plot for the very fast isomerising compound (III), measured in hexane, is non-linear. The data suggest that the activation energy and collision factor above and below *ca.* −15° are different (Figure). A similar plot from measurements in carbon tetrachloride between −23 and +11° does not show this break. The correlation coefficients of the straight lines drawn in the Figure are not very high (0.946 in CCl_4; 0.930 in hexane below −15°) and the accuracy of the Arrhenius parameters indicated in Table 3 by 95% confidence limits is lower than for (IV) and (V). In Table 3 our results are compared with those of (II) and several simple olefins.

The values of log A for the isomerisations of (III) (at least above −15°), (IV), and (V) are about equal to that of the addition step in the isomerisation of (II). In view of the discussion in the preceding paper these data strongly suggest that the addition of an iodine atom leading to the intermediate radical is rate determining in these cases. Below *ca.* −15° or in carbon tetrachloride as the solvent the temperature dependence of the rate constant of (III) increases. Moreover, the rate constant

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[3] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1940, p. 103.

[4] K. Lunde and L. Zechmeister, *J. Amer. Chem. Soc.*, 1954, **76**, 2308.

[5] L. Zechmeister and J. H. Pinckard, *J. Amer. Chem. Soc.*, 1954, **76**, 4144.

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

TABLE 2

Isomerisation rate constants ($l^{\frac{1}{2}}\ mol^{-\frac{1}{2}}\ s^{-1}$)

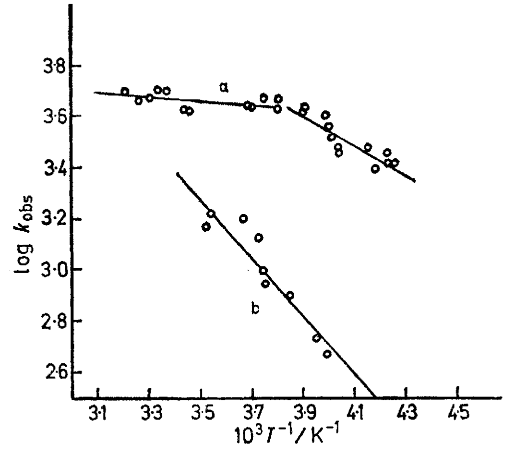
Compound	T (°C)	$10^6[I_2]$/M	k_{min}	k	k_{max}
(IV) in hexane lamp with log $f = -5.99$	64.2	84.2	4.09	4.18	4.27
	51.5	84.2	3.19	3.27	3.35
	37.3	84.2	2.35	2.40	2.44
	22.6	84.2	1.78	1.81	1.84
	6.7	84.2	1.24	1.30	1.36
	−9.7	84.2	0.82	0.86	0.91
	−22.8	84.2	0.62	0.63	0.65
	−39.2	84.2	0.37	0.40	0.42
lamp with log $f = -5.96$	27.4	113	2.09	2.16	2.22
	37.4	113	2.90	3.10	3.31
	52.2	113	3.24	3.37	3.49
	63.2	113	4.40	4.57	4.73
	52.2	113	3.64	3.70	3.76
	37.3	113	2.71	2.84	2.79
	3.8	113	1.24	1.31	1.38
	−32.8	113	0.44	0.47	0.51
	−44.1	113	0.28	0.30	0.31
(V) in hexane lamp with log $f = -5.99$	−38.5	84.2	40	42	44
	−25.3	84.2	50	54	59
	−10.4	84.2	67	69	71
	6.5	84.2	75	78	81
	22.3	84.2	100	105	111
	37.3	84.2	114	117	120
	51.4	84.2	131	134	138
	64.6	21.0	145	157	169
(III) in hexane lamp with log $f = -5.99$	38.3	10.5	4 700	4 920	5 130
	32.4	10.5	4 290	4 620	4 950
	29.0	10.5	4 460	4 680	4 890
	25.8	10.5	4 700	5 010	5 320
	23.3	10.5	4 890	5 040	5 180
	17.3	21.0	4 090	4 200	4 300
	15.8	21.0	4 020	4 180	4 340
	−2.4	21.0	4 090	4 280	4 470
	−3.2	21.0	4 120	4 290	4 460
	−6.6	21.0	4 420	4 610	4 810
	−9.7	21.0	3 940	4 220	4 500
	−10.3	21.0	4 530	4 610	4 690
	−16.2	21.0	3 790	3 980	4 370
	−17.1	21.0	3 920	4 100	4 270
	−17.3	21.0	3 820	4 250	4 680
	−24.4	21.0	3 100	3 300	3 510
	−25.6	21.0	2 820	1 930	2 050
	−25.8	21.0	2 820	2 910	3 000
	−34.4	21.0	2 340	2 450	2 560
	−23.6	42.1	3 270	3 580	3 890
	−32.8	42.1	2 830	2 940	3 060
	−37.8	42.1	2 460	2 590	2 710
	−37.4	84.2	2 420	2 570	2 720
	−37.5	84.2	2 600	2 690	2 790
(III) in CCl_4 lamp with log $f = -5.99$	10.5	21.0	1 457	1 463	1 468
	9.2	21.0	1 560	1 650	1 740
	0.3	21.0	1 510	1 570	1 620
	−5.0	21.0	1 230	1 340	1 450
	−5.5	21.0	946	974	1 006
	−6.8	21.0	843	871	900
	−13.5	21.0	732	790	850
	−20.3	21.0	464	537	610
	−23.1	21.0	440	460	481

is solvent dependent which was not found in the case of 3,3′,5,5′-tetramethyl-*cis*-stilbene.

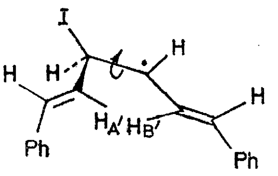
These observations suggest that the isomerisation of (III) at lower temperatures gradually becomes diffusion controlled. Especially in carbon tetrachloride k_{diff} is apparently much lower than k_{add}.

The activation energy and the high log A value found in this solvent agree very well with Arrhenius parameters of other diffusion-controlled reactions[7,8] (E_a 2—6; log $A > 11$).

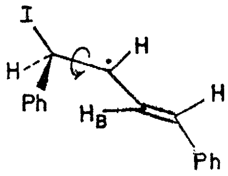
The activation energy for the addition of an iodine atom to (IV) is *ca.* 2 kcal mol^{-1} larger than the corresponding value for (II). Both reactions lead to a cinnamyl type radical [(1) and (2), respectively] but the resonance energy of (1) is 2 kcal mol^{-1} larger due to the presence of an additional styrene group. The difference between the resonance energies of the starting compounds (IV) and (II) is not exactly known but will certainly be much larger. It can be estimated at 6—8 kcal mol^{-1}.* The addition of an iodine atom to (IV) will then be 4—6 kcal mol^{-1} less endothermic than that of addition to (II). The transition state will be reached at a later stage in the former case and the activation energy will, indeed, be higher. On the other hand, the activation energy for the reverse reaction, *i.e.* the decomposition of the intermediate radical into the starting compound and an iodine atom, will be 2—4 kcal mol^{-1} larger for (II) than for (IV); assuming that the frequency factors are about equal in both reactions, $(k_{-1})_{(II)}$ will be smaller than $(k_{-1})_{(IV)}$.



Arrhenius plots for the isomerisation of *cis,trans,trans*-1,6-diphenylhexa-1,3,5-triene (a, in n-hexane and b, in carbon tetrachloride)



(1)



(2)

It is known that $(k_{-1})_{(II)}$ is about equal to the rate constant of the rotation step, $(k_2)_{(II)}$, because the isomerisation of (II) is a multiple rate-determining process. For (IV), however, k_{-1} is smaller than k_2. It may thus be concluded that $(k_2)_{(II)} \ll (k_2)_{(IV)}$. This rather

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* The resonance energy of (II) was estimated at 6—8 kcal mol^{-1} in the preceding paper. Using similar reasoning here, the difference in resonance energy between the coplanar compound (IV) and *trans*-stilbene will be about equal to that between a compound such as cycloheptatriene and buta-1,3-diene (6.7 kcal mol^{-1}, see ref. 3, p. 79). The resonance energy should then be *ca.* 14 kcal mol^{-1}.

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

[8] H. G. Curme and G. K. Rollefson, *J. Amer. Chem. Soc.*, 1952, **74**, 3766.

large difference between these rotation rate constants can be ascribed to the occurrence of much less steric strain in the intermediate radical (1) than in (2).

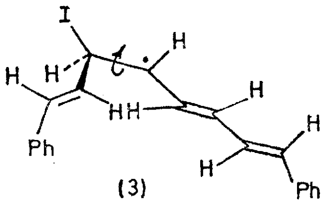
The addition of an iodine atom to (V) is more exothermic than that to (IV); the activation energy is 1.7 kcal mol^{-1} lower. This difference and the corresponding increase in the isomerisation rate constant can certainly be ascribed to the formation of a pentadienyl type radical (3) from (V) instead of a cinnamyl type radical (4). The extension of conjugation from (IV) to (V) will cause a larger increase in resonance energy in the intermediate radical than in the starting compound itself, as was also found in going from *cis*-stilbene to *cis,trans*-diphenylbutadiene. Rotation in (3), possible without much steric strain, will certainly be very fast.

TABLE 3

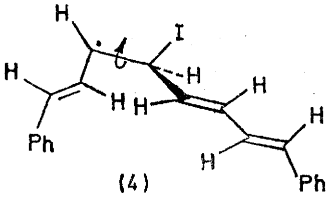
Activation parameters and relative rate constants for isomerisations of olefins, catalysed by thermally or photochemically generated iodine atoms

Compound	Method	Solvent	log (A/ l mol^{-1} s^{-1})	E_a/ kcal mol^{-1}	$k_{rel.}$ at 25°	Rate determining step	Ref.
cis-But-2-ene	Δ		8.5	9.4	3.6×10^{-4}	Rotation	6
trans-1,2-Di-iodoethylene [a]	Δ		8.85	11.0	5.2×10^{-5}	Rotation	*b*
Methyl *cis*-cinnamate	Δ	CCl_4	7.5	5.0	6×10^{-2}	Rotation	*c*
3,3′,5,5′-Tetramethyl-*cis*-stilbene	*hν*	Hexane	7.76	3.7	1	Rotation	1
cis,trans-Diphenylbutadiene (II)	*hν*	Hexane	6.6	−2.7	6.8×10^{-2}	Rotation + addition	1
			9.3	1.5			
(III)	*hν*	Hexane, > −15°	9.9 (±0·3)	0.3 (±0.3)	4.4×10^{-4}	Addition	
		Hexane, < −15°	11.8 (±0.6)	2.62 (±0.73)		Diffusion controlled	
		CCl_4	13.4 (±1.3)	5.32 (±1.62)		Diffusion controlled	
(IV)	*hν*	Hexane	8.9 (±0.1)	3.53 (±0.17)			
			9.1 (±0.1)	3.82 (±0.19)			
			Mean 9.0	Mean 3.68	1.7×10	Addition	
(V)	*hν*	Hexane	9.5 (±0.1)	1.96 (±0.15)	9.8×10^{2}	Addition	

[a] *trans–cis*-Isomerisation. [b] D. M. Golden, S. Furuyama, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 57. [c] A. J. G. van Rossum, W. J. Muizebelt, and R. J. F. Nivard, *J. Chem. Soc.* (*B*), 1970, 733.



(3)



(4)

The isomerisation of (III) also proceeds *via* a highly stabilized phenylpentadienyl radical. In this case it arises from a non-planar starting compound in which crowding is similar to that in (II). In consequence, a very low activation energy and a very fast isomerisation rate may be expected, as is indeed found.

Summarising, it appears that the differences in the isomerisation rate constants for compounds (II)—(V) are mainly determined by differences between the activation energies.

The log A factors for these reactions are not identical, but the differences between them are rather small. As a general trend in the whole series a slight increase of the collision factor with decreasing activation energy may be observed. In the addition step the entropy is reduced by the reduction of the number of species and by stiffening of bonds due to increasing resonance stabilisation during the formation of the intermediate radicals. The latter effect is stronger when the transition state is reached at a later stage. On the basis of Hammond's postulate the transition state will be more similar to the final state when the addition step is less exothermic or when the activation energy is higher.

In rotation-controlled isomerisations, the log A factors for various compounds are much more variable. The highest values are found when the intermediate radical is least stabilised (*cis*-butene, di-iodoethylene) and this trend causes log A to be higher for the isomerisation of *cis*-stilbene (*via* a benzyl radical) than for (II) (*via* a cinnamyl radical).

Finally, it may be noted that the ratio $k_{(III)} : k_{(II)}$ (non-planar compounds) is about equal to $k_{(V)} : k_{(IV)}$ (planar compounds), namely *ca.* 60 at 25°. The ratio represents the increase in the rate constant in consequence of the introduction of an additional *trans*-substituted double bond, which extends the conjugation in the parent compound and in the intermediate radical in precisely the same way.

Addition of a double bond at the other side of the polyene chain (which does not lead to variation of the type of intermediate radical) reduces the rate constant *ca.* 40-fold ($k_{(II)} : k_{(IV)} \simeq k_{(III)} : k_{(V)} \simeq 40$ at 25°).

[4/2304 *Received, 6th November*, 1974]