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Mechanism of the Electrophilic Iodination of 1,3-Diarylallenes

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Kinetic data are given for the addition of iodine to 12 substituted 1,3-diphenylallenes in 1,2-dichloroethane as solvent. A linear Hammett plot, based on σ^+ values, is found for diphenylallenes substituted in one ring, providing a p value of -3.2 at 5°. This has been taken as evidence that the transition state resembles a planar 1,3-diphenylallyl cation. The conclusion is supported by the observation that the addition is accompanied by racemisation, and that racemisation and addition rate constants are equal at the same temperature. The p value for the iodination of 1 - phenyl-3-(p-tolyl)allenes, substituted in the phenyl ring is only -2.3 at 5°. The diminished influence of substituents in this series is ascribed to the alteration of the charge distribution in the transition state by the fixed p-methyl substituent in the other ring.

DETERMINATION of the structure and configuration of addition products of allenes has revealed that the intermediate in these reactions has a variable character. The stereospecific *trans*-additions found in the halogenation and methoxymercuriation of (-)-1,3-dimethylallene¹ and in the bromination of (+)-cyclonona-1,2diene² point to dissymmetric bridged carbonium ions (1) as reaction intermediates. The optical purity of the reaction products from the iodination of 1,3-dimethylallene³ and from the ethoxymercuriation of (-)-cyclonona-1,2-diene⁴ appeared to depend, however, on the nature of the electrophile used. This suggests that symmetric allyl carbonium ions (3) are also involved in these reactions.

We have investigated the iodination of a series of ¹ W. L. Waters, W. S. Linn, and M. C. Caserio, J. Amer. Chem. Soc., 1968, **90**, 6741. ² L. R. Byrd and M. C. Caserio, J. Amer. Chem. Soc., 1971, **93**,

² L. R. Byrd and M. C. Caserio, J. Amer. Chem. Soc., 1971, 93, 5758.

substituted 1,3-diphenylallenes by kinetic methods since the study of substituent effects on the addition rate

)c=c=c(



state involved. In additions occurring *via* a transition ³ M. C. Findlay, W. L. Waters, and M. C. Caserio, *J. Org. Chem.*, 1971, 36, 275.

⁴ R. D. Bach, J. Amer. Chem. Soc., 1969, 91, 1771.

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state which resembles the dissymmetric structures (4) or (5) the transition state should be different for 1,3diphenylallenes with electron-donating and -withdrawing substituents (S), viz. (4A) or (5A), and (4B) or (5B), respectively. The free energy relationship, $\log k$ versus σ^+ , will then be curved, as observed for the bromination of monosubstituted trans-stilbenes⁵ and the acidcatalysed isomerisation of cis-stilbenes.⁶ When iodination proceeds, however, via a symmetric transition state resembling (6), a linear Hammett plot should be found.

EXPERIMENTAL

Materials.---1,3-Diphenylallenes were obtained via prototropic rearrangements of 1,3-diphenylpropynes.7,8 The in tightly stoppered flasks at -25° since they discolour ¹¹ at room temperature on exposure to air.

Most benzyl bromides were obtained according to standard procedures.¹² p-Trifluoromethylbenzyl bromide was prepared from p-trifluoromethylphenylmagnesium bromide by treatment with carbon dioxide, reduction of the resulting acid with lithium aluminum hydride, and reaction of the alcohol with phosphorus bromide.13

For the rearrangement of the propynes into the corresponding allenes a 1,3-diarylpropyne (2 g) was dissolved in a few ml of benzene, and the solution was poured onto a column (diameter 3 cm), filled with normal alumina (10 cm) and basic alumina 7 (7 cm). A red band appeared immediately at the top of the column. On elution with light petroleum (b.p. 40-60°) the allene was washed out with the



required propynes were synthesized by the coupling of phenyl- or p-tolyl-ethynylmagnesium bromide 9 with a suitably substituted benzyl bromide in tetrahydrofuran as

TABLE 1

Physical constants of 1,3-diphenylpropynes, XCHCHC=CCH.Y

	Δ			
x	Y	B.p. (°C) [p/mmHg]	M.p. (°C)	Yield (%)
н	н	116-118 [0.1]	Oil	73
p-CH,	н	134—138 [0.5]	Oil	55
₽-C1	н	140 - 142 [0.7]	Oil	55
<i>.</i> <i>φ</i> -F	\mathbf{H}	125 - 132 [0.4 - 0.6]	Oil	60
β-C ₁₀ H,	н	160-166 [0.3]	64 - 65	27
φ-CF	н	134 - 136 [1.0]	Oil	55
m-Cl	\mathbf{H}	132 - 136 [0.3]	Oil	46
$m, m-Cl_2$	\mathbf{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	p-CH ₃	138 [0.6]	48 - 50	56
m,m-Cl,	p-CH ₃	170 - 172 [0.4 - 0.5]	Oil	45

solvent, in the presence of copper(I) chloride. The procedure used 10 gave the diphenylpropynes as oils or low melting solids in good yields (Table 1). They were stored

⁵ M. F. Ruasse and J. E. Dubois, Tetrahedron Letters, 1970, 1163; J. Org. Chem., 1972, 37, 1770.
 ⁶ D. S. Noyce, D. R. Hartter, and F. B. Miles, J. Amer. Chem.

Soc., 1968, **90**, 4633. ⁷ T. L. Jacobs and D. Dankner, J. Org. Chem., 1957, **22**, 1424.

first 200 ml of the eluate. It was isolated by evaporation of the solvent in vacuo at room temperature as a light yellow oil which could be crystallized in most cases from hexane, yielding 50-60% of a pure product (Table 2). The lower melting allenes undergo ready dimerisation and oxidation in air. Therefore, all operations were carried out as fast as possible and the products (oils dissolved in hexane) were stored at -25° in tightly stoppered flasks. Under these conditions they remained pure for several months.

A sample of partially resolved 1,3-diphenylallene, having $\left[\alpha\right]_{D}^{27}$ -50° (c 0.5, CHCl₃) was obtained as described by Caserio.1

Kinetic Measurements.—All measurements were carried out in 1,2-dichloroethane [Baker; dried (CaCl₂) and distilled] between 20 and -35° . Under these conditions homolytic iodination, which occurred in less polar solvents such as hexane or carbon tetrachloride, may be neglected, as may the iodine-catalysed dimerisation of diphenylallenes. The electrophilic iodination proved to be first

⁸ T. L. Jacobs and S. Singer, J. Org. Chem., 1952, 17, 475.
⁹ A. D. Allen and C. D. Cook, Canad. J. Chem., 1963, 41, 1084.
¹⁰ H. Taniguchi, I. M. Mathai, and S. I. Miller, Org. Synth.,

1970, 50, 97. ¹¹ J. R. Johnson, T. L. Jacobs, and A. M. Schwartz, J. Amer.

Chem. Soc., 1938, 60, 1885. ¹² A. I. Vogel, 'Practical Organic Chemistry,' Longmans,

Green and Co., London, 1957, p. 701. ¹³ J. D. Turner and C. K. Bradsher, J. Org. Chem., 1967, **32**,

1163.

order in the allene (A) and second order in iodine, and leads to equilibrium (1). Since the equilibrium is on the side of

$$\mathbf{A} + 2\mathbf{I}_2 \xrightarrow[k_{-1}]{k_1} \mathbf{A}\mathbf{I}_2 + \mathbf{I}_2 \tag{1}$$

the products, determination of rate constants can be done using the simple rate equation (2) when a large excess of

$$-d[I_2]/dt = k[A][I_2]^2$$
(2)

A is used. For several compounds, which react very fast, this is not possible, however, and the reverse reaction has to be taken into account. Therefore, k values were

diphenylallenes. A rough estimation of the complexation constant revealed that only a small percentage of the iodine is bound in this way. The small difference between the optical densities of the reaction mixture at zero time and a comparable iodine solution was in agreement with this estimate.

RESULTS

On the whole the precision of the measured rate constants (k),* expressed in l² mol⁻² min⁻¹, was quite satisfactory. The lower accuracy, found for very slow reactions may be due to slight variations of temperature during the long

TABLE 2

Physical and chemical data of substituted 1,3-diphenylallenes, XC₆H₄C=C=CC₆H₄Y

		λ_{max} (EtOH)/nm		C (%)		H (%)	
X	Y	(10 ⁻³ ε)	M.p. (°C)	Found	Calc.	Found	Ćalc.
Н	H a	255 (43.0)	53.5 - 55	93.3	93.7	6.3	6.3
p-CH ₃	н	256(41.3)	51.0 - 52.5	93.0	93.1	6.9	6.9
p-C1	н	259 (47.6)	54.0 - 55.5	79.4	79.45	4.9	4.9
p-F	Н	253 (41.6)	43.0 - 44.0	85.6	85.7	5.3	5.25
β-C ₁₀ H ₇	н	258 (81.5)	91.5 - 92.5	93.4	94.2	5.7	5.8
p-CF3	н	258(40.4)	54-55	73.6	73.85	4.1	4.25
m-Cl	н	256 (36.0)	Oil	76.8	79.45	4.8	4.9
$m,m-Cl_2$	н	258 (32.6)	Oil	66.1	68.45	4.2	4.6
p-CH ₃	<i>p</i> -CH₃	259 (45.5)	75.5 - 77.5	92.3	92.7	7.4	7.3
p-Br	p-CH ₃	265 (48.3)	8990	67.5	67.4	4.8	4.6
p-CF ₃	p-CH ₃	261 (43.8)	60 - 61	74.1	74.45	4.7	4.8
$m, m-Cl_2$	p-CH₃	261 (35.3)	Oil	69.3	69.85	4.7	4.4

^a Ref. 7 gives λ_{max} . 255 nm (ε 52.2 \times 10³), m.p. 49–51°.

derived from expression (3), which transforms into equation (4) with $K_e = k_1/k_{-1}$; $[A] = [A]_0 - [I_2]_0 + [I_2]$; and $[AI_2] = [I_2]_0 - [I_2]$.

$$-d[I_2]/dt = k_1[A][I_2]^2 - k_{-1}[AI_2][I_2]$$
(3)

$$-d[I_2]/dt = k_1[I_2]\{[I_2]^2 + ([A]_0 - [I_2]_0 + 1/K_e)[I_2] - [I_2]_0/K_e\}$$
(4)

A photometer cuvette (1 cm), equipped with a side-arm and placed in a chamber 14 with optically flat windows which fitted into a Cary 1 spectrophotometer, was used as the reaction vessel. Allene solution (2 ml) was placed in the cuvette and iodine solution (1 ml) (Merck) in the sidearm. The vessel was brought to the desired temperature with a Cryoson apparatus, and the extinction of the allene solution was measured. The reactants were mixed in the dark and iodine concentrations were determined at intervals by measurement of the extinction at 500 nm against a blank solution and comparison with a standard solution at the same temperature. Most reactions were followed between 15 and 80% conversion; very fast reactions were measured from ca. 50% conversion. The $K_{\rm e}$ values required for the calculation of k were estimated by following the reaction until the optical density became constant. It should be noted that a K_e value thus obtained is presumably not the value of a single reaction since cis- and trans-addition products may be formed, and from unsymmetrically substituted diphenylallenes products with a different substitution pattern may also arise.

The iodine concentrations were not corrected for formation of charge-transfer complexes between iodine and reaction times. For very fast reactions the precision was lower because slow removal of iodine as a consequence of dimerisation of the allene restricted the exact determination of $K_{\rm e}$ values.

By plotting log k values for any compound against 1/T, Arrhenius parameters (log A and E_a) were determined (Table 3). Plots of log A as well as E_a against log k at an

TABLE 3

Frequency factors [log $(A/l^2 \text{ mol}^{-2} \text{ min}^{-1})$] and activation energies $(E_a/\text{kcal mol}^{-1})$ for the iodination of 1,3-diphenylallenes, $XC_6H_4C=C=CC_6H_4Y$

		log	log	\log			
X	Y	A_{\min}	\check{A}	$A_{\rm max.}$	$E_{\mathbf{a}, \min}$	$E_{\mathbf{a}}$	$E_{a, max}$
Н	н	5.39	6.12	6.84	1.72	2.58	3.44
β-C ₁₀ H ₇	\mathbf{H}	4.09	4.70	5.30	-0.64	0.11	0.85
p-F	\mathbf{H}	5.82	6.28	6.73	2.28	2.82	3.38
p-Cl	\mathbf{H}	4.06	4.93	5.80	0.61	1.72	2.28
m-Cl	\mathbf{H}	4.83	5.42	6.00	2.57	3.26	3.96
p-CF ₃	\mathbf{H}	2.54	4.66	6.80	0.58	3.08	5.58
$m, m-Cl_2$	н	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-Čl,	p-CH	4.23	4.63	5.04	1.25	1.72	2.19

arbitrary temperature (5°) show that the influence of substituents on the k values can only be ascribed to variation of the activation energy.

The addition rate constants could not be well correlated for the whole series with the sum of σ^+ or σ values of the substituents. Graphs of log k against σ^+ for compounds in which the substitution pattern is varied in only one of the

¹⁴ A. J. G. van Rossum, A. H. M. de Bruin, and R. J. F. Nivard, *J.C.S. Perkin II*, 1975, 1036.

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^{*} The numerical data, together with 95% confidence limits are presented in Supplementary Publication No. SUP 21796 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

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aromatic rings give, however, good linear correlations (Figures 1 and 2). From these and similar plots from measurements at -20° the ρ values given in Table 4 were determined.



0·0

0.4

TABLE 4

 ρ -Values for the iodination of 1,3-diphenylallenes, C₆H₅-C=C=CC₆H₄X (A) and 1-phenyl-3-(p-tolyl)allenes, p- $CH_3C_6H_4C=C=CC_6H_4X$ (B)

	T (%C)	•			Correlation
	I(0)	Pmin.	P	Pmax.	coemcient
Α	5.0	-2.93	-3.18	-3.44	-0.998
Α	-20.0	-3.19	-3.54	-3.89	-0.996
в	5.0	-1.95	-2.26	-2.57	-0.997
в	-20.0	-1.98	-2.39	-2.79	-0.996

Stereospecificity of the Iodination Reaction .--- Preliminary experiments with a partially resolved sample of 1,3-di-

 J. A. Pincock and K. Yates, Canad. J. Chem., 1970, 48, 2944.
 R. E. Buckless, J. L. Miller, and R. J. Thurmaier, J. Org. Chem., 1967, 32, 888.

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phenylallene revealed that the optical activity of the reaction mixture from the iodine addition gradually vanished. This points to the involvement of a symmetrical transition state (3). The racemisation rate constant (k_r) was measured by following the change of the optical rotation (α) after the mixture had reached equilibrium. In this way complex kinetics are avoided; the integrated rate equation is (5).

$$\ln \alpha_0 / \alpha = k_{\rm r} [{\rm I}_2]_{\rm e}^2 t \tag{5}$$

Measurements were performed with a JASCO spectropolarimeter (ORD/DC/UV-5) at 355 nm, at which wavelength iodine absorption is very low. The results of three experiments at 11° are given in Table 5. The equilibrium

TABLE 5 Racemisation rate constant (k_r) at 11° $10^{3}[I_{2}]_{0}/M$ 10³[A]₀/M $10^{4}[I_{2}]_{e}/M$ $10^{4}k_{r}$ 16.48 4.28 $\frac{4.35}{7.3}$ 1.85.51 14.131.311.83 5.519.1 1.6

concentration of iodine $[I_2]_e$ was calculated from the K_e value $(7.1 \times 10^2 \text{ l mol}^{-1})$ at this temperature.

DISCUSSION

The third-order kinetic form for the addition of iodine to diphenylallenes is quite common for halogen additions to unsaturated systems in solvents of moderate polarity.¹⁵⁻¹⁷ It is consistent with a polar mechanism as outlined in the Scheme. It is generally accepted 18

$$A + I_{2} \xrightarrow{} A, I_{2}$$

$$A, I_{2} + I_{2} \xrightarrow{} AI^{+}, I_{3}^{-}$$

$$AI^{+}, I_{3}^{-} \xrightarrow{} AI^{+} + I_{3}^{-}$$

$$AI^{+} + I_{3}^{-} \xrightarrow{} AI_{2} + I_{2}$$

$$SCHEME$$

that the formation of the ion-pair in the second step is rate determining. Thus the observed rate constant (k)equals $K_{c}k'$, where K_{c} and k' represent the complexation constant of A,I_2 and the rate constant of the formation of the ion-pair, respectively. The second iodine molecule is involved in the dispersion of negative charge. The unfavourable nature of the termolecular transition state is reflected in the high negative value of the activation entropy (ca. -46 cal mol⁻¹ K⁻¹) which can be derived from the mean value of the frequency factors (log A ca. 5.3; Table 3).

The linear Hammett plots, found over a wide range of σ^+ values for the iodination of monosubstituted 1,3-diphenylallenes as well as 1-phenyl-3-(p-tolyl)allenes (Figures 1 and 2, Table 4), indicate that the transition state is very similar to the planar diphenylallyl cation (6). Therefore, iodination is accompanied by racemisation. The equal values for the racemisation rate

istry,' Holt, Rinehart, and Winston, New York, 1962, p. 524.



FIGURE 1 Hammett plot for the iodination at 5° of 1,3-diphenylallenes, substituted in one ring

-Br

-CF3

0.8

mm-Cl₂

- CH3

6.0

5:0^{-,} 5:00 boj

4.0

3.0

- 0.4

¹⁷ P. B. D. de la Mare, ' Electrophilic Additions to Unsaturated Systems,' Elsevier, Amsterdam, 1966, p. 128. ¹⁸ E. S. Gould, 'Mechanism and Structure in Organic Chem-

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constant and the addition rate constant $(1.55 \times 10^4 \text{ and})$ 1.41×10^4 l² mol⁻² min⁻¹, respectively, at 11°) are in agreement with a symmetrical intermediate formed in a rate-determining step common to both reactions.

The variation in the character of the transition state in going from the stereospecific trans-additions to dialkylallenes 1,3 to the non-stereospecific iodination of diarylallenes via symmetrical intermediates is guite similar to that found for additions to olefins. Halogenation of dialkylolefins proceeds as a stereospecific trans-addition, ascribed to the occurrence of bridged halogenonium ions as intermediates.¹⁹⁻²¹ Halogen additions to mono-^{19,21} and di-arylolefins²² are non-stereospecific and proceed apparently via open α -phenyl carbonium ions.

The effects of substituents in the different rings of 1,3-diphenylallene are not simply additive. A similar observation has previously been made for the bromination of substituted 1,1-diphenylethylenes.²³ To explain this result it is supposed that introduction of a substituent (Y) in one aryl residue varies the charge distribution in the transition state and by that the effective charge with which substituents (X) in the other ring interact. Introduction of an electron-donating group (Y) (e.g. p-Me) will lower the effective charge in electrophilic iodination, and consequently reduce the ρ value for variations of X (Table 4). A comparison of the variation of ρ with the σ^+ value of Y ($\Delta \rho / \Delta \sigma^+ = -2.95$) with $\Delta \rho / \Delta \sigma^+$ in two other reactions to which the multiple p treatment has been applied, viz. the bromination of 1,1-diphenylethylenes 23 (-1.54) and the solvolysis of diphenylmethyl chlorides 23 (-1.68), shows that Y has a much larger influence in the iodine addition to diphenylallenes. This is understandable since Y does not only alter the effective charge in the reaction centre as in diphenylethylenes and diphenylmethyl chlorides but also the charge distribution in the allyl cation. A similar situation has been observed in the solvolysis of *p*-nitrobenzoates of substituted chalcols.²⁴

The *p* value of the iodination of monosubstituted diphenylallenes (ca. -3.0 at 25°) is lower than for re-

¹⁹ R. C. Fahey and C. Schubert. J. Amer. Chem. Soc., 1965, 87, 5172.

²⁰ R. C. Fahey, J. Amer. Chem. Soc., 1966, 88, 4681.
 ²¹ J. H. Rolston and K. Yates, J. Amer. Chem. Soc., 1969, 91, 1469, 1477, 1483.

 J. A. Pincock and K. Yates, *Canad. J. Chem.*, 1970, 48, 3332.
 A. F. Hegarty, J. S. Loman, W. V. Wright, E. D. Bergmann, and J. E. Dubois, J. Org. Chem., 1972, 37, 2222.

actions via open benzyl cations ($\rho -4$ to -5). This must be due to charge dispersion over the allylic system. A similar reduction of p values has also been observed for reactions via carbonium ions in which conjugation was progressively extended by one, two, or three phenyl rings.25

A transition state resembling a diphenylallyl cation can assume three different conformations (6a-c).



Structure (6a) is unlikely since the opposing phenyl rings prevent coplanarity and this lowers the resonance stabilisation. The same conclusion can be drawn from the application of Yukawa and Tsuno's modification²⁶ of the Hammett relation [equation (6)] in which R is a

$$\log k/k_0 = \rho_{meta}(\sigma^0 + R\Delta\sigma^+) \tag{6}$$

resonance transmission coefficient and $\Delta \sigma^+ (= \sigma^+ - \sigma^0)$ a measure of the resonance contribution of the substituent. From Figures 1 and 2 it appears that even the compounds with the largest $\Delta \sigma^+$ values (p-fluoro- and p-chloro-derivatives) hardly deviate from the linear plots. So R will be close to unity, which points to a planar cation intermediate. Although Stuart models indicate slightly less steric hindrance in planar (6b) than in (6c) a preference for one of these conformations cannot be established from the kinetic data. Structure (6c) for the allylic cation is, however, unlikely since this would only be produced by attack of iodine from the side *cis* to phenyl in the starting allene.

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Japan, 1966, 39, 2274.