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## Nucleophilic Substitution by Thiolate lons in Some 1,1-Diaryl-2-Halogenoethylenes

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Six 1,1-diaryl-2-arylthioethylenes were obtained by displacement of chloride or bromide ion from diaryl-halogenoethylenes by aryl thiolate ions in amidic solvents.

The reaction of compounds (p-R-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C:CHCl (R = H, Me, and OMe) with sodium toluene-p-thiolate in dimethylformamide was studied kinetically in the range 30-90°. The order of reactivity is H > Me > OMe, with a high value of the Hammett p constant. The reaction appears a case of direct nucleophilic substitution at a nonactivated vinylic carbon atom.

As first noted by Fritsch et al.,1 when 1,1-diphenyl-2chloroethylene and 2-bromo-ethylene and their methyl or methoxy ring-substituted derivatives react with a basic nucleophile, such as ethoxide ion in ethanol, they usually give, in competition with nucleophilic substitution or instead of it, a-elimination with rearrangement. Replacement of the  $\alpha$ -hydrogen with a methyl group fails to lead to a clean nucleophilic substitution because of  $\beta$ -elimination; <sup>2,3</sup> this is overcome, however, by p-nitro-substitution in the aromatic rings,<sup>4</sup> or replacement of chlorine and bromine by fluorine.<sup>5</sup>

Another possible method is the use of less basic nucleophiles, such as chloride ion; <sup>6</sup> in this connection thiolate ions also appear to be suitable reagents. Benzenethiolate and toluenethiolate were chosen for reactions with compounds (I)--(III), the expected products being compounds (IV)-(VI).

$$\begin{array}{ccc} p \cdot R \cdot C_{\mathfrak{g}} H_{\mathfrak{q}} \\ p \cdot R \cdot C_{\mathfrak{g}} H_{\mathfrak{q}} \end{array} \xrightarrow{} C = C \\ X \\ (II) R = Me \\ (III) R = OMe \\ (III) R = OMe \\ (IV) R = H \\ (V) R = Me \\ (V) R = Me \\ (V) R = OMe \\ (V)$$

The choice of the solvent proved a critical factor in order to obtain good yields in reactions carried out on a preparative scale and to obtain reproducible results in kinetic runs. Ethanol was unreliable and amidic sol-

vents, already employed for similar reactions with thiolate ions,<sup>7</sup> were finally chosen.

## EXPERIMENTAL

Materials .--- NN-Dimethylformamide was dried on 4A molecular sieves at flow rates around 40 ml./hr., collected under nitrogen and distilled under reduced pressure. Its density was measured as a function of temperature by a ca. 10 ml. pyknometer, calibrated with air-free distilled water:  $d (g./cm.^3) = 0.9442 (25^\circ), 0.9397 (30^\circ), 0.9349$ (35°), 0.9299 (40°), 0.9250 (45°), and 0.9199 (50°). These values fit the equation d = 0.9688 - 0.000974 t (°c).

Ultraviolet spectra were recorded on a Beckmann DK-2A spectrophotometer. Results are given in Table 1. Nuclear magnetic resonance spectra were scanned on a Perkin-Elmer R-10 apparatus (60 Mc./sec.), using tetramethylsilane as reference; solutions in deuteriated chloroform of concentration less than 5 mole %, where employed.

Gas-chromatographic analyses were effected on a flame ionisation apparatus, using a 2-m. column of 5% Silicone SE-30 on Chromosorb W.

Thiophenol was a commercial product (B.D.H.), distilled under nitrogen; it was used only when perfectly clear. Toluene-p-thiol, prepared from toluene-p-sulphonyl chloride, was treated with sodium in toluene; <sup>8</sup> sodium toluene-pthiolate was filtered off, dried, and kept in vacuo over phosphorous pentoxide.

<sup>4</sup> P. Beltrame, P. L. Beltrame, O. Sighinolfi, and M. Simonetta, preceding Paper. <sup>5</sup> E. Silversmith and D. Smith, J. Org. Chem., 1958, 23, 427.

<sup>6</sup> P. Beltrame, I. R. Bellobono, and A. Feré, J. Chem. Soc. (B), 1966, 1165.

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<sup>&</sup>lt;sup>1</sup> P. Fritsch, W. P. Buttenberg, and H. Wiechell, Annalen, 1894, 279, 319, 324, 337.
<sup>2</sup> P. Beltrame, S. Carrà, P. Macchi, and M. Simonetta, J.

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2-Chloro-1, 1-diphenylethylene (Ia), 2-bromo-1, 1-diphenylethylene (Ib), 2-chloro- and 2-bromo-1, 1-di-(p-tolyl)ethylene [(IIa) and (IIb), respectively], and 2-chloro- and 2-bromo-1,1-di-(p-methoxyphenyl)ethylene [(IIIa) and (IIIb). respectively] were prepared as previously.9,10 Nuclear spectra of chloro-derivatives: magnetic resonance (Ia)  $\tau 2.5-2.8m$  (10H), 3.34s (1H); (IIa)  $\tau 2.35-3.2m$ (8H), 3.44s (1H), 7.61s (3H), and 7.66s (3H); (IIIa)  $\tau 2.5$ — 3.25m (8H), 3.51s (1H), 6.16s (3H), and 6.19s (3H).

1,1-Diphenyl-2-(phenylthio)ethylene (IVc).-The bromoethylene (Ib) (10.5 mmoles) was added to potassium benzenethiolate (13.0 mmoles) in NN-dimethylacetamide (25 ml.) at 150°, and then heated under reflux for 4 hr. The mixture was filtered and the solution evaporated to give an oil from which crystals were obtained (6.8 mmoles), m. p. 72-73° (from methanol) (Found: C, 83.55; H, 5.8; S, 10.8. C20H16S requires C, 83.3; H, 5.6; S, 11.1%); n.m.r. peaks at  $\tau 2.4$ —2.8m (15H) and 3.09s (1H). The same compound was also obtained from (Ia) and sodium benzenethiolate in ethanol in a sealed tube at  $90^{\circ}$  (68 hr.).

1,1-Diphenyl-2-(p-tolylthio)ethylene (IVd).-This was prepared from (Ia) in dimethylformamide, at 80° for 160 hr. (under the conditions employed for kinetic runs); the solvent was evaporated off and water and ether were added. The ether layer was separated and the solvent was removed. The product was obtained as crystals (from ethanol), m. p. 85° (Found: C, 83.65; H, 6.2; S, 10.25. C21H18S requires C, 83.4; H, 6.0; S, 10.6%); n.m.r. spectrum: 7 2.4-2.9m (14H), 3.11s (1H), and 7.64s (3H). The compound (200 mg.) was ozonised at room temperature in chloroform; the solution was washed with aqueous sodium hydrogen carbonate, the solvent was evaporated off, methanol was added, and a 2,4-dinitrophenylhydrazone was prepared (225 mg.; 94% yield), m. p. 236° (benzophenone 2,4-dinitrophenylhydrazone has m. p. 238-239° 11).

1,1-Di-(p-tolyl)-2-(phenylthio)ethylene (Vc).-This was prepared from (IIa) (10.3 mmoles) and potassium benzenethiolate in NN-dimethylacetamide, as described for (IVc). The product (9.5 mmoles) had m. p. 69° (from methanol) (Found: C, 83.7; H, 6.45. C22H20S requires C, 83.5; H, 6.35%). Ozonisation was effected as for (IVd) and a 2,4dinitrophenylhydrazone was obtained in 64% yield, m. p. 218-219° (from acetic acid), as indicated <sup>11</sup> for the derivative of di-*p*-tolyl ketone.

1,1-Di-(p-tolyl)-2-(p-tolylthio)ethylene (Vd).-This was prepared from (IIa) by the method described for (IVd). The product had m. p. 125° (from ethanol) (Found: C, 83.75; H, 6.85; S, 9.95. C<sub>23</sub>H<sub>22</sub>S requires C, 83.6; H, 6.7; S, 9.7%); n.m.r. spectrum  $\tau$  2.5-3.1m (12H), 3.22s (1H), 7.63s and 7.71s (3 + 6H).

1,1-Di-(p-methoxyphenyl)-2-(phenylthio)ethylene (VIc). This was prepared from (IIIb) (14.9 mmoles) in dimethylacetamide, as described for (IVc). The product, an oil, was purified by column chromatography on alumina (6% water) with elution by ethyl acetate-n-hexane (1:9);  $n_{\rm D}^{25}$  1.6645 (Found: C, 75.7; H, 5.85.  $C_{22}H_{20}O_2S$  requires C, 75.85; H, 5.8%). The product was shown to be pure by thin-layer chromatography [silica gel G; ethyl acetaten-hexane (1:4)].

1,1-Di-(p-methoxyphenyl)-2-(p-tolylthio)ethylene (VId).-This was prepared from (IIIa) by the method described for

<sup>10</sup> P. Beltrame and G. Favini, Gazzetta, 1963, 93, 757. **4** D

(IVd). Reactions conditions: 70° for 27 days. The compound, an oil, was purified by preparative g.l.c. on a 2 m. column of 20% Silicone SE-30 on Chromosorb W, column temperature 280°, evaporator 300°, carrier gas hydrogen;  $n_{\rm D}^{25} = 1.6658$  (Found: C, 76.85; H, 5.9; S, 8.7. C<sub>23</sub>H<sub>22</sub>O<sub>2</sub>S requires C, 76.2; H, 6.1; S, 8.85%), n.m.r. spectrum 7 2.5-3.2m (12H), 3.31s (1H), 6.13s (3H), 6.19s (3H), and 7.66s (3H).

Products (I)—(VI) were shown to be pure by gas-liquid chromatography (temperature 200-250°). Reaction mixtures, tested by g.l.c. at low conversions, showed reagents and main products with only traces of impurities.

1,2-Di-(p-tolyl)-2-(phenylthio)ethylene.—Thiophenol (2.62 mmoles) was added, under nitrogen, to a solution of di-ptolylacetylene (2.56 mmoles) and sodium ethoxide (2.56 mmoles) in ethanol (25 ml.). The reaction was heated in a sealed glass tube at 120° for 92 hr. and gave a precipitate, m. p. 114° (from ethanol) (0.66 mmoles) (Found: C, 83·25; H, 6·25. C<sub>22</sub>H<sub>20</sub>S requires C, 83·5; H, 6·35%),  $\lambda_{max}$  (n-hexane) 316, 301sh, 278, and 228sh (log  $\varepsilon$  4.22, 4.24, 4.30, 4.21) of unknown configuration. Starting material was recovered when the reaction was carried out at  $80^{\circ}$ for 10 or 84 hr.

Kinetics.—Weighed amounts of sodium toluenethiolate and diaryl-chloroethylene were separately dissolved in dimethylformamide and the thermostatted solutions were mixed, under nitrogen, in a stoppered 'Pyrex' vessel. The stream of nitrogen, saturated with solvent at the temperature of the run, was also employed during the withdrawal of kinetic samples. Circulation of thermostatted fluid into a jacket kept the reaction vessel at constant temperature  $\pm 0.1^{\circ}$ .

Samples for titrimetric analyses were quickly poured into an excess of 0.1m-iodate-iodide solution and acidified with hydrochloric acid; the excess of iodine was titrated with 0.1M-thiosulphate.12 Samples for spectrophotometric analyses were quenched by dilution with 'Spectrograde' methanol. Analyses were based on absorbance at  $310 \text{ m}\mu$ for compounds (IVd) and (Vd), and at 305 mµ for compound (VId). At 'infinite time ' the absorbance was  $98 \pm 7\%$  of the theoretical; theoretical values were used for rateconstant calculations.

For all reactions, most of which were followed up to 50%completion or more, results fitted the second-order rate equation. Initial concentrations were corrected, when required, for solvent expansion. Rate constants (k) were calculated by the graphical procedure, as slopes of linear regression lines obtained by the least-squares method. From the values of log k and 1/T, Arrhenius activation energies ( $\Delta E^{\ddagger}$ ) and frequency factors (Z) were similarly calculated. Activation entropies ( $\Delta S^{\ddagger}$ ) were derived from Z values. Probable errors were evaluated for these quantities.13

## RESULTS AND DISCUSSION

Displacement of halide ions in compounds (I)—(III) by benzenethiolate and toluenethiolate ions could have taken the route of  $\alpha$ -elimination, with rearrangement to

<sup>&</sup>lt;sup>8</sup> W. E. Truce and R. F. Heine, J. Amer. Chem. Soc., 1959, 81, 592.

<sup>&</sup>lt;sup>9</sup> P. Beltrame and S. Carrà, Gazzetta, 1961, 91, 889

<sup>&</sup>lt;sup>11</sup> M. Frankel and S. Patai, 'Tables for Identification of Organic Compounds,' Chemical Rubber Co., Cleveland, 1964,

 <sup>&</sup>lt;sup>12</sup> S. Siggia, 'Quantitative Organic Ana Groups,' Wiley, New York, 1954, p. 131.
 <sup>13</sup> R. T. Birge, *Phys. Rev.*, 1932, **40**, 207. Quantitative Organic Analysis via Functional

diaryl-acetylenes and subsequent addition of thiol. If this had occurred stilbenic isomers of the products of direct substitution would have been obtained. No diarylacetylenes were detected by gas-chromatographic analysis of samples taken during the course of the reactions whilst the following evidence shows that the products are 1,1-diaryl-ethylenic derivatives, *i.e.*, compounds (IV)--(VI).

Ultraviolet spectra of reaction products are strictly analogous to the spectra of the corresponding diarylhalogenoethylenes (I)-(III), as shown in Table 1.

TABLE 1

Ultraviolet spectra in methanol ( $\lambda_{max}$ in m $\mu$ ;	log ε
values in parenthesis)	

		-		
$\setminus X =$	Cl	Br	PhS	<i>p</i> -Me-C <sub>6</sub> H₄S
$R = \backslash$	[Ia]	[Ib] <sup>ø</sup>	[IVc]	[IVd]
Н	255 (4·14) 222 <sup>a</sup> (4·23)	259 (4·19)	310 (4·27) 268 <sup>a</sup> (4·03) 226 <sup>a</sup> (4·22)	309 (4·28) 265 <sup>a</sup> (4·07) 223 <sup>a</sup> (4·30)
	[IIa]°	[IIb]°	[Vc]	[Vd]
			310 (4.27)	310 (4.27)
Me	260 (4·18)	264 (4.17)		$270^{a}$ (4.07)
	<b>240 (4·30</b> )	240 (4.22)	235 (4.21)	234ª (4·23)
	[IIIa]	[IIIb]	[VIc]	[VId]
			<b>306</b> (4·30)	<b>305</b> (4·32)
OMe	265 <sup>a</sup> (4·29)	270 (4·29)	290 <sup>a</sup> (4·25)	290ª (4·27)
	250 (4.38)	$252 \ (4.34)$	256 (4.29)	$254^{a} (4 \cdot 35)$
	<sup>a</sup> Should	ler. <sup>b</sup> Ref. 9.	e Ref. 10.	

In almost all compounds listed, a couple of bands in the range 290–220 m $\mu$  may be noted; in every case, the shorter wavelength band has the higher intensity. Whatever the X group, both bands show a bathochromic shift when R is changed from H to Me and OMe.

Typically, 1,1-diaryl-ethylenic derivatives of this kind (Table 1) show at least one band in the range 275-230 mµ. The spectrum of 1,2-di-(p-tolyl)-2-(phenylthio)ethylene, the stilbenic sulphide that was prepared as a reference compound ( $\lambda_{max}$  316, 301sh, 278, and 228sh m $\mu$ ) has no maxima in that range. This feature is common to other stilbenic compounds, such as the cis- and transisomers of stilbene itself  $^{14}$  and of  $\alpha\text{-chlorostilbene.}^{15}$ 

In view of the spectroscopic analogies between the products, the ozonolysis of compounds (IVd) and (Vc) was considered sufficient for characterisation; benzophenone and di-p-tolyl ketone, respectively, were obtained in good yields.

Ultraviolet spectra of sulphides (IV)-(VI) show, besides bands typical of the diphenyl-vinyl system, intense absorption at 310-305 mµ. This is almost unaffected by substitution in the phenylthio-

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<sup>16</sup> C. C. Price and S. Oae, 'Sulfur Bonding,' Ronald Press, New York, 1962, ch. 2. <sup>17</sup> R. C. Passerini, 'Organic Sulphur Compounds,' eds. N.

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<sup>18</sup> F. Bergmann, S. Israelashvili, and D. Gottlieb, J. Chem.

Soc., 1952, 2523.
 <sup>19</sup> J. C. D. Brand and G. Eglinton, 'Applications of Spectroscopy to Organic Chemistry,' Oldbourne, London, 1965.

group or the diphenylethylene system. The sulphide linkage is known to allow only weak 'through conjugation ' in diaryl sulphides,<sup>16</sup> probably because of the steric inhibition of ring coplanarity; for instance, the absorption bands of diphenyl sulphide at 250 and 274 m $\mu$ can be assigned to separate benzenoid and sulphidebenzene chromophores, respectively.<sup>17</sup>

Similarly, in compounds (IV)-(VI) 'through conjugation,' if present, is weaker than for a compound where an ethylenic bond is substituted for the sulphur atom; 1,1,4-triphenylbutadiene has its first band at ca. 340 mµ (log  $\varepsilon$  ca. 4.6).<sup>18</sup>

In the n.m.r. spectra of the chloro- and the p-tolylthioderivatives, bands attributable to aromatic protons and alkyl hydrogen atoms adjacent to oxygen and to benzene ring showed the expected chemical shifts.<sup>19</sup> Vinylic protons gave signals as shown in Table 2, where an

TABLE 2

Chemical shifts ( $\tau$  values) of vinylic protons

X = X =	OMe	Me	н	$NO_2$	
Cl <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub> S	(IIIa) 3·51 (VId) 3·31	(IIa) 3·44 (Vd) 3·22	(Ia) 3·34 (IVd) 3·11	3.06*	
* Ref. 4.					

additional compound <sup>4</sup> is also considered for comparison.

Chemical shifts of vinylic protons are in the order expected for substituents in the phenyl rings. It is well known that in aryl derivatives, some degree of correlation can be found between chemical shifts and Hammett  $\sigma$ -constants.<sup>20</sup> For p-substituted benzenes. when chemical shifts  $(\delta, p.p.m.)$  of the proton at the para-position to the substituent are plotted against  $\sigma_p$ -values of the substituent, near straight lines are obtained; the slope of one such line, given by Diehl, is  $\rho' = 0.49$ ;<sup>21</sup> from the data of Bothner-By and Glick<sup>22</sup> and of Spiesecke and Schneider <sup>23</sup> we obtained  $\rho' = 0.70$ and 0.64 (p.p.m./ $\sigma$ ), respectively. For *p*-substituted phenylacetylenes a similar correlation <sup>24</sup> gave  $\rho' = 0.37$ p.p.m./ $\sigma$  for the acetylenic hydrogen. For  $\beta$ -aryl acrylic acids, chemical shifts of a-hydrogens from ten compounds were correlated; 25 in this series  $\rho'$  has the value 0.37 p.p.m./ $\sigma$ .

The corresponding least-squares straight line drawn through the points of our chloro-derivatives (Table 2) gives  $\rho' = 0.21$  p.p.m./ $\sigma$  (r = 0.992), when  $\sigma_p$ -values of the two substituents are assumed additive. The behaviour of compounds having  $X = p - Me - C_{g}H_{a}S$ seems similar. p-Substituents in the conjugated phenyl

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<sup>21</sup> P. Diehl, Helv. Chim. Acta, 1961, 44, 829.

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<sup>23</sup> H. Spiesecke and W. G. Schneider, J. Chem. Phys., 1961, **35**, 731.

<sup>24</sup> S. H. Marcus, W. F. Reynolds, and S. I. Miller, J. Org. Chem., 1966, 31, 1872.

<sup>25</sup> A. R. Katritzky and F. J. Swinbourne J. Chem Soc., 1965, 6707.

rings of our compounds appear to have a limited effect on the shielding of vinylic hydrogen nuclei, which is not only less than on the aromatic proton of benzene, but also markedly less than in aryl-acetylenes and in  $\beta$ aryl acrylic acids. Besides the weakening effect of the unsaturated side-chain on the transmittance of the substituent effects, the lack of coplanarity of the phenyl rings with the ethylenic system seems to play a role in the present case. The result is that the substituent effects are transmitted with a lower efficiency, corresponding to lower absolute  $\sigma$ -values, than in the simple aryl-ethylenic case. Furthermore, such modified ovalues can be different for identical p-substituents on the two phenyl rings; in fact the aromatic rings, cis and trans with respect to the halogen, are rotated by different angles around the bonds connecting them to the ethylenic carbons.26

Kinetic measurements were made on the reaction of the chloroethylenes (Ia), (IIa), and (IIIa) with toluenep-thiolate in dimethylformamide at various temperatures between 30 and 90°. Results fitted the second-order rate equation. Several reactions were followed both by titrimetric and spectrophotometric analysis. The resulting rate constants were reasonably close to each other,  $k_{\rm sp}$  values being on the average 8% lower than  $k_{\rm tit}$ values. They were eventually averaged. In some cases only one analytical method was employed.

Rate constants for the different reactions are given in Table 3; frequency factors, activation energies, and entropies are also shown. Differences existing between  $k_{\rm sp}$  and  $k_{\rm tit}$  values do not affect the values of the activation parameters beyond the indicated probable errors.

The reactivity order, as a function of the p, p'-substituents, is H,H > Me,Me > MeO,MeO. Although only three points are available, a Hammett correlation has been tried, using the principle of additivity of  $\sigma_p$ values. As pointed out above, effective  $\sigma$ -constants lower in absolute value than the ordinary ones, would have been necessary; as a consequence, the Hammett e-value that was obtained is actually an approximate lower limit of the reaction constant for this substitution. The resulting  $\rho$ -value is  $3.4 \pm 0.4$  at 50°. The  $\rho$ value for the ethoxide-ion substitution in ethanol, calculated on the same assumption of additive Hammett  $\sigma_p$ -values, was 3.38 at 120°.<sup>4</sup> Aromatic nucleophilic substitution of 4-substituted 2-nitro-chlorobenzenes by sodium benzenethiolate in 60% dioxan at 25° gave  $\rho = 4.5^{27}$  and for 5-substituted 2-nitrochlorobenzenes with sodium benzenethiolate in methanol at  $35^{\circ} \rho$  was 5.1.28 A rough analogy can be recognised, despite variations in several reaction conditions.

Lack of kinetic data in the same solvent system made a direct comparison of thiolate and ethoxide ions as nucleophiles in the reaction with 1.1-diaryl-2-chloroethylenes impossible. However, chloride ion has been tested as a nucleophile on compounds of this type in dimethylformamide; <sup>6</sup> kinetic results obtained for cisand trans-2-chloro-1-p-methoxyphenyl-1-phenylethylene can be assumed to be intermediate between the unknown reactivities of (Ia) and (IIIa) under these conditions. On the basis of such an hypothesis, and using Arrhenius parameters for extrapolation purposes, at 100° the rate constant ratio  $k_{\text{NaSC6H4Me}-p}/k_{\text{LiCl}}$  for nucleophilic displacement has a minimum value of  $1.4 \times 10^5$  and a maximum value of  $1.2 \times 10^7$ . This large factor is not surprising, considering that in typical  $S_{\rm N}$ Ar reactions, at 0° in dimethylformamide, thiolate ion has been found to be 3-5 orders of magnitude more reactive than azide ion, and the latter  $10^5$  times more reactive than bromide ion.29

Differences in reactivity of diarylchloroethylenes so far studied in dimethylformamide are connected with large variations in activation energy. Compounds (Ia), (IIa), and (IIIa) show increasing values of  $\Delta E^{\ddagger}$ (16.8, 19.5, and 21.8 kcal./mole respectively) accompanying the reduction in rate in the reaction with toluene-pthiolate (Table 3); both activation energies for (Ia) and

## TABLE 3

Rate constants (l. mole<sup>-1</sup> sec.<sup>-1</sup>) for substitution of diarylchloroethylenes (0.04-0.08M) by sodium toluene-pthiolate (0.08-0.10M) in dimethylformamide

2-Chloro-1,1-diphenylethylene (Ia)

Temp	30·0°	$40.0 \\ 2.21$	50·0	60·0
104k	0·823		4·47	10·59
$\Delta E^{\ddagger} = 16.8 \pm 0$ -23.9 + 1.8 e.u.	<b>)·6</b> kcal./mole; (at 50°)	$\log Z =$	$= 8.0 \pm 0.4;$	$\Delta S^{\ddagger} =$

2-Chloro-1,1-di-(p-tolyl)ethylene (IIa)

Temp 104k .		50·0° 0·623	60-0 1-384	$70.0 \\ 3.21$	$80.0 \\ 8.34$
$\begin{array}{c} \Delta E^{\ddagger} = 1 \\ -19.6 \pm 1 \end{array}$	$19.5 \pm 0.6$ 1 1.9 e.u. (at	kcal./mole; 50°)	$\log Z =$	$9.0 \pm 0.4;$	$\Delta S^{\ddagger} =$

2-Chloro-1,1-di-(p-methoxyphenyl)ethylene (IIIa)

Temp	50·0°	70·0	$79.9 \\ 1.321$	90·0
10 <sup>4</sup> k	0·0637	0·444		2·48
$\Delta E^{\ddagger} = 21.8 \pm 0.7$ k -17.0 ± 1.9 e.u. (at 5	cal./mole; 0°)	$\log Z =$	$9.6 \pm 0.4;$	$\Delta S^{\ddagger} =$

(IIIa) are markedly lower than the values (34-36)kcal./mole) found for the slower reactions of 2-chloro-1-(p-methoxyphenyl)-1-phenylethylenes with chloride ion.Smaller variations of entropic factors partially compensate for the differences in activation energy.

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