

842. Kinetics and Mechanism of the Reaction of 2-Chloro- and 2-Bromo-1,1-diphenylpropene with Sodium Ethoxide in Ethanol.

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The rates of reaction of 2-chloro- and 2-bromo-1,1-diphenylpropene with ethoxide ions in ethanol have been measured titrimetrically in the temperature range 80—125°. Both from the chloro- and the bromo-compound two reaction products have been isolated and identified: 2-ethoxy-1,1-diphenylpropene and 1-diphenylmethylene-2-methylene-3,3-diphenylcyclobutane. According to kinetic data and the ratio of products, the most probable mechanism is an elimination to the unstable 1,1-diphenylallene, followed by concurrent reactions of this molecule with itself or with ethoxide ion.

THE kinetic behaviour of 1,1-diaryl-2-halogenoethylenes (halogen = Cl, Br) towards ethoxide ions in ethanolic solutions has recently been studied.¹ In the present work the reactivity of 2-halogeno-1,1-diphenylprop-1-enes (*Ia*; X = Cl, *Ib*; X = Br) has been examined towards the same reagent. The reaction of 2-bromo-1,1-diphenylprop-1-ene with ethanolic potassium hydroxide studied by Pansevich-Koliada² gave one oil and a smaller amount of white crystals. The liquid product was not identified, and for the solid only a probable (but not correct) structure was suggested. Information about the reactivities of 1,1-di-*p*-chlorophenyl-2-nitroprop-1-ene and 2-bromo-1,1-di-*p*-chlorophenylprop-1-ene towards potassium *t*-butoxide in *t*-butyl alcohol was given by Bordwell and Garbisch.³

A quantitative study of the reactivity of *Ia* and *Ib* with sodium ethoxide seemed of interest in connection with the previous results on the ethylenes, because the introduction of the methyl group on carbon atom 2 prevents the Fritsch rearrangement and makes a β -elimination reaction possible as an alternative to the nucleophilic displacement. Besides the product of this elimination could be either the monomeric diphenylallene or a dimer.

EXPERIMENTAL

Materials.—Dry ethanol for kinetic purposes was prepared from “99.9%” ethanol by the usual treatment with magnesium and distillation. The solvents used for ultraviolet spectra were methanol (C. Erba) and cyclohexane (B.D.H.) of “spectrograde” purity. Anhydrous sodium perchlorate was obtained by crystallization from water at 60° and drying at 130°.

Gas chromatograms were obtained on a “FractoVap B/f” (C. Erba) using a 2-metre column of 10% Apiezon L grease on Celite, at 230°. Ultraviolet and infrared spectra were obtained, respectively, from a Beckman DU spectrophotometer (up to 210 m μ) and a Perkin-Elmer 21 apparatus with rock salt optics.

2-Chloro-1,1-diphenylprop-1-ene. 1,1-Diphenylpropanol was prepared⁴ and dehydrated to 1,1-diphenylprop-1-ene by adding with stirring to 1 : 2 sulphuric acid–water at 100° and heating for 4—5 hr. 1,1-Diphenylprop-1-ene (90 g.) in CCl₄ (400 ml.) was treated with chlorine at 0—10° until absorption stopped, the solvent was removed, and the residue heated at 70°. When evolution of hydrogen chloride stopped, the oil was carefully distilled (b. p. 150°/5 mm.) giving a liquid, later crystallized with m. p. 39° (from light petroleum) (Found: C, 79.0; H, 6.0; Cl, 15.6. Calc. for C₁₅H₁₃Cl: C, 78.8; H, 5.7; Cl, 15.5%). Its purity was checked by gas chromatography. Spectrum in methanol: λ_{max} = 242 m μ (ϵ = 13,150).

2-Bromo-1,1-diphenylprop-1-ene. Prepared from 1,1-diphenylprop-1-ene by bromination and dehydrobromination according to Hell and Bauer,⁵ it had b. p. 160°/5 mm., m. p. 48—49°

¹ (a) Beltrame and Carrà, *Gazzetta*, 1961, **91**, 889; (b) Beltrame and Favini, *Gazzetta*, 1963, **93**, 757; (c) Simonetta and Carrà, *Tetrahedron*, 1963, **19** suppl. **2**, 467.

² Pansevich-Koliada, *Zhur. obschei Khim.*, 1960, **30**, 3898.

³ Bordwell and Garbisch, *J. Org. Chem.*, 1962, **27**, 3049.

⁴ Masson, *Compt. rend.*, 1902, **135**, 533.

⁵ Hell and Bauer, *Ber.*, 1904, **37**, 232.

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(from glacial acetic acid) (Found: C, 65.8; H, 4.7; Br, 28.7. Calc. for $C_{15}H_{13}Br$: C, 65.95; H, 4.8; Br, 29.25%). The purity of the product was checked by gas chromatography. Spectrum in methanol: $\lambda_{max} = 243 m\mu$ ($\epsilon = 10,300$), $222 m\mu$ (sh) ($\epsilon = 15,300$).

Kinetics.—An exactly weighed amount of organic compound was dissolved in an ethanolic sodium ethoxide of the appropriate concentration, containing, when required, a known amount of sodium perchlorate, in a 100 ml. volumetric flask. On three 5 ml. samples of the final solution the exact EtO^- concentration was determined by titration with hydrochloric acid. The reaction was carried on in sealed Pyrex tubes in a thermostat with temperature control better than $\pm 0.2^\circ$, and followed by potentiometric titration of the halogen ions by means of 0.04996M-silver nitrate in a mainly alcoholic medium. The reaction was quenched by cooling of tubes with water for the runs at 80–100°, or quick acetone–solid carbon dioxide cooling for the runs at 125°. Reactions were usually conducted up to about 50% for the bromo-compound and 30% for the chloro-compound.

Second-order rate constants were obtained graphically from the linear plots of $(2.303/B - A) \log (B - x/A - x)$ against time, where B = initial concentration of EtO^- ; A = initial concentration of the organic halide; x = concentration of halide ion at time t . Deviations of the experimental points from the best straight line were in every case used to calculate the probable error by means of the Bessel formula.⁶ The rate constants were eventually corrected for solvent expansion, by means of the solvent density ratio (d_{20}/d_T). Arrhenius activation energies were obtained from plots of $\log k_2$ against $1/T$. Activation entropies were calculated by the formula: $\Delta S^\ddagger = 4.576 (\log Z - \log T_m) - 49.207$, where Z = frequency factor; T_m = temperature at a medium point of the experimental temperature range, in our case 373.2°K.

Example on (Ib): Temperature = 100.0°.

Time (min.)	$A = 0.0401M$	$B = 0.1936M$	$[NaClO_4] = 0.3404M$	Y *
	0.04996M-AgNO ₃ (ml.)	x	Reaction (%)	
210	0.40	0.0040	10	10.805
380	0.52	0.0052	13	10.985
1275	1.48	0.0148	37	12.740
1560	1.61	0.0161	40	13.038
1780	1.81	0.0181	45	13.530
2715	2.36	0.0236	58	15.195
3040	2.47	0.0247	62	15.610
4140	2.94	0.0294	75	17.795

$$* Y = \frac{2.303}{B - A} \log \frac{B - x}{A - x}$$

From the plot of Y against time a good straight line is obtained, with a slope of 2.927×10^{-5} l. mole⁻¹ sec.⁻¹. After correction for solvent expansion and calculation of the probable error, $k_2 = (3.23 \pm 0.04) \times 10^{-5}$ l. mole⁻¹ sec.⁻¹.

Products.—Larger amounts of the organic halides (*ca.* 0.1 mole each time) were dissolved in ethanolic solutions of sodium ethoxide of known concentration in a large open Pyrex tube in a stainless steel autoclave. Heating at the desired temperature, roughly controlled ($\pm 3^\circ$), lasted at least eight half-lives. Finally, after cooling, a solid product was filtered off (solid A); the solution was concentrated and diluted with water: a small amount of solid precipitate was filtered off (solid B). It having been shown that solid B, apart from impurities, is identical with A (see below) the two solids were put together, thoroughly washed with water to remove the sodium halide, dried, and crystallized from glacial acetic acid: the white crystals had *m. p.* 190°. The aqueous-alcoholic residue was further evaporated and extracted with ether, the ether layer dried (MgSO₄), and the solvent removed: the liquid product was then distilled in a Vigreux flask (*b. p.* 142°/1 mm.).

The distillate was a pale yellow liquid (*b. p.* 133°/0.5 mm.) (n_D^{25} 1.5794), the same product both from (Ia) and (Ib), of good gas-chromatographic purity (Found: C, 85.6; H, 7.4. Calc. for $C_{17}H_{18}O$: C, 85.7; H, 7.6%). The infrared spectrum showed strong absorption bands at 1220, 1053, 760, 696 cm.⁻¹, and medium-intensity bands at 3000, 2930, 1630, 1600, 1495, 1440,

⁶ Crumpler and Yoe, "Chemical Computations and Errors," Wiley, New York, 1946.

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1375, 1185, 1108, 1085, (1070), 1030, 1015 cm^{-1} . Ultraviolet spectrum in methanol: $\lambda_{\text{max.}} = 260 \text{ m}\mu$ ($\epsilon = 11,400$). A sample of the liquid product (5 g.) was refluxed for 2.5 hr. with 1 : 4 sulphuric acid-water (100 ml.) giving an oil, later crystallized, m. p. 55° (recryst. from ethanol, m. p. 58°), semicarbazone m. p. 168° . 1,1-Diphenylacetone has m. p. $58.5\text{--}59.5^\circ$; semicarbazone m. p. $169\text{--}170^\circ$.

Solid B was shown to be identical, when recrystallized, with solid A, by means of mixed m. p., elemental analysis, and spectra. Furthermore, the solids from (Ia) and (Ib) were identical; they had m. p. 190° , unchanged by recrystallization from benzene, carbon tetrachloride-light petroleum, or glacial acetic acid. It is almost insoluble in diethyl ether, light petroleum, methanol, and ethanol, fairly soluble in benzene and acetic acid, easily soluble in chloroform and carbon tetrachloride. Its molecular weight is 345 (cryoscopic in benzene); 395, 347 (vapour pressure osmometer in chloroform) which corresponds to a diphenylallene dimer (Found: C, 93.6—94.05; H, 6.0—6.1. Calc. for $\text{C}_{30}\text{H}_{24}$: C, 93.7; H, 6.3%; M , 384.5).

The infrared spectrum (in KBr) shows strong bands at 1447, 779, 758, 752, 698 cm^{-1} , and medium intensity bands at 3070, 1597, 1482, 1181, 1077, 1034, 1014, 916, 726, 656 cm^{-1} . Ultraviolet spectrum in cyclohexane: $\lambda_{\text{max.}} = 312 \text{ m}\mu$ ($\epsilon = 10,690$), $243 \text{ m}\mu$ (sh) ($\epsilon = 18,500$).

The nuclear magnetic resonance spectrum (Varian 60) has several peaks in the range 2.5—3.5 τ , two peaks at 4.40 and 5.07 τ , and a peak at $\tau = 8.19$ (intensity ratio about 20 : 1 : 1 : 2).

The solid product (1.0 g.) was hydrogenated in ethyl acetate (40 ml.) with 0.1 g. PtO_2 for 2 hr. at room temperature and pressure (H_2 absorbed = 1.4 moles/mole dimer). The hydrogenated product was crystallized twice from ethanol, yielding *ca.* 0.7 g. (m. p. *ca.* 60°) (Found: C, 92.95; H, 7.0. Calc. for $\text{C}_{30}\text{H}_{26}$: C, 93.2; H, 6.8. Calc. for $\text{C}_{30}\text{H}_{28}$: C, 92.7; H, 7.3%). Its infrared spectrum (part in hexachloro-1,3-butadiene, part in Nujol) had main bands at 3080—3050, 2940, 1600, 1495, 1445, 1035, 752, 744, 718, 698 cm^{-1} , and among the weaker bands, a doublet at 1380—1370 cm^{-1} [Found: M , 400 (cryoscopic in benzene), 380 (vapour pressure osmometer). Calc. for $\text{C}_{30}\text{H}_{26} = 386.5$]. Ultraviolet spectrum in methanol: $\lambda_{\text{max.}} = 277 \text{ m}\mu$ (sh) ($\epsilon = 4550$), $270 \text{ m}\mu$ ($\epsilon = 4910$), $264 \text{ m}\mu$ ($\epsilon = 4930$).

The dimer (182 mg.) was ozonized at room temperature in acetic acid (70 ml.), with a large excess of ozonized oxygen. Zinc was added, and partial distillation into 10% hydrochloric acid containing 2,4-dinitrophenylhydrazine (600 mg.) gave a product (95 mg.; 0.96 mole CH_2O /mole dimer) of m. p. 164° , not depressed by mixing with formaldehyde 2,4-dinitrophenylhydrazine. In a second similar ozonolysis (dimer 636 mg., acetic acid 200 ml.) the product was exhaustively steam-distilled into 10% hydrochloric acid containing 2,4-dinitrophenylhydrazine (656 mg.): the final product (250 mg.; 0.72 mole CH_2O /mole dimer) had m. p. and mixed m. p. 158° . By column chromatography on silica gel, and elution with 6 : 1 hexane-ether it was confirmed that this product is slightly impure, but it was not possible to isolate any benzophenone 2,4-dinitrophenylhydrazone.

Two Diels-Alder reactions on the dimer (0.5 g.) with maleic anhydride (0.5 g.) in benzene (30 ml.), refluxing for 7 hr. or heating in a sealed Pyrex tube at 160° for 7 hr., were both unsuccessful, leaving the dimer unaltered.

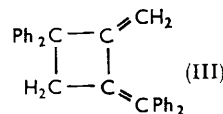
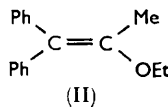
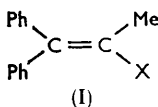
Distribution of Products.—The relative amounts of the solid and the liquid products were determined by weighing them after the separation described above. As the crude products were fairly pure, in order to reduce losses they were weighed before crystallization (or distillation). The overall molar yield was always around 90%, the solid being considered as a diphenylallene dimer and the liquid as diphenyl-ethoxy-propene. The "product distribution ratio" (p.d.r.) mentioned later is the ratio: (moles of liquid product) \div (2 \times moles of solid product).

Example on (Ia): Temperature = $125\text{--}130^\circ$; calcd. half-life = *ca.* 1 hr.; heating time = 14 hr.

$$\begin{array}{lll} [\text{EtONa}]_0 = 1.0\text{M.} & [\text{Ia}]_0 = 0.2\text{M.} & \text{Soln. volume} = 1000 \text{ ml.} \\ & & \text{Starting material: } 46.041 \text{ g.} = 201.3 \text{ mmoles.} \\ \text{Crude products: Solid (4.95 g. of A + 0.30 g. of B):} & & 5.25 \text{ g.} = 13.65 \text{ mmoles.} \\ \text{Liquid:} & & 38.125 \text{ g.} = 160.0 \text{ mmoles.} \\ \text{Overall yield} = \frac{160.0 + 2 \times 13.65}{201.3} = 93.0\%; \text{ p.d.r.} = \frac{160.0}{27.3} = 5.85. \end{array}$$

RESULTS AND DISCUSSION

Product Identification.—We found that both (Ia) and (Ib) on reaction with ethoxide ions give one liquid and one solid product. The formula (II) was assigned to the liquid product on account of the analysis and the following arguments: the infrared spectrum shows, besides all the most probable bands for monosubstituted benzenes,⁷ a band at 1220 cm^{-1} , typical for the $=\text{C}-\text{O}-$ group in ethers and a band at 1053 cm^{-1} typical of the ethers having a $-\text{CH}_2-\text{O}-$ group;⁸ the intensity of the 260 $\text{m}\mu$ band in the ultraviolet spectrum is in accord with the presence of a diphenylethylenic group; the acid hydrolysis gives diphenylacetone.



Analysis and molecular weight of the solid product are in agreement with the formula of a dimer of diphenylallene. Two of the possible dimers are known: 1,2-bisdiphenylmethylenecyclobutane⁹ and 1,3-bisdiphenylmethylenecyclobutane.¹⁰ Also a rearranged linear product is known: 1,1,6,6-tetraphenylhexatri-1,3,5-ene.¹¹ All differ from our product. Our experimental results are well accounted for by formula (III). In the ultraviolet spectrum the strong band at 312 $\text{m}\mu$ indicates conjugation of two phenyl groups with the two double bonds. In fact the first long wavelength band appears at 256 $\text{m}\mu$ in diphenylmethylenecyclobutane,¹⁰ at 267 $\text{m}\mu$ in 1,3-bisdiphenylmethylenecyclobutane,¹⁰ at 351 $\text{m}\mu$ in 1,2-bisdiphenylmethylenecyclobutane,⁹ at 372 or 380 $\text{m}\mu$ in 3,4-dichloro-1,2-bisdiphenylmethylenecyclobutane,^{12,13} at 325 $\text{m}\mu$ in 4-chloro-2-chloromethylene-1-diphenylmethylene-3-diphenylcyclobutane.¹⁴ Infrared evidence is not quite clear; however, one of the probable bands for substituted cyclobutanes is present at 916 cm^{-1} , together, of course, with all the monosubstituted benzene bands. The nuclear magnetic resonance spectrum shows the presence of 20 aromatic hydrogen atoms (peaks at $\tau = 2.5-3.5$), two non-equivalent ethylenic hydrogens ($\tau = 4.40$ and 5.07) and two equivalent hydrogens in a $-\text{CH}_2-$ group ($\tau = 8.19$), in complete agreement with formula (III). The result of ozonolysis, about one mole of formaldehyde for one mole of dimer, proves the presence of one exo-methylenic group. The hydrogenation was not complete: less than two moles of H_2 were absorbed per mole of dimer. The ultraviolet spectrum of the product shows the presence of some absorption by an unaltered diphenylmethylene group. The infrared spectrum shows the typical band of the CH_3 group at 1375 cm^{-1} . Furthermore the characteristic band of paraffinic C-H bond stretching, very weak in the dimer's spectrum, appears now with medium intensity at 2940 cm^{-1} .

Kinetic Data.—The order of the reaction with respect to the base has been tested for (Ib) in three runs in which the substrate and total salt concentrations were kept roughly constant and the $[\text{EtO}^-]$ varied from about 0.1 to 0.5M. From the results (Table 1), the order 1.1 was found. We assume that the discrepancy from unity can be attributed to specific salt effects. Second-order rate constants at various temperatures, both for (Ia)

⁷ Ulery and McClenon, *Tetrahedron*, 1963, **19**, 749.

⁸ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

⁹ Albermann and Kipping, *J.*, 1951, 779.

¹⁰ Griffin and Velluro, *J. Org. Chem.*, 1961, **26**, 5183, and personal communication of Professor Griffin.

¹¹ Schmitt, *Annalen*, 1941, **547**, 103.

¹² Nagase, *Bull. Chem. Soc. Japan*, 1961, **34**, 139; *Scient. Pap. Inst. Phys. Chem. Res. (Tokyo)*, 1961, **55**, 165.

¹³ Landor and Landor, *Proc. Chem. Soc.*, 1962, 77.

¹⁴ Nagase, *Scient. Pap. Inst. Phys. Chem. Res. (Tokyo)*, 1961, **55**, 172.

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and (Ib), are reported in Table 2; frequency factors, activation energies, and entropies are also shown. When required, interpolated or extrapolated rate constants were calculated from these data.

As the k_2 's are overall rate constants, it was necessary to investigate the products distribution by other means. For this, runs on large quantities of (Ia) and (Ib) were taken practically to completion, the products being separated and weighed. The influence

TABLE 1.

Bromodiphenylpropene (init. concn. = A) reacting with sodium ethoxide (init. concn. = B) at 100.0°.

A (mole/l.)	0.0400	0.0401	0.0400
B (mole/l.)	0.0935	0.1936	0.5075
[NaClO ₄] (mole/l.)	0.4500	0.3404	—
Total salt concn.	0.5435	0.5340	0.5075
Reaction range examined	7—48%	10—75%	13—38%
10 ⁵ k ₂ (l. mole ⁻¹ sec. ⁻¹)	2.92 ± 0.04	3.23 ± 0.04	3.72 ± 0.06

TABLE 2.

Rate constants for (Ia) and (Ib) in the reaction with sodium ethoxide.

Temp.	80.0°	90.0°	100.0°	125.0°
Chlorodiphenylpropene (Ia).				
A (mole/l.)	0.0400	0.0400	0.0400	0.0401
B (mole/l.)	0.4991	0.5087	0.5170	0.4557
10 ⁵ k ₂ (l. mole ⁻¹ sec. ⁻¹)	0.148 ± 0.005	0.441 ± 0.007	1.46 ± 0.04	23.3 ± 0.4
ΔE‡ = 31,700 ± 400 cal./mole; log Z = 13.7 ± 0.3; ΔS‡ = +1.8 ± 1.2 e.u. (at 100°).				
Bromodiphenylpropene (Ib).				
A (mole/l.)	0.0400	0.0400	0.0400	0.0400
B (mole/l.)	0.4991	0.5170	0.5075	0.5407
10 ⁵ k ₂ (l. mole ⁻¹ sec. ⁻¹)	0.412 ± 0.011	1.20 ± 0.02	3.72 ± 0.06	59.2 ± 0.2
ΔE‡ = 31,300 ± 500 cal./mole; log Z = 13.9 ± 0.3; ΔS‡ = +2.8 ± 1.4 e.u. (at 100°).				
Relative rates:	$\frac{k_2(Ib)}{k_2(Ia)} = 2.79$	2.72	2.55	2.54

TABLE 3.

Product distribution.

Temp.	ca. 100°	125—130°	125—130°	125—130°
[B ⁻] ₀ (mole/l.)	1.0	0.25	1.0	2.0
[RHX] ₀ (mole/l.)	0.20	0.10	0.20	0.20
([B ⁻]/[RHX]) ₀ = C ₀	5.0	2.5	5.0	10
(p.d.r.) _{Cl}	4.35	3.6	5.85	10
(p.d.r.) _{Br}	3.1	2.3	3.6	8.15
(p.d.r.) _{Cl} /(p.d.r.) _{Br}	1.4	1.6	1.6	1.2

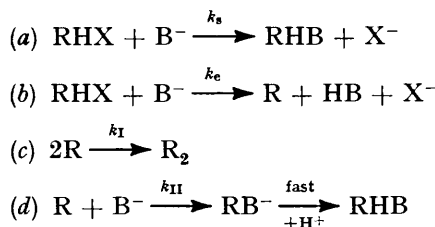
Symbols: [B⁻] = concn. of EtO⁻; [RHX] = concn. of organic halide; [RHB] = concn. of ethereal product; [R₂] = concn. of dimeric product.

(p.d.r.)_{Cl} = $\frac{[RHB]}{2 \times [R_2]}$ in the products from (Ia). (p.d.r.)_{Br} = $\frac{[RHB]}{2 \times [R_2]}$ in the products from (Ib).

of the ratio of the initial reagent concentrations on the product distribution was studied; results are in Table 3. In our experimental conditions the dimer was 7.4—26.2% by weight of the isolated products.

Mechanism.—The first order of reaction with respect to the base found for (Ib) rules out the possibility of an S_N1-E1 mechanism. The breaking of the C-Cl bond in the

rate-determining step is even less probable. A reasonable reaction mechanism can then be formulated as follows:



where the symbols are as below Table 3 and R is diphenylallene. Chemical evidence suggests that the assumption $k_I \gg k_e$ can be made.

Two limiting cases can be envisaged: (A) k_{II} is zero and all the ether comes from nucleophilic attack of the base on α -carbon atom; (B) the nucleophilic substitution constant k_s is zero and all the products come from attack of the base on the β -hydrogen atom.

In case (A), as reactions (a) and (b) are both of first order with respect to the substrate and the base, the product distribution ratio is given by:

$$\text{p.d.r.} = \frac{[\text{RHB}]}{2 \times [\text{R}_2]} = \frac{k_s}{k_e}$$

that is, p.d.r. is not dependent on $[\text{B}^-]/[\text{RHX}]$. The values of k_s and k_e could be found, it being kept in mind that $k_s + k_e = k_2$. Unless steric acceleration is present, the k_s 's should be smaller than for the respective 2-halogeno-1,1-diphenylethylenes, analogously to what has been verified for 2-halogeno-1,1-di-*p*-tolylethylenes.^{1b} From Table 3 it appears that p.d.r. is strongly dependent on the reagent concentration ratio. Furthermore, the constants k_s ($\approx 0.9 k_2$ in this approximation) are about 200 times bigger than the substitution constants for the corresponding ethylenes:

$$k_s \text{ (l. mole}^{-1} \text{sec.}^{-1}) \text{ at } 120^\circ: (\text{C}_6\text{H}_5)_2\text{C} = \text{CHBr}, 1.2 \times 10^{-6}; (\text{C}_6\text{H}_5)_2\text{C} = \text{C}(\text{CH}_3)\text{Br}, (307 \times 10^6)$$

$$k_s \text{ (l. mole}^{-1} \text{sec.}^{-1}) \text{ at } 130^\circ: (\text{C}_6\text{H}_5)_2\text{C} = \text{CHCl}, 2.25 \times 10^{-6}; (\text{C}_6\text{H}_5)_2\text{C} = \text{C}(\text{CH}_3)\text{Cl}, (320 \times 10^6)$$

This corresponds to a decrease of about 4.0–4.3 kcal./mole in activation free energy, which seems too high to be accounted for by steric acceleration in these molecules.

In case (B), step (b) is rate-determining and the distribution of products can be calculated from the following kinetic equations:

$$(b') \quad \frac{d[\text{X}^-]}{dt} = k_c [\text{RHX}][\text{B}^-]$$

$$(c') \quad \frac{d[\text{R}_2]}{dt} = k_I [\text{R}]^2$$

$$(d') \quad \frac{d[\text{RB}^-]}{dt} = \frac{d[\text{RHB}]}{dt} = k_{II} [\text{R}][\text{B}^-]$$

Adopting the pseudo-stationary-state approximation, we find the concentration of R given by:

$$[\text{R}] = \frac{k_e [\text{RHX}][\text{B}^-]}{2k_I [\text{R}] + k_{II} [\text{B}^-]}$$

from which:

$$[\text{R}] = \frac{-k_{II} [\text{B}^-] + \sqrt{(k_{II}^2 [\text{B}^-]^2 + 8k_I k_e [\text{RHX}][\text{B}^-])}}{4 k_I}$$

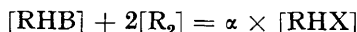
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Dividing eqn. (d') by twice eqn. (c') and introducing the above expression for [R] we obtain

$$\frac{d[\text{RHB}]}{2d[\text{R}_2]} = \frac{2}{-1 + \sqrt{\left(1 + K \frac{[\text{RHX}]}{[\text{B}^-]}\right)}} = f(\alpha)$$

where $K = \frac{8k_1k_e}{k_2^2k_{II}}$ and α is the "advancement" of the reaction.

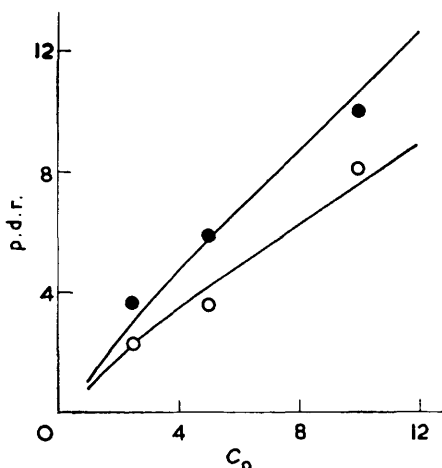
Taking into account the stoichiometric relation



we obtain the following value of p.d.r.

$$\text{p.d.r.} = \frac{1}{\int_0^1 \frac{\sqrt{\left(1 + K \frac{1-\alpha}{C_0-\alpha}\right)} - 1}{\sqrt{\left(1 + K \frac{1-\alpha}{C_0-\alpha}\right)} + 1} d\alpha} - 1$$

Numerical integration by the Gauss quadrature method (with 16 points), performed on a IBM 1620 computer, has allowed the choice of the values of K that give the best fit to the experimental data. They are: $K_{\text{Cl}} = 8.33$; $K_{\text{Br}} = 12.3$. Curves of $\text{p.d.r.} = f(C_0)$, calculated with these K -values are plotted in the Figure.



Experimental values of $(\text{p.d.r.})_{\text{Cl}}$ (full circles) and $(\text{p.d.r.})_{\text{Br}}$ (open circles) at 125–130° against C_0 ($K_{\text{Cl}} = 8.33$; $K_{\text{Br}} = 12.3$).

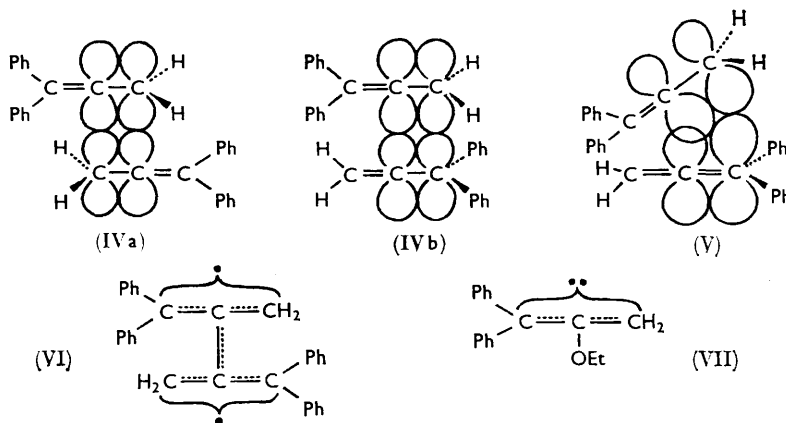
The agreement between the calculated curves and the general trend of experimental values for both compounds suggests that the mechanism is very close to case (B). Of course, k_2 is then practically equal to k_e and no direct comparison can be made with substitution constants. Comparing the reactivities of (Ia) and (Ib) we find that the bromo-compound reacts faster than the chloro-compound; in particular at 125° $k_{e\text{Br}}/k_{e\text{Cl}} \simeq k_{2\text{Br}}/k_{2\text{Cl}} = 2.54$. If k_I and k_{II} do not depend on the nature of the halogen, $K_{\text{Br}}/K_{\text{Cl}}$ should have the same value. The actual ratio is 1.48.

The value 2.54 for the Br/Cl "element effect" is rather low for an elimination reaction and suggests that the reaction mechanism is E2, leaning towards the side of the E1cb according to Bunnett's classification.¹⁵

The dimerization has been written as a thermal cycloaddition (eqn. c), where no base is

¹⁵ Bunnett, *Angew. Chem. (Intern. Edn.)*, 1962, **1**, 225.

involved, owing to the many examples of such reactions given by Roberts and Sharts¹⁶ and by Roedig and Niedenbrück.¹⁷ Furthermore Nagase^{12,14} obtained the dimers of 3-chloro-1,1-diphenylallene in acidic or buffered conditions.



We justify the assumption that the rate of the dimerization of 1,1-diphenylallene is much faster than its formation on the ground that no 1,1-diphenylallene was found either in our products or by Pansevich-Koliada,² although similar compounds have been isolated in cases when their preparation could be effected without prolonged heating. For instance 3-bromo-1,1-diphenylallene could be prepared from 2,3-dibromo-1,1-diphenylprop-1-ene with alcoholic potassium hydroxide, only moderate heating being required;² furthermore, some 1,1-diaryl-3,3-dichloroallenes were obtained by a different route at room temperature¹⁷ and were dimerized by refluxing with acetone or heating in petroleum solution on a water-bath for about half an hour.

Qualitative arguments can be found to justify the fact that dimerization leads almost exclusively to compound (III). Owing to steric hindrance it is conceivable that the two molecules approach each other with the bulky diphenylmethylenic groups at opposite ends. Two useful ways of approach can then be symbolized as in (IVa) and (IVb). If the transition state is formulated as one in which the formation of one bond is more advanced than the other, the transition state (V) is favoured by resonance effects. Should the reaction proceed through a diradical intermediate, the most stable form would be (VI), which again would lead to dimer (III).

As to reaction (d), we can only suggest that in the first step the carbanion (VII) is formed, which is the most stable for resonance effects, and to this the proton is added in the position that leads to the most stable product. The fact that direct nucleophilic substitution, if present, is only a small amount of the overall reaction is in line with previous results¹ showing that, in ethanol and with sodium ethoxide there is a strong tendency for diaryl-chloro(bromo)ethylenes to follow reaction paths other than nucleophilic substitution.

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¹⁶ Roberts and Sharts, *Org. React.*, 1962, **12**, 1.

¹⁷ Roedig and Niedenbrück, *Ber.*, 1957, **90**, 673.