

694. *The Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part III.* The Reactions of 3 : 3 : 3-Trichloro-2-methylprop-1-ene with Nucleophilic Reagents.*

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The compound $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$ reacts with sodium thiophenoxide in ethyl alcohol to form the product of substitution with rearrangement, $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{SPh}$. This process, being kinetically of the second order, is a further example of the $\text{S}_{\text{N}}2'$ mechanism, and the rate is somewhat faster than that of the corresponding reaction of 3 : 3-dichloroprop-1-ene.

1-METHYLLALLYL CHLORIDE reacts bimolecularly with alcoholic sodium ethoxide to give the product of normal ($\text{S}_{\text{N}}2$) substitution (cf. Catchpole, Hughes, and Ingold, *J.*, 1948, 11). In Parts I and II (*loc. cit.*), however, it has been shown that the presence of an α -chloro-substituent, as in 3 : 3-dichloroprop-1-ene (*i.e.*, 1-chloroallyl chloride) is unfavourable to the $\text{S}_{\text{N}}2$ mechanism, and promotes bimolecular substitution with anionotropic rearrangement ($\text{S}_{\text{N}}2'$). As a result, therefore, the $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}2'$ mechanisms of substitution contribute nearly equally to the reactions of this compound with ethoxide, phenoxide, and thiophenoxide ions. It was suggested (cf. Hughes and Ingold, *J. Chim. phys.*, 1948, 45, 241) that the $\text{S}_{\text{N}}2'$ reaction is favoured, in such an example, by the inductive influence of the CHCl_2 group, which displaces the screen of unsaturation electrons in such a way as to make less difficult the attack of a nucleophilic reagent on the unsaturated carbon atom, as may be represented thus : $\text{EtO} \curvearrowright \text{CH}_2 \cdot \overset{\curvearrowright}{\text{C}} \text{H} \cdot \text{CHCl}_2$.

It would be a consequence of this interpretation that the CCl_3 group should be still more effective in promoting reaction by this mechanism, the more so since $\text{S}_{\text{N}}2$ attack on this group is still more difficult. Kirrmann and Jacob (*Bull. Soc. chim.*, 1940, 7, 586) have indeed recorded that the compounds $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$ and $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$ react, the former much less readily than the latter, with water, sodium acetate, potassium *p*-nitrobenzoate, and sodium ethoxide, to give, in each case in good yield, the product expected from the second isomer (*e.g.*, $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{OEt}$ in the reaction of either isomer with sodium ethoxide). Since these authors made no kinetic measurements, they were unable to discuss adequately the mechanism involved in the anionotropic rearrangements which they were observing in the reactions of $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$. For this reason, we have examined the kinetics and products of the reaction of this compound with sodium thiophenoxide in ethyl alcohol. The reaction is kinetically of the second order, and the first equivalent of chloride is released from the compound considerably more rapidly than the second and third. The velocity constant at 24.7° was found to have the value $k_2 = 6.2 \times 10^{-3}$ l. mole⁻¹ min.⁻¹,† and the energy of activation in the range 24.7 — 64.9° was 20.3 kcal. These values indicate that the reaction occurs more readily than that of the $\text{S}_{\text{N}}2'$ component of the similar reaction of 3 : 3-dichloroprop-1-ene (k_2 at 24.7° , 2.5×10^{-3} ; $E = 21.2$ kcal.). From 8 g. of trichloride, with the equivalent quantity of sodium thiophenoxide, there was obtained in 64% yield the compound $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{SPh}$, identical in properties with a sample obtained similarly from $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$. It is concluded, therefore, that $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$ reacts with thiophenoxide ion almost exclusively by $\text{S}_{\text{N}}2'$ displacement of chloride.

3 : 3-Dichloroprop-1-ene thus reacts with thiophenoxide ion to give the product of anionotropic rearrangement, at about half the rate found for $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$; the activation energy for the reaction of the former compound is correspondingly slightly higher. A similar difference in reactivity by this mechanism is found for the reaction with sodium ethoxide. The CCl_3 group, as compared with the CHCl_2 group, would be expected to favour the $\text{S}_{\text{N}}2'$ reaction by an even greater factor; but in the present example, the additional 2-methyl substituent has an opposing effect, which, as might be expected, partly cancels the influence of the third chlorine substituent.

* Parts I and II, *J.*, 1952, 3325, 3331.

† All velocity coefficients given in this paper are in these units.

We hope in due course to study the similar reactions of 3 : 3 : 3-trichloroprop-1-ene. The compound which has customarily been assigned this structure (Victoria, *Rec. Trav. chim.*, 1905, **24**, 280; Kharasch, Rossin, and Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2558), although moderately reactive with sodium ethoxide at 65°, hardly reacts with sodium thiophenoxide under the same conditions. Substitution reactions in such circumstances are usually some 10²–10³ more rapid with sodium thiophenoxide than with sodium ethoxide, as, for example, we have shown herein for CCl₃·CMe·CH₂. We therefore concluded that the compound usually described as 3 : 3 : 3-trichloroprop-1-ene is probably 1 : 1 : 2-trichloroprop-1-ene, as seemed not unlikely, since this compound might be formed from the addition of hydrogen chloride to 1 : 1-dichloroallene, and both of these substances are reported (Kharasch, Rossin, and Fields, *loc. cit.*) as by-products in the usual preparation of this trichloropropene. During the course of the experiments described herein, our attention was called to an abstract (*Chem. Abstr.*, 1952, **46**, 1957) of a paper by Nesmayanov, Freidlina, and Firstov (*Doklady Akad. Nauk. S.S.S.R.*, 1951, **78**, 717), in which chemical evidence is given of the correctness of this view (cf. also Ladd and Shinkle, U.S.P. 2,561,516).

EXPERIMENTAL

(a) *Preparation of Trichlorobutenes.*—Jacob (*Bull. Soc. chim.*, 1940, **7**, 584) described the synthesis, as well as the proofs of structure, of CCl₃·CMe·CH₂ and CCl₂·CMe·CH₂Cl. Although poor yields of pure product were obtained by this method, it proved in our hands more satisfactory than that of Price and Marshall (*J. Org. Chem.*, 1943, **8**, 532). Anhydrous chlorobutol was dehydrated in small batches by phosphoric oxide in the presence of dimethylaniline, and the combined product was dissolved in ether, washed with sodium carbonate and then with water, dried (CaCl₂), and fractionated in a helix-packed column, giving 3 : 3 : 3-trichloroisobutene (13 g. from 400 g. of chlorobutol), n_D^{25} 1.4760, b. p. 52–53°/45 mm., which appeared to be kinetically pure. Its isomer, 1 : 1 : 3-trichloroisobutene, was obtained in good yield as a subsequent fraction, b. p. 75°/45 mm., n_D^{25} 1.4961.

(b) *Products.*—1 : 1 : 3-trichloroisobutene (22 g.) was gradually added to 200 ml. of 0.6N-sodium thiophenoxide in alcohol. After the reaction mixture had been kept overnight, the product was extracted with pentane, and the extract was washed with water, dried, and fractionated, giving 13 g. of 1 : 1-dichloro-2-methyl-3-thiophenoxyprop-1-ene, b. p. 112–114°/ca. 0.7 mm., n_D^{25} 1.5853 [Found: C, 51.1; H, 4.5; S, 14.1; Cl, 14.1; (determined by reaction with sodium in ethylene glycol at 200°), 31.0. C₁₀H₁₀SCl₂ requires C, 51.5; H, 4.3; S, 13.7; Cl, 30.5%].

By a similar method, there were obtained, from 3 : 3 : 3-trichloroisobutene (8 g.) and an equivalent quantity of sodium thiophenoxide, 7.5 g. of 1 : 1-dichloro-3-phenylthioisobutene, b. p. 107–113°/ca. 0.5 mm., n_D^{25} 1.5863, of which a middle fraction (4.5 g.) had b. p. 111–112°/ca. 0.5 mm., n_D^{25} 1.5857 (Found: C, 52.1; H, 4.3; S, 13.3; Cl, 29.9%). Both these compounds reacted slowly at the same rate with sodium thiophenoxide; the kinetics of this reaction are outlined later, but the products have not been further investigated.

(c) *Kinetics.*—Reagents and methods were as described in Parts I and II (*loc. cit.*). Here-with are the results of a typical kinetic run. 3 : 3 : 3-Trichloroisobutene (0.1150M) was made up in 0.319N-sodium thiophenoxide. Samples (5 ml.) were removed from the thermostat (24.7°) at appropriate intervals, added to 20 ml. of ice-cold 0.1153N-hydrochloric acid, and rapidly back-titrated with 0.02716N-sodium hydroxide (bromophenol-blue). The initial sample was allowed 50 minutes to warm to thermostat temperature.

Time (min.)	0	70	166.5	250	338	368	402	442	∞
RCI ₃ destroyed (ml. of 0.02716N-NaOH)	0.00	1.95	4.35	6.10	7.70	8.50	8.60	9.50	19.20
10 ³ k ₂	—	5.1	5.2	5.3	5.3	5.6	5.2	5.5	—

The mean velocity coefficient, $k_2 = 5.3 \times 10^{-3}$ for [NaSPh] = 0.319, is only slightly raised, owing apparently to the usual small negative salt effect, by changing the concentration of thiophenoxide to 0.164 ($k_2 = 6.2 \times 10^{-3}$). Solvolysis is negligibly slow. Hence the reaction is of the second order ($d[\text{Cl}^-]/dt = k[\text{RCI}_3][\text{SPh}^-]$).

At 64.9°, the corresponding second-order rate-coefficient ([NaSPh] = 0.326) was 0.314. It was necessary to show that the stage of the reaction under kinetic observation resulted in the release of only one equivalent of chlorine; for this would be the result of an S_N2' reaction, whereas normal S_N2 substitution would be expected to lead to the liberation of all the chlorine in the molecule, as in the reactions of chloroform with nucleophilic reagents (Huntress, "Organic

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Chlorine Compounds," Wiley and Sons, New York, 1948, p. 552). The above second-order velocity coefficients have been calculated by using the usual formula

$$k_2 = 2.303 \{ \log_{10} b(a-x)/a(b-x) \} / t(a-b)$$

where a is the measured initial concentration of sodium thiophenoxide, and b is the molar concentration of trichlorobutene. The constancy of these values indicates that only 1 equiv. of chlorine is released in the rate-determining process, but attempts to measure an experimental value for the release of chlorine at complete reaction indicated a slow further release of chlorine, as shown in the following results, for $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2 = 0.101\text{M}$ and $\text{NaSph} = 0.326\text{N}$:

Time (min.)	0	5.0	11.0	24.5	33.5	41.4	137	214	410	4330
Release of chloride equiv. per mol. of $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$	0.348 *	0.582	0.747	0.912	0.968	1.015	1.166	1.280	1.431	1.903

* This represents reaction occurring in the time (5 mins.) required for warming to the temperature (64.9°) of the thermostat.

This further release of chloride was not the result of a part of the initial process proceeding by the $\text{S}_{\text{N}}2$ mechanism, but of the subsequent reaction of the product, $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{Sph}$, formed by the initially rapid substitution. The following experiment shows the rate of reaction of $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{Sph}$ (0.0450M) with sodium thiophenoxide (0.1491N) at 64.9° .

Time (min.)	109	196	292	1223	1700	2800
Release of chloride, equiv. per mol. of $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{Sph}$	0.170	0.272	0.374	0.942	1.094	1.284

The initial second-order rate-coefficient for the release of the first equiv. of chloride from this compound ($k_2 = 6.0 \times 10^{-3}$, based on the release of 2 equiv. of chloride at completion of reaction), corresponds well with the value ($k_2 = 5.2 \times 10^{-3}$) obtained from the above data for $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$, considering the rate of release of the *second* equivalent of chloride, as a proportion of the release of the last 2 equiv. of chloride. The initial $\text{S}_{\text{N}}2'$ reaction of $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$ is, however, some 50 times faster than the subsequent decomposition of the product, which does not, therefore, interfere with the determination of the velocity of the former reaction. It is concluded that the second-order reaction, which results in the liberation of the first equivalent of chloride from $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$, leads to formation of $\text{CCl}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{Sph}$, and is therefore an example of the $\text{S}_{\text{N}}2'$ mechanism.

The following shows the rate of development of chloride from $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$ (0.0305M) with sodium ethoxide (0.514N) in ethyl alcohol at 64.9° . Samples (5.03 ml.) were titrated with 0.0100N-silver nitrate.

Time (min.)	0	965	1225	2340	2720	4220	∞
Titre (ml.)	0.00	5.32	6.30	9.44	10.44	12.14	15.24
$10^4 k_2$	—	8.3	8.2	8.0	8.1	7.2	—

Solvolysis of the compound was found to be considerably slower at this temperature, as shown by the rate of development of acid from 5.0-ml. samples of $\text{CCl}_3\cdot\text{CMe}\cdot\text{CH}_2$ (0.0250M) in ethyl alcohol at 64.9° , titrated in alcohol with sodium hydroxide, lacmoid being used as indicator:

Time (min.)	0	200	315	2780	4545	∞
Titre (ml. of 0.02716N-NaOH)	0.11	0.20	0.27	0.80	1.18	4.60

Hence the reaction with sodium ethoxide is bimolecular, and, since Kirrmann and Jacob (*loc. cit.*) showed that the product involved rearrangement, this reaction also is to be classified as $\text{S}_{\text{N}}2'$. Its rate, as for the reaction with thiophenoxide, is faster than that recorded in Part I (*loc. cit.*) for the $\text{S}_{\text{N}}2'$ component of the reaction of $\text{CHCl}_2\cdot\text{CH}\cdot\text{CH}_2$ with sodium ethoxide ($k_2 = 3.6 \times 10^{-4}$).

(d) "*Trichloropropene*."—The product of dehydration of 1:1:1-trichloropropan-2-ol with phosphoric oxide gave a product, b. p. 116—118°/762 mm., n_{D}^{20} 1.4790 (Kharasch, Rossin, and Fields, *loc. cit.*, record, for a product prepared similarly, n_{D}^{20} 1.4827). This material (0.0279M) reacted at 64.9° with sodium ethoxide (0.471N) to release 1 equiv. of chloride in 500 min., 2 equiv. in 1600 min., and 2.7 equiv. at completion of reaction (1 week at 75°). With sodium thiophenoxide (0.155N) at 64.9° , less than 0.1 equiv. of chloride was released in 500 minutes, and hence the rate of reaction of this material with thiophenoxide is slower than that with ethoxide. The latter reaction, therefore, is most probably not a substitution, but an elimination, and the compound is probably $\text{CCl}_2\cdot\text{CCl}\cdot\text{CH}_3$ (cf. Nesmayanov, Freidlina, and Firstov, *loc. cit.*). Attempted dehydration of trichloropropan-2-ol by phosphoric oxide in the presence of

quinoline gave only material of b. p. 106° , n_D^{25} 1.4548. This may be the substance described by Kharasch *et al.* (*loc. cit.*) as dichloroallene, b. p. $52-55^{\circ}/103$ mm., n_D^{20} 1.4650; on treatment with sodium ethoxide in ethyl alcohol, the solution immediately darkened, and sodium chloride was precipitated, but only a quarter of the amount of chlorine expected for the above compound was detected, either immediately or after 4 days at room temperature.

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