714. *The Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part IV.* The Reaction of* 1 : 1-*Dimethylallyl Chloride with the Thiophenoxide Ion.*

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1 : 1-Dimethylallyl chloride reacts with sodium thiophenoxide by a reaction of the second order, to give the product, 3-methylbut-2-enyl phenyl sulphide, of substitution with anionotropic rearrangement. The reaction proceeds more rapidly, and has a lower energy of activation, than the corresponding reaction of 3 : 3-dichloroprop-1-ene. 1-Methylallyl chloride reacts, more slowly, but also by a reaction of the second order, to give a product from which can be isolated (cf. Cope, Morrison, and Field, *J. Amer. Chem. Soc.*, 1950, **72**, 59) the non-rearranged, contaminated with a small amount of the rearranged, product. The theoretical implications of these results are discussed.

In previous papers (Parts I—III, *J.*, 1952, 3326, 3331, 3628) it has been shown that bimolecular nucleophilic substitution with anionotropic rearrangement (S_N2') can be realised experimentally in allylic halides in which direct nucleophilic displacement (S_N2) is hindered by the presence of appropriate substituents at the reacting centre. A typical example is 3 : 3-dichloroprop-1-ene, in which the S_N2 reaction is hindered, and the S_N2' process is favoured, by the presence of the second chlorine substituent.

In 1 : 1-dimethylallyl chloride, $CH_2{:}CH{\cdot}CMe_2Cl$, the inductive effect of the two methyl substituents would be expected to inhibit somewhat the attack by a nucleophilic reagent at the double bond, but at the same time to facilitate the concerted removal of the chloride ion. Hence it could not be predicted *a priori* whether the S_N2' reaction would be faster for this than for simpler compounds.

The more usual reactions of 1 : 1-dimethylallyl chloride are unimolecular in character, as indicated by the fact that this compound and its allylic isomer, 3 : 3-dimethylallyl chloride (3-methylbut-2-enyl chloride), give on solvolysis similar mixtures of isomeric alcohols (Ultee, *Rec. Trav. chim.*, 1949, **68**, 483). It is also known (Young, Winstein, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1958) that solvolysis in acetic acid is accompanied by a rearrangement in which the ionisation of the migrating chlorine does not become complete, as is indicated by the non-intervention in the reaction of chloride ions from the environment.

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* Part III, *J.*, 1952, 3628.

Sodium thiophenoxide, however, is a very powerful reagent for nucleophilic substitutions. Consistently, it has been found that 1 : 1-dimethylallyl chloride reacts with sodium thiophenoxide in alcohol by a reaction which is of the second order, is considerably faster than the corresponding solvolysis, and gives 3-methylbut-2-enyl phenyl sulphide.

This reaction does not involve a bimolecular displacement to form $CH_2{:}CH{\cdot}CMe_2{\cdot}SPh$, followed by rearrangement of the latter compound, for the following reason. Such a bimolecular displacement would of necessity be considerably slower than the corresponding bimolecular displacement of thiophenoxide ions on 1-methylallyl chloride, for it is well known that a retardation in rate results from the introduction of methyl substituents on a carbon atom undergoing bimolecular substitution, both for steric, and, as Dostrovsky, Hughes, and Ingold (*J.*, **1946**, 173) consider, for polar reasons. In the present instance, however, the introduction of the second methyl group has the result of facilitating, by a factor of about two, the observed rate of bimolecular displacement. Hence the more rapid reaction cannot be an S_N2 process. The possibility has also been excluded that the reaction involves an elimination to give isoprene, followed by the addition of thiophenol; for it has been shown that thiophenol does not add to isoprene under the conditions of the kinetic measurements. Taking into account these facts, together with the kinetic behaviour, the reaction can best be interpreted as a bimolecular substitution with anionotropic rearrangement (S_N2'). It proceeds some forty times more rapidly than the corresponding reaction of 3 : 3-dichloroprop-1-ene, and has a smaller energy of activation.

The reaction of 1-methylallyl chloride with sodium thiophenoxide in ethanol has been studied by Cope, Morrison, and Field (*J. Amer. Chem. Soc.*, 1950, **72**, 59). These workers isolated both 1-methylallyl and but-2-enyl phenyl sulphides from the product, the yields of pure isomers isolated being respectively 57 and 8%. Their work has been repeated, with essentially similar results. As judged from the refractive index of the product obtained by reaction at 5°, it contains only about 16% of the rearranged isomer, and this amount is somewhat increased when the temperature of the reaction is changed to 80°. Pure 1-methylallyl phenyl sulphide, after contact with sodium thiophenoxide, on recovery has increased refractive index, suggesting either that isomerisation occurs to the isomeric product under these conditions, or that the samples become contaminated with a trace of material of higher refractive index. The former possibility is the more likely, since in our experience fractionation or even simple distillation under reduced pressure of mixtures, which from their refractive index contain much 1-methylallyl phenyl sulphide, gives a distilled product containing an increased amount of the isomeric sulphide; no fractions of boiling points and refractive indices lower than those of 1-methylallyl phenyl sulphide, or higher than those of but-2-enyl phenyl sulphide, are obtained in these distillations.

It is considered, therefore, that the amount of but-2-enyl phenyl sulphide formed from 1-methylallyl chloride and sodium thiophenoxide by the S_N2' reaction, certainly less than 16% for reaction at 5°, is small, and probably approximates to the amount of rearranged ether formed in the reaction of this chloride with sodium ethoxide. For the latter reaction, Roberts, Young, and Winstein (*ibid.*, 1942, **64**, 2157) found less than 4% for reaction at 25°, and we have obtained only about 4·5% for reaction at 81° (cf. Catchpole and Hughes, *J.*, 1948, 4).

The following structural comparisons can now be made, using the data of earlier parts (*locc. cit.*) :

Compound	$Me_2\underset{\vert}{\overset{}{C}}{\cdot}CH{:}CH_2$ Cl	$Me{\cdot}\underset{\vert}{CH}{\cdot}CH{:}CH_2$ Cl	$Cl{\cdot}\underset{\vert}{CH}{\cdot}CH{:}CH_2$ Cl
k_2 (S_N2', for reaction with SPh^- in EtOH at 25°)...	0·090	$\ngtr$0·007	0·0025
E (kcal./mole)	19·6	—	21·2

It is clear that, so far as the effect of the methyl group on the S_N2' process is concerned, the facilitation of the breaking of the C–Cl bond dominates over the inductive retardation of attack by the nucleophilic reagent. In the S_N2' reaction, as in the S_N2 process (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 628), the polar requirements for the breaking of one bond are opposite to those required for the making of another, and hence the reaction may, in some circumstances, be facilitated either by electron-withdrawing or by electron-donating substituents. For the S_N2' process, it has now been made probable that reactivity is enhanced both by a 1-chlorine (Part III, *loc. cit.*) and by a 1-methyl substituent, by facilitating, in the former case, the formation of the bond with the reagent, and in the latter, the breaking of the C–Cl bond. The effects of 2- and 3-substituents are under investigation; in these cases, it seems likely that the inductive influence on the formation of the new bond will become relatively of greater importance.

It is now becoming clear that S_N2' attack on the system $\mathrm{CH_2{:}\overset{|}{C}{\cdot}\overset{|}{\underset{|}{C}}{\cdot}Cl}$ is more common than was once thought, and various examples have been recorded in the past without recognition of their mechanism. Thus, for example, we were unaware, when Part II was published, that 3 : 3-dichloroprop-1-ene has been recorded (Rothstein, *J.*, 1940, 1550) as reacting with the ethyl sulphide ion to give, in roughly equal amounts, 3 : 3-di(ethylthio)prop-1-ene and 1-chloro-3-ethylthioprop-1-ene. This reaction is probably bimolecular, and is analogous to the corresponding reaction of the thiophenoxide ion, in that products of normal and abnormal substitution are formed in nearly equal amounts. The differences in free energy of activation which determine the ratio of products for the reaction of 3 : 3-dichloroprop-1-ene with the different reagents $\mathrm{OEt^-}$, $\mathrm{SEt^-}$, $\mathrm{OPh^-}$, $\mathrm{SPh^-}$ (cf. Part II, *loc. cit.*) are clearly rather small, and the presence of a second centre in the molecule, which may help attack on the unsaturated carbon atom by participation in a cyclic transition complex, is clearly advantageous for the observation of rearrangement, as Young, Webb, and Goering (*J. Amer. Chem. Soc.*, 1951, **73**, 1076) have demonstrated for the reaction of secondary amines with 1-methylallyl chloride.

EXPERIMENTAL

The general methods have been described in previous Parts (*locc. cit.*). 1 : 1-Dimethylallyl chloride, prepared as described by Ultee (*J.*, 1948, 530) and fractionated under reduced pressure, had b. p. 30°/120 mm. Its refractive index (n_D^{25} 1·4170) was always checked before use, to guard against isomerisation. 3 : 3-Dimethylallyl (3-methylbut-2-enyl) chloride, prepared similarly, had b. p. 112—115°/770 mm., n_D^{25} 1·4468.

3-*Methylbut*-2-*enyl phenyl sulphide* was prepared by the action of sodium thiophenoxide on 3-methylbut-2-enyl chloride in ethanol. The product had b. p. 124—126°/14 mm., f. p. −3·5°, n_D^{25} 1·5644 (Found : C, 74·2; H, 8·1. $\mathrm{C_{11}H_{14}S}$ requires C, 74·2; H, 7·9%). Its sulphilimine derivative, prepared by the method of McCall, Tarbell, and Havill (*J. Amer. Chem. Soc.*, 1951, **73**, 4476), had m. p. 47° after recrystallisation from ethanol and from pentane.

1 : 1-Dimethylallyl chloride (20 g.) was allowed to react overnight at 30° with 250 ml. of N-sodium thiophenoxide in ethanol. The product was dissolved in ether, washed well with aqueous alkali and with water, and distilled, giving a sulphide (21 g.), b. p. 128—132°/16 mm., n_D^{25} 1·5632, f. p. −5·0°, not depressed on admixture with an authentic specimen. This material, and an authentic sample, were examined by Dr. L. C. Bateman and Dr. E. S. Waight, of the British Rubber Producers' Research Association, Welwyn Garden City, Herts. We are indebted to these investigators for showing that these two specimens had virtually identical infra-red spectra; the presence of bands at 1665 and 834 cm.$^{-1}$, together with the absence of bands at 1640 and 920 cm.$^{-1}$, were consistent with the structure $\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}SPh}$, and indicated contamination with less than 2% of $\mathrm{PhS{\cdot}CMe_2{\cdot}CH{:}CH_2}$.

For the kinetic measurements, thiophenol was added to the equivalent amount of a standardised solution of sodium ethoxide in ethanol. This solution (*ca.* 100 ml.) was allowed to reach the temperature of the thermostat, and to it was added *ca.* 0·5 ml. of 1 : 1-dimethylallyl chloride. The following are details of a typical set of measurements, at 24·9°, in which 5·00-ml. portions were added to cooled alcohol containing 10 ml. of 0·0878N-hydrochloric acid, and back-titrated with 0·0190N-sodium hydroxide (lacmoid indicator); values of k_2 were calculated by using the usual formula $k_2 = 2{\cdot}303\{\log_{10}[b(a-x)/a(b-x)]\}/t(a-b)$, where b and a are the initial concentrations of the reactants, and x is the concentration of product at time t; E and B are the Arrhenius parameters, obtained from the equation $k_2 = Be^{-E/RT}$, the units of k_2 and B being l. mole^{-1} min.$^{-1}$, and E being in kcal./mole :

Time (min.)	0	7·30	16·75	26·70	34·6	48·0	83·0	∞
Titre (ml. 0·0190N-NaOH)	2·50	3·88	5·40	6·62	7·58	8·92	11·25	15·80
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·092	0·092	0·088	0·089	0·090	0·089	—

From these values and those at other temperatures (35·1°, $k_2 = 0{\cdot}267$; 44·6°, $k_2 = 0{\cdot}701$) it can be deduced that the reaction has $E = 19{\cdot}6$ kcal., $\log_{10} B = 13{\cdot}35$. The reaction is bimolecular; the velocity coefficient at 44·6° ($k_2 = 0{\cdot}701$, for NaSPh = 0·159) is changed only slightly, and in accordance with the usual small negative salt effect, by an increase in the concentration of sodium thiophenoxide ($k_2 = 0{\cdot}661$, for NaSPh $= 0{\cdot}220$). The solvolysis of the halide is considerably slower. The following are details of the development of acid from 1 : 1-dimethylallyl chloride in ethanol at 44·6°; 5·53-ml. portions were added to excess of cold ethanol, and titrated with 0·0110N-sodium hydroxide (lacmoid). Values of k_1 were calculated by using the formula $k_1 = 2{\cdot}303\{\log_{10} [a/(a - x)]\}/t$.

Time (min.)	0	6·0	12·3	18·0	30·6	45·0	60·0	∞
Titre (ml. 0·0110N-NaOH) ...	3·41	4·69	5·82	7·01	8·93	10·85	12·50	23·34
k_1 (min.$^{-1}$)	—	0·0111	0·0105	0·0111	0·0106	0·0104	0·0102	—

To check that $\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}SPh}$ could not have been formed by the route $\mathrm{Me_2\overset{\overset{\textstyle Cl}{|}}{C}{\cdot}CH{:}CH_2} \xrightarrow{-\mathrm{HCl}} \mathrm{CH_2{:}CMe{\cdot}CH{:}CH_2} \xrightarrow{\mathrm{PhSH}} \mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}SPh}$, it was shown that isoprene does not add thiophenol under the conditions of the kinetic measurements. Sodium (3·25 g.) was dissolved in ethanol (100 ml.), and to the mixture were added thiophenol (15 ml.) and isoprene (10 g.). The mixture was heated at 60° for 18 hr. (sealed tube). Working up the product in the usual way gave a small amount of polymer, and a negligible quantity of material, b. p. >180°. A similar experiment was carried out with half the above quantity of sodium; the result was the same.

1-Methylallyl chloride, n_D^{25} 1·4124, was prepared as described by Catchpole and Hughes (*loc. cit.*). 1-Methylallyl phenyl sulphide was prepared by the method of Cope, Morrison, and Field (*loc. cit.*), as follows. Sodium (13·8 g.) was dissolved in absolute ethanol (600 ml.), and to the solution was added thiophenol (63 g.). The mixture was cooled to 5°, and 1-methylallyl chloride (50 g.) was added. After the mixture had been kept overnight at 5°, it was poured into water and extracted with ether. The extract was washed with sodium hydroxide solution and with water, dried ($CaCl_2$), and fractionated through a 2-ft. column packed with glass helices. The following fractions were obtained (b. p. at 2 mm.) : (1) (5·0 g.), b. p. 57—58°, n_D^{25} 1·5547,* (2) (5·0 g.), b. p. 57—58°, n_D^{25} 1·5547, (3) (5·0 g.), b. p. 57—58°, n_D^{25} 1·5570, (4) (6·2 g.), b. p. 58—70°, n_D^{25} 1·5630, (5) (4·0 g.), b. p. 70°, n_D^{25} 1·5672, (6) (43·0 g.), b. p. 70°, n_D^{25} 1·5681,* residue (*ca.* 3·0 g.). The mean refractive index (1·5649) of fractions 1—6 indicates that a considerable amount of rearrangement had occurred during the fractionation. The following experiment shows that the true refractive index of the sulphide produced in the reaction is much lower. 1-Methylallyl chloride (9 g.) was added at 5° to 100 ml. of a solution of N-sodium thiophenoxide. Next morning the mixture was poured into excess of N-sodium hydroxide. The sulphides were extracted with pentane, and the pentane extract was washed with water, dried ($CaCl_2$), filtered, and distilled. When most of the pentane had been removed on a water-bath, the product was evacuated for some hours, without heating, at about 1 mm. It was then molecularly distilled from a flask at room-temperature into a trap at −80°, under the vacuum of a mercury diffusion pump. A first fraction of about 1 g., which might have had a low refractive index because of the presence of a trace of pentane, was rejected. The remainder (10 g.; n_D^{25} 1·5568) was a mixture of 1-methylallyl phenyl sulphide (84%) and but-2-enyl phenyl sulphide (16%), as judged by its refractive index. There remained a small residue (<1 g.) of undistilled solid product, probably diphenylene disulphide produced by slight oxidation of thiophenol. A similar experiment, in which the reaction was allowed to proceed at 80°, gave a product of n_D^{25} 1·5578. A sample of nearly pure 1-methylallyl phenyl sulphide, n_D^{25} 1·5555, was kept overnight at room temperature with 1·44N-sodium thiophenoxide (80 ml.). The sulphide was then recovered by the above technique, and had refractive index 1·5608.

The reaction of 1-methylallyl chloride with sodium thiophenoxide was studied kinetically in the usual way. The following are the results of an experiment at 25·0°. Portions (5·00 ml.) of the reaction mixture, initially containing 0·2266N-sodium thiophenoxide and 0·1132N-1-methylallyl chloride, were pipetted into ethanol and titrated with 0·0412N-hydrochloric acid (lacmoid indicator).

Time (min.)	0	2·92	8·73	14·80	25·28	42·40	90·1	197·0	∞
Titre (ml. 0·0412N-HCl)	27·50	27·08	26·40	25·68	24·10	23·00	20·10	16·80	13·76
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·048	0·043	0·044	0·053	0·044	0·046	0·045	—

The mean velocity coefficient at 42·5° was found to be 0·252 l. mole^{-1} min.$^{-1}$, from which the energy of activation for this reaction is 18 kcal.

* There was no indication of the presence of any material intermediate in b. p. between ether and fraction 1. Cope, Morrison, and Field (*loc. cit.*) record n_D^{25} 1·5546 and 1·5680 respectively for 1-methylallyl and but-2-enyl phenyl sulphide.

The product of the reaction of 1-methylallyl chloride with sodium ethoxide in ethanol was re-examined (cf. Roberts, Young, and Winstein; Catchpole and Hughes, *locc. cit.*). 1-Methylallyl chloride (74 g.) was heated for 48 hr. at 81° with ethanolic 2N-sodium ethoxide (500 ml.) in sealed tubes. The product was poured into water and extracted six times with pentane. The pentane extracts were washed with saturated calcium chloride solution and with water, dried, and fractionated, giving the fractions: (*a*) 9·1 g., b. p. 40—75°, n_D^{25} 1·3678; (*b*) 11·5 g., b. p. 75—78°, n_D^{25} 1·3855; (*c*) 25·8 g., b. p. 78—80°, n_D^{25} 1·3862; (*d*) 3·8 g., b. p. 80—98°, n_D^{25} 1·3906; (*e*) 1·0 g., b. p. 98—101°, n_D^{25} 1·4031. By assuming that pentane, ethyl 1-methylallyl ether, and but-2-enyl ethyl ether have respectively n_D^{25} 1·3550, 1·3862,* and 1·4031,* it can be estimated that there were isolated 54·6 g. (55%) of mixed ethers containing 4·5% of but-2-enyl ethyl ether.

We are indebted to Professor E. D. Hughes, F.R.S., for valued discussions. Analyses are by Mr. A. V. Winter of this Department.

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[*Received, July* 11*th*, 1953.]