2. *Rearrangement and Substitution in Anionotropic Systems. Part II. Test for Bimolecular Rearrangement, and Confirmation of the Ionic Mechanism of Rearrangement, from Product Compositions in Substitutions of α- and γ-Methylallyl Halides.*

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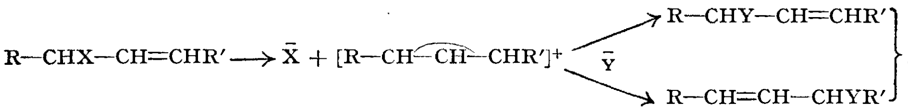
In continuation of the investigations outlined in the preceding paper, we show in the example of the etholysis of α- and γ-methylallyl chlorides that, whereas the first-order solvolytic reactions of the chlorides, which are largely unimolecular in mechanism, give rise to a mixture of isomeric ethers of approximately the same composition in both cases, the bimolecular reactions with sodium ethoxide in ethyl alcohol give only the ether of corresponding structure to the chloride used. Thus, while there is evidence for a unimolecular mechanism of replacement, involving the formation of a mesomeric carbon cation (S_N1—see below), and for a direct bimolecular substitution without rearrangement (S_N2), we find no indication of bimolecular replacement with rearrangement (S_N2'). The observations are entirely consistent with our failure to realise a bimolecular mechanism of isomerisation (preceding paper). The full significance of both results is discussed in the following paper.

In Part I we outlined the application of recent advances in our knowledge of the mechanism of aliphatic substitution to the problems of rearrangement and substitution in anionotropic compounds and discussed in more detail the special case of isomerisation in these systems. We now proceed with a further consideration of the mechanism of anionotropic substitution. Burton and Ingold's mechanism, now regarded as a particular form of the general unimolecular mechanism of nucleophilic substitution, may for this case be formulated as follows :



$$\mathrm{R{-}CHX{-}CH{=}CHR'} \longrightarrow \bar{\mathrm{X}} + [\mathrm{R{-}CH\overset{\frown}{-}\overset{\frown}{CH}{-}CHR'}]^{+} \overset{\bar{\mathrm{Y}}}{\rightrightarrows} \left.\begin{array}{l} \mathrm{R{-}CHY{-}CH{=}CHR'} \\ \mathrm{R{-}CH{=}CH{-}CHYR'} \end{array}\right\} \ldots (S_N1)$$

Obviously, this mechanism provides for substitution without or with rearrangement of the anionotropic system. It is undoubtedly operative over a wide range of substances and conditions : the evidence, partly derived from this paper, will be collated in Part III.

The analogous particularisation of the bimolecular mechanism of substitution is represented below; in theory, this scheme also provides for substitution either without rearrangement of the anionotropic system, S_N2, or with such rearrangement, S_N2' :

$$\bar{\mathrm{Y}} + \mathrm{R{-}CHX{-}CH{=}CHR'} \longrightarrow \mathrm{R{-}CHY{-}CH{=}CHR'} + \bar{\mathrm{X}} \ldots (S_N2)$$

$$\mathrm{R{-}CHX{-}CH{=}CHR'} + \bar{\mathrm{Y}} \longrightarrow \bar{\mathrm{X}} + \mathrm{R{-}CH{=}CH{-}CHYR'} \ldots (S_N2')$$

We set ourselves two experimental problems, one relating to each of these two main types of mechanism. The first was to set up conditions of substitution, kinetically consistent with the unimolecular mechanism, for two isomerides $\mathrm{R{-}CHX{-}CH{=}CHR'}$ and $\mathrm{R{-}CH{=}CH{-}CHXR'}$, and then to ascertain whether each yields an identical mixture of the substitution products $\mathrm{R{-}CHY{-}CH{=}CHR'}$ and $\mathrm{R{-}CH{=}CH{-}CHYR'}$, both the reactants and the products being sufficiently stable not to undergo mutual isomerisation under the experimental conditions employed. An identical mixture should result if the reaction proceeds by way of a carbonium ion which is common to both of the original substances and to both of the products. The second problem was to set up, for each of the two original isomerides, conditions of substitution in which the bimolecular mechanism could kinetically be proved to have taken substantially complete control; and then to ascertain by a similar study of the product composition whether each substitution, besides pursuing the familiar route in which the entering group becomes attached to the carbon atom from which the removed group is expelled (S_N2), also assumes a form in which the entering group becomes attached to the other end of a rearranged anionotropic system (S_N2'). Our failure to establish bimolecular rearrangement in isomerisation lent special interest to the question of the existence of bimolecular rearrangement in the substitution reactions of an anionotropic system.

Desiring a system of simple constitution and limited mobility, we considered the case of α- and γ-methylallyl bromides, our attention having been drawn to these compounds by previous studies of their formation and interconversion and particularly by the work of Young and of Kharasch and their collaborators (Winstein and Young, *J. Amer. Chem. Soc.*, 1936, **58**, 104; Young and Lane, *ibid.*, 1937, **59**, 2051; Kharasch, Margolis, and Mayo, *J. Org. Chem.*, 1936, **1**, 393). The corresponding chlorides (Kharasch, Kritchevsky, and Mayo, *J. Org. Chem.*, 1937, **2**, 489) are, however, much more easily purified to the extent necessary for the kinetic and product experiments, as well as having a wider margin of stability; consequently, we selected these compounds for our investigations. The substitution studied was their ethyl alcoholysis, both in ethyl alcohol alone and in solutions containing various concentrations of sodium ethoxide.

It is convenient to include the detailed account of the preliminary kinetic experiments in a forthcoming paper, since, in the subsequent course of our work, these experiments have been extended into a kinetic investigation of considerably wider scope (which is not yet quite complete) involving a number of simple and substituted allyl halides other than those with which we are now concerned, as well as a general consideration of medium effects, activation energies, and other matters which are only indirectly connected with the present problem. The main point for our immediate purpose is the determination of the limits of sodium ethoxide concentration above which the kinetic order is substantially second. These limits follow from the measured first- and second-order rate constants for alcoholysis in alcohol solutions containing different concentrations of sodium ethoxide. The alcoholysis of α-methylallyl chloride under the conditions used is a nearly pure second-order reaction in the presence of ethoxide concentrations above about 0·5N. For γ-methylallyl (crotyl) chloride the tendency to second-order substitution is greater, to the extent that the approximate limit may be set about five times lower than that applying to the α-methylallyl compound.

In order to exclude any trace of accompanying unimolecular reactions the experiments on the products formed in bimolecular substitution were carried out in 2·7N-ethyl-alcoholic sodium ethoxide. The first-order solvolytic reactions, on the other hand, were conducted in substantially neutral alcoholic solutions.

It is by now a commonplace that first-order solvolytic substitutions are not proved by their kinetic order alone to be unimolecular, because bimolecular substitutions with the solvent molecule as the substituting agent require the same kinetic order. The latter interpretation is definitely excluded only when we can show, for instance, that the compound substituted is insensitive to substituting agents which are more strongly basic than the solvent molecule. With α- and γ-methylallyl chlorides in dry ethyl alcohol as solvent there is sensitivity to the very strongly basic ethoxide ion, as shown by the results contained in Table I.

TABLE I.

Rates of Alcoholysis of α- and γ-Methylallyl Chlorides.

(Temp. 99·5°. Initial [Halide] ~ 0·05M. k_1 = first-order constant in min.$^{-1}$. k_2 = second-order constant in min.$^{-1}$ g.-mol.$^{-1}$ l.)

	α-Methylallyl chloride.	γ-Methylallyl chloride.
NaOEt = 0 : 10^3k_1	1·76	4·88
NaOEt = 1M : 10^3k_2	91·5	1630

Taking account of the concentration of the solvent for the purpose of an order-of-magnitude calculation, the specific rates which would have to represent the activity of alcohol in assumed bimolecular reactions with α- and γ-methylallyl chlorides are about 10^{-3}—10^{-4} times smaller than the corresponding rates for the reactions with ethoxide ions. In reactions for which other evidence indicates a bimolecular mechanism this rate ratio is of order 10^{-5}—10^{-6} (cf. Bateman, Cooper, Hughes, and Ingold, *J.*, 1940, 925). In the case of α-methylallyl chloride, the sensitivity is such as to suggest a substantially unimolecular mechanism in the complete absence of added ethoxide ions, though it is not sufficiently limited definitely to establish a unimolecular mechanism to the complete exclusion of any bimolecular contribution. A duplex constitution for the reaction between γ-methylallyl chloride and ethyl alcohol is rendered very probable by the results indicated. Nevertheless, since the second-order reactions with sodium ethoxide are indubitably bimolecular, we have two conditions of reaction, corresponding to first- and second-order kinetics, for which product analyses are of interest.

The bimolecular replacement was effected with a saturated solution of sodium ethoxide (2·7N) in ethyl alcohol at the boiling point of the solution. All the usual precautions having been taken with regard to the standardisation and checking of the method of isolation (see experimental section), the ethers formed were isolated and analysed refractometrically. The results are in Table II. They show that each halide gives an ethyl ether of corresponding structure; in other words that, while bimolecular substitution without rearrangement of the anionotropic system (S_N2) freely occurs with both halides, there is no accompanying bimolecular substitution with rearrangement (S_N2').

TABLE II.

Product Composition in Second-order Ethyl Alcoholysis of α- and γ-Methylallyl Chlorides.

Chloride or mixture of chlorides used.	Ethyl γ-methylallyl ether in product (%).
α-Methylallyl chloride	0
γ-Methylallyl chloride	100
Mixture of chlorides {71% α-methylallyl 29% γ-methylallyl}	28

For the first-order reactions, the experiments were again carried out at the boiling point of the solution, which was prevented from running acid by adding an indicator and titrating with alcoholic sodium ethoxide during the course of the reaction. The solutions were thus kept as near the neutral point as possible, but, of course, momentary local concentrations of alkali were impossible to avoid, though by rapid agitation they could be minimised. The results, summarised in Table III, show that each of the isomeric chlorides, on alcoholysis under the conditions mentioned, gives a mixture of isomeric ethyl ethers of similar composition. The direction of the differences in composition is such that they may be attributed either to our failure entirely to avoid such momentary local concentration of alkali during the experiments as would lead to a small amount of simultaneous substitution with ethoxide ions, or to a limited concomitant bimolecular reaction with solvent molecules. Doubtless, the incursion of a bimolecular replacement would be more important in the case of γ-methylallyl chloride, as the results of Table I clearly show, and we regard the figures obtained with α-methylallyl chloride as approximating more closely to the probable result of substitution by a unimolecular mechanism.

TABLE III.

Product Composition in First-order Ethyl Alcoholysis of α- and γ-Methylallyl Chlorides.

Chloride or mixture of chlorides used.	Ethyl γ-methylallyl ether in product (%).
α-Methylallyl chloride	82
γ-Methylallyl chloride	92
Mixture of chlorides {32% α-methylallyl 68% γ-methylallyl}	92

In the bimolecular reaction, it is evident from the product studies themselves (Table II) that no isomerisation of the halides takes place under the conditions used. For the first-order reaction, on the other hand, the product analysis does not provide a similar check, and it is necessary to discuss the possibility that isomerisation of the halides occurs by some mechanism which does not involve ionisation.* Evidence is available indicating that any considerable

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* Isomerisation of the halides through an ionic intermediate would not vitiate our conclusion with regard to the mesomeric nature of the ion, but we think it is unlikely to occur to any considerable extent under the conditions employed.

isomerisation of this type is improbable under the conditions employed in our solvolytic reactions. Briefly, the chief items of evidence are as follows : First, the pure isomers did not undergo any detectable change on being boiled under reflux for several hours, either alone or in solution in an inert solvent such as acetone. Secondly, when the two pure chlorides are dissolved in ethyl alcohol under conditions approximating to those used in our product experiments, the first-order rate constants for the formation of the mixed ethers are different in the two cases (cf. Table I : see also Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157), thus eliminating the possibility that a prior isomerisation may occur in the alcoholic solvent, to give in each case the same equilibrium mixture of chlorides. The absence of isomerisation in the products of reaction (after their formation) under the conditions of our experiments is proved by the results for the bimolecular substitution reactions (Table II) ; evidently no change occurs when the ethers are boiled under reflux in alcoholic solution. Further evidence on this point was obtained by conducting " recovery " experiments involving known mixtures of the two ethers; no change in composition was detected under the conditions employed for either the first- or the second-order substitution reactions.

After the publication in summary of these results (*Trans. Faraday Soc.*, 1941, **37**, 627) a paper by Roberts, Young, and Winstein appeared (*loc. cit.*) recording the results of an independent investigation which provides excellent confirmation as far as there is overlap. These authors studied the reactions of α- and γ-methylallyl chlorides with both ethoxide ions in ethyl alcohol and acetate ions in acetic acid. In neither of these substitutions did they isolate the first-order reaction for both halides, but they showed that acetolysis which contained a first-order reaction led to mixtures of acetates, and that the heterogeneous substitution of the isomeric chlorides by means of silver acetate gave mixtures of the methylallyl acetates which were of similar composition for both halides. On the other hand, they did establish conditions for the second-order substitution of both chlorides in the case of alcoholysis, and on examining the products they found, just as we did, that each chloride gives only an ethoxy-compound of its own type of constitution. Similar results were obtained for acetolysis with acetate ions in acetone or acetic anhydride. In a later paper (*ibid.*, 1944, **66**, 421) Young and Andrews reported on an analogous investigation of the hydrolysis of the isomeric chlorides in aqueous or aqueous-alcoholic media. From a study of the reaction kinetics and products in the presence of varying concentrations of alkali, they concluded that the secondary chloride reacts only by the unimolecular mechanism under these conditions, to give a mixture of alcohols containing about 65% of the secondary isomer, while the primary chloride has a tendency to follow the bimolecular mechanism, and gives, under conditions most favourable to bimolecular substitution, high proportions of the primary alcohol. Evidence was obtained that the first-order (solvolytic) reaction of the primary chloride is in part a bimolecular reaction with the solvent. The heterogeneous hydrolysis with an aqueous suspension of silver oxide gave a mixture of alcohols from both halides, the composition of the mixture being similar, but not identical, in the two cases.

A notable outcome of the work described in this paper, and also that of Young and his co-workers, is that bimolecular substitution with rearrangement (S_N2') does not occur under the conditions employed. There is, of course, an obvious correspondence between this result and that of Part I in which we failed to find a bimolecular isomeric rearrangement. The significance of both results is discussed in the following paper.

EXPERIMENTAL.

γ- and α-Methylallyl Chlorides.—The pure chlorides were isolated from mixtures of the two isomers by fractional distillation (Kharasch, Kritchevsky, and Mayo, *J. Org. Chem.*, 1937, **2**, 489). It was found expedient to use for this purpose two different mixtures, each rich in either γ- or α-methylallyl chloride. γ-Methylallyl chloride (b. p. 84·0—84·2°/760 mm.; $n_D^{20°}$ 1·4350) was thus obtained from crotyl alcohol and hydrogen chloride, while α-methylallyl chloride (b. p. 63·9—64·2°/760 mm.; $n_D^{20°}$ 1·4151) was isolated from the addition product of butadiene and hydrogen chloride (Kharasch *et al.*, *loc. cit.*). Neither chloride was isomerised by being boiled under reflux for 5 hours, either alone or in solution in acetone.

Ethyl γ- and α-Methylallyl Ethers.—A mixture of γ- and α-methylallyl bromide (110 ml.) obtained from α-methylallyl alcohol and hydrogen bromide (Young and Lane, *J. Amer. Chem. Soc.*, 1937, **59**, 2051) was mixed with dry ethyl alcohol (200 ml.) and boiled under reflux for 2 hours, the solution being kept substantially neutral by frequent titration with alcoholic sodium ethoxide, using phenolphthalein as indicator. The product was diluted with an equal volume of water and saturated with sodium chloride, and the mixture was distilled. Distillation was continued until a test sample of distillate gave no separation into layers on dilution with water. The whole distillate obtained up to this point was diluted with an equal volume of water, and the upper layer was separated and washed with water, the washings being added to the aqueous layer. An equal volume of water was added to the aqueous portion, and, after being saturated with salt, the mixture was fractionally distilled as before. This process was repeated until no ether separated from the first few ml. of distillate on addition of water. The crude ether thus obtained (124 ml.) was dried (P_4O_{10}) and distilled from barium oxide. Repeated fractional distillation to constant refractive index gave ethyl α-methylallyl ether, b. p. 75·5—76·0°/760 mm., $n_D^{25^\circ}$ 1·3872, and ethyl γ-methylallyl ether, b. p. 100—100·5°/760 mm., $n_D^{25^\circ}$ 1·4020 (Found, for a mixture of the two ethers: C, 71·8; H, 11·7. Calc.: C, 72·0; H, 12·0%). The refractive index–composition plot for synthetic mixtures of the isomeric ethers was shown to be linear.

Isolation and Examination of Ethers from the Etholysis of γ- and α-Methylallyl Chlorides.—The alcoholysis of each of the isomeric chlorides was carried out in absolute ethyl alcohol under two sets of experimental conditions, namely, (*a*) in substantially neutral solution, and (*b*) in 2·7N-solution of sodium ethoxide—these being conditions conducive to the operation of the unimolecular (S_N1) and the bimolecular (S_N2) mechanism respectively. The aim of our isolation technique was to obtain samples of the ethers, the composition of which would correspond to the proportions of ethyl γ- and α-methylallyl ether produced under the conditions stated. The method adopted (see below) has been shown to give reliable results by carrying out the procedure with synthetic mixtures containing the two ethers in known proportions. For the solvolytic reaction, the halide (10 ml.) was dissolved in dry ethyl alcohol (100 ml.) and boiled under reflux for 72 hours, the solution being kept nearly neutral by frequent titration with alcoholic sodium ethoxide, phenolphthalein being used as indicator. Bimolecular alcoholysis of each chloride (10 ml.) was carried out by boiling it under reflux with 2·7N-sodium ethoxide in ethyl alcohol (100 ml.) for 12 hours.

In illustration of the experimental method, details are given below of the isolation of the ether mixture formed by the solvolysis of γ-methylallyl chloride in ethyl alcohol. The reaction mixture, after dilution with an equal volume of water, was saturated with sodium chloride and distilled to give the following fractions: (1*a*) 5 ml., b. p. 75—78°; (1*b*) 7 ml., b. p. 78—81°; (1*c*) 10 ml., b. p. 81—83°; (1*d*) 10 ml., b. p. 83—85°; (1*e*) 40 ml., b. p. 85—88°. With water (equal volume), (1*a*) and (1*b*) gave an upper layer of ether, which was separated and washed with water, whilst (1*c*), (1*d*), and (1*e*) gave no separation of layers. Fractions (1*c*), (1*d*), (1*e*), the washings from (1*a*) and (1*b*), and an equal volume of water, were combined, saturated with salt, and redistilled: (2*a*) 3 ml., b. p. 80—82°; (2*b*) 6 ml., b. p. 82—83°, (2*c*) 10 ml., b. p. 83—85°; (2*d*) 25 ml., b. p. 85—89°. With water (2*a*) gave an upper layer which was washed with water, whilst (2*b*), (2*c*), and (2*d*) gave no separation. Fractions (2*b*), (2*c*), and (2*d*), the washing from (2*a*), and an equal volume of water were combined, saturated with salt, and redistilled: (3*a*) 2 ml., b. p. 82—84°; (3*b*) 4 ml., b. p. 84—87°; (3*c*) 6 ml., b. p. 87—88°. With water (3*a*) gave an upper layer, and the washings, together with fractions (3*b*) and (3*c*), were again treated as above: (4*a*) 1 ml., b. p. 84—85°; (4*b*) 1 ml., b. p. 85°. With water (4*a*) gave a very small upper layer which was separated and washed with water.

The top layers (crude ethers, totalling 8·5 ml.) from (1*a*), (1*b*), (2*a*), (3*a*), and (4*a*) were distilled completely, first from fused barium oxide, and then from sodium. The refractive index ($n_D^{25^\circ}$ 1·4008) of the final distillate (8·0 ml.) showed it to have the following composition: ethyl γ-methylallyl ether 92%, ethyl α-methylallyl ether 8%.

The percentage compositions of the various halide and ether mixtures were in all cases determined from their refractive indices. The results are summarised below:

Reactant (Halide).		Condition of reaction.*	Product (Ether).	
$n_D^{25^\circ}$.	% of primary.		$n_D^{25^\circ}$.	% of primary.
1·4123	0	1	1·3993	82
1·4123	0	2	1·3872	0
1·4324	100	1	1·4008	92
1·4324	100	2	1·4020	100
1·4260	68	1	1·4007	91
1·4179	28	2	1·3915	29

* 1 = Solvolysis in EtOH; 2 = Reaction with OEt in EtOH.

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