

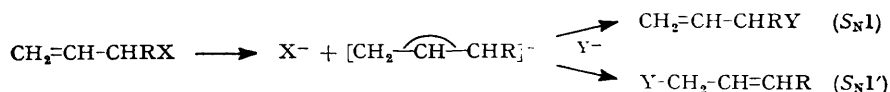
*Demonstration of Bimolecular Substitution with Anionotropic
Rearrangement (S_N2') in 1-Methylallyl Bromide.*

By B. D. ENGLAND

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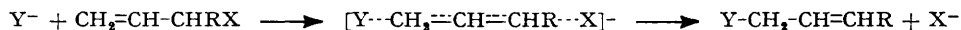
Rates and activation energies for the S_N2 exchange reactions of 1- and 3-methylallyl bromide with lithium bromide in acetone have been measured. The rearrangement of 1-methylallyl bromide under similar conditions has been investigated and shown to be bimolecular, in accordance with the S_N2' mechanism of rearrangement in anionotropic systems. Rates and Arrhenius parameters for the corresponding rearrangement of 3-methylallyl bromide have been inferred from these results. Experiments on the *thermal* rearrangement of these compounds in the pure state are recorded, and a method of stabilising them described.

For aliphatic substitution in allyl halides, much evidence has been obtained for the operation of the S_N2 mechanism of substitution (see, especially, Catchpole and Hughes, *J.*, 1948, 4; Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Vernon, *J.*, 1954, 4462) and the S_N1 (Catchpole, Hughes, and Ingold, *J.*, 1948, 8; Vernon, *J.*, 1954, 423). Indeed, as these mechanisms are well established in the general field of nucleophilic aliphatic substitution, it would be surprising if they had no counterparts in the reactions of the allyl compounds. As applied to substitution in allylic systems, the unimolecular mechanism may lead to substitution without (S_N1) or with rearrangement (S_N1'):



Since the cation-forming step in such a substitution is independent of the nucleophilic reagent, the compound should, ideally, undergo isomeric rearrangement in the same environment if the nucleophilic reagent is omitted. With the S_N2 mechanism, the entering substituent always occupies the position of the displaced atom or group.

Unequivocal evidence for a third mechanism, peculiar to anionotropic systems and involving bimolecular substitution with rearrangement (S_N2'), *viz.*,



has been much more difficult to obtain. The mechanism was first suggested as a possibility by Hughes (*Trans. Faraday Soc.*, 1938, **34**, 194) but, until recently, no convincing demonstration had been published. With the simpler allylic halides and nucleophilic reagents, the conditions favouring the S_N2' mechanism are just those which promote S_N2 substitution which then dominates the substitution process, forming a product resistant to attack by either mechanism. Thus, Roberts, Young, and Winstein (*loc. cit.*), on treatment

of 1- and 3-methylallyl chloride with sodium ethoxide in absolute ethanol, obtained at least 96 and 99% respectively of the corresponding ethers, a result confirmed by Catchpole and Hughes (*loc. cit.*) and by de la Mare and Vernon (*J.*, 1953, 3555).

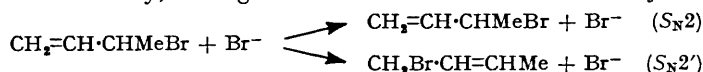
With more complex systems, rearranged products may be obtained but it may not be certain that they have been formed in an S_N2' reaction. A demonstration that the reaction is bimolecular is a necessary part of the evidence. Hence, the conversion of 3-phenylallyl alcohol into 1-phenylallylacetone and of 1-phenylallyl alcohol into 3-phenylallylacetone by Carroll (*J.*, 1940, 1266), quoted by Wilson (*Trans. Faraday Soc.*, 1941, 37, 631), cannot rank as a demonstration of the S_N2' reaction because this kinetic evidence has not been supplied; furthermore, an alternative interpretation of Carroll's results is available (Kimel and Cope, *J. Amer. Chem. Soc.*, 1943, 65, 1922). Likewise, bimolecular kinetics have been demonstrated neither for the acid-catalysed rearrangement of allylic alcohols, claimed by Braude (*Ann. Reports*, 1949, 46, 128) to involve such a mechanism, nor for the rearrangements of the halocodides (Manske and Holmes, "The Alkaloids," Vol. 2, Academic Press, New York, 1952, p. 185; cf. Stork and White, *J. Amer. Chem. Soc.*, 1953, 75, 4119).

A bimolecular substitution reaction which involves re-arrangement does not necessarily involve the S_N2' mechanism; the rearranged products may result from the rapid intramolecular rearrangement S_Ni' (Ingold, "Structure and Mechanism in Organic Chemistry," Cornell, 1953, p. 596) of the products of substitution without rearrangement. The stability to rearrangement of the starting compound and of possible products of "normal" substitution reactions should therefore be demonstrated. An objection (Dewar, *Bull. Soc. chim.*, 1951, 18, c43) to the claim (Kepner, Young, and Winstein, *J. Amer. Chem. Soc.*, 1949, 71, 115) that the formation of rearranged products in the reaction of 1-methyl- and 1-ethyl-allyl chloride with diethyl sodiomalonate in absolute ethanol proceeds by the S_N2' mechanism has been based on this point. Young, Webb, and Goering (*ibid.*, 1951, 73, 1076) used the formally neutral reagents di- and tri-ethylamine in reaction with 1-methylallyl chloride in benzene and found, with the secondary amine, that a large yield of rearranged products was formed in an apparently bimolecular reaction: the S_N2 substitution product was absent but was prepared by a different method and shown to be stable to rearrangement under the conditions of the reaction. The authors pointed out, however, that the products might be formed by the rearrangement of a pre-formed, hydrogen-bonded complex, a process that might also require second-order kinetics. Young and Clement (*Science*, 1952, 115, 488) have however now claimed similar rearrangements with tertiary amines where no assistance from hydrogen-bonding is possible.

The most significant tests of the S_N2' mechanism have arisen from deliberate attempts to increase the ratio of the specific rate of the S_N2' reaction to that of the S_N2 reaction by a variety of methods. Hughes and his co-workers (cf. Ingold, *op. cit.*, p. 594) find that the S_N2' rearrangement is easily observable in the reaction of 1-*tert*-butylallyl chloride with ethoxide ion in absolute ethanol, where the S_N2 reaction is sterically hindered. Alkyl substituents may also increase the S_N2' rate by assisting the displacement of halogen, for de la Mare and Vernon (*loc. cit.*) observed virtually complete rearrangement in the reaction of 1:1-dimethylallyl chloride with sodium thiophenoxide, a reaction that is faster than the S_N2 substitution of 1-methylallyl chloride with the same reagent. Independent experiments showed that an S_N2' reaction was undoubtedly under observation. Likewise, additional halogen atoms on the 1-carbon atom appear both to retard the S_N2 substitution and to promote the S_N2' rearrangement, in this case by their inductive effect on the electron density at the 3-carbon atom. Thus de la Mare and Vernon (*J.*, 1952, 3325, 3331, 3628) have observed S_N2' rearrangement in the reactions of 3:3-dichloroprop-1-ene and 3:3:3-trichloro-2-methylprop-1-ene with ethoxide and thiophenoxide ions. In view of the lability of α -chloro-ethers it is most unlikely that an S_N2 substitution followed by an S_Ni' rearrangement is responsible for the rearranged products.

In the simpler alkyl derivatives of allyl halides the S_N2' rearrangement undoubtedly occurs with common nucleophilic reagents, but to such a small extent that an investigation of its characteristics is usually impracticable. In the present work (cf. England and Hughes, *Nature*, 1951, 168, 1002) the mechanism has been studied in 1-methylallyl bromide by using bromide ions as nucleophilic reagent. This choice ensures that the S_N2 reaction

does not use up the original compound before S_N2' rearrangement has proceeded to a measurable extent: theoretically, the organic bromide is available indefinitely for rearrangement.



Furthermore, by using radioactive bromide ion, the kinetic features of the much faster S_N2 reaction can be investigated. 1- and 3-Methylallyl bromide as ordinarily prepared, are unstable compounds rearranging rapidly in the absence of solvent to an equilibrium mixture (Winstein and Young, *J. Amer. Chem. Soc.*, 1936, **58**, 104). We have succeeded in reducing the rate of this type of rearrangement to the point where it does not compete with the heterolytic mechanism S_N2' .

EXPERIMENTAL

Materials.—Acetone was purified by standard methods, and, immediately before use, distilled from anhydrous magnesium perchlorate. For S_N2' runs, diphenylamine was added to the perchlorate in the final distillation, which was conducted in a stream of nitrogen. This procedure prevented the development of colour in the organic bromide solutions (cf. Baker and Nathan, *J.*, 1935, 519).

Radioactive lithium [^{82}Br]bromide was prepared from ammonium bromide after irradiation by the Atomic Energy Research Establishment at Harwell. The product was thoroughly dried and freed from insoluble material before being made up in acetone, inactive bromide being added when necessary. In most cases the [^{80}Br] isotope of 4.4-hr. half-life, which was also produced in the irradiation, had decayed to a negligible activity before the material was used.

All methods of preparation of 1- or 3-methylallyl bromide yield a mixture of the two. 1:3-Butadiene was found to be a more convenient starting material than either acraldehyde (Claisen and Tietze, *Ber.*, 1926, **59**, 2344) or crotonaldehyde (Young, Hartung, and Crossley, *J. Amer. Chem. Soc.*, 1936, **58**, 100). Dry diethyl ether (150 ml.) containing a trace of diphenylamine was cooled to -80° . Dry butadiene (54 g., 1 mole) was dissolved in this ether, followed by dry hydrogen bromide (81 g., 1 mole) (*Org. Synth.*, Coll. Vol. 2, Wiley, New York, 1943, p. 338); at this stage, yellow addition products (Archibald and McIntosh, *J.*, 1904, **85**, 925) of hydrogen bromide and ether were formed. The mixture was allowed to warm slowly to room temperature, left for a day, then washed with water and dried (CaCl_2). Ether and unchanged butadiene were removed on the water-bath and the residue was fractionated at 93 mm. until the b. p. of 1-methylallyl bromide (31°) was reached. The bromide fraction was then distilled into a trap (-80°) at 1 mm. pressure and room temperature to remove high-boiling impurities. A crude mixture (93 g., 69%) of bromides was obtained. Unfortunately, we were not then aware of the work of Voigt (*J. pr. Chem.*, 1938, **151**, 307) who obtained 81.5% of mixed bromides by passing butadiene into concentrated aqueous hydrogen bromide.

The separation of the bromides requires fractionation below room temperature (Winstein and Young, *loc. cit.*), and a 4 ft., vacuum-jacketed column packed with glass helices was used. The still-head was of conventional design but the condenser and take-off tube (surrounded by thin lead tubing) were kept at about -30° by the circulation of cold alcohol; the receiver was at -80° . To reduce isomerisation, receivers were cleaned with hot chromic acid followed by dilute ammonia solution and water. After being dried, they were heated to redness, flushed with steam, dried again, and cooled in dry nitrogen. Distillations were conducted in a nitrogen atmosphere, usually at 34 mm. pressure. Fractions of 1-methylallyl bromide isolated by this procedure were of constant b. p. but had low and variable purity. The difficulty was avoided by isolating the 3-methylallyl bromide fraction from a mixture stabilised with ammonia (see below) and isomerising this to the equilibrium mixture (Winstein and Young, *loc. cit.*) by 10 mins.' heating on the water-bath. Fractionation of the mixture then yielded pure secondary bromide. More than the theoretical 14% of 1-methylallyl bromide was often isolated from the mixture, as isomerisation occurred in the still-pot. The bromide fractions were brought up to room temperature, and dry ammonia (about 15 ml. to 10 ml. of bromide) was introduced into the air space in the receivers, which were then stored at -80° until required. Physical constants were: 1-methylallyl bromide, b. p. $11.5\text{--}11.7^\circ/34\text{ mm.}$, $n_D^{25}\ 1.4599$, $d_4^{25}\ 1.2990$; 3-methylallyl bromide, b. p. $26.8^\circ/34\text{ mm.}$, $n_D^{25}\ 1.4795$, $d_4^{25}\ 1.3372$; equilibrium mixture at 25° , $n_D^{25}\ 1.4767$. These values compare well with data in the literature (Kharasch, Margolis, and Mayo, *J. Org. Chem.*, 1936, **1**, 393; Winstein and Young, *loc. cit.*) and the bromine content, as determined by quantitative

hydrolysis, had the theoretical value. No evidence for the existence of two forms of 3-methylallyl bromide [but-2-enyl bromide] was obtained (cf. Winstein and Young, *loc. cit.*; Gredy and Piaux, *Bull. Soc. chim.*, 1934, 1, 1481). Glass surfaces, after long contact with bromide mixtures, became opaque.

Stability of 1- and 3-Methylallyl Bromide.—Previous workers have noted the small and variable stability of these compounds as ordinarily prepared, especially the secondary isomer, observations which were fully confirmed in the present work. However, 3-methylallyl bromide [but-2-enyl bromide] samples remaining in the still-pot after removal of the lower-boiling isomer were often remarkably stable although brown. Such samples resisted isomerisation after 2 hr. at 100° even after addition of charcoal which is a catalyst (Winstein and Young, *loc. cit.*). The same samples were easily isomerised in 10 min. at 100° after fractionation to remove the colour. Secondary bromide samples could be stored indefinitely at -80° under nitrogen without isomerisation, but, on being warmed and transferred to another vessel or to a refractometer at room temperature after a few days at -80°, isomerised very rapidly forming 30% of primary bromide in about 10 min. Freshly distilled samples were usually quite stable enough to allow a careful determination of refractive index at 25°.

Investigations of the stabilising effect of various substances were carried out by sealing about 1 ml. of unstabilised secondary bromide and a trace of the substance in Pyrex tubes (*ca.* 10 cm. long and 8 mm. internal diameter) previously treated in the same manner as the receivers (see above) and heating them in a thermostat at 75° for 30 min. The percentage of isomerisation was measured by the refractive index, which is linear with composition. Freshly distilled samples usually showed about 25% isomerisation under these conditions, but values as small as 5% or as large as 80% were not uncommon. Consequently, in evaluating the effect of any treatment, several "blanks" were used. Filling the tubes with nitrogen or oxygen or adding powdered glass or sodium hydrogen carbonate to the contents was found to have no reproducible effect on the rate of isomerisation. A trace of diphenylamine generally had a slight stabilising effect when the tubes were filled with nitrogen, but quinol, unexpectedly, catalysed the formation of primary bromide. Erratic results were obtained with samples exposed to light during isomerisation but the rate was rather faster when the tubes were evacuated before sealing.

Mayo and Walling (*Chem. Reviews*, 1940, 27, 399) have proposed a free-radical mechanism for the rearrangement of these bromides, mainly on the basis of an observation by Kharasch, Margolis, and Mayo (*loc. cit.*), who found that hydrogen bromide and peroxides in conjunction were powerful catalysts. However, this observation does not necessarily imply that the considerable instability of secondary bromide samples in the absence of added substances is due to the fortuitous presence of these materials. None of the samples which we examined gave a positive test for peroxides, and the effect of quinol (which is among the best inhibitors of abnormal addition of hydrogen bromide to olefins) was opposite to that expected on the above hypothesis.

Concerning the stabilisation of the bromides which was an important feature of the work, by far the most satisfactory results were obtained by introducing a little dry ammonia gas into the the air space in the tubes, a procedure which invariably retarded the isomerisation though not always to the same extent. Some typical results are given below.

Sample	A	B	C
Time at 75° (hr.)	4	0.5	0.5
Isomerisation (%):			
(a) untreated	83, 70, 66, 82	25, 17, 26	31, 40, 30
(b) treated with ammonia ...	12	9, 5	3, 3

The ammonia technique enabled the secondary bromide to be stored satisfactorily. Samples so treated were stable for weeks in a refrigerator and for several days at room temperature. The bromide was also sufficiently stable in acetone under the conditions of kinetic experiments to enable the test for bimolecular rearrangement to be carried out.

Kinetic Measurements.—*S_N2 Exchange reactions.* For temperatures above -10° thermostats were of conventional design: below this temperature the bath was a large Dewar flask containing alcohol kept at a low temperature by a partially insulated cold-finger containing acetone-solid carbon dioxide mush.

The exchange reactions were carried out in Y-tubes, the separate arms containing, initially, organic bromide (10 ml., *ca.* 0.2M) and lithium bromide (10 ml., *ca.* 0.08M) in acetone. Four tubes were normally used: one, which was allowed to react for about 2 min., served as blank. With 1-methylallyl bromide the reaction was stopped by pouring the Y-tube contents into a

flask at -80° . Acetone and organic bromide were removed at about -20° by a mechanical pump, leaving lithium bromide as a white deposit to which two separate 5-ml. portions of acetone were added and evaporated off, ensuring complete removal of the organic bromide. The lithium bromide samples, including one from the original acetone solution, were made up to a suitable volume in water and counted in a 10-ml. liquid counter (Twentieth Century Electronics, Type M6) connected to a conventional high-voltage supply and scaling circuit. The samples were each counted for two periods of 12 min. separated by some 80 min., and for a further 12 min. period if, owing to statistical fluctuations, the slope of the log counts/min.-time plot differed considerably from that characteristic of the 36.2 hr. half-life. Parallel straight lines were drawn through the groups of points for each sample, and the relative activities thereby estimated at the same time, after correction for the small background count. A total of at least 10^4 counts was recorded for each. The concentration of lithium bromide was then determined by weight titration, enabling the specific activity of each sample to be calculated.

3-Methylallyl bromide reacted too quickly to allow the evaporation technique to be used and, instead, the reaction was stopped by pouring the Y-tube contents into water (15 ml.) and pentane (40 ml.) in a separating funnel. After shaking, the water layer was run off into more pentane (20 ml.), shaken again, separated, and evaporated to dryness, and the lithium bromide was dissolved in water and estimated.

Specific rates of the exchange reactions were calculated by a modification of Le Roux and Sugden's equation (J., 1939, 1279), viz.,

$$k_2 = 2.303 \{ \log_{10} [1 - z_1(1 + b/a)] / [1 - z_2(1 + b/a)] \} / (a + b)(t_2 - t_1)$$

where a and b are the concentrations of organic and inorganic bromide respectively, corrected for solvent expansion or contraction from Thorpe's data (J., 1880, 37, 212), and $z = (1 - y)$, where y is the specific activity of a sample of recovered lithium bromide compared with that of the original sample taken as unity. Data for a typical run (1-methylallyl bromide at 30.0°) are given in Table 1 where k_2 is expressed in $l \text{ mole}^{-1} \text{ sec}^{-1}$; $a = 0.0994M$, $b = 0.0430M$.

TABLE 1.

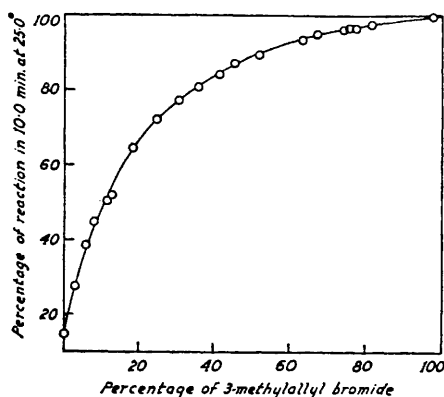
Aqueous lithium bromide.				Aqueous lithium bromide.			
t (sec.)	ct./min.	Concn.	z	$10^3 k_2$	t (sec.)	ct./min.	Concn.
115	2702	0.0435	0.0373	—	4735	2350	0.0647
1820	2460	0.0493	0.2263	1.39	Original	2494	0.0387
3015	3064	0.0699	0.3204	1.36	LiBr		
							Mean k_2
							1.41
							1.39

In another run at the same temperature with $b = 0.0254M$ the mean rate was 1.66×10^{-3} . The reaction thus shows a salt effect of the same sign and magnitude as that observed for saturated bromides by de la Mare (Thesis, University of London, 1948) and by Evans and Sugden (J., 1949, 270), and all results were corrected to a standard concentration (0.04M). A similar salt effect was observed with 3-methylallyl bromide.

S_N2' Reactions. Attempts to follow the rearrangement by isolating the organic bromide mixture and measuring the refractive index were unsuccessful because thermal isomerisation always occurred during the removal of the acetone solvent by fractional distillation. However, no products other than 3-methylallyl bromide were isolated in the reaction of 1-methylallyl bromide with lithium bromide at temperatures up to 80° . The pseudo-first-order kinetics of an S_N2' rearrangement of this type are well suited to a dilatometric study, but the small density difference of the two isomers again made accurate measurements impossible. The method finally used depended on the large difference in the rates of S_N2 substitution of the two bromides: for convenience radioactive bromide ion was chosen as nucleophilic reagent. The very rapid exchange of the primary bromide with this reagent at 25° allowed conditions to be chosen for the kinetic analysis under which further S_N2' rearrangement was negligible though it was not great enough to allow exchange of the secondary bromide to be neglected. Consequently, an empirical curve was prepared connecting the composition of bromide mixtures with the extent of exchange with radioactive lithium bromide under standard conditions (see Figure). The results were obtained as follows. Mixtures of the pure bromides (total concentration ca. 0.2M) were made up in acetone. Aliquot parts (10 ml.) of these solutions were mixed at 25° with the same volume of radioactive lithium bromide (0.02M): after 10.0 min. the reaction was stopped by rapid quenching at -80° . The specific activity of the lithium bromide which was isolated by evaporation was measured as above, greater precision being secured by recording more counts and using

more than one original sample. The value of z was computed for each mixture and multiplied by $100(1 + b/a)$, where a is the total organic bromide concentration, to obtain a function which increased from 0 at zero exchange to 100 when equilibrium between inorganic and organic bromides was attained. This "percentage reaction" is plotted against the percentage of 3-methylallyl bromide for 20 different mixtures in the Figure.

For the S_N2' rate measurements, aliquot parts (10 ml.) of 1-methylallyl bromide (0.5M) and lithium bromide (usually 0.08M) were mixed at room temperature and allowed to react in sealed Monax test-tubes. Precautions were taken to exclude oxygen. After reaction, the mixtures



were carefully evaporated at low pressure to separate lithium bromide, the distillate being collected in a trap at -80° . Further acetone (5 ml.) was added to and evaporated off the lithium bromide deposit to remove all traces of organic bromide and yield as distillate an acetone solution (*ca.* 0.2M) of the mixed bromides. Precautions were taken to exclude moisture. An aliquot portion of this distillate was then allowed to react with radioactive lithium bromide exactly as above; a second aliquot portion was completely hydrolysed and titrated for bromide ion to measure the exact concentration of organic bromides.

Both bromides were found to produce, after 260 hr. at 50.0° , a mixture of the same composition within experimental error, and eight separate determinations of this composition, using both pure bromides and thermal equilibrium mixtures as

starting materials with 0.04M-lithium bromide, yielded 75.0% as the mean equilibrium percentage of 3-methylallyl bromide. In the same time, 1-methylallyl bromide, in the absence of lithium bromide, yielded 4.7 and 6.7% of 3-methylallyl bromide, and this compound yielded, very approximately, 14% and 17% of 1-methylallyl bromide. To prove the absence of hydrogen bromide (which would be recorded as 3-methylallyl bromide by the method of analysis) a reaction mixture at equilibrium was separated from lithium bromide and allowed to react with radioactive lithium bromide at -80° . There was no exchange of bromide within experimental error.

The rearrangement of 1-methylallyl bromide was found to have the kinetic form of a reversible, pseudo-first-order reaction; second-order specific rates were calculated from the equation $k_2 = 2.303 \times 0.75[\log_{10}(x_e - x_1)/(x_e - x_n)]/b(t_n - t_1)$, where b is the lithium bromide concentration, x is the concentration of 3-methylallyl bromide at time t , and x_e its concentration at equilibrium. The reaction was followed, until at least 48% of primary bromide was produced, at four different temperatures. In no case was any drift of the constant k_2 observed. Details of a run at 50.0° are given in Table 2, where k_2 is in l. mole $^{-1}$ sec. $^{-1}$.

TABLE 2.

Initial concns.: 1-methylallyl bromide, 0.236M; LiBr, 0.0400M.						
Tube No.	Time (min.)	3-Methylallyl-bromide, %	$10^5 k_2$	Tube No.	Time (min.)	3-Methylallyl-bromide, %
1	12	1.6	—	5	1265	38.7
2	143	6.6	16.8	6	1598	44.8
3	317	13.0	17.3	7	1913	48.3
4	548	20.3	17.1			Mean 17.2

Kinetic analysis (radioactive LiBr, 0.01020M):

Aqueous LiBr				Aqueous LiBr			
Tube No.	a	ct./min.	Concn. $\times 10^5$	Tube No.	a	ct./min.	Concn. $\times 10^5$
1	0.0961	6783	1120	5	0.0986	2597	1367
2	0.0998	4742	984.8	6	0.0982	2663	1587
3	0.0997	4090	1097	7	0.0950	2407	1526
4	0.0989	2827	959.4		Original LiBr	4618	608.6
			$z(1 + b/a)$				$z(1 + b/a)$
			$\times 100$				$\times 100$
			22.3				82.7
			40.3				86.0
			56.1				87.7
			67.5				—

The effect of varying the initial lithium bromide concentration on the rate of the reaction at 60.2° is shown in Table 3.

TABLE 3.
Initial concn., 1-methylallyl bromide, 0.247M; k_2 in l. mole⁻¹ sec.⁻¹.

Tube No.	<i>b</i>	Time (min.)	3-Methylallyl bromide, %	10 ⁵ k_2	Tube No.	<i>b</i>	Time (min.)	3-Methylallyl bromide, %	10 ⁵ k_2
1	0.0101	970	29.4	63.5	5	0.0503	199	23.3	46.5
2	0.0201	1245	49.9	54.7	6	0.0603	172	22.0	41.8
3	0.0302	343	25.6	50.4	7	0.0804	120	19.2	38.3
4	0.0402	245	22.4	45.0	8	0.1005	98	20.4	40.3

DISCUSSION

The results in Table 3 show that the rearrangement has an order of approximately 0.75 with respect to lithium bromide. That this order should be less than unity is not unexpected since Evans and Sugden (*loc. cit.*), investigating the S_N2 exchange reactions of *n*-butyl and *sec*-octyl bromides with lithium bromide in acetone, found a similar effect which they attributed to incomplete dissociation of lithium bromide in this solvent, and de la Mare (Thesis, University of London, 1948) has observed a similar "dilution effect" with *tert*-butyl bromide. It is therefore concluded that the rearrangement is bimolecular.

In the reactions of alkyl halides with nucleophilic reagents the possible elimination of hydrogen halide must always be borne in mind. In the present case the possibility that the rearranged products are due to elimination of hydrogen bromide followed by re-addition may be discounted since 1-methylallyl halides do not readily undergo elimination reactions even with reagents whose nucleophilic affinity for hydrogen is very much more marked than that of bromide ion. For example, Vernon (*J.*, 1954, 4462) found that only 10% of butadiene was formed in the reaction of 1-methylallyl chloride with sodium ethoxide. We therefore conclude that 1-methylallyl bromide undergoes rearrangement by the S_N2' mechanism in the presence of lithium bromide.

The exchange reactions of the bromides with radioactive lithium bromide should show first-order kinetics in a single run whatever the mechanism (Duffield and Calvin, *J. Amer. Chem. Soc.*, 1946, 68, 557) but, since the dependence of the rate on lithium bromide concentration is similar to that mentioned above, the S_N2 mechanism is indicated, a conclusion which is confirmed by the much greater rate of the primary isomer (cf. Vernon, *J.*, 1954, 423). Rearrangement does not interfere with the exchange measurements since it can be calculated that, at most, 0.5% of primary bromide was formed by the S_N2' reaction during measurement of the S_N2 exchange. The kinetic data (k_2 and A_2 in l. mole⁻¹ sec.⁻¹) and Arrhenius parameters are given below. In the final column, rates are compared at 25° by interpolation or extrapolation.

Allyl bromide	Temp.	10 ⁵ k_2	E_A (kcal. mole ⁻¹)	$\log_{10} A_2$	10 ⁵ k_2 (25°)
1-Methyl- (S_N2)	30.00°	142	16.5	9.06	879
	24.80	86.6			
	16.05	36.7			
	-6.20	3.44			
1-Methyl- (S_N2')	75.15	157	19.4	9.40	14.9
	60.20	44.2			
	50.00	17.2			
	30.05	2.42			
3-Methyl- (S_N2)	-18.80	198	14.7	9.93	141,000
	-27.25	71.3			
	-33.10	34.9			
3-Methyl (S_N2')	—	—	ca. 19	ca. 9	5

The S_N2 substitution of 1-methylallyl bromide is 60 times faster than the corresponding S_N2' rearrangement at 25° and this difference arises largely from a difference of 3 kcal. in the activation energy. It is likely that the bimolecular substitution reactions of all 1-substituted allyl halides involve at least a small percentage of rearrangement, which, in 1-methyl halides, is just beyond the usual limit of detection in a product analysis. It is also understandable that some derivatives (cf. de la Mare and Vernon, *loc. cit.*) have been found to react exclusively by the S_N2' mechanism.

The corresponding ratio of rates in 3-methylallyl bromide is much greater (28,000 : 1) and this is due largely to the facilitation of the S_N2 reaction by the 3-methyl group. The

contribution of the S_N2' mechanism to the bimolecular reactions of halides substituted only in the 3-position may generally be expected to be quite negligible.

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