Kinetics and Mechanisms of Nucleophilic Displacements in Allylic Systems. Part VIII. The Reactivities of Allylic Chlorides towards Bimolecular Substitution without Rearrangement.*

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The reactivities of a series of allylic chlorides towards the S_N2 mechanism of nucleophilic substitution have been determined. The reactions principally studied have been those with ethoxide ions in ethanol and with chloride ions in acetone. In the latter case, the radio-isotope ^{36}Cl has been used to follow the reactions. Similar studies have been made, for comparison, on propargyl chloride and on some alkyl chlorides. It has been found that, towards the S_N2 mechanism, allylic chlorides are more reactive than the corresponding saturated compounds, and that, unlike the latter, they do not give elimination products (except in the case of 1-methylallyl chloride). Electron-releasing substituents in the γ-position facilitate bimolecular substitution but the effect is small compared with that found for the unimolecular processes. The effect of change of solvent has been investigated and shown to be frequently opposite in direction to that found for alkyl chlorides. The theoretical implications of the findings are discussed.

In Part V (Vernon, *J.*, 1954, 423) the reactivities of a series of allylic chlorides towards the unimolecular mechanism of nucleophilic substitution were studied; in the present paper a similar study of bimolecular substitution without rearrangement (S_N2) is reported. The range of nucleophilic substituting agents employed included ethanol and aqueous ethanol, in solvolytic reactions, and the basic ions derived from them; also chloride ions (giving a symmetrical exchange) in acetone.

Several investigations of the S_N2 substitution process in allylic chlorides have been reported, the most extensive being that by Hatch and his co-workers (see, especially, Hatch and Alexander, *J. Amer. Chem. Soc.*, 1949, **71**, 1037; Hatch, Gordon, and Russ, *ibid.*, 1948, **70**, 1093), who measured rates of reaction, mostly at one temperature, between allylic chlorides and ethoxide ions in ethanol and iodide ions in acetone. This work and that by other authors is later referred to and discussed in conjunction with results obtained in the present investigation, the main objects of which have been to study the effect of alkyl-group substitution and of solvent changes on the S_N2 reactivity of allylic chlorides, and to compare the behaviour of these compounds with that of their saturated analogues.

EXPERIMENTAL

(*a*) *Materials.*—*n*-Butyl chloride and *sec.*-butyl chloride were prepared from commercial samples, which were washed with aqueous sodium hydrogen carbonate, dried ($CaCl_2$), and fractionated. The products had, respectively, b. p. 78·4—78·6°/760 mm., n_D^{25} 1·3986, and b. p. 68·3—68·6°/760 mm., n_D^{25} 1·3948.

*iso*Butyl chloride was obtained from a good commercial sample, which was washed with potassium carbonate solution until no more acid was liberated, dried ($CaCl_2$), and fractionated. The product had b. p. 69·2—69·3°/769 mm., n_D^{25} 1·3942.

Propargyl chloride was prepared by adding dropwise a slight excess of purified thionyl chloride to a cooled mixture (0°) of anhydrous propargyl alcohol (18 g.) and benzene (100 c.c.), efficient stirring being maintained throughout the addition. The mixture was then refluxed for 1 hr., pyridine (1 g.) added, and refluxing continued for a further hour. The resulting solution was fractionated, all the material boiling below 78° being collected. The distillate was then washed with water and aqueous sodium hydrogen carbonate until neutral, dried (Na_2SO_4) and refractionated in a helix-packed, externally heated column 3′ long, a small quantity of benzene being used as a "chaser." There were obtained 17 g. (70%) of propargyl chloride, b. p. 56·3—56·6°/753 mm., n_D^{25} 1·4317 * (Found: C, 48·2; H, 4·6; Cl, 47·6. Calc. for C_3H_3Cl: C, 48·3; H, 4·1; Cl, 47·6%).

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* Part VII, *J.*, 1954, 3679.

Dioxan was purified by Vogel's method (" A Textbook of Practical Organic Chemistry," p. 175, Longmans, Green & Co., 1948) and dried by refluxing with metallic sodium. Acetone was purified by refluxing for several hours with potassium permanganate, followed by fractionation through a small Vigreux column. Immediately before use, the acetone was distilled from anhydrous magnesium perchlorate.

Nitromethane was purified by distillation, followed by refluxing for several hours in a stream of nitrogen. After drying ($CaCl_2$), it was refractionated, the fraction of b. p. 101° being collected.

Other materials and solvents were as described in Part V (*loc. cit.*).

(*b*) *Rate Measurements on Reactions in Ethanol and Aqueous Ethanol.*—Techniques were as described in earlier parts (see especially Part V, *loc. cit.*).

First- and second-order rate coefficients were calculated from the formulæ, $k_1 = (2\cdot303/t) \log_{10} a/(a - x)$; $k_2 = [2\cdot303/t(a - b)] \log_{10} b(a - x)/a(b - x)$, the symbols having their customary significance. In cases where the value of the appropriate rate coefficient decreased as the reaction progressed, as for example, in the solvolytic reactions in ethanol where the liberated acid was partly removed by reaction with the solvent, the initial value was found by graphical extrapolation.

For those reactions involving ethoxide ions in ethanol or hydroxide ions in aqueous solvents in which mixed-order kinetics were observed, owing, formally, to the incursion of a substantial solvolytic contribution, second-order rate coefficients were calculated by the method of Hughes, Ingold, and Shapiro (*J.*, 1936, 225). In these instances the coefficient calculated by the straightforward application of the above formula is written as k_2' and the corrected coefficient as k_2. The analysis was not attempted where k_2' and k_2 would differ by more than 20%.

Details of a typical run with allyl chloride (0·1079M) and sodium ethoxide (0·1396M) in ethanol at 44·6° are given below, k_2 being in the units l. mole^{-1} min.$^{-1}$ (here and later) :

Portions of 5·51 c.c. titrated after addition of 15·34 c.c. of 0·0722N-HCl; 0·0338N-NaOH was used for titration.

t (min.)	Titre	10^2k_2	*t* (min.)	Titre	10^2k_2	*t* (min.)	Titre	10^2k_2	*t* (min.)	Titre	10^2k_2
0	10·0	—	141	13·02	1·06	260	14·98	1·07	354	16·14	1·06
50	11·19	1·06	185	13·78	1·06	300	15·50	1·07	1390	22·69	1·08
89	12·01	1·06	231	14·53	1·07	330	15·87	1·07	∞	27·57	—

10^2k_2 (mean) = 1·07.

Details of a run with 3 : 3-dimethylallyl chloride (0·0519M) and sodium ethoxide (0·0977M) in ethanol at 35·0°, in which the correction for concomitant solvolysis has been applied, are :

Portions of 5·00 c.c. titrated. After addition of 10·34 c.c. of ethanolic hydrochloric acid (0·0875N) and 50 c.c. of cooled ethanol, sodium ethoxide (0·0254N) in ethanol was used for the titrations and lacmoid was employed as indicator.

t (min.)	Titre	$10^2k_2'$	10^2k_2	*t* (min.)	Titre	$10^2k_2'$	10^2k_2	*t* (min.)	Titre	$10^2k_2'$	10^2k_2
0	16·40	—	—	93·0	21·02	7·84	6·36	202	23·58	8·16	6·65
19·5	17·74	7·77	6·37	143	22·33	7·78	6·30	254·5	24·39	8·54	6·95
40·0	18·83	7·55	6·13	165	22·90	8·02	6·51	∞	26·64	—	—
59·5	19·78	7·76	6·30								

10^2k_2 (mean) = 6·45.

Arrhenius parameters were found from measurements of rate coefficients at different temperatures. Where accurate measurements over an extended temperature range were possible, determinations at five different temperatures were made, and the results treated by the method of linear regression. For example, with 3-methylallyl chloride (0·10M) and sodum ethoxide (0·15M) in ethanol, the following data were obtained :

Temp.	25·3°	35·1°	44·6°	60·2°	74·95°
10^2k_2 (l. mole^{-1} min.$^{-1}$)	0·344	1·08	2·95	13·2	49·5

These results give E = 20·47 kcal./mole (standard deviation 0·11 kcal./mole), $\log_{10} B$ = 12·60.

(*c*) *Determination of the Amount of Olefin produced from Saturated Chlorides.*—An extraction method, similar to that described by Hughes, Ingold, Masterman, and MacNulty (*J.*, 1940, 911), was used, the difference being that the extraction was carried out in a closed apparatus designed by Dr. B. M. Wepster, to whom the author is indebted, in which the pressure was

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* These physical constants are in good agreement with those reported by Hatch and Chiola (*J. Amer. Chem. Soc.*, 1951, **73**, 360). The correct boiling point is 9° lower than that originally given by Henry (*Ber.*, 1875, **8**, 398).

initially reduced below atmospheric, thus allowing the introduction of several portions of carbon tetrachloride for extraction purposes. The apparatus had an upper and a lower section, and by suitable adjustment of the initial pressure in the two sections, the extract from the upper could be run into the lower without opening the apparatus to the atmosphere. By the use of this closed apparatus losses of olefin due to volatility were eliminated. The olefin produced in tubes taken at the time-zero ($t = 0$, after the period of warming in the thermostat) and in tubes taken at complete reaction ($t = \infty$) was estimated by extraction, as described above, of the acidified solution with three portions of carbon tetrachloride, followed by reaction in the dark with a slight excess of standard bromine in carbon tetrachloride. After addition of potassium iodide solution, the residual halogen was titrated with standard sodium thiosulphate solution. Details of a typical experiment with *iso*butyl chloride (0·0907N) and sodium ethoxide (0·1800M) in ethanol at 76·9° are given below :

Portions of 10·0 c.c. of bromine solution (0·0504N) were added to the extract in each case. Titres refer to c.c. of 0·0344N-sodium thiosulphate.

$t = 0$ titres	15·22	15·20	14·91	15·05	—	Mean, 15·09
$t = \infty$ titres	2·91	2·71	2·72	2·69	2·69	„ 2·75

Mean % of olefin formed = 42·5. The total second-order rate coefficient for the reaction (k_2) was found to be $11 \cdot 4 \times 10^{-4}$ l. mole^{-1} min.$^{-1}$. Hence $10^4 k_2$ (E_2) and $10^4 k_2$ (S_N2) are respectively 4·84 and 6·56 l. mole^{-1} min.$^{-1}$.

(*d*) *Search for the Products of Elimination from Allylic Chlorides.*—The bromination method described above (*c*) could not be used satisfactorily where the substitution product was itself unsaturated. For allyl and 1- and 3-methylallyl chlorides, the possible products of elimination of hydrogen chloride were therefore sought by direct isolation. Reaction mixtures containing 10—20 g. of organic chloride were sealed in tubes and heated at 44·6° until no further reaction occurred. The resulting solution was then fractionated in a column especially designed to detect small quantities of low-boiling substances. The column, which had a sealed-on, silvered, evacuated jacket, consisted of a tube, 45 cm. in length and of 7 mm. internal diameter, down the centre of which was a coaxial glass rod of 5 mm. diameter. Use of a partial condensation still-head enabled a small proportion of the vapour traversing the length of the column to be passed through a capillary tube and condensed in a cooled receiver. The temperature of the vapour was measured by a copper–constantan couple.

1-Methylallyl chloride (10·98 g.) and 150 c.c. of ethanol containing sodium ethoxide (1·6N) were allowed to react completely in a sealed tube at 44·6°. By using the fractionating column described above, there was obtained from the products, 0·65 g. of butadiene, b. p. −5°, representing 10% of elimination. By reaction with bromine in carbon tetrachloride (Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, **58**, 146) there were isolated, after recrystallisation from ethanol, colourless needles of racemic 1 : 2 : 3 : 4-tetrabromobutane, m. p. 115·5°, unchanged on admixture with an authentic specimen. A duplicate experiment gave 11·4% of elimination. In 50% aqueous ethanol,* both in the absence and on the presence of sodium hydroxide (1·7N), 1-methylallyl chloride gave no butadiene.

From the products of reaction of 3-methylallyl chloride and sodium ethoxide (1·6N) in ethanol no fraction boiling below the b. p. of ethanol was obtained. Presumably no elimination product was formed. Similarly, allyl chloride and sodium ethoxide (1·6N) in ethanol gave no allene.

The absorption at 2200 Å of the products of reaction of 3 : 3-dimethylallyl chloride and sodium ethoxide (0·50N) in ethanol was determined in a Unicam ultra-violet spectrophotometer, Model S.P. 500. The optical density recorded corresponded to a yield of isoprene of not more than 2·5%.

(*e*) *Exchange Reactions with Radioactive Chloride Ions.*—An acetone solution of lithium chloride, containing the radio-active isotope ^{36}Cl, was prepared as described by Brown and Ingold (*J.*, 1953, 2680). The following technique (de la Mare, Ph.D. Thesis, London, 1948) was used for the kinetic experiments. Aliquot portions of a solution of the organic chloride in acetone and of the lithium chloride solution were sealed in tubes, which were heated in a thermostat, removed at appropriate time intervals, and cooled in alcohol–carbon dioxide slush. The volatile components of the solution (acetone and organic chloride) were then pumped off at low temperature, several additions of dry acetone being made to ensure complete removal of the organic chloride. The remaining lithium chloride was then dissolved in water and the radioactivity and chloride-ion concentration of the solution were determined by conventional

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* An x% aqueous solvent means that x vols. of water and (100 − x) vols. of the solvent were mixed.

means. A " blank " tube taken at the end of the warming period in the thermostat and an aliquot portion of the original lithium chloride solution were similarly treated. Comparison of these two gave the extent of exchange occurring in the warming period. The counts per minute found for all the samples were corrected to refer to a solution of some fixed chloride-ion concentration. Second-order rate coefficients were calculated from the formula

$$k_2 = \frac{2{\cdot}303}{t(a + b)} \log_{10} \frac{1 - x_1(1 + b/a)/c}{1 - x_2(1 + b/a)/c}$$

where t measures the time from the time-zero (the blank tube), a and b are the concentrations of organic chloride and lithium chloride respectively, x_1/c and x_2/c are the ratios of the concentration of radioactive organic chloride to the total concentration of radioactive chloride at the time zero and at any time t, respectively. Details of a typical run with *n*-propyl chloride (0·1040M) and lithium chloride (0·0268M) in acetone at 44·6° are given below. The original lithium chloride solution gave 2942 counts per min.

t (min.)	0	4325	5518	8563	10,080	11,520
Counts/min.	2947	2647	2515	2386	2282	2202
10^4k_2 (l. mole^{-1} min.$^{-1}$)	—	2·41	2·81	2·34	2·52	2·52

$$k_2 = 2{\cdot}52 \times 10^{-4} \text{ l. mole}^{-1} \text{ min.}^{-1}.$$

Results.—Data for the reactions of some allylic chlorides in ethanol and aqueous ethanol are given in Table 1. First-order rate coefficients (k_1) (see Table 1) have been calculated in most cases, initial values being given where the reactions were of second order. The effect of addition of alkali on reaction rate can hence conveniently be found by comparison of the appropriate values of k_1.

The reaction between propargyl chloride and sodium ethoxide in ethanol gave, as previously noted by Hatch and Chiola * (*loc. cit.*), values of k_2 which decreased as the reaction progressed. A similar effect was found to occur in aqueous ethanol; the solvolytic reaction in this solvent was, however, normal and gave constant coefficients. Because of this disturbance, which appeared to be due to changes occurring later in the reaction, the initial values of the rate coefficients were taken as representing the rates of the substitution processes.

The products of reaction of 1-methylallyl chloride with sodium ethoxide in ethanol have been investigated by several groups of workers (Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Catchpole and Hughes, *J.*, 1948, 4; de la Mare and Vernon, *J.*, 1953, 3555), and it has been shown that the substitution product arises almost completely from normal (S_N2) substitution. It has now been found that an elimination process, comprising about 10% of the total reaction, is also present. The extent of this has been determined, at an alkali concentration *ca.* 1·6N, by direct isolation of the volatile elimination product (butadiene), and the value recorded (10·7%) may well be too low. This error is likely to be partially compensated, however, by assuming the same value to be correct at the lower concentration of base (*ca.* 0·2N) used in the kinetic study. On this basis an approximate value of k_2 for the S_N2 process is recorded.

The reactions with sodium ethoxide in ethanol of cinnamyl chloride and 3 : 3-dimethylallyl chloride have been reported (Hatch and Alexander, *J. Amer. Chem. Soc.*, 1950, **72**, 5645; Hatch and Gerhardt, *ibid.*, 1949, **71**, 1677) as being too rapid for measurement. This conclusion is erroneous and arises from the use of an analytical method which is inapplicable for compounds readily hydrolysed by water. In fact, both reactions can be studied conveniently in the temperature range 20—50°; appropriate rate coefficients are given in Table 1.

The results of a study of the elimination and substitution reactions of four alkyl chlorides, chosen for purposes of comparison with allyl chloride and the three monomethyl-substituted allyl chlorides, are given in Table 2. No extensive data for these compounds have previously been reported; the corresponding bromides have, however, been thoroughly investigated (Dhar, Hughes, Ingold, and Masterman, *J.*, 1948, 2055; Dhar, Hughes, and Ingold, *ibid.*, p. 2058). The mixture of olefins formed from *sec.*-butyl chloride has not been analysed; it has been assumed that the proportions in which the two possible isomers are formed are the same as from the corresponding bromide (Dhar, Hughes, and Ingold, *loc. cit.*).

Rates of the exchange reactions, measured by the use of the radioactive isotope ^{36}Cl, of some allylic chlorides and chloride ions in acetone are given in Table 3. Corresponding data for

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* These workers were, however, in error in supposing that the reaction did not go to 100% completion.

TABLE 1. *Kinetic data for allylic chlorides in ethanol and 50% aqueous ethanol at 44·6° (unless otherwise noted).*

	Ethanol					50% Aqueous ethanol		
Compound	NaOEt (M)	10^3k_1	10^2k_2	E_A	log *B*	NaOH (M)	10^3k_1	10^2k_2
$\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}Cl}$ ...	0·0000	(0·0038) §	—	—	—	0·0000	0·101	—
	0·0450	(0·560)	1·21	—	—	0·1307	(2·04)	1·51
	0·1396	(1·44)	1·07	20·6 ± 0·2	12·27	0·5156	(6·54)	1·31
	0·4918	(4·62)	0·94	—	—	—	—	—
$\mathrm{CH_2{:}C(CH_3){\cdot}CH_2Cl}$	0·0000	(0·0048) §	—	—	—	0·0000	0·154	—
	0·0677	(0·690)	1·06	—	—	0·1552	(2·30)	1·50
	0·1544	(1·40)	0·95	20·5 ± 0·15	12·14	—	—	—
$\mathrm{CH{\vdots}C{\cdot}CH_2Cl}$	0·1925	—	(1·10)	—	—	0·0000	0·0049 §	—
	0·2383	—	(1·07)	—	—	0·1480	—	(1·02)
$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH_2Cl}$	0·0000	(0·06) §	—	—	—	0·0000	9·22	—
	0·1617	(4·53)	2·81	20·5 ± 0·1	12·60	0·1500	16·7	—
$\mathrm{Bu^t{\cdot}CH{:}CH{\cdot}CH_2Cl}$	0·1500	—	2·10	—	—	—	—	—
$\mathrm{CH_2{:}CH{\cdot}CHCl{\cdot}CH_3}$	0·0000	(0·0126) §	—	—	—	0·0000	8·23	—
	0·1864	—	*ca.* 0·052 ‖	*ca.* 22·9	*ca.* 12·67	0·0845	8·59	—
						0·2388	8·92	—
$\mathrm{Ph{\cdot}CH{:}CH{\cdot}CH_2Cl}$	0·0000	(0·527)	—	—	—	0·0000	773 §	—
	0·0974	(7·40)	7·87	—	—	0·0000	94·6 †	—
	0·1849	(13·6)	7·31	—	—	0·0150	104 †	—
$\mathrm{(CH_3)_2C{:}CH{\cdot}CH_2Cl}$	0·0000	(3·92)	—	—	—	0·0000	*ca.* 13 × 10³ §	—
	0·5270	(84·8)	16·1	19·7	12·78			
	0·0000	(1·32) *	—	—	—	0·0000	93 ‡	—
	0·0250	(3·00) *	—	—	—	0·1000	*ca.* 95 ‡	—
	0·1488	(10·0) *	6·47	—	—	—	—	—
	0·5564	(30·3) *	5·50	—	—	—	—	—
$\mathrm{CH_2{:}CH{\cdot}CCl(CH_3)_2}$	0·0000	(11·2)	—	—	—	0·0000	*ca.* 55 × 10³ §	—
	0·0529	12·0	—	—	—			

Values of k_1 and k_2 are expressed in min.$^{-1}$, and l. mole^{-1} min.$^{-1}$, respectively. E_A is in kcal./mole. RCl concentration *ca.* 0·10M.

Parentheses enclose initial values of decreasing coefficients.

* At 35·0°. † At 25·8° ‡ At 0°.

§ Extrapolated from values at other temperatures.

‖ Accompanied by an elimination reaction with 10^2k_2 = *ca.* 0·006.

TABLE 2. *Kinetic data for alkyl chlorides in ethanol.*

				Substitution			Elimination		
Compound	*T*	NaOEt (M)	Olefin, %	10^2k_2	E_A	log *B*	10^2k_2	E_2	log *B*
$\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2Cl}$	74·95°	0·1617	5·70	0·647	21·1	11·1	0·0391	24·0	11·7
	101·6	0·1559	7·40	5·93	—	—	0·473	—	—
	120·0	0·1517	8·95	21·8	—	—	2·14	—	—
$\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl}$	76·9	0·1690	4·75	0·624	21·2	11·1	0·0311	24·7	12·0
	101·6	0·1553	6·15	4·77	—	—	0·313	—	—
	120·0	0·1490	7·85	17·8	—	—	1·51	—	—
$\mathrm{CH_3{\cdot}CH(CH_3){\cdot}CH_2Cl}$	76·9	0·1915	42·5	0·0656	22·4	10·85	0·0484	24·2	11·8
	101·6	0·1879	47·3	0·580	—	—	0·520	—	—
	120·0	0·1638	49·8	2·28	—	—	2·26	—	—
$\mathrm{CH_3{\cdot}CH_2{\cdot}CH(CH_3)Cl}$	100·8	0·5596	71·6	0·51	23·5	11·49	1·28	24·0	11·93
	120·0	0·5505	72·2	2·41	—	—	6·26	—	—

k_2 and *E* are expressed in l. mole^{-1} min.$^{-1}$, and kcal./mole, respectively. RCl concentrations *ca.* 0·10M.

n-propyl and propargyl chlorides are included for comparison. Since a fixed lithium chloride concentration was used throughout, the orders of the reactions (and hence the molecularities) cannot be deduced from the experimental data. It has been assumed, however, that the reactions are bimolecular, since all the compounds listed readily react with sodium ethoxide in ethanol by the bimolecular (S_N2) mechanism, and the weakly ionising solvent acetone is unlikely to promote a change of mechanistic type. The absence of production of free acid showed the reactions to be unaccompanied by elimination processes, and constant rate coefficients (within the range of the experimental error) were obtained in each case.

TABLE 3. *Kinetic data for the reaction with lithium chloride* (ca. 0·03M) *at* 44·6°.

Compound	Solvent	10^3k_2	Compound	Solvent	10^3k_2
$CH_3\cdot CH_2\cdot CH_2Cl$	$COMe_2$	0·252	$CH\vdots C\cdot CH_2Cl$	$COMe_2$	3·94
	20% $MeNO_2$–$COMe_2$	0·104	$CH_3\cdot CH{:}CH\cdot CH_2Cl$	,,	8·88 *
$CH_2{:}CH\cdot CH_2Cl$	$COMe_2$	3·52	$CH_2{:}CH\cdot CH(CH_3)Cl$ ...	,,	0·109 *
	20% $MeNO_2$–$COMe_2$	2·52	$(CH_3)_2C{:}CH\cdot CH_2Cl$	,,	75·0

k_2 is expressed in l. mole^{-1} min.$^{-1}$. RCl concentration *ca.* 0·10M.
* These values are due to England and Hughes (unpublished work), to whom the author is indebted for permission to quote.

TABLE 4. *Effect of change of solvent on reactivities of allyl chloride and* n-*propyl chloride.*

Compound	*T*	Solvent	Base	Concn., M	10^3k_1	$10^2k_2(S_N2)$	$10^2k_2(E_2)$
$CH_2{:}CH\cdot CH_2Cl$	44·6°	Ethanol	—	0·0000	0·0038 *	—	—
			NaOEt	0·4918	—	0·94	—
			KOEt	0·1580	—	1·21	—
		25% Aq. ethanol	—	0·0000	0·0242	—	—
			NaOH	0·5540	—	1·03	—
			KOH	0·1447	—	1·41	—
		50% Aq. ethanol	—	0·0000	0·101	—	—
			NaOH	0·5156	—	1·31	—
			KOH	0·1698	—	1·58	—
	64·9	40% Aq. dioxan	KOH	0·1704	—	3·64	—
		60% Aq. dioxan	KOH	0·1626	—	7·39	—
$CH_3\cdot CH_2\cdot CH_2Cl$	101·6	Ethanol	—	0·0000	0·024	—	—
			NaOEt	0·5116	—	5·44	0·43
		25% Aq. ethanol	—	0·0000	0·183	—	—
			NaOH	0·5803	—	3·60	0·20
		50% Aq. ethanol	—	0·0000	0·580	—	—
			NaOH	0·5266	—	*ca.* 3·54 †	*ca.* 0·15 †

k_1 and k_2 are expressed in min.$^{-1}$, and l. mole^{-1} min.$^{-1}$, respectively. RCl concentration *ca.* 0·10M.
* Extrapolated from values at other temperatures.
† Inaccurate because of attack by alkali on glass.

In Table 4 are presented data on the effect of solvent changes on the bimolecular reactivities of allyl and *n*-propyl chloride.

DISCUSSION

(*a*) *Mechanisms.*—The reactions of allyl and *n*-propyl chlorides with sodium ethoxide in ethanol are unquestionably bimolecular, being kinetically of second order and much faster, by a factor of *ca.* 1000 for 0·5N-sodium ethoxide, than the corresponding solvolytic reactions. Similarly in 25% and 50% aqueous ethanol, in the presence of added hydroxide ions, second-order kinetics were observed and the reactions were faster than the corresponding solvolyses; the increases in rate produced by the same concentration of base were, however, much smaller, *ca.* 65 and *ca.* 30 for allyl and *n*-propyl chlorides, respectively, in 50% aqueous ethanol.

It will be noticed that the formal order of reactions referred to above as second order, are actually less than 2, the second-order rate coefficients increasing slightly as the stoicheiometric concentration of base decreases. This effect, common among reactions between a negative ion and a neutral molecule, is usually known as the " dilution effect " and its origin has been ascribed to incomplete dissociation of the electrolyte from which the negative ion arises (Robertson and Acree, *J. Amer. Chem. Soc.*, 1915, **37**, 1902; Marshal and Acree, *J. Phys. Chem.*, 1915, **19**, 589). This hypothesis, which may well be correct in some circumstances (see, *e.g.*, Evans and Sugden, *J.*, 1949, 270), is clearly unattractive where strong electrolytes are involved (cf. Lauer and Shingu, *Ber.*, 1936, **69**, 273). In the present case the most pronounced effect was found to occur in 50% aqueous ethanol and it is unlikely that in this solvent sodium hydroxide is appreciably undissociated. The dilution effect in these systems is most likely a salt effect but, whatever its origin, it introduces no mechanistic ambiguity and its occurrence does not imply a deviation from bimolecular character.

The mechanisms of the solvolytic reactions of allyl and *n*-propyl chlorides, since a kinetic criterion is necessarily absent, can be deduced only by indirect arguments. The following are reasons for supposing that the reactions are bimolecular: (*a*) The increase in solvolytic rate in passing from ethanol to 50% aqueous ethanol (*ca.* 25 times for each compound) is much smaller than that observed for unimolecular reactions (cf. the data for 1 : 1-dimethylallyl chloride) but is consistent with the expected magnitude of a solvent effect if the reactions were bimolecular. (*b*) The unimolecular reactivites of both compounds are small (Vernon, Part V, *loc. cit.*), rates of hydrolysis in slightly aqueous formic acid being much less than in 50% aqueous alcohol, whereas a rough equality of rates in these two solvents is normally found for unimolecular reactions. (*c*) The increases in rate produced by a given amount of alkali in ethanol and in 50% aqueous ethanol were similar to those found for *trans*-1 : 3-dichloroprop-1-ene, the solvolytic reactions of which are known to be bimolecular from the non-appearance of anionotropically rearranged products (de la Mare and Vernon, Part VII, *loc. cit.*).

The reactions of 1 : 1-dimethylallyl chloride in ethanol and aqueous ethanol represent the other extreme of mechanistic behaviour, and are clearly unimolecular. Ethoxide ions were found to be without effect on the rate of ethanolysis; consistently, the solvolytic rate was enormously increased (by a factor of *ca.* 5000) by change to 50% aqueous ethanol.

Of the other compounds listed in Table 1, 2-methylallyl chloride and propargyl chloride behaved similarly to allyl chloride, and the reactions of both these compounds are therefore predominantly bimolecular. On the other hand, 3 : 3-dimethylallyl chloride behaved like its anionotropic isomer, and its reactions are hence largely unimolecular in character; a facile bimolecular reaction appeared, however, in ethanol when sufficient ethoxide ions were present.

The behaviour of 3-methylallyl chloride was intermediate in type. In ethanol a bimolecular reaction was observed, in the presence of ethoxide ions, but the solvolytic reaction is known to be partly unimolecular since it gives a proportion of rearranged products (Catchpole and Hughes, *J.*, 1948, 4). Change to 50% aqueous ethanol increased the rate by a factor intermediate in value between that found for the two extremes of mechanistic behaviour, while the effect of addition of alkali in the more aqueous solvent, though still significant, was small. Cinnamyl chloride and 1-methylallyl chloride behaved similarly, but the tendency to unimolecularity is more pronounced in these two compounds, and in 50% aqueous ethanol no evidence of a bimolecular component was found.

Hatch and Alexander (*loc. cit.*) have suggested that the bimolecular reactions of allylic chlorides with sodium ethoxide in ethanol proceed by electrophilic attack by a sodium ethoxide molecule. This suggestion, which is completely implausible on general chemical grounds, can be formally disposed of by noting that it is inconsistent with the observed direction of the dilution effect, since if molecular sodium ethoxide were the active substituting agent, the second-order rate coefficients would increase with the stoicheiometric concentration of the base and the dilution effect would be in the opposite direction to that observed.

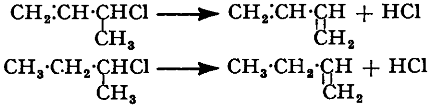
(*b*) *Structural Comparisons.*—The following table gives the relative rates, at 44·6°, of bimolecular substitution reactions of the compounds listed, with sodium ethoxide, *ca.* 0·15M, in ethanol.

$CH_2{:}CH{\cdot}CH_2Cl$	100	$CH_2{:}CH{\cdot}CH(CH_3)Cl$	*ca.* 4·9
$CH_3{\cdot}CH_2{\cdot}CH_2Cl$	2·7 *	$CH_3{\cdot}CH_2{\cdot}CH(CH_3)Cl$	0·19 *†
$CH_2{:}C(CH_3){\cdot}CH_2Cl$	89	$CH{\vdots}C{\cdot}CH_2Cl$	103
$CH_3{\cdot}CH(CH_3)CH_2Cl$	0·24 *	$Bu^t{\cdot}CH{:}CH{\cdot}CH_2Cl$	196
$CH_3{\cdot}CH{:}CH{\cdot}CH_2Cl$	262	$Ph{\cdot}CH{:}CH{\cdot}CH_2Cl$	683
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$	2·65 *	$(CH_3)_2C{:}CH{\cdot}CH_2Cl$	1500 †

* Extrapolated from values at higher temperatures. † At NaOEt = *ca.* 0·5M.

The S_N2 mechanism of nucleophilic substitution by ethoxide ions in ethanol is seen to occur in the allylic chlorides more readily than in the corresponding saturated compounds; for allyl and *n*-propyl chlorides the rate factor at 44·6° is about 37 and is similar in magnitude to that found for the unimolecular reactivities (Vernon, Part V, *loc. cit.*). Because of the differences in the effect of methyl substitution in the two series of compounds, the rate factors are not the same for each pair of substances, but the allylic chloride is always the more reactive. It is noteworthy that the increases in rate produced by the allyl double bond appear to depend on variation of the non-exponential Arrhenius parameters (*i.e.*, on differences in the entropies of activation) as well as on differences in the energies of activation.

Of the allylic compounds studied, only in the case of 1-methylallyl chloride was a bimolecular elimination mechanism detected. The rate of this reaction was found to be greater than the total rate of bimolecular elimination from *sec.*-butyl chloride, and if the proportions in which the isomeric olefins are produced from the latter compound are assumed to be the same as from the corresponding bromide (*i.e.*, 19% $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$), approximate second-order rate coefficients ($k_2 \times 10^5$) for the two



$$CH_2{:}CH{\cdot}\underset{CH_3}{CHCl} \longrightarrow CH_2{:}CH{\cdot}\underset{\overset{\|}{CH_2}}{CH} + HCl$$

$$CH_3{\cdot}CH_2{\cdot}\underset{CH_3}{CHCl} \longrightarrow CH_3{\cdot}CH_2{\cdot}\underset{\overset{\|}{CH_2}}{CH} + HCl$$

reactions can be calculated as 6 and 0·79 l. mole^{-1} min.$^{-1}$, respectively. The greater ease of the process in the allylic system arises from the greater energy of conjugation of the vinyl group, as compared with an alkyl group, with the incipient double bond in the transition state of the reaction (cf. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., 1953, p. 436). No elimination reactions occur in allyl chloride or in the 3-substituted allylic chlorides, first, because in these compounds the S_N2 process is more facile than in 1-methylallyl chloride, and secondly, because 1 : 2-elimination reactions would produce allene or its derivatives, and on this account would be energetically unfavoured.

The results obtained for the four alkyl chlorides are very similar to those obtained by Hughes, Ingold, and their co-workers (*loc. cit.*) for the corresponding bromides, with the usual difference that the bimolecular elimination reactions in the chlorides were relatively less important.

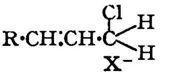
Propargyl chloride undergoes bimolecular substitution by ethoxide ions about as easily as allyl chloride. Similarly, the rate of chloride exchange in acetone, which, unlike substitution by ethoxide ions is uncomplicated by side reactions, is about the same as for allyl chloride and faster than for *n*-propyl chloride. These results show that a triple bond or a double bond will equally facilitate a substitution of the S_N2 type occurring at a reaction centre one atom removed from the point of unsaturation.

Considering structural effects within the allylic series of compounds, an α-methyl group produces the same effect as in the saturated series, *i.e.*, it retards bimolecular substitution. A γ-methyl group, in contrast, has a facilitating influence, 3-methylallyl chloride being more reactive than allyl chloride, by a factor of *ca.* 2·5, both in the reactions with ethoxide ions and with chloride ions. A β-methyl group has no significant effect. Essentially similar results have been obtained by other workers (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 602; Tamele, Ott, Marple, and Hearne, *Ind. Eng. Chem.*, 1941, **33**, 119; Young and Andrews, *J. Amer. Chem. Soc.*, 1944, **66**, 421; Hatch and Nesbitt, *ibid.*, 1951, **73**, 358; Hatch, Gordon, and Russ, *loc. cit.*; Hatch and Alexander, *loc. cit.*; Kirmann, Schmitz, and Saito, *Bull. Soc. chim.*, 1952, 515). The polar requirements of an S_N2 reaction are not clear-cut, and unambiguous prediction of the direction of a polar effect is not possible in general terms. Electron-releasing groups attached to the reaction centre in saturated compounds are generally thought, however, to exert, apart from their steric effect, a small retarding influence on bimolecular substitution (Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173). In contrast, such groups when conjugated with the reaction centre through an unsaturated system produce small accelerations in rate. For example, substitution of a methyl or a *tert.*-butyl group in the *para*-position of benzyl chloride increases slightly ($CH_3 > Bu^t$) the rates of bimolecular substitutions with ethoxide ions and with iodide ions (Bevan, Hughes, and Ingold, *Nature*, 1953, **171**, 301), and from the present results, a methyl group in the γ-position of allyl chloride is seen to behave in like fashion. A *tert.*-butyl group or two methyl groups similarly increase reaction rate in the allylic system, the magnitudes of the effects produced being in the order $(CH_3)_2 > CH_3 > Bu^t > H$*. A phenyl group has an effect greater than one methyl group, but smaller than two, although in this case the direction of the polar effect is not known. It should be noted that the accelerating powers of the groups are in the same order as in the unimolecular reactions (Vernon, *locc. cit.*) but the magnitudes of the individual effects are very much smaller.

(*c*) *Solvent Effects.*—Bimolecular reactions between alkyl halides and negative ions are slightly retarded in rate by an increase in the polarity of the solvent. This generalisation, for which there is much experimental support (Ingold, *op. cit.*, pp. 347, 348), follows from the theory in which the direction and magnitude of solvent effects are related to differences of charge or distribution of charge as between the initial and transition states of the reaction. Allylic chlorides, however, frequently behave differently; for example, the rate of reaction of allyl chloride and hydroxide ions in 60% aqueous dioxan was about twice as fast as that in 40% aqueous dioxan. Similarly, change of solvent from ethanol to 50% aqueous ethanol slightly increased the bimolecular reactivities of allyl and 2-methylallyl chlorides, whereas the reactivity of *n*-propyl chloride decreased under these conditions (Table 4). The latter reactions are, however, more complicated than those in aqueous dioxan, since change of solvent also involves a change of nucleophilic reagent.

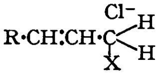
Exceptions to this behaviour of allylic chlorides are known. For example, whereas the S_N2 reactivity of *cis*-1 : 3-dichloroprop-1-ene is greater in 50% aqueous ethanol than in anhydrous ethanol, the reverse is true for the *trans*-isomer (Andrews and Kepner, *J. Amer. Chem. Soc.*, 1948, **70**, 3456). Similarly, the addition of nitromethane to the acetone solvent retards the rate of chloride exchange of allyl chloride although the retardation is less pronounced than with *n*-propyl chloride (Table 3).

The most interesting points which emerge from the present investigation are: (*a*) the reactivities of allylic chlorides by the S_N2 mechanism of substitution are greater than those of the corresponding saturated chlorides; (*b*) electron-releasing groups in the γ-position increase the rate; and (*c*) increase in the polar character of the solvent in many, but not in all cases, also increases the rate. These observations may be accommodated in the general theory of bimolecular nucleophilic substitution by noting that, in valence-bond terms, contributions to the transition state from " structure " (III), which in the allylic system, is additional to the normal " structures " (I) and (II), will lower the activation energy and facilitate the reaction :



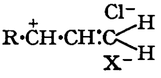
$\mathrm{R{\cdot}CH{:}CH{\cdot}\overset{Cl}{\underset{X^-}{C}}{<}^{H}_{H}}$

(I)



$\mathrm{R{\cdot}CH{:}CH{\cdot}\overset{Cl^-}{\underset{X}{C}}{<}^{H}_{H}}$

(II)



$\mathrm{R{\cdot}\overset{+}{C}H{\cdot}CH{:}\overset{Cl^-}{\underset{X^-}{C}}{<}^{H}_{H}}$

(III)

Further, structure (III) is highly polar, and when its contribution is considerable, the reaction, while remaining kinetically of strictly bimolecular form, will take on, although to a much reduced extent, the characteristics of a S_N1 reaction, *i.e.*, it will be accelerated by suitably placed electron-releasing substituents and by change to a more polar medium.

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* This " hyperconjugation order " is not without ambiguity, since it has been shown that differences in geometrical configuration may affect reaction rate (Hatch and his co-workers, *locc. cit.*). The samples of 3-methylallyl chloride and cinnamyl chloride used had the *trans*-configuration; the 3-*tert.*-butylallyl chloride had unknown configuration.