

545. *The Synthesis and Isomeric Rearrangement of 1-Phenylallyl Chloride.*

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1-Phenylallyl chloride has been prepared by the reaction of 1-phenylallyl alcohol and thionyl chloride either in ether in the presence of tri-n-butylamine or in chloroform in the presence of triethylamine. It rearranges rapidly and quantitatively to *trans*-cinnamyl chloride, and this reaction, which also accompanies its solvolyses, has been investigated kinetically in various solvents. The rearrangement is of the first order and its rate is related to parameters measuring the ionizing power of the medium, but not to the dielectric constant. It is concluded that in aqueous dioxan the formation of an intimate ion-pair is rate-determining, but that in other media an S_Ni' mechanism may be involved. The rate is increased by the addition of salts and of carboxylic acids, and the increase is proportional to the concentration of lithium chloride in ethanol and in *NN*-dimethylformamide, and to the concentration of acid in chlorobenzene.

WHEREAS migration of double bonds accompanying nucleophilic substitution in allylic halides has been much investigated,¹ the isomeric rearrangements of the halides themselves have been studied only for interconversions of 1- and 3-methylallyl chloride² and bromide,³ 1,1- and 3,3-dimethylallyl chloride,⁴ and *cis*- and *trans*-5-methylcyclohex-2-enyl chloride.⁵ The low anionotropic mobility of such halides and the difficulty of obtaining quantitative rate data led us to turn to the phenylallyl chlorides, particularly since the anionotropy of phenylallyl alcohols⁶ and esters⁷ has been extensively studied. One of the required isomers, 3-phenylallyl (cinnamyl) chloride (II), is well known but the

¹ De Wolfe and Young, *Chem. Rev.*, 1956, **56**, 753.

² Kharasch, Kritchevsky, and Mayo, *J. Org. Chem.*, 1937, **2**, 489.

³ England, *J.*, 1955, 1615; England and Hughes, *Nature*, 1951, **168**, 1002.

⁴ Young, Winstein, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1958.

⁵ Goering, Nevitt, and Silversmith, *ibid.*, 1955, **77**, 5026.

⁶ Braude, Jones, and Stern, *J.*, 1946, 396.

⁷ Braude, Turner, and Waight, *J.*, 1958, 2396; Braude and Turner, *J.*, 1958, 2404.

preparation of the other, 1-phenylallyl chloride (I), proved difficult although ultimately very simply achieved.

Synthesis.—Since the equilibrium in the system:



should very largely favour the conjugated isomer, the preparation of (I) can only succeed under non-equilibrating conditions. After unsuccessful attempts by other routes,⁸ direct replacement of the hydroxyl group in 1-phenylallyl alcohol was investigated. The disadvantage of this lies in the known sensitivity of the alcohol and the suspected sensitivity of the product to the acidic reagents required. Cinnamyl chloride proved, indeed, to be the only isolable product from the reactions of 1-phenylallyl alcohol with phosphorus trichloride, phosphorus pentachloride, or thionyl chloride in ether, even in the presence of pyridine or triethylamine.* Following the discussion of the reaction of thionyl chloride with allylic alcohols given by Young, Caserio, and Brandon,⁹ we tried the reaction of 1-phenylallyl alcohol with thionyl chloride in ether in the presence of tri-*n*-butylamine, whose hydrochloride is ether-soluble. A mixture of phenylallyl chlorides containing a high proportion of the 1-phenyl isomer was obtained. A much more convenient procedure was the treatment of the alcohol with thionyl chloride and triethylamine in dry chloroform, a good solvent for triethylamine hydrochloride. 1-Phenylallyl chloride is probably formed by bimolecular (S_N2) attack of chloride ion on the intermediate chlorosulphinate, but the latter also rearranges intramolecularly (S_Ni') to cinnamyl chloride. Rapid fractionation of the product under reduced pressure gave a chloride which had the correct elemental composition for (I) and exhibited strong infrared bands characteristic of a vinyl group (983 and 930 cm^{-1}), but which also showed a weaker band at 965 cm^{-1} indicative of *trans* $-\text{CH}=\text{CH}-$ in cinnamyl chloride. The presence of the latter was confirmed by the ultraviolet absorption (λ_{max} 2530 Å, ϵ 3500). The spectral data indicate that the product consists of 1-phenylallyl and cinnamyl chlorides in the ratio of about 5 : 1. The presence of some cinnamyl chloride, which could not readily be removed, did not in the main prove objectionable, and for brevity the mixture will be referred to as 1-phenylallyl chloride.

Rearrangement.—1-Phenylallyl chloride can be kept unchanged for some weeks under anhydrous conditions at -196° , or for shorter periods in ether solution at room temperature. At room temperature the undiluted chloride isomerizes rapidly and quantitatively to *trans*-cinnamyl chloride, identified by its ultraviolet and infrared absorption spectra. This isomerization, in conjunction with the analytical data, establishes the structure of the chloride as (I). Hydrolysis yields mainly 1-phenylallyl alcohol together with a little cinnamyl alcohol, and is accompanied by a competitive rearrangement to cinnamyl chloride, which is hydrolysed much more slowly to a mixture of the same alcohols but in different proportion.¹⁰

The very marked contrast in stability between the chloride itself and its solutions, and the variations observed from preparation to preparation, suggest that the apparently spontaneous isomerization may in fact be partly catalysed by traces of impurities. One of the most likely catalysts is hydrogen chloride, either from the preparation or more probably produced by interaction of 1-phenylallyl chloride with traces of water.

Initial kinetic studies of the rearrangement were made in chlorobenzene, the increase in intensity of the 2530 Å absorption band of cinnamyl chloride being used to follow the reaction. The rearrangement is of the first order, the product being essentially pure *trans*-cinnamyl chloride as in the absence of solvent. The rate constants (k) are reasonably

* Martin and Trinh (*Compt. rend.*, 1949, **228**, 688) claim to have isolated 1-phenylallyl chloride in 2% yield from the reaction of either 1-phenylallyl alcohol or cinnamyl alcohol with dry hydrogen chloride. We have been unable to repeat their preparation.

⁸ Cf. Braude and Waight, *J.*, 1952, 1116.

⁹ Young, Caserio, and Brandon, *Science*, 1953, **117**, 473.

¹⁰ Valkanas and Waight, *Proc. Chem. Soc.*, 1959, 8.

reproducible for runs with samples from a particular preparation but vary quite widely with samples from different preparations.

Isomerization accompanies all solvolyses of 1-phenylallyl chloride so far investigated, so that rate data for a range of solvents of widely differing dielectric constants and ionizing powers are available (Table 1). In most of the solvents used the rate constants are far

TABLE 1. Rearrangement of 1-phenylallyl chloride, 40°. The effect of medium.

Medium	$10^4 k$ (min. ⁻¹)	D^{20}	Z	E (kcal. mole ⁻¹)
Chlorobenzene	~0.28 *	5.9	55.8 †	~22
2-Nitropropane	~0.28 *	25	—	—
Dimethylformamide	3.4 *	36.7	68.5	19
2-Methylbutan-2-ol	20.4	12	70.4 †	—
Propan-2-ol	206	26	76.3	—
Ethanol	632	25.7	79.6	16
85% Dioxan-water	740	8	79.2	16
Methanol	~3800 *	34	83.6	—

* Estimated.

† Unpublished measurements by J. Crossley.

more reproducible than in chlorobenzene, but otherwise the kinetic features are identical in all solvents. For comparison, k 's are referred to a temperature of 40°; where no direct measurements were made at this temperature, values have been estimated by

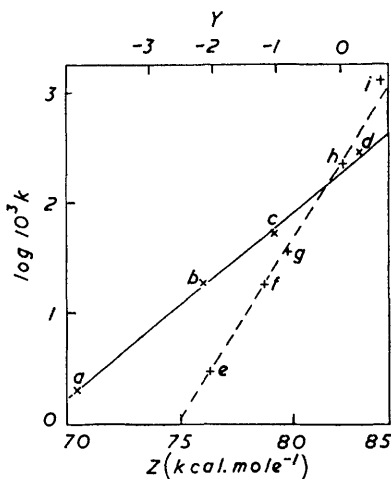


FIG. 1.

- a 2-Methylbutan-2-ol at 40°.
- b Propan-2-ol at 40°.
- c Ethanol at 40°.
- d Methanol at 40°.
- e 90% Dioxan-water at 25°.
- f 85% " " "
- g 80% " " "
- h 70% " " "
- i 60% " " "

extrapolation of the Arrhenius curve. There is obviously no parallel between k and the dielectric constant of the medium (D) but $\log k$ is directly related to parameters measuring the ionizing power of the solvent, such as Grunwald and Winstein's Y values¹¹ and Kosower's Z values,¹² as shown in Fig. 1. Straight lines of different slope are obtained for a series of alcohols, and for various mixtures of dioxan and water. The values for chlorobenzene and NN -dimethylformamide lie below the extrapolation of the alcohol plot but give a line of similar slope. Z is the energy of the charge-transfer transition of 1-ethyl-4-methoxycarbonylpyridinium iodide in the solvent, and its use as a measure of solvent-ionizing power has been criticized by Winstein and Robinson.¹³ However, Y , which is derived from the rate of solvolysis of t -butyl chloride in the medium, cannot be determined for all solvents, so that the use of Z is appropriate in the present instance. In the Grunwald-Winstein relation, $\log k = mY + \text{constant}$, m provides a measure of the susceptibility of the system to the ionizing power of the medium, referred to t -butyl

¹¹ Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

¹² Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

¹³ Winstein and Robinson, *J. Amer. Chem. Soc.*, 1958, **80**, 169.

chloride in aqueous ethanol as unity. m is large for reactions occurring by the S_N1 mechanism, for example the solvolyses of *t*-butyl halides, and low for reactions occurring by the S_N2 (or S_{N_i}) mechanism. For the isomeric rearrangement of 1-phenylallyl chloride in aqueous dioxan, m is 1.0, but in the alcoholic solvents m , derived from the plot of $\log k$ against Z , is only 0.5.

The energy of activation, E_A , also varies with the medium, paralleling the rate variation. Values of E_A derived from Table 2 are 22 kcal. mole⁻¹ in chlorobenzene, 19 kcal. mole⁻¹ in dimethylformamide, and 16 kcal. mole⁻¹ in 85% dioxan.

TABLE 2. *Rearrangement of 1-phenylallyl chloride. The effect of temperature.*

(a) *In chlorobenzene containing p-nitrobenzoic acid. (Chloride concn. 0.177 mole l.⁻¹, acid concn. 0.024 mole l.⁻¹.)*

Temp.	90°	100°	110°	120°
10 ⁴ <i>k</i> (min. ⁻¹)	59	132	255	590

(b) *In dimethylformamide. (Chloride concn. 0.15 mole l.⁻¹.)*

Temp.	61°	70°	80°	90°
10 ⁴ <i>k</i> (min. ⁻¹)	22.3	45.5	103	217

(c) *In 85% dioxan-water. (Chloride concn. 0.159 mole l.⁻¹.)*

Temp.	25°	30°	35°	40°
10 ⁴ <i>k</i> (min. ⁻¹)	213.5	319	514	740

TABLE 3. *Rearrangement of 1-phenylallyl chloride in chlorobenzene, 90°. (Chloride concn. 0.30 mole l.⁻¹.) The effect of acid.*

Acid	None	Monochloro- acetic	Dichloro- acetic	Trichloro- acetic	Trichloro- acetic	Trichloro- acetic	Trichloro- acetic
Concn. (mole l. ⁻¹) ...	—	0.010	0.010	0.004	0.006	0.008	0.010
10 ⁴ <i>k</i> (min. ⁻¹)	40	146	230	160	250	280	360

Braude¹⁴ suggested that the isomeric rearrangement of allyl chlorides should exhibit acid-catalysis* and accordingly we have investigated the effect of various carboxylic acids in chlorobenzene. The rate of rearrangement is in fact increased by the addition of acid and the increase is proportional to the acid concentration and related to the strength of the acid, as shown in Table 3. Cinnamyl esters could not be detected in the reaction products although they are stable in chlorobenzene in the presence of hydrogen chloride at 90°. The energy of activation is decreased by the addition of acid. In the presence of 0.024M-*p*-nitrobenzoic acid, which has little effect on the rate, E_A is 22 kcal. mole⁻¹, and this value is probably not very different from that of the uncatalysed reaction in chlorobenzene. In the presence of trichloroacetic acid E_A is much lower, about 15 kcal. mole⁻¹. In comparison, E_A for 1-phenylallyl *p*-nitrobenzoate in chlorobenzene is about 26 kcal. mole⁻¹,⁷ and the difference of 4 kcal. mole⁻¹ accounts almost entirely for the much lower mobility, about one-thousandth, in the ester compared with the chloride, since the non-exponential factors are similar for the two derivatives.

The effect of adding lithium chloride has also been examined. In both dimethylformamide and ethanol the increase in the rate of rearrangement is directly proportional to the salt concentration up to 0.5M in dimethylformamide and 1.0M in ethanol as shown in Fig. 2. In the former the salt appears to reduce the final intensity of light absorption and since the addition of lithium chloride to solutions of pure cinnamyl chloride in dimethylformamide results in a slow decrease to similar light-absorption intensities, it is

* In view of a comment by the Referees it must be emphasized that at no time did the late Professor Braude suggest that the presence of acid was a *necessary* condition for the isomeric rearrangement of allyl halides.

¹⁴ Braude, *Ann. Reports*, 1949, **46**, 114; *Quart. Rev.*, 1950, **4**, 404.

conceivable that the position of equilibrium is affected, being no longer almost entirely in favour of the conjugated isomer. It has not been possible to prove this directly since the presence of unconjugated material cannot be detected in the product isolated after equilibrium is attained. An alternative explanation may be that the salt is merely catalysing a slow reaction between the organic halide and dimethylformamide such as has been observed by Kornblum and Blackwood.¹⁵ It is perhaps significant that solutions of cinnamyl bromide in this solvent at 80° are considerably less stable than those of the chloride, and show a much larger decrease in light-absorption intensity on the addition of lithium bromide, but again only the cinnamyl isomer can be recovered.

Conductivity measurements indicate that in dimethylformamide the concentration of free chloride ion is not directly proportional to salt concentration over the range 0—0.5M, so we suggest that the linear increase in rate is unlikely to be due to a bimolecular reaction of 1-phenylallyl chloride with free chloride ion. If free chloride ions were involved the derived second-order rate constants (k_2) would decrease with salt concentration. Such a behaviour has been reported by England³ for the rearrangement, kinetically of first

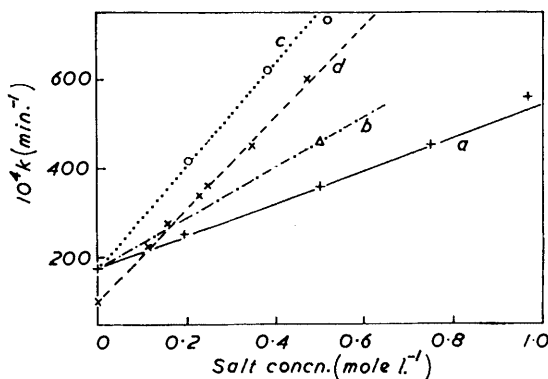


FIG. 2.

- a Lithium chloride in ethanol at 25°.
- b Lithium bromide in ethanol at 25°.
- c Lithium azide in ethanol at 25°.
- d Lithium chloride in dimethylformamide at 80°.

order, of 1-methylallyl bromide in the presence of lithium bromide (up to 0.1005M) in acetone. In view of the apparent discrepancy with our own results we have re-examined England's. He found that the rate of isomerization of the methylallyl bromides in the absence of salt is very slow and assumed that it could be neglected in calculating the rate in the presence of salt. England's second-order rate constants can be converted into first-order rate constants by multiplying them by the salt concentration and dividing by 0.75. These values, when plotted against salt concentration, give a reasonably straight line over the whole range used, which has an intercept of $0.4 \times 10^{-5} \text{ sec.}^{-1}$ at zero salt concentration, considerably higher than the value of $0.01\text{--}0.1 \times 10^{-5} \text{ sec.}^{-1}$ which can be estimated for the rate constant of the spontaneous isomerization from England's data. Our observations thus accord with England's except that in our case the rate of the uncatalysed rearrangement falls on the straight line given by the rates in the presence of lithium chloride. In the reaction studied by England the rate plot may become sharply curved at very low salt concentrations; in our example, owing perhaps to the presence of traces of hydrogen chloride, we may have been unable to measure the rate of the truly spontaneous rearrangement.

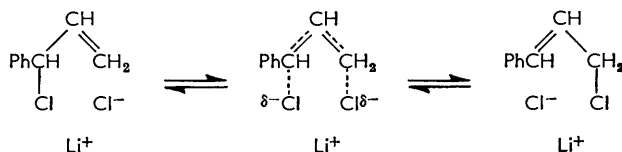
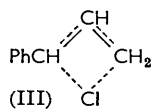
The effect of lithium bromide on the rate in ethanol is larger than that of the chloride, and the effect of the azide is yet larger (Fig. 2). Similar results are observed in dimethylformamide where the effect of azide is particularly pronounced. In the latter case the first-order rate constants fall during the run owing to the formation of cinnamyl azide which may be produced in an S_N2' reaction. However, catalysis of the isomerization

¹⁵ Kornblum and Blackwood, *J. Amer. Chem. Soc.*, 1956, **78**, 4037.

followed by very rapid S_N2 reaction of the cinnamyl chloride with lithium azide cannot be excluded for certain. Cinnamyl azide is also formed in ethanol, but the first-order rate constants of the rearrangement do not appear to decrease with time. Nevertheless it is clear that little if any 1-phenylallyl azide is formed in ethanol or in dimethylformamide since it should be relatively stable under the reactions conditions towards both solvolysis and rearrangement.

Mechanisms.—The variation of rate with ionizing power of the solvent suggests that, in aqueous dioxan at least, the rearrangement involves ionization of the C-Cl bond in the rate-determining step. Since solvolysis occurs independently to give largely the 1-phenylallyl products¹⁰ we suggest that the chloride and carbonium ions are not separated by solvent molecules, *i.e.*, that formation of an ion-pair of the intimate type proposed by Winstein⁴ is rate-determining. The much lower value of m obtained for the alcoholic solvents could indicate a different mechanism in these cases, namely, an S_N2' reaction involving a transition state to which covalent structures such as (III) make an important contribution.

The rate increase in the presence of lithium chloride is, as previously remarked, unlikely to be due to an S_N2' reaction with halide ion of the type suggested by England.³ It is conceivable that an S_N2' reaction with lithium chloride ion-pairs occurs in which the lithium ion acts as a bridge:



However the rate constant k_2 derived on this basis varies with ionizing power of the solvent in almost exactly the same way as does the rate constant of the uncatalysed rearrangement. This suggests that the salt is merely catalysing the unimolecular rearrangement and that even the modified S_N2' reaction does not occur. The increase in rate of the isomerization of 1,1-dimethylallyl chloride in aqueous ethanol due to added lithium chloride has been explained by de la Mare and Vernon¹⁶ as due to salt catalysis. In the present case and particularly that of the methylallyl bromides the rate increase is much too large to be accounted for by an ionic-strength effect. On the other hand, from the variation of k_2 with temperature a value for E_A of about 26 kcal. mole⁻¹ can be derived, about 7 kcal. mole⁻¹ higher than for the uncatalysed reaction, and this suggests that a bimolecular reaction is involved. England found that E_A for the " S_N2' reaction" of the methylallyl bromides is larger than E_A for the S_N2 reaction by about 3 kcal. mole⁻¹. That lithium bromide and azide have larger effects on the rate than the chloride again suggests that a bimolecular displacement is involved, since nucleophilicity increases in the order $Cl^- < Br^- < N_3^-$. Clearly, the present evidence is insufficient to decide the mechanism of rearrangement in the presence of lithium salts.

Since in the presence of acids the increase in the rate of rearrangement is proportional to the stoichiometric acid concentration and related to the strength of the acid, it is reasonable to suggest that one molecule of the acid associates with one molecule of the chloride so that the C-Cl bond is weakened. The nucleophilicity of an undissociated carboxylic acid is much lower than that of a chloride ion so that rearrangement remains essentially intramolecular; cinnamyl esters are not formed. Braude¹⁴ suggested that a halonium ion analogous to an oxonium ion, might be formed under these conditions, but although information concerning the ionization of carboxylic acids in chlorobenzene is lacking we prefer the alternative explanation given.

¹⁶ de la Mare and Vernon, *J.*, 1954, 2504.

EXPERIMENTAL

Analyses were by Miss J. Cuckney and the staff of the Organic Chemistry Microanalytical Laboratories. Infrared spectra were determined for liquid films by Mr. R. L. Erskine, B.Sc., A.R.C.S. Ultraviolet absorption data refer to cyclohexane solutions.

1-Phenylallyl Chloride.—To 1-phenylallyl alcohol (0.1 mole) and dry triethylamine (0.12 mole) in alcohol-free chloroform (150 ml.) at -10° was added with stirring over 25 min. thionyl chloride (0.11 mole) in alcohol-free chloroform (10 ml.). The solution was stirred for a further 10 min. and then quickly washed with water, aqueous sodium hydrogen carbonate, and water (all at 0°), and then dried (Na_2SO_4). The solvent was removed under vacuum at as low a temperature as possible and the crude *chloride*, n_D^{25} 1.5616, λ_{max} 2530 Å ($E_1^{1\%}$ 660), rapidly distilled giving fractions: (i) b. p. 48—52°/0.4 mm. (0.4 g.), n_D^{22} 1.5448; (ii) b. p. 52—58°/0.4 mm. (2.2 g.), n_D^{22} 1.5475; (iii) b. p. 58—65°/0.35 mm. (1.0 g.), n_D^{22} 1.5682; (iv) b. p. 65—70°/0.35 mm. (1.1 g.), n_D^{22} 1.5805; (v) b. p. 70—72°/0.35 mm. (2.5 g.), n_D^{22} 1.5832. Fractions (i) and (ii) combined had λ_{max} 2530 Å (ϵ 3500), ν_{max} 1636 (C=C), 983, 930 (—CH=CH₂), and 965 (*trans* —CH=CH—) cm^{-1} (Found: C, 70.5; H, 6.09; Cl, 22.6. $\text{C}_9\text{H}_9\text{Cl}$ requires C, 70.8; H, 5.95; Cl, 23.3%). Alternatively the reaction mixture was worked up as follows: The washings were omitted and the solvent immediately removed at low temperature under vacuum. The chloride was extracted from the residue with pentane. After removal of the pentane, the crude product had n_D^{25} 1.5601, λ_{max} 2530 Å ($E_1^{1\%}$ 640) and was practically identical with that above.

The refractive index and absorption intensity of samples prepared at various times varied somewhat, and the best sample, obtained after three distillations of material having initially b. p. 50—60°/0.35 mm., had n_D^{22} 1.5420, λ_{max} 2530 Å (ϵ 1900).

Samples were stored in stoppered tubes at -196° . A sample after being heated at 90° for 6 hr. (sealed tube) had n_D^{18} 1.5820, λ_{max} 2530 Å (ϵ 20,000) and an infrared spectrum identical with that of *trans*-cinnamyl chloride prepared by the action of thionyl chloride on *trans*-cinnamyl alcohol in ether.

Cinnamyl Trichloroacetate.—Trichloroacetyl chloride (4 g., from trichloroacetic acid and thionyl chloride) in dry benzene (10 ml.) was added in portions to cinnamyl alcohol (4 g.) in pyridine (3 g.) and dry benzene (50 ml.) at 0° . After storage at room temperature for 18 hr., pyridine hydrochloride was filtered off and the filtrate diluted with ether (100 ml.), washed with water and aqueous sodium hydrogen carbonate, and dried (Na_2SO_4). Distillation gave the *ester*, b. p. 101—103°/0.001 mm. (4 g.), n_D^{22} 1.5612, λ_{max} 2520 Å (ϵ 19,000), ν_{max} 1785 cm^{-1} (C=O) (Found: C, 47.0; H, 3.44; Cl, 37.2. $\text{C}_{11}\text{H}_9\text{O}_2\text{Cl}_3$ requires C, 47.2; H, 3.22; Cl, 38.1%)

Rearrangement Products.—(a) The chloride (1.2 g., n_D^{22} 1.5499), trichloroacetic acid (1.2 g.), and chlorobenzene (15 ml.) were heated at 90° for 15 min. The cooled solution was diluted with ether, washed with aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and distilled. The product (0.8 g.) had n_D^{22} 1.5812, λ_{max} 2530 Å (ϵ 19,000), and an infrared spectrum identical with that of cinnamyl chloride. There was no residue. To show that cinnamyl trichloroacetate if formed would be stable under the reaction conditions, the ester (1.4 g.) was dissolved in chlorobenzene (50 ml.) saturated with hydrogen chloride ($\sim 0.6M$) at room temperature, and heated at 90° for 10 min. (sealed tube). The mixture was worked up as before and the product (1.0 g.) had n_D^{19} 1.5612, λ_{max} 2520 Å (ϵ 19,000), and an infrared spectrum identical with that of cinnamyl trichloroacetate. No evidence of the presence of cinnamyl chloride was obtained. (b) The chloride (1.0085 g., n_D^{23} 1.5452), lithium chloride (0.107 g.), and *NN*-dimethylformamide (10 ml.) were heated at 80° for 3 hr. The solvent was removed by distillation and the residue extracted with light petroleum (b. p. 40—60°). The extract was washed with water, dried (Na_2SO_4), and distilled, giving a product (0.72 g.), b. p. 56°/0.05 mm., n_D^{22} 1.5814, λ_{max} 2530 Å (ϵ 20,600), with an infrared spectrum identical with that of cinnamyl chloride (Found: C, 70.6; H, 6.05; Cl, 22.7. Calc. for $\text{C}_9\text{H}_9\text{Cl}$: C, 70.8; H, 5.95; Cl, 23.3%).

Kinetic Measurements.—Solvents were carefully purified and dried by the following methods: Chlorobenzene was washed with aqueous sodium hydrogen carbonate, dried (CaCl_2), and distilled from a trace of sodium. *NN*-Dimethylformamide was kept for some days over sodium sulphate and then distilled under reduced pressure; this procedure was repeated three times. Dioxan was refluxed with sodium for 6—8 hr. and then distilled. Methanol was refluxed with magnesium (4 hr.) and then distilled. Propan-2-ol and 2-methylbutan-2-ol were

refluxed over calcium oxide (6 hr.) and then distilled. Burnett's absolute alcohol was not further purified. Lithium salts were freed from water by dissolution in ethanol followed by evaporation to dryness and heating at 100° *in vacuo*. Chloroacetic acids were redistilled.

The kinetic method previously described was employed,¹⁷ the reaction being followed by measuring the absorption intensity at 2530 Å. Carboxylic acids and salts were added as accurately measured volumes of stock solutions.

First-order rate constants (k , min.⁻¹) are calculated from the expression,

$$k = (2.3/t) \log_{10} [(a - x_0)/(a - x)],$$

where t is the time (min.), a is the final intensity, x_0 the initial intensity, and x the intensity of light absorption at time t . In media such as aqueous dioxan, the solvolysis of cinnamyl chloride is much slower than the solvolysis and isomeric rearrangement of 1-phenylallyl chloride; thus the calculated k represents the sum of the competing first-order reaction rate constants. The rate constant for isomeric rearrangement (k_r) is obtained by multiplying by the fraction of cinnamyl chloride produced, *i.e.*,

$$k_r = k [1 - cs/(c - x_0)]$$

where c is the light absorption intensity of pure cinnamyl chloride, and s the fraction of solvolysis. s was determined by adding 0.5 ml. of the reaction mixture at t_∞ to water (*ca.* 70 ml.) and light petroleum (*ca.* 30 ml.). The mixture was shaken and titrated with standard alkali, Methyl Red being used as indicator. Typical runs are in Table 4.

TABLE 4.

(a) *Rearrangement in chlorobenzene, 90°. Chloride concn., 0.332 mole l.⁻¹. Trichloroacetic acid concn., 0.005 mole l.⁻¹.*

t (min.)	0	10	15	20	27	40	55	∞
$E_{1\text{cm.}}^{1\%}$	244	361	428	478	544	662	784	1200
10^2k (min. ⁻¹)	—	1.31	1.42	1.40	1.40	1.44	1.51	— (mean 1.41)

(b) *Rearrangement and solvolysis in 85% aqueous dioxan, 25°. Chloride concn., 0.162 mole l.⁻¹.*

t (min.)	0	4	5	8	10	15	69
$E_{1\text{cm.}}^{1\%}$	290	375	400	450	480	560	1005
10^2k (min. ⁻¹)	—	3.12	3.22	3.16	3.08	3.17	— (mean 3.15)

After 75 min. 0.5 ml. of reaction mixture required 0.54 ml. of 0.0377M-sodium hydroxide for neutralization, giving $s = 0.251$ and $10^2k_r = 2.14$ min.⁻¹.

(c) *Rearrangement in dimethylformamide in the presence of lithium azide, 40°. Chloride concn., 0.149 mole l.⁻¹. Lithium azide concn., 0.21 mole l.⁻¹.*

t (min.)	0	1	2	5	9	240
$E_{1\text{cm.}}^{1\%}$	280	701	865	1050	1160	1270
10^2k (min. ⁻¹)	—	55.4	44.6	30.0	24.4	— (extrap. ~75)

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[Received, February 26th, 1959.]

¹⁷ Braude and Jones, *J.*, 1944, 436 *et seq.*