803. *Solvolytic Reactions of* 1- *and* 3-*Phenylallyl Chloride.*

By G. VALKANAS, E. S. WAIGHT, and M. WEINSTOCK.

Solutions of 1-phenylallyl chloride in aqueous dioxan produce 1- and 3-phenylallyl alcohol and cinnamyl chloride which in turn is hydrolysed much more slowly to give the same alcohols but in different proportions. Analogous results are obtained when alcohols are employed as solvents. The effects of added salts and variations in the ionizing power of the solvent on the spectrometric rate of reaction and on the product ratio have been investigated and it is concluded that for both isomers the formation of an ion-pair is rate-determining. This conclusion is supported by rates of loss of optical activity of (+)-1-phenylallyl chloride which are larger than the spectrometric rates.

THE rearrangement of 1-phenylallyl chloride (I) to cinnamyl chloride (II) in a variety of media, including common hydroxylic solvents in which it accompanies solvolysis, has already been reported.[1] We now discuss the solvolytic reactions of these halides. Kinetic studies of solvolytic reactions of cinnamyl halides have been made before:[2] mixtures of allylic isomers are produced,[3] but little quantitative information about medium and salt effects on product ratios is available.

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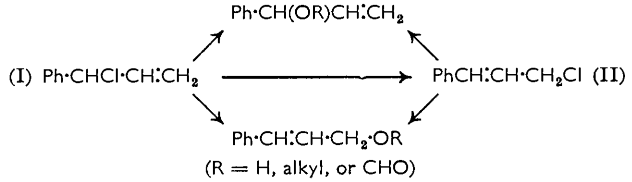
[1] Valkanas and Waight, *J.*, 1959, 2720.

[2] Vernon, *J.*, 1954, 423, 4462.

[3] Meisenheimer and Link, *Annalen*, 1930, **479**, 211; Meisenheimer and Beutter, *ibid.*, 1933, **508**, 58.

The phenylallyl system presents several advantages compared with simple alkyl-substituted allylic systems. The secondary halide (I) is much more reactive than the primary isomer (II), so that solvolysis of the former is not complicated by concurrent reaction of any of the latter which may be formed; in the acetolysis of 1,1-dimethylallyl chloride [4] the 3,3-isomer is formed but reacts with solvent at a rate similar to that of the tertiary isomer. The styryl chromophore has high absorption intensity at about 2500 Å; reactions of phenylallyl halides are thus conveniently followed by observing the intensity at 2530 Å, the final value together with a titrimetric determination of acid or halide ion formed sufficing to give a complete analysis of the products without the necessity of isolation. Finally, optically active 1-phenylallyl chloride can be prepared [5] and a study of its racemization gives further information on the intermediates involved in the solvolysis and rearrangement reactions.



EXPERIMENTAL

Unless otherwise stated, ultraviolet light absorption measurements refer to solutions in ethanol.

1-*Phenylallyl Alcohol.*—The product from the reaction of acraldehyde and phenylmagnesium bromide contained two unidentified impurities and cinnamyl alcohol. It was purified by way of the hydrogen phthalate, m. p. 73° (lit.,[6] m. p. 73—74°), and then had b. p. 96°/6·5 mm., n_D^{26} 1·5385, $\lambda_{max.}$ 2520 Å (ε 178) [lit.,[6] n_D^{25} 1·5386, $\lambda_{max.}$ 2520 Å (ε 187)]. The infrared and nuclear magnetic resonance spectra indicated the removal of the contaminants and the purity was further demonstrated by gas–liquid chromatography.

1-*Phenylallyl Chloride.*—This was prepared as described previously.[1] A sample from purified 1-phenylallyl alcohol (see above) had b. p. 35—36°/0·15 mm., n_D^{22} 1·5410, $\lambda_{max.}$ 2530 Å (ε 602 in cyclohexane), representing *ca.* 98% of 1-phenylallyl chloride. More usually the samples contained about 5% of cinnamyl chloride and some preparations contained 2—5% of two other impurities, derived from those in the alcohol, which did not significantly alter the rate constants but were allowed for in calculating product ratios.

(+)-1-*Phenylallyl Chloride.*—(−)-1-Phenylallyl alcohol, $[\alpha]_D^{23}$ $-9{\cdot}05°$ (liquid), prepared through the quinidine salt of 1-phenylallyl hydrogen phthalate,[6] was converted, as for the racemic alcohol, into (+)-1-phenylallyl chloride, b. p. 42—46°/0·5 mm., $[\alpha]_D^{23}$ $+14{\cdot}85°$ (in cyclohexane), $\lambda_{max.}$ 2530 Å (ε 680 in cyclohexane), having an infrared spectrum (liquid film) identical with that of inactive material. Heating at 80° (18 hr., sealed tube) caused total loss of optical activity and the infrared spectrum of the product became identical with that of cinnamyl chloride except for weak hydroxyl absorption at 3380 $cm.^{-1}$.

Cinnamyl Alcohol.—A commercial sample was recrystallized four times from ether–pentane. It then had $\lambda_{max.}$ 2510 Å (ε 18,180) [lit.,[6] $\lambda_{max.}$ 2510 Å (ε 17,900)].

Cinnamyl Ethyl Ether.—Cinnamyl chloride and 2N-sodium ethoxide in ethanol were heated under reflux for 1 hr. The product had b. p. 127°/15 mm., $\lambda_{max.}$ 2530 Å (ε 17,800), and was shown to be pure by gas–liquid chromatography.

Cinnamyl Chloride.—This was prepared by the action of thionyl chloride on cinnamyl alcohol. It had b. p. 51—53°/0·1 mm., n_D^{25} 1·5815, and $\lambda_{max.}$ 2530 Å (ε 19,300, in cyclohexane), and contained only traces of impurities as shown by gas–liquid chromatography.

Reaction of Cinnamyl Chloride and Alcoholic Lithium Azide.—Cinnamyl chloride (1·05 g.), lithium azide (0·5 g.), and ethanol (40 ml.) were kept at 50° for 16 hr. The product, b. p.

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[4] Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Young, *J. Chem. Educ.*, 1962, 455.

[5] Waight and Weinstock, *Proc. Chem. Soc.*, 1961, 334.

[6] Duveen and Kenyon, *J.*, 1939, 1697; Goering and Dilgren, *J. Amer. Chem. Soc.*, 1959, **81**, 2556.

70°/0·2 mm., n_D^{20} 1·5719, contained only carbon, hydrogen, and nitrogen but did not give satisfactory elemental analyses. From its infrared spectrum (liquid film) which showed strong bands at 2115 (N_3) and 975 (*trans*-CH:CH) cm.$^{-1}$ and only weak absorption at *ca.* 1100 (C–O), 983, 930 (CH:CH_2) cm.$^{-1}$ it was evidently mainly cinnamyl azide.

Kinetic Measurements.—Solvents were purified as described previously,[1] except that Burnett's absolute alcohol was further dehydrated with magnesium ethoxide (cf. Vogel [7]). Formic acid was distilled through a Fenske column to remove low-boiling impurities, kept over boric anhydride (80 g./l.), and redistilled from fresh boric anhydride. Water was boiled over potassium permanganate, redistilled, and passed through a column of "Biodemineralit." Commercial anhydrous lithium chloride was kept for several hours at 100° *in vacuo* and subsequently handled in a dry-box. For reactions in aqueous media it was used in aqueous solution (*ca.* 3M), standardized by titration with silver nitrate solution. Lithium perchlorate (cf. Fainberg and Winstein [8]) still contained water after the molten salt had been heated at 300°. A satisfactory sample of lithium azide could not be prepared, even by the method of Gray and Waddington.[9] Tetraethylammonium azide was obtained by acidifying (to Bromothymol Blue) tetraethylammonium hydroxide in ethanol with ethereal hydrazoic acid. The solvent was removed *in vacuo* and the resulting solid twice dissolved in chloroform–acetone (1 : 1) and reprecipitated with ether, finally being dried *in vacuo*. Only very weak hydroxyl absorption was evident in the infrared spectrum of the solid.

Typical kinetic runs are in Table 1. Preliminary results were obtained (*a*) by using the spectrometric method of Braude, Jones, and Stern [10] and (*b*) by titrating the acid produced with standard alkali.[1] Although reasonable first-order constants were obtained, terminal values of absorption intensity and degree of solvolysis were not very reproducible. Accordingly for measurements below 50° the method of Braude and Gore [11] was adopted. A stock solution of the chloride (0·1 ml.; *ca.* 0·125 g./l.; in dioxan or cyclohexane) was added to 2·40 ml. of the medium contained in a 1 cm. spectroscopic cell, placed in the thermostat-controlled cell-holder of a Beckman DU spectrophotometer. This method had the advantage that the low concentration of acid produced had a negligible catalytic effect on the rearrangement of 1-phenylallyl solvolysis products. The degree of solvolysis was obtained by adding a weighed quantity (*ca.* 0·05 g.) of 1-phenylallyl chloride to the reaction medium (25 ml.) kept at the required temperature. After nine reaction half-lives, 5 ml. samples were added to pentane (25 ml.), which was then shaken twice with water (10 ml.); the aqueous solution was titrated with 0·01N-sodium hydroxide to Methyl Red, or analysed by the Volhard method. Recovery of hydrochloric acid from the reaction medium was better than 99%. Cinnamyl chloride was unaffected.

In reactions of cinnamyl chloride first-order rate constants (k_T; min.$^{-1}$) are calculated from

$$k_T = (2{\cdot}3/t)\log_{10}[(E_0 - E_\infty)/(E_t - E_\infty)],$$

where E_0 is the initial, E_∞ the final, and E_t the observed optical density (at time t). The ratio of the concentrations of 1-phenylallyl and cinnamyl solvolysis products (c_P and c_C, respectively) is given by

$$c_P/c_C = (\varepsilon_C c_0 - E_\infty)/(E_\infty - \varepsilon_P c_0),$$

where ε_P and ε_C are, respectively, the molecular extinction coefficients (at 2530 Å) of pure 1-phenylallyl and cinnamyl solvolysis products and c_0 is the initial molar concentration. For reactions of 1-phenylallyl chloride first-order rate constants are calculated from

$$k_T = (2{\cdot}3/t)\log_{10}[(E_\infty - E_0)/(E_\infty - E_t)].$$

The molar concentrations of the three products are given by:

$$\begin{aligned} c_C &= [E_\infty + T(\varepsilon_{CCl} - \varepsilon_P) - \varepsilon_{CCl}\cdot c_0]/(\varepsilon_C - \varepsilon_P), \\ c_P &= T - c_C, \\ c_{CCl} &= c_0 - c'_{CCl} - (c_P + c_C), \end{aligned}$$

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[7] Vogel, "Practical Organic Chemistry," Longmans, London, 1948, p. 166.

[8] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2767.

[9] Gray and Waddington, *Proc. Roy. Soc.*, 1956, *A*, **235**, 106.

[10] Braude, Jones, and Stern, *J.*, 1946, 396.

[11] Braude and Gore, *J.*, 1959, 41.

where T is the molar concentration of liberated acid referred to the initial concentration of phenylallyl chlorides, c_0, in the spectrometric run, ε_{CCl} is the molecular extinction coefficient of pure cinnamyl chloride, and c'_{CCl} the concentration of cinnamyl chloride originally present. The total hydrolysable chloride ($c'_{\text{CCl}} + c_{\text{PCl}}$) was determined by keeping a sample (*ca.* 0·05 g.) in 50% dioxan–water for 3 hr. at 30°, the acid formed being titrated with standard aqueous sodium hydroxide. The values obtained (95—100%) were used to correct the amount of

TABLE 1.

(*a*) Hydrolysis of cinnamyl chloride in 60% dioxan–water at 30·0°.
Chloride 3·269 × 10^{-5}M.

(min.)	0	13	80	110	154	180	210	240	1600	
E	0·610	0·583	0·489	0·458	0·420	0·402	0·382	0·367	0·283	(% ROH 51·2)
10^3k (min.$^{-1}$) ...	—	5·74	5·77	5·69	5·65	5·62	5·69	5·66	—	(Mean 5·69)

(*b*) 1-Phenylallyl chloride in 96% ethanol–cyclohexane at 30·0°. Chloride 4·730 × 10^{-5}M.
Lithium chloride 0·055M.

t (min.) ...	0	1	1·5	2	3	4	5	6	7	80	
E	0·145	0·168	0·180	0·190	0·210	0·229	0·246	0·265	0·281	0·515	
10^3k (min.)	—	64·5	66·3	65·0	64·5	64·6	63·8	65·5	65·4	—	(Mean 65·0)

The chloride (0·03909 g., containing 9·0% of cinnamyl chloride) was kept in 96 : 4 ethanol–cyclohexane (25 ml.) containing lithium chloride (0·055M) at 30°, for 90 min. Two samples (5 ml.) were extracted with water as described above; the aqueous extracts required 2·05 ml. and 2·16 ml., respectively, of 1·49 × 10^{-2}N-aqueous sodium hydroxide for neutralization. Thus the concn. of acid formed was 6·27 × 10^{-3}M, corresponding to 67·3% hydrolysis of the secondary chloride.

(*c*) Loss of optical activity of (+)-1-phenylallyl chloride in 90% dioxan–water
at 30·0°. Chloride 0·147M. Lithium chloride 0·014M.

t (min.)	0	5	10	15	20	25	30	35	40	45	1080
α (°)	0·623	0·570	0·530	0·481	0·441	0·399	0·369	0·333	0·299	0·275	0
10^3k (min.$^{-1}$)	—	17·7	16·1	17·2	17·1	17·8	17·5	17·9	18·3	18·2	—
											(Mean 17·5)

TABLE 2.

Hydrolysis of cinnamyl chloride (~3·3 × 10^{-5}M) in aqueous dioxan at 30·0°.

Dioxan (%) *	Salt	(M)	10^3k_T †	ROH (%) ‡	Dioxan (%) *	Salt	(M)	10^3k_T †	ROH (%) ‡
30	—	—	703	59	50	LiBr	0·10	39·8	54
,,	LiCl	0·10	643	57	,,	$LiClO_4$	0·10	39·3	52
,,	,,	0·50	508	56	,,	,,	0·50	53·2	51
40	—	—	165	56	,,	NaOH	0·117	30·2	50
,,	LiCl	0·10	152	57	,,	,,	0·234	23·9	47
,,	,,	0·50	110	51	60	—	—	5·72	52
,,	$LiClO_4$	0·50	233	55	,,	LiCl	0·10	5·20	51
50	—	—	31·6	54	,,	,,	0·50	4·08	43
,,	LiCl	0·10	27·3	54	,,	$LiClO_4$	0·50	10·6	48
,,	,,	0·50	20·0	48					

* x% means that dioxan (x ml.) was mixed with water (100 − x ml.). † Mean values of several runs. ‡ Mean values; R = 1-phenylallyl.

TABLE 3.

Ethanolysis of cinnamyl chloride.

Temp.	Salt	(M)	10^3k_T	ROEt (%)	Temp.	Salt	(M)	10^3k_T	ROEt (%)
45·0°	—	—	0·60 *	—	50·0°	LiCl	0·507	1·68 †	54
,,	LiCl	1·00	1·56 *	—	,,	,,	0·560	1·76 *	—
,,	LiBr	1·00	10·9 *	—	,,	,,	0·760	1·96 †	55
50·0	—	—	1·04 †	52	,,	$LiClO_4$	0·240	2·36 †	57
,,	—	—	1·07 *	—	,,	,,	0·480	3·71 †	59
,,	LiCl	0·254	1·44 †	52	60·0	—	—	2·85 †	52
,,	,,	0·410	1·53 *	—	70·0	—	—	8·92 †	51

* By titrimetric method, extrapolated to zero time; chloride ~0·15M. † By spectrometric method, solvent containing 2% of cyclohexane; chloride ~3·3 × 10^{-5}M; mean values of several runs.

TABLE 4.

Reaction of 1-phenylallyl chloride with aqueous dioxan at 30·0° (chloride ~5 × 10^{-5}M).

Dioxan (%)	Salt	(M)	10^3k_T *	Hydrolysis † (%)	ROH (%)	Dioxan (%)	Salt	(M)	10^3k_T *	Hydrolysis † (%)	ROH (%)
70	—	—	1023	45·0	70	80	$LiClO_4$	0·056	197	47·4	68
,,	LiCl	0·180	1039	36·4	71	,,	,,	0·113	236	47·0	69
75	—	—	412	43·3	71	,,	,,	0·226	281	47·5	66
80	—	—	169	43·4	70	85	—	—	51·0	41·5	71
,,	LiCl	0·045	163	39·6	70	90	—	—	9·71	36·1	67
,,	,,	0·090	169	36·4	72	,,	LiCl	0·029	13·2	32·9	68
,,	,,	0·180	172	30·8	78						

* Mean values. † 100 $T/(c_0 - c'_{\infty})$.

TABLE 5.

Reaction of 1-phenylallyl chloride with other solvents.

Solvent	Temp.	Salt	(M)	10^3k_T *	Solv. (%)	ROS † (%)
MeOH (*a*)	20°	—	—	186	71·8	
,, (*b*)	25	—	—	356	72·0	
,, (*a*)	40	—	—	~1390		
96% EtOH–C_6H_{12} (*c*)	30	—	—	56·6	69·8	78
,,	,,	LiCl	0·017	58·7	67·6	75
,,	,,	,,	0·034	59·3	67·4	75
,,	,,	,,	0·055	63·5	67·3	75
,,	,,	,,	0·111	66·3	67·3	72
,,	,,	,,	0·557	74·1	61·2	70
,,	,,	NaOEt	0·522	48·9		
,,	,,	$LiClO_4$	0·071	73·0	68·8	77
,,	,,	,,	0·142	86·8	67·6	75
,,	,,	,,	0·282	134	65·1	78
,,	,,	,,	0·565	244	63·5	77
EtOH (*d*)	,,	NEt_4N_3	0·100	92·3	44·6	11,700 ‡
,,	,,	,,	0·200	118	35·5	12,500 ‡
,,	,,	,,	0·400	158	22·2	13,900 ‡
,,	,,	,,	0·600	165	16·9	15,900 ‡
,, (*b*)	40	—	—	153	~60	
Pr^iOH (*e*)	,,	—	—	37·2	~45	
t-C_5H_{11}·OH (*e*)	,,	—	—	2·48	~14	
22% HCO_2H–dioxan (*c*)	30	HCO_2Li	0·065	25·3	10·6	(100)

Chloride concns.: (*a*) 0·146M; (*b*) 0·268M; (*c*) ~5 × 10^{-5}M; (*d*) ~4 × 10^{-3}M; (*e*) ~0·10M.

* Mean values. † 1-Phenylallyl ether or ester. ‡ Final ε of solution.

TABLE 6.

Racemization of (+)-1-phenylallyl chloride (chloride ~0·15M).

Solvent	Temp.	Salt	(M)	10^3k_{α}	10^3k_T
96% EtOH–C_6H_{12}	22°	—	—	27·4	22·3
,, ,,	30	—	—	66·2	56·6
90% ,,	22	—	—	20·8	18·4
80% ,,	,,	—	—	11·6	11·5
70% ,,	,,	—	—	9·28	8·50
60% ,,	,,	—	—	6·24	5·32
90% Dioxan–H_2O	30	—	—	13·9	9·71
,, ,,	,,	LiCl	0·014	17·5	
,, ,,	,,	,,	0·029	19·3	13·2

chloride weighed out to give the initial concentration of phenylallyl chlorides (c_0). The non-hydrolysable material was assumed to have ε < 200 and this gave good agreement for product ratios obtained for different batches of chloride of differing purity. Calculated amounts of the solvolysis products of 1-phenylallyl chloride were reproducible to ±3%.

Polarimetric runs in 90% dioxan–water and in ethanol at 22° were carried out with ~0·15M-solutions in a jacketed polarimeter tube (*l.* 2 dm., *ca.* 2 ml. capacity). Water at the appropriate temperature was circulated through the outer jacket and the tube was immersed in a thermostat-controlled water-bath between measurements made at 5893 Å with a Hilger and Watts Microptic photoelectric polarimeter. When filled with pure solvent the polarimeter tube had a small positive rotation from which final readings in the kinetic runs were indistinguishable. First-order polarimetric rate constants are calculated from

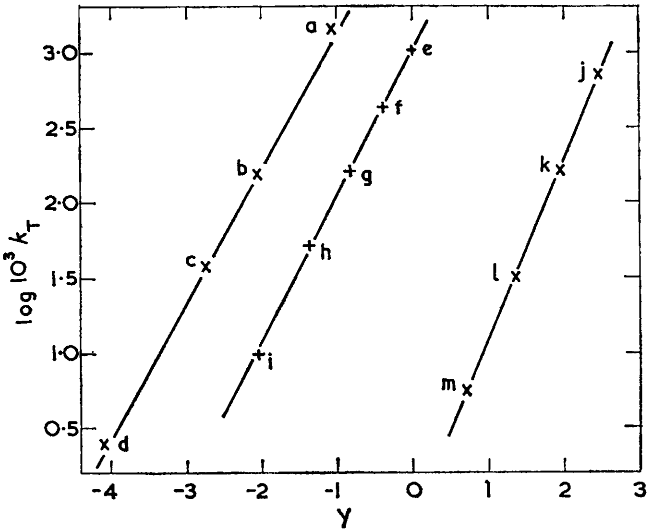
$$k_\alpha = (2{\cdot}3/t)\log_{10}(\alpha_0/\alpha_t),$$

where α_0 and α_t are, respectively, the rotations initially and at time t (min.). Rate measurements at 30° were made by withdrawing samples (0·10 ml.) at intervals of one min. and quenching them in cyclohexane at 0°. The rotations of the cyclohexane solutions were measured at 3030 Å with a Rudolph spectropolarimeter. We are indebted to Professor W. Klyne and Miss J. Jackson for these measurements.

Results are tabulated.

RESULTS

The rates of hydrolysis of both 1-phenylallyl and cinnamyl chloride in aqueous dioxan are sensitive to medium composition (see Tables 2 and 4) and give good correlation with the ionizing power, as measured by Grunwald and Winstein's Y-values.[12] In the Figure, log k_T is plotted against Y; the slopes (m) of the lines, 1·23 for the primary and 0·93 for the secondary isomer, are typical of unimolecular (S_N1) reactions. The fraction of 1-phenylallyl chloride undergoing hydrolysis decreases as the concentration of water decreases but the relative amounts of 1-phenylallyl and cinnamyl alcohol produced are scarcely affected. The proportion of the secondary alcohol is significantly larger than expected by considering reactions, such as the acid-catalysed rearrangement of 1-phenylallyl alcohol[6,13] and the deamination of 1-phenylallylamine with nitrous acid,[14] thought to proceed by attack of water on a free phenylallyl carbonium ion. The mixture of alcohols obtained from cinnamyl chloride approximates to



1-Phenylallyl chloride in: (a) methanol, (b) ethanol, (c) propan-2-ol, (d) 2-methylbutan-2-ol * at 40°; (e) 70%, (f) 75%, (g) 80%, (h) 85%, (i) 90% dioxan–H_2O at 30°.

Cinnamyl chloride in: (j) 30%, (k) 40%, (l) 50%, (m) 60% dioxan–H_2O at 30°.

* Y-value from Y–Z plot (Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, and ref. 1).

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[12] Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; Fainberg and Winstein, *ibid.*, 1956, **78**, 2770.

[13] Bunton, Pocker, and Dahn, *Chem. and Ind.*, 1958, 1516.

[14] Pocker, *Chem. and Ind.*, 1959, 195.

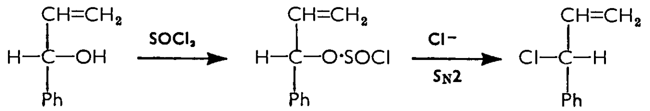
that expected from hydration of the free carbonium ion, but the composition does vary with the proportion of water in the medium. Early work[15] suggested that even larger amounts of 1-phenylallyl alcohol were produced in the hydrolysis of the secondary chloride; the difference between those claims and the values now favoured seems due to the original chloride samples containing large amounts (*ca.* 20%) of cinnamyl chloride and to less accurate analytical methods.

For the secondary chloride k_T (Tables 4 and 5) is about six times larger in ethanol than in 90% dioxan–water and has an intermediate value in 22% formic acid–dioxan, all three media having about the same ionizing power as judged by Y-values.[12] Cinnamyl chloride comprises only 30% of the total product in ethanol compared with 64% in 90% dioxan–water and 89% in 22% formic acid–dioxan. The major product of ethanolysis is 1-phenylallyl ethyl ether. In other alcohols (Table 5) k_T again gives good correlation with Y (see Figure), m being 0·94. The degree of solvolysis also increases with ionizing power.

Vernon[2] showed that sodium ethoxide increases the rate of ethanolysis of cinnamyl chloride. Lithium bromide (1·0M) increases k_T (Table 2) to about half that of cinnamyl bromide under similar conditions, while sufficient lithium azide completely inhibits ether formation owing to the rapid production of cinnamyl azide. Lithium chloride also increases the rate and (very slightly) the proportion of secondary ether; both effects are less marked than with lithium perchlorate. Vernon[2] also showed that in 50% aqueous ethanol sodium hydroxide has little effect on the rate of hydrolysis of cinnamyl chloride. In 50% dioxan–water sodium hydroxide decreases the rate (Table 2), as in the hydrolysis of t-butyl nitrate and diphenylmethyl bromide.[16] Lithium bromide and perchlorate cause similar rate increases, while lithium chloride decreases the rate of hydrolysis. These salts at 0·1M-concentration have little effect on the solvolysis product ratio.

Sodium ethoxide decreases k_T for 1-phenylallyl chloride in ethanol (Table 5). Lithium perchlorate and tetraethylammonium azide increase k_T by similar amounts and have a much larger effect than lithium chloride. All three salts decrease the proportion of solvolysis; the effect of azide is particularly pronounced and the main product is cinnamyl azide. In 70% and 80% dioxan–water (Table 4) lithium chloride has hardly any effect on the overall rate but does decrease the degree of solvolysis, whereas lithium perchlorate (in 80% dioxan–water) has little effect on the product ratio but increases the rate; the hydrolysis thus exhibits a common-ion rate depression.

Polarimetric rate constants for (+)-1-phenylallyl chloride in ethanol and in 90% dioxan–water (Table 6) exceed k_T under the same conditions, as in solvolyses of *cis*- and *trans*-5-methylcyclohex-2-enyl chloride,[17] 4-chlorodiphenylmethyl chloride, and 1-mesitylethyl chloride,[18] and the 1-phenylallyl alcohol or ethyl ether formed is largely or completely racemic. Solutions of the (+)-chloride in ethanol or aqueous dioxan, kept until all the (secondary) chloride had reacted, occasionally showed small positive rotations but never negative rotations. From the mechanism of its formation the (+)-chloride probably has the configuration opposite to that of the (−)-alcohol:[19]



$$\mathrm{H{-}\overset{\displaystyle CH{=}CH_2}{\underset{\displaystyle Ph}{C}}{-}OH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{H{-}\overset{\displaystyle CH{=}CH_2}{\underset{\displaystyle Ph}{C}}{-}O{\cdot}SOCl} \xrightarrow[S_N2]{\mathrm{Cl^-}} \mathrm{Cl{-}\overset{\displaystyle CH{=}CH_2}{\underset{\displaystyle Ph}{C}}{-}H}$$

Bimolecular displacements (S_N2) on the (+)-chloride might thus be expected to produce the (−)-alcohol.

DISCUSSION

Cinnamyl Chloride.—Vernon[2] has concluded that the solvolysis of cinnamyl chloride in 50% aqueous ethanol occurs by a unimolecular mechanism and that in pure ethanol

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[15] Valkanas and Waight, *Proc. Chem. Soc.*, 1959, 8.

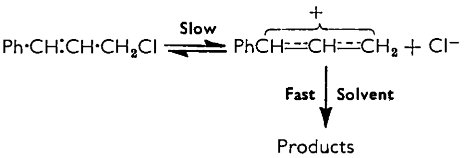
[16] Benfey, Hughes, and Ingold, *J.*, 1952, 2494.

[17] Goering, Nevitt, and Silversmith, *J. Amer. Chem. Soc.*, 1955, **77**, 5026.

[18] Winstein, Gall, Hojo, and Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 1010; Winstein, Hojo, and Smith, *Tetrahedron Letters*, 1960, No. 22, 12.

[19] Young, Caserio, and Brandon, *J. Amer. Chem. Soc.*, 1960, **82**, 6163; Young and Caserio, *J. Org. Chem.*, 1961, **26**, 245.

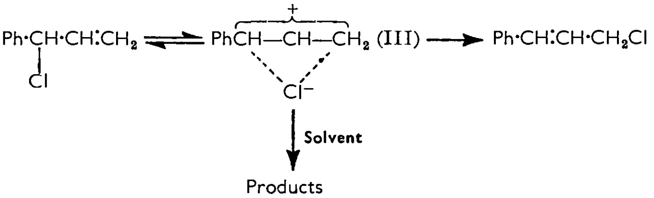
there is a bimolecular component; the results presented now support this general conclusion. However, it is difficult to account for the variation of product ratio with water content of the medium if the product-forming step is the reaction of solvent with a free mesomeric phenylallyl carbonium ion:



It is suggested that an ion-pair is formed in the rate-determining step without nucleophilic assistance by the solvent. In the most highly aqueous (*i.e.*, ionizing) media the counter-ions are sufficiently well separated before reaction with solvent for the positive charge to be completely delocalized, and the isomeric alcohols are thus obtained in about the same ratio as from the free carbonium ion. In less highly ionizing media, water reacts when the chloride ion is still closer to the 3-carbon atom than to the 1-carbon atom, so that the carbonium ion is polarized with the positive charge localized at the 3-position and more cinnamyl alcohol is formed. The common-ion rate depression is not accompanied by an increase in the proportion of 1-phenylallyl alcohol; 1-phenylallyl chloride is not formed. Either return from an intermediate, such as the mesomeric carbonium ion-pair, which can give secondary chloride, is negligible or anions have a much greater differential reactivity with the 3-position of such an intermediate than have neutral molecules. The former seems unlikely (see below) and some molecular-orbital calculations on the phenylallyl carbonium ion by Professor L. M. Jackman and Dr. A. Hardisson [20] * support the latter view.

The ethanolysis of cinnamyl chloride requires nucleophilic assistance by solvent in the rate-determining step, as suggested by Streitwieser [21] for the solvolysis of but-2-enyl chloride, or unimolecular and bimolecular mechanisms may occur concurrently.[22]

1-*Phenylallyl Chloride.*—By analogy with the structurally similar diphenylmethyl halides,[23] this isomer would be expected to undergo solvolysis by the unimolecular (S_N1) mechanism. That the rate-determining step involves ionization of the carbon–chlorine bond is supported by (*a*) the sensitivity of the rate of reaction to the ionizing power of the medium, (*b*) the relative insensitivity of the rate to the presence of lyate ions, (*c*) the ionic-strength effect and common-ion rate retardation, and (*d*) the formation of largely or completely racemic products in the reactions of an optically active isomer. The formation of cinnamyl chloride in amounts almost independent of the halide concentration but



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* The self-consistent field treatment in the Pariser–Parr approximation was used. Although the static charge densities ($q_r = 0{\cdot}627\beta$) are identical at the 1- and the 3-position, the self-atom polarizability, π_{33} ($0{\cdot}416\beta$), is larger than π_{11} ($0{\cdot}389\beta$). Since $\pi_{rr} = \partial q_r/\partial\alpha_r$, where α_r is the Coulomb integral, on the approach of a charged reagent the charge density at the 3-position would be expected to increase compared with that of the 1-position and the former position thus become the more reactive.

[20] Jackman and Hardisson, personal communication.

[21] Streitwieser, *Chem. Rev.*, 1956, **56**, 571.

[22] Dostrovsky, Hughes, and Ingold, *J.*, 1954, 634; Hughes, Ingold, and Rose, *J.*, 1953, 3839.

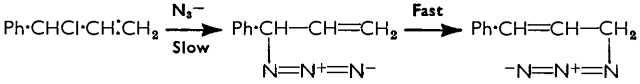
[23] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

dependent on the nucleophilicity of the medium suggests an ion-pair intermediate[4] and, in agreement, rates of loss of optical activity of the (+)-isomer are larger than spectrometric rates. The intermediate returns to 1-phenylallyl chloride with loss of configuration at a rate similar to its conversion into cinnamyl chloride, the relative rates of the two return processes being unaltered by the presence of lithium chloride. The sensitivity of the rates of isomeric rearrangement and of solvolysis, separately, to changes in ionizing power of the medium are similar, although not identical; the rate-determining step of both reactions is the same. The previous conclusion[1] that the rearrangement is less sensitive to ionizing power in alcoholic media than in aqueous dioxan is incorrect.

de la Mare and Vernon[24] have suggested that the analogous rearrangement of 1,1-dimethylallyl chloride in acetic acid or aqueous ethanol is independent of the accompanying solvolysis. On this view, species (III) should be regarded as a transition state and not as an intermediate. Streitwieser[21] has adduced arguments against this interpretation. Formulation of the reaction as a competition of chloride ion and solvent for an intermediate is favoured by the large variation in the amount of cinnamyl chloride formed when the reaction is carried out in media of similar ionizing power but very different nucleophilicity. Such large differences would not be expected if isomerization and solvolysis were independent reactions with rather similar sensitivity to solvent ionizing power.

Surprisingly large proportions of secondary solvolysis product are formed, but there is no kinetic evidence that 1-phenylallyl chloride can undergo bimolecular displacements in hydroxylic solvents. In the intermediate (III) the positive charge can be localized so that attack by solvent occurs at the 1-position, but as easily from the same side as the leaving group as from the opposite to give racemic products. Species (III) can rearrange to cinnamyl chloride and also dissociate further to the free carbonium ion which reacts with any nucleophile to give the expected products.

The reaction with ionic azide in ethanol is anomalous. The major product is cinnamyl azide but the observed rate constants exclude an S_N2' reaction. Evidently azide ion competes effectively with solvent for the intermediate (III) but the expected main product, the secondary azide, must be isomerized very rapidly:



$$\mathrm{Ph{\cdot}CHCl{\cdot}CH{:}CH_2} \xrightarrow[\text{Slow}]{N_3^-} \mathrm{Ph{\cdot}\underset{\displaystyle N{=}N^+{=}N^-}{CH}{-}CH{=}CH_2} \xrightarrow{\text{Fast}} \mathrm{Ph{\cdot}CH{=}CH{-}\underset{\displaystyle {}^-N{=}N^+{=}N}{CH_2}}$$

The rapid isomerization of allylic azides has been noted previously.[25]

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[24] de la Mare and Vernon, *J.*, 1954, 2504.

[25] Gagneux, Winstein, and Young, *J. Amer. Chem. Soc.*, 1960, **82**, 5956.