MECHANISTIC STUDIES OF SOME REACTIONS OF 1- AND 3-PHENYLALLYL CHLORIDES

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Presented By
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ABSTRACT

A brief review is given of recent work on the mechanism of the solvolysis and isomerization reactions of allylic halides. The advantages of the phenylallyl chloride system as a model for such studies are mentioned, and an account is given of some kinetic investigations of the solvolysis and rearrangement reactions of both 1- and 3-phenylallyl chlorides. In the light of the results obtained, possible mechanisms are proposed and discussed. Some work is also included on the isomerization of 1-phenylallyl chloride under non-solvolytic conditions.

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INTRODUCTION

General Properties of Allylic Halides

Allylic compounds owe their importance to the high reactivity that they display towards nucleophilic substitution and to the fact that they readily undergo rearrangement reactions. The latter involve the migration of an electronegative substituent from one end of the allylic system to the other and are frequently found to accompany nucleophilic displacements in allylic systems.

$$RR^1C{=}CR^2{-}CR^3R^4X \longrightarrow RR^1YC{-}CR^2{=}CR^3R^4$$

X and Y may be the same or different functional groups. Rearrangement reactions of this type belong to the class of reactions known as anionotropic rearrangements. They are characterized by the migration of an anion or other group together with its bonding electrons. A study of the anionotropic rearrangement occurring during a displacement reaction can yield valuable information concerning the mechanism of the latter reaction. Allylic halides display the properties of ease of nucleophilic substitution and anionotropic mobility to a high degree, and in the following sections mechanistic aspects of these reactions will be discussed with particular reference to solvolysis reactions.

Solvolytic substitutions can be broadly classified as being either unimolecular or bimolecular; in addition, there is a large group of reactions which do not fall under either heading and are sometimes termed borderline reactions. In the case of allylic compounds there is the additional possibility of rearrangement accompanying the solvolysis, and the degree and conditions under which this occurs can illuminate details of the solvolysis mechanism.

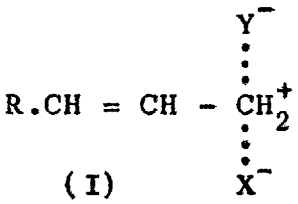
Normal Bimolecular Nucleophilic Substitution

Normal bimolecular nucleophilic substitutions involving allylic halides closely resemble the corresponding reactions of saturated alkyl halides and bear the mechanistic designation S_N2. The reactions are characterized by second order kinetics (pseudo first order where the substituting agent is in excess) and by the appearance of only normal substitution products in which the substituting group occupies the position in the molecule which had previously belonged to the displaced group.

$$R.CH{=}CH{-}CH_2X \quad + \quad Y^- \longrightarrow R.CH{=}CH{-}CH_2Y \quad + \quad X^-$$

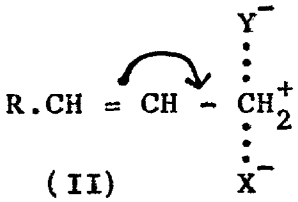
The above illustration is for the replacement of a primary halogen by a negative ion since these are the most common conditions, but an uncharged nucleophilic molecule could act in place of the ion, and the substrate could in principle be secondary or tertiary. The mechanism is generally understood to involve the formation of a new bond between the central carbon atom and the substituting group as the old bond is broken, the action occurring simultaneously at opposite corners of the carbon tetrahedron. When such displacements are carried out on an asymmetric carbon atom, it is found that inversion of configuration has accompanied each act of displacement.

In order to achieve reaction, a free energy maximum associated with the transition state (I) shown below must be overcome.



(I)

$$\mathrm{R.CH = CH - \underset{\underset{X^-}{\vdots}}{\overset{\overset{Y^-}{\vdots}}{CH_2^+}}}$$



(II)

$$\mathrm{R.CH \overset{\curvearrowright}{= CH -} \underset{\underset{X^-}{\vdots}}{\overset{\overset{Y^-}{\vdots}}{CH_2^+}}}$$

Since the transition state can be stabilized by the tautomeric release of electrons from the double bond (II), S_N2 displacements of allylic halides are more rapid than those of the corresponding alkyl compounds, e.g. 3-methylallyl chloride reacts 95 times faster than *n*-butyl chloride with ethanolic sodium ethoxide at 44.6°C. (54).

The rate of a bimolecular reaction is affected by substituents in the carbon chain. In the 1- position, substituents, whether electron releasing or withdrawing, retard the reaction by steric interference with the approach of the nucleophilic reagent. Tertiary halides are therefore rather unreactive towards direct displacement reactions, e.g. <u>tert</u>-butyl halides react about 0.07 - 0.34 times as fast as <u>iso</u>-propyl halides with halide ions in acetone (13, 41). In the case of tertiary allylic halides, displacement by the normal S_N2 mechanism is not usually observed (62), and reaction occurs by either the unimolecular or the abnormal bimolecular mechanism. Electron releasing substituents on the 3-carbon atom of the allylic system facilitate the direct displacement by assisting the departure of the leaving group as a negative ion. A number of examples involving substitution by sodium ethoxide in ethanol and by potassium iodide in acetone are quoted in a review by Young and DeWolfe (62).

The rate of direct displacement reactions is dependent on the nucleophilic ability of the attacking reagent. This is determined by its solvation energy, the strength of its bond with a carbon 2p orbital, its steric effect, and the electronegativity and polarizability of the reacting atom. Streitwieser (49) has compiled a table of relative nucleophilic abilities of a number of bases. The nucleophilicity of thiophenoxide ion is of the order of 470 times as great as that of ethoxide ion.

In agreement with expectation, it has been found that 3:3-dichloropropene undergoes S_N2 substitution with thiophenoxide ion in ethanol about 250 times as fast as with ethoxide ion (14).

Effects of changes in the medium on the rate of bimolecular displacement reactions are not large. The magnitude and direction of the change would be expected to depend on the disposition of charges in the reactants and in the transition state of the reaction. Where a neutral molecule is the substituting agent, as in a solvolysis, an increase in the solvent polarity should cause a small increase in the rate. An increase in the ionic strength should have a similar effect.

Abnormal Bimolecular Nucleophilic Substitution

In an abnormal substitution, the nucleophilic reagent attacks the 3- carbon atom of the allylic system and displaces the substituent on the 1- carbon atom in a concerted process.

$$Y^- + C{=}C{-}C{-}X \longrightarrow \overset{\delta-}{Y}\cdots\overset{\delta+}{C}\overset{\cdots}{-}C\overset{\cdots}{-}\overset{\delta+}{C}\cdots\overset{\delta-}{X} \longrightarrow$$

$$Y{-}C{-}C{=}C + X^-$$

The mechanism is designated S_N2'.

The first published evidence for the occurrence of the S_N2' mechanism concerned the reaction of 1-ethylallyl chloride with sodium malonic ester in ethanol (36). About 23% of rearranged product was obtained, the reaction having been shown to be kinetically of the second order. The S_N2' mechanism was subsequently shown to be involved in several other cases, notably in the bromide exchange reactions of 1- and 3-methylallyl bromides (23), the reaction of 1-methylallyl chloride with diethylamine (63), and the reactions of a number of allylic chlorides having 1- carbon atoms sterically hindered by additional chlorine atoms or methyl groups (14, 15, 16, 17).

The structure of the allylic system and the nature of the reagent are both important in determining whether the S_N2' mechanism will operate. Since the formation of the transition state involves the approach of a nucleophilic substituting agent to an electron-rich area, the mechanism rarely occurs in cases where normal bimolecular substitution is unhindered by additional substituents on the 1- carbon atom. The ratio $k_{S_N2}/k_{S_N2'}$ for the bromide ion exchange reaction of 1-methylallyl bromide is 59; for 3-methylallyl bromide the ratio is 28,200 (22). Uncharged nucleophilic reagents such as secondary or tertiary amines appear to cause S_N2' substitution more readily than ionic reagents, possibly because the latter are more effective in facilitating the separation of the leaving group when attacking at the 1- rather than the 3- position (62).

There have been no well established cases of the S_N2' mechanism involving simple hydroxylic solvents, e.g. water or alcohols, as substituting agents.

Unimolecular Nucleophilic Substitution

The unimolecular mechanism of nucleophilic substitution in allylic systems is a first order process closely resembling the corresponding mechanism for substitution in saturated aliphatic systems and designated S_N1. The S_N1 reaction was described by Ingold and his collaborators (26) as involving the heterolysis of the organic compound into a carbonium ion and an anion, followed by reaction of the carbonium ion with any available nucleophile to form the product. The degree to which the intermediate carbonium ion becomes free of the departing anion has long been a subject of conjecture. It was recognised by Hughes, Ingold, and their collaborators that the departing anion was in some cases sufficiently close so as to enable it to shield part of the molecule from attack by the nucleophile. This explained the observation that the unimolecular solvolysis of many optically active compounds did not result in complete racemization as would have been expected from a planar carbonium ion intermediate. Hammett (31) suggested that the first product of ionization was an ion-pair which would react with inversion of configuration. Later work, notably by Winstein, Goering, and their associates, has shown experimental evidence for the existence of ion-pairs as intermediates in unimolecular displacement reactions. We may consider the S_N1 mechanism as one in which an electron-deficient organic intermediate, either a free carbonium ion, or an ion-pair, is formed in the rate-determining step without nucleophilic assistance by the solvent or external nucleophiles.

The S_N1 mechanism of substitution occurs most readily in compounds giving rise to carbonium ions which can be stabilized by inductive or mesomeric effects. Steric hindrance to nucleophilic attack is another important point in determining whether the unimolecular or the bimolecular mechanism will operate. The S_N1 mechanism is promoted by solvents having a high ionizing power and by electrophilic catalysts such as Ag^+.

The allylic carbonium ion, being mesomeric, can react with a nucleophilic reagent at either the 1- or the 3-carbon atoms:

$$\mathrm{R.CH{=}CH{-}CH_2X} \longrightarrow \mathrm{R.\overset{\delta+}{CH}\,\underline{\cdots}\,CH\,\underline{\cdots}\,\overset{\delta+}{CH_2}} \quad + \quad \mathrm{X^-}$$

$$\begin{aligned}\mathrm{R.\overset{\delta+}{CH}\,\underline{\cdots}\,CH\,\underline{\cdots}\,\overset{\delta+}{CH_2}} \quad + \quad \mathrm{Y^-} \longrightarrow \quad & \mathrm{R.CH{=}CH{-}CH_2Y} \quad + \\ & \mathrm{R.CH(Y){-}CH{=}CH_2}\end{aligned}$$

Thus, for asymmetric allylic systems, substitution by the S_N1 mechanism may be accompanied by partial rearrangement.

Much of the recent work on the mechanism of the unimolecular substitution of allylic halides is due to Vernon. He measured the rates of solvolysis of a number of halides in moist formic acid, a solvent of high ionizing power and low nucleophilicity in which solvolyses could be assumed to occur entirely by the unimolecular mechanism. He found that electron-releasing substituents on both the 1- and the 3- carbon atoms greatly increased the rate of solvolysis, e.g. 1-methylallyl chloride reacted with the solvent more than 5600 times as rapidly as allyl chloride. The corresponding factor for the solvolysis of the primary isomer was in excess of 3500. A rather similar but slightly smaller rate increase was observed when the methyl groups were replaced by <u>tert</u>-butyl groups, the difference being probably due to the greater hyperconjugative electron release (53).

Vernon also demonstrated the pronounced dependence on solvent ionizing power of the rate of a unimolecular solvolysis. 1:1-Dimethylallyl chloride and 3:3-dimethylallyl chloride are both known to react with solvents by the unimolecular mechanism. It was shown that the rates of solvolysis of both these compounds were about 5000 times as great in 50% aqueous ethanol as in absolute ethanol, the former being the more polar solvent. Those compounds, which would not be expected to react entirely by the unimolecular route in ethanol or aqueous ethanol, exhibited a smaller rate increase when the polarity of the solvent was raised.

Mechanisms of Solvolysis of Allylic Halides

Solvolysis reactions are displacements in which the solvent is the nucleophilic reagent. Since the latter is always present in great excess, solvolysis reactions display first order kinetics whatever the number of molecules involved in the rate determining step. The mechanism of solvolytic displacements is a subject on which much work has taken place and on which many diverse opinions have been held. Two extreme mechanistic possibilities are generally recognised, the pure S_N1 and the pure S_N2 processes. Examples of the former include the solvolytic reactions of tertiary alkyl or di- and triphenylmethyl halides, systems which afford considerable resonance stabilization to a carbonium ion and are sterically unfavourable to bimolecular displacement reactions. Primary alkyl halides are among those whose solvolysis may be wholly bimolecular since the above two conditions do not apply.

Of particular interest are an intermediate set of borderline cases which cannot be fully described by either one of the two extreme mechanisms. Most solvolyses of secondary alkyl halides and many of allylic halides are to be described as belonging in this category. Hughes, Ingold, and their co-workers, while recognising that borderline cases are to be represented by some sort of intermediate mechanism (5, 26), have in a number of cases preferred to regard these as mixtures of S_N1 and S_N2 solvolyses, occurring simultaneously and in competition (20, 34). More recent work by Pocker (46) on the substitution reactions of diphenylmethyl halides by anionic reagents in nitromethane, and by Kohnstam, Queen and Shillaker (39) on the substitution of 4-methoxybenzyl chloride by azide ions in aqueous acetone, has produced results which are interpreted by the authors as being explicable only on the basis of concurrent S_N1 and S_N2 mechanisms. However, no unambiguous cases of solvolyses occurring by the dual mechanism have been reported.

Winstein, Grunwald and Jones (57) have suggested that solvolysis reactions may have a continuous spectrum of mechanisms of which the S_N1 and S_N2 mechanisms are special cases. They considered that nucleophilic interaction between the solvent and the substituted carbon atom, and electrophilic interaction between the solvent and the leaving group would, in general, both contribute to the driving force of the reaction. Those cases in which the former interaction was negligible were termed 'limiting', and correspond to the pure S_N1 mechanism of Hughes and Ingold. As there are in principle infinite gradations in the relative contributions of nucleophilic and electrophilic solvation to the driving force of the reaction, there is no sharp dividing line between the mechanisms S_N1 and S_N2.

In support of the hypothesis, Winstein and his associates presented experimental results of a study of the variation in the rates of solvolysis of some 'borderline' compounds with solvent ionizing power. For those compounds, the dual mechanism idea requires that the solvolysis be purely bimolecular in solvents of high nucleophilicity but low ionizing power, and that it should gradually change to a purely unimolecular process as the ionizing power is raised, the nucleophilicity being unchanged. According to the theory of Grunwald and Winstein (30), a plot of the logarithm of the solvolysis rate constant against their measure of the solvent ionizing power should show a distinct curvature corresponding to the transition from S_N2 to S_N1. Since very good straight lines were obtained (60), this was considered as evidence that some type of single intermediate mechanism rather than two competing mechanisms was involved.

A structural hypothesis for displacement reactions lies in the molecular orbital representation of the so-called pentacovalent carbonium ion intermediate introduced by Doering and Zeiss (19). In this structure both lobes of the central p orbital of the carbonium ion overlap with orbitals of two Lewis bases which may be solvent molecules, other nucleophiles, or the leaving group. The two bonds are weak and are considered at best as half bonds. The hypothesis implies a number of corollaries relating to the structure of the rate-determining transition state. The greater the solvation forces on the leaving group, the more these will stabilize charge separation and hence the closer the transition state will be to tetrahedral. For orbital overlap whith a nucleophile to be possible, a configuration of the transition state tending towards coplanarity is required, the tetrahedral configuration sterically hindering such interaction. The limiting case of Winstein, Grunwald and Jones corresponds to those cases where the positive charge can be well stabilized internally with the result that little orbital is available at the rear, and nucleophilic participation is both sterically hindered and energetically unimportant.

Some aspects of investigations of solvolyses of allylic halides are considered in more detail in the following sections:

(a) Solvent Effects

As has been pointed out previously, bimolecular solvolyses are less dependent on solvent ionizing power than are unimolecular solvolyses. Reference has already been made to the examination by Vernon of the effect of ionizing power variation on the rate of ethanolysis of some allylic chlorides. A more quantitative investigation was carried out by Winstein and his associates who stressed the need of a standard measure of ionizing power. Such a measure is the rate constant of solvolysis of an alkyl halide which reacts by preliminary ionization. Grunwald and Winstein (30) defined the ionizing power, Y, of a solvent as the logarithm of the rate constant for the solvolysis of tert-butyl chloride therein relative to the rate constant for its solvolysis in 80% aqueous ethanol, and measured Y values for a large number of solvent mixtures (24, 30). They found that the logarithms of the solvolysis rates of many compounds gave linear correlations in Y expressed as the equation:

$$\log k = mY + \log k_o$$

where k_o is the rate constant for the solvolysis in the standard solvent, 80% aqueous ethanol. The slope m measures the susceptibility of the substrate to the ionizing power of the solvent relative to <u>tert</u>-butyl chloride. Usually m has a value of about 0.4 for reactions which definitely belong in the unimolecular category, and a value of about 0.9 - 1.0 for reactions which are definitely unimolecular. Borderline reactions have intermediate values. On the basis of m values, Winstein and his associates (60) found that the solvolysis of allyl chloride was largely bimolecular in aqueous ethanol ($m = 0.455$). The solvolysis of 1:1- and 3:3- dimethylallyl chlorides in aqueous ethanol or aqueous acetone was clearly unimolecular ($m = 0.974 - 1.085$). The m values for crotyl chloride indicated an intermediate mechanism in aqueous ethanol but a unimolecular one in the less nucleophilic aqueous acetone (m = 0.655 and 0.904 respectively).

It had previously been observed (61) that crotyl chloride solvolyzed more rapidly in aqueous ethanol than 1-methylallyl chloride. This was explained by the postulation that there was a bimolecular component in the solvolysis of the primary chloride. Roberts, Young and Winstein (47) later showed that in the less nucleophilic solvent, acetic acid, the order of reactivity was reversed, and Vernon (53) found the same to be true in the weakly nucleophilic moist formic acid. Evidently there is a negligible bimolecular component to the solvolysis in the two latter solvents. In non-borderline cases, variation in solvent nucleophilicity does not show the same effect. 1:1-Dimethylallyl chloride is more reactive than its primary isomer both in acetic acid and in aqueous ethanol (53, 61).

(b) Effects of Added Nucleophiles

A common method of detecting the presence of a bimolecular component in a solvolysis reaction consists of the addition of anionic nucleophilic reagents different from the allylic substituent (non-common ions). These should accelerate a bimolecular reaction but have no effect on a unimolecular one other than through the accompanying ionic strength increase (35). Lyate ions, i.e. ions derived by loss of a proton from the functional group of the solvent, are often used for the purpose. It should be pointed out that a rate increase by lyate ions does not necessarily prove that the solvolysis in the absence of these ions has a degree of bimolecular character, but merely that the transition state (19) of the reaction can involve orbital overlap with nucleophiles should these be sufficiently powerful or abundant. Absence of a rate increase by lyate ions does, however, definitely indicate that the solvolysis is unimolecular.

An investigation of the effects of added lyate ions on the rates of solvolysis of a number of allylic halides was undertaken by de la Mare and Vernon (14, 54). They measured the rates of solvolysis of allyl chloride and of mono- and di-alkyl substituted homologues in absolute and 50% aqueous ethanol, alone, and in the presence of ethoxide or hydroxide ions. They found that secondary or tertiary allylic chlorides were virtually or completely unaffected by added alkali in both the solvents. All the other chlorides were affected to different extents in the pure solvent, the smallest rate increase being observed for primary chlorides with strong electron releasing substituents on the 3- carbon atom, viz. 3:3-dimethyl and cinnamyl chlorides. The rate of solvolysis of these two compounds, and that of crotyl chloride, were only slightly accelerated by alkali in the aqueous solvent, but a large rate increase was observed for non-activated primary chlorides. It was concluded that the alkali-insensitive compounds underwent unimolecular solvolysis and the alkali-sensitive ones bimolecular solvolysis.

(c) Composition of Reaction Products

Indispensable to the understanding of the mechanistic details of an allylic solvolysis reaction is a knowledge of the composition of the product mixture. If only normal substitution product is obtained, it is very likely that a bimolecular displacement mechanism is in operation. Excluding the possibility of an S_N2' displacement or the isomerization of the starting material by an intramolecular mechanism, the appearance of some rearranged product definitely means that a mesomeric carbonium ion, or ion-pair, is formed at some stage of the reaction, with or without nucleophilic assistance. However, to determine the extent of the formation of the mesomeric ion, and also the extent to which it becomes free of the departing anion, a quantitative analysis of the product mixture is necessary.

Most of the investigations of allylic solvolyses reported in the literature have been concerned with simple alkenyl halides where experimental difficulties arise. Separation of the isomeric alcohols, esters, or ethers, and their estimation under conditions which do not cause them to isomerize is a hard task allowing only rough estimates of the product composition to be made. Results of product determinations by Young and his associates have been quoted in the literature (62) for a number of simple allylic halides. A quantitative infra-red spectrophotometric technique was employed, but in the absence of any experimental details no estimate of its accuracy can be made.

The results of Young and of others do indicate that for unimolecular solvolyses, more normal than rearranged product is generally formed. The addition of electrophilic catalysts such as silver ions causes the compositions of the product mixtures of isomeric halides to be closer together. These results are consistent with the idea that part of the reaction in each case is bimolecular, and that the tendency towards formation of the mesomeric common ion intermediate is enhanced by electrophilic catalysis. However, if this is the case, it is not apparent why variations are observed in the product composition for solvolyses which show no other evidence of bimolecularity. The ethanolysis of 1:1-dimethylallyl chloride has been shown by Vernon (53, 54) and by Winstein (60) to be entirely unimolecular. On ethanolysis in the presence of silver oxide, Young reports that 20% of the resulting ether mixture is primary; in ethanol alone the figure is 30%. The postulate of a competing S_N2 mechanism to explain the product variations is thus not always tenable assuming the latter to have been accurately observed.

The value of accurate product data would be greatly increased if one knew the product compositions for the reactions of free allylic carbonium ions with the solvolysis medium. Young and DeWolfe (62) assumed these to be identical with the compositions obtained from the solvolysis of secondary or tertiary allylic halides in the presence of silver oxide. They found considerable differences in the product compositions when different solvents were used, e.g. for the butenyl ion, water, ethanol and acetic acid gave 35%, 50% and 56% primary products respectively. The corresponding figures for the 1:1-methylethylallyl ion were found to be 12%, 26% and 55%.

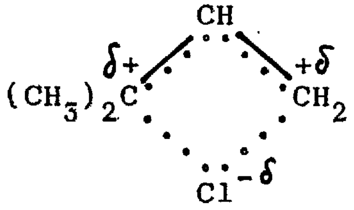
(d) Polarimetric Studies

The comparisonof the rates of racemization of optically active compounds with their rates of reaction has been an important means of collecting evidence for the presence of ion-pairs as intermediates preceding carbonium ions in solvolysis reactions (58). The chief work of this nature in the field of allylic halides is due to Goering, Nevitt and Silversmith (27). They investigated the ethanolysis and acetolysis of cis- and trans-5-methyl-2-cyclohexenyl chloride, measuring the rate constants for solvolysis and racemization, k_t and k_a. For both isomers in both solvents, k_a exceeded k_t and the rate constants were virtually unaffected by added chloride ions. Unsolvolyzed chloride recovered from the partly acetolyzed solutions of the starting material was shown not to have undergone cis-trans isomerization. The same solvolysis product mixture was obtained from either chloride in both the solvents. The latter observation indicated that the same mesomeric carbonium ion was the only intermediate in either case leading to solvolysis products. A preceding symmetrical ion-pair was postulated to explain the discrepancy between k_a and k_t, racemization resulting from the return to the covalent state as well as from solvolysis. Owing to the absence of cis-trans isomerization during racemization, the ion-pairs obtained from the two isomers were given different structures; in each case the anion remained on the original side of the ring and a degree of covalent binding between it and the two carbon atoms at the ends of the allylic system was invoked. If the bonding in the ion-pair were purely ionic, one would have expected relatively free rotation of each of the ions and, therefore, facile cis-trans isomerization.

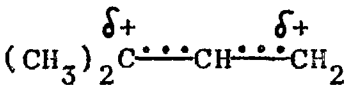
(e) Allylic Isomerization Reactions

The racemization of the cyclic allylic chlorides described above is an example of an allylic isomerization reaction, in which the original substituent migrates from one end of the three carbon system to the other. Such isomerizations have been detected to accompany the solvolysis of 1:1-dimethylallyl chloride (18, 64) and have also been studied under non-solvolytic conditions for 1-methylallyl chloride (37) and bromide (22), as well as for the phenylallyl system.

In the case of the simple alkenyl halides, the relative reactivities of the two isomers is such that the isomerization occurring during solvolysis cannot be followed directly. Its presence can be inferred, and its rate constant estimated, from the change in the instantaneous solvolysis rate constant with time, the magnitude of the latter falling from a value typical of the starting material to one typical of its isomer. Young, Winstein and Goering (64) obtained a rate constant for the isomerization of 1:1-dimethylallyl chloride in acetic acid. No increase in the isomerization rate was observed on addition of a small quantity of chloride ions, and no isomerization was detected in the liquid state or during solvolysis in pure ethanol. Isomerization was, however, detected in 75% aqueous ethanol by de la Mare and Vernon (18) who also noted that the rearranged product had partially exchanged its chlorine atom with added Cl^{36} ions. The latter workers interpreted their results on the basis of two simultaneous reactions, an intramolecular cyclization involving structure (I) as a transition state, and an S_N1 ionization reaction involving the free carbonium ion (II). The ion could react with the solvent to give a mixture of products, or with chloride ions to give the starting material or its isomer. Young, Winstein and Goering considered structure (I) to be an intermediate ion-pair rather than a transition state, and to be common to all the reactions. They ruled out free carbonium ion formation because added chloride ions did not affect the isomerization rate.



(I)



$(CH_3)_2\overset{\delta+}{C}\cdots CH\cdots\overset{\delta+}{CH_2}$

(II)

The alternative mechanisms were discussed by Streitwieser (49) who favoured the second owing to the fact that isomerization was not observed in pure ethanol. He argued that since the transition state (I) possessed considerable charge separation, increase in the solvent polarity by the substitution of ethanol for acetic acid should have increased the rate of isomerization, particularly as the rate was increased in 75% aqueous ethanol. If, however, (I) is regarded as an intermediate one could explain the non-appearance of isomerization in ethanol as having been due to the greater nucleophilicity of this solvent, the intermediate ion-pair being captured by it rather than the chloride ion. The argument involves the assumption that pure ethanol is considerably more nucleophilic than 75% aqueous ethanol.

The Phenylallyl System

The isomeric phenylallyl chlorides are two compounds that are particularly suitable for a study of the mechanism of allylic solvolysis and rearrangement reactions. The system possesses two distinct advantages over the alkyl-substituted allylic systems on which the greater part of the previous work in this field has been concentrated. The advantages derive from the fact that in one of the isomers the allylic system is in conjugation with the benzene ring and in the other it is not. The first consequence is that 1-phenylallyl chloride has a far higher reactivity than its conjugated isomer towards unimolecular substitution, the rate constant for hydrolysis being about 600 - 800 times as large. In an alkyl-substituted primary-secondary allylic system, e.g. methylallyl chloride, the secondary isomer is only 1.6 times as reactive as the primary towards unimolecular solvolysis (53). Because of the large reactivity difference, the kinetics of the solvolysis of the phenylallyl chlorides are not complicated by simultaneous isomerization followed by reaction of the isomer at a comparable rate to the starting material. When 1-phenylallyl chloride undergoes solvolysis, the reaction is accompanied by a considerable amount of isomerization, but the cinnamyl chloride so formed is stable under the reaction conditions. The isomerization reaction can therefore be followed directly, and its rate need not be estimated from the change in the instantaneous rate constant of the solvolysis.

The second advantage of the system lies in the large difference in the ultra-violet absorption intensity of the two isomers. Cinnamyl chloride and its normal solvolysis products absorb light at 2530 Å with a molecular extinction coefficient of about 18,000. At the above wavelength the molecular extinction coefficient for 1-phenylallyl compounds is about 200. Since both compounds undergo solvolysis with rearrangement, the reactions can be followed by measurement of the light absorption intensity. This enables one to employ very low concentrations of chloride and thereby avoid the need of adding bases to neutralize the acid produced on solvolysis. A large concentration of acid would catalyze the isomerization of the products (7). A still more important point is that the relative amounts of the primary and secondary solvolysis products can be calculated accurately from the final light absorption. This obviates the need for isolation and separation of the products, or even of removing the solvent.

An account of some of the previous work concerned with the phenylallyl chlorides is given below.

Cinnamyl Chloride

Cinnamyl chloride has been known for many years. Its preparation, by the treatment of cinnamyl alcohol with hydrogen chloride, was described by Klages and Klenk (38) in 1906. Of the early work on the solvolysis and displacement reactions, that of Meisenheimer and his coworkers (43, 44) is perhaps the most significant. Meisenheimer noticed a great similarity in the reactions of cinnamyl chloride, bromide and iodide. Treatment of any of these compounds with ethanolic potassium hydroxide resulted in the exclusive formation of cinnamyl ethyl ether. However, when the ethanolysis was performed in the presence of silver oxide, a considerable part - ca. 25-40% - of the product was found to be 1-phenylallyl ethyl ether. Rearrangement to a similar extent was also observed for the acetolysis when carried out in the presence of potassium or silver acetate.

In a later investigation, Vernon (53) compared the rate constants for the solvolysis of cinnamyl chloride in pure and 50% aqueous ethanol with the corresponding rate constants for allyl and 1:1-dimethylallyl chlorides. He found the ratios $k_{50\%\ C_2H_5OH} / k_{C_2H_5OH}$ for the three chlorides to be 1500, 27 and 4800 respectively. That for crotyl chloride, whose solvolysis in ethanol is known to have a bimolecular component (see above), was 154. Vernon also found (54) that the rate of ethanolysis of cinnamyl chloride was greatly increased by the addition of ethoxide ions in the pure solvent but that the rate of solvolysis in the aqueous solvent was virtually independent of added hydroxide ions. On the basis of the results of these investigators, the solvolysis of cinnamyl chloride must be included among those regarded as borderline reactions, appearing to be unimolecular in solvents of high ionizing power but to have some bimolecular character where the conditions are favourable, i.e. in solvents of low or moderate ionizing power in the presence of strong nucleophiles.

The mechanism of the solvolysis of cinnamyl chloride was re-examined by Valkanas (50) in conjunction with his work on the reactions of 1-phenylallyl chloride. He obtained rate constants for the solvolysis in ethanol and 60% aqueous dioxan and noted the effects of added salts containing anions of differing nucleophilicities. By making use of the final U.V. light absorption, he was able to estimate the amount of rearrangement that occurred during the reaction. As much of his measurements are repeated in the present work, discussion of his results and conclusions is deferred to a later chapter. It was thought necessary to repeat some of his measurements for the following reasons:

(a) There was a large discrepancy between those rate constants that he measured by titrating liberated acid and those that were obtained by spectrophotometric technique. This was explained as being due to the triethylamine that was added to the solvolysis medium to prevent it from becoming acidic.

(b) His final U.V. light absorptions were measured in the presence of triethylamine. It was considered preferable to dispense with this additive and to prevent acid catalyzed isomerization of the products by employing a much lower concentration of chloride.

(c) His use of sodium perchlorate as a means of measuring the ionic strength effect may have led to misleading results owing to the insolubility of sodium chloride in ethanol. Repetition of the measurements using the lithium salt would avoid this difficulty.

1-Phenylallyl Chloride

The preparation of this compound was first described in detail by Valkanas and Waight (52). After unsuccessful attempts by other routes (9), they investigated the direct replacement of the hydroxyl group in 1-phenylallyl alcohol. Basic conditions were required since the isomerization of the alcohol is catalyzed by acid (7). It was further found necessary to use a base whose hydrochloride was soluble in the reaction medium, so as to maintain a high chloride ion concentration. This would have the effect of diverting the reaction of the intermediate chlorosulphinate towards an S_N2 displacement yielding the required product, and away from an intramolecular S_Ni' process which would yield cinnamyl chloride. Tri-n-butylamine in ether and triethylamine in chloroform were both found to be suitable, the latter being the more convenient on account of the ease with which the hydrochloride could be subsequently washed out of the chloroform solution with water. The product obtained by Valkanas and Waight consisted of a mixture of the isomeric chlorides which, after three distillations, contained about 85% 1-phenylallyl chloride. They considered this mixture to be azeotropic since further purification by distillation could not be achieved.

In a preliminary note (8) the authors referred to two earlier reports claiming the successful preparation of 1-phenylallyl chloride. The first, by Martin and Trinh (42), involved the treatment of either 1-phenylallyl or cinnamyl alcohol with dry hydrogen chloride, followed by repeated fractionation of the product. A yield of 2% of the secondary chloride was claimed. Its refractive index was much lower than that reported by Valkanas and Waight, and these workers were unable to repeat the preparation. Young and his associates (11) reported a quantitative yield of 1-phenylallyl chloride from the reaction of cinnamyl alcohol with thionyl chloride in dilute ethereal solution. No experimental details were given and the physical constants of the product were not recorded. On repetition of the experiment, Valkanas and Waight obtained a mixture of chlorides containing at least 45% cinnamyl chloride before distillation.

Valkanas and Waight studied the isomerization of the chloride in solvents of high and low ionizing power. The variation of rate with ionizing power in highly polar media such as aqueous dioxan suggested that isomerization involved ionization of the C-Cl bond in the rate determining step. In alcoholic solvents, they found that the dependence of the rate of isomerization on solvent ionizing power was much lower than for the aqueous dioxan media, indicating the possibility of an S_Ni' mechanism with little charge separation in the transition state. However, the above conclusion depended on the validity of using Z values (see below) as a measure of ionizing power and obtaining m values through the use of published Z - Y correlations. This procedure can lead to misleading results, as will be shown in the present work.

In a preliminary note on their investigations into the solvolysis reaction (51), they stated that 1-phenylallyl solvolysis products were invariably found to predominate in a ratio of at least 6:1. This was taken to indicate that the chloride and carbonium ions were not separated by solvent molecules and that the formation of an intimate ion-pair was rate determining. Full details of the work were given in a thesis by Valkanas (50). Owing to the interesting and unusual nature of the above result it was considered desirable to re-investigate the solvolysis mechanism as it was apparent that improvements could be made on the technique of Valkanas. The improvements can be described under three headings.

(a) Purity of material

The chloride used by Valkanas contained cinnamyl chloride varying in proportion with different batches from 10-20%. The reproducibility of rate constants obtained with different batches of chloride was not always good. It was considered that an attempt should be made to prepare purer material to eliminate this difficulty.

(b) Accuracy of rate constants

Valkanas measured rate constants by two methods, titration of liberated acid and measurement of U.V. light absorption of aliquots withdrawn from the reaction mixture at various times. He considered that the rate constants found by the first method were too high owing to reaction of the chloride with water during the titration; the rate constants obtained by the second method were too low owing to some rearrangement of the unconjugated solvolysis products, the result of acid catalysis (7). In the present work, rate constants were measured accurately by the spectrophotometric method. Acid catalyzed rearrangement was avoided by employing a far lower concentration of chloride than had been used by Valkanas.

(c) Accuracy in the determination of the product composition

In view of the published result of Valkanas and Waight (see above) it was particularly necessary to ensure that the product composition had been accurately estimated. The final light absorptions measured by Valkanas were too high owing to acid catalyzed rearrangement of the products. In addition, an incorrect method of calculation of the composition from the final light absorption was used. No account was taken of the small but significant absorption of the unconjugated products, and no account was taken of the difference in absorption intensity between cinnamyl chloride, alcohol and ethyl ether. The error thus caused was considerable as will be demonstrated in a later chapter. In the present work, pure samples of cinnamyl chloride, cinnamyl alcohol and cinnamyl ethyl ether were prepared so that their absorption intensities at the required wavelength would be known accurately, and account was taken of the absorption of the unconjugated products.

The results and conclusions of Valkanas will be discussed in later chapters alongside those of the present work.

RESULTS

Hydrolysis in Aqueous Dioxan

The reactions of the two phenylallyl chlorides with water follow the scheme shown below:

$$\begin{tikzcd}
\mathrm{Ph.CH(Cl).CH = CH_2} \arrow[rr, "k_r"] \arrow[dr, "k_s"'] & & \mathrm{Ph.CH = CH.CH_2Cl} \arrow[dl, "k'_s"] \\
& \begin{array}{c} \mathrm{Ph.CH(OH).CH = CH_2} \\ + \\ \mathrm{Ph.CH = CH.CH_2OH} \end{array} &
\end{tikzcd}$$

A mixture of 1- and 3-phenylallyl alcohols is obtained from both isomers. 1-Phenylallyl chloride also gives rise to some cinnamyl chloride. The first order rate constants for the isomeric rearrangement and hydrolysis of 1-phenylallyl chloride, k_r and k_s, are both approximately 600-800 times as large as k'_s, the first order rate constant for the hydrolysis of cinnamyl chloride. Rate constants have been obtained for the formation of the various products in a series of aqueous dioxan mixtures, and the effects of added nucleophiles determined.

The Effect of Solvent Ionizing Power

Tables (I) and (II) show the mean results of measurements of the rate of hydrolysis and isomeric rearrangement of the two chlorides in aqueous dioxan. In the case of 1-phenylallyl chloride, the overall rate constants for the reactions in 80 and 85% aqueous dioxan can be compared with those obtained by Valkanas. The agreement is quite good, the results in the present work verifying his statement that his spectrometric rates were too low and his titrimetric rates too high (Table IIa).

For both isomers, the rates of reaction are very sensitive to the amount of water present in the medium and correlate quite well with the ionizing power of the medium as measured by the Y values of Fainberg and Winstein (24). In figs. (I) and (II), $\log_{10}(k_{total})$ is plotted against Y; the slopes of both lines are close to unity, typical of reactions in which the rate determining step is thought to be a unimolecular ionization.

The proportion of the total reaction of 1-phenylallyl chloride resulting in isomeric rearrangement increases as the concentration of water in the medium is decreased, but little trend is observable in the relative amounts of the two alcohols produced. The secondary alcohol accounts for about 70% of the total solvolysis product in each case. This figure is far lower than that reported by Valkanas for hydrolysis in 80 and 85% aqueous dioxan.

In the case of cinnamyl chloride, the alcohol product ratio does vary significantly, although only slightly, with the medium composition, approaching in the most highly ionizing medium the value expected for the attack of water molecules on a mesomeric phenylallyl carbonium ion (10, 45). The value of 51.7% 1-phenylallyl alcohol can be compared with a value of 67% reported by Valkanas for the reaction in the same solvent, 60% aqueous dioxan. He did not investigate how the rate of hydrolysis of cinnamyl chloride was affected by variations in solvent ionizing power.

TABLE I

Solvolysis of Cinnamyl Chloride in Aqueous Dioxan. The Effect of Solvent Ionizing Power. Chloride Concn., ca. 3.3×10^{-5}M. Temp., 30.0°C.

Dioxan (% v/v)	k'_s (min.^{-1})	Product Composition (% ROH)
60	0.00572	51.7
50	0.0316	54.2
40	0.165	56.4
30	0.703	58.5

/¯R = 1-phenylallyl_7

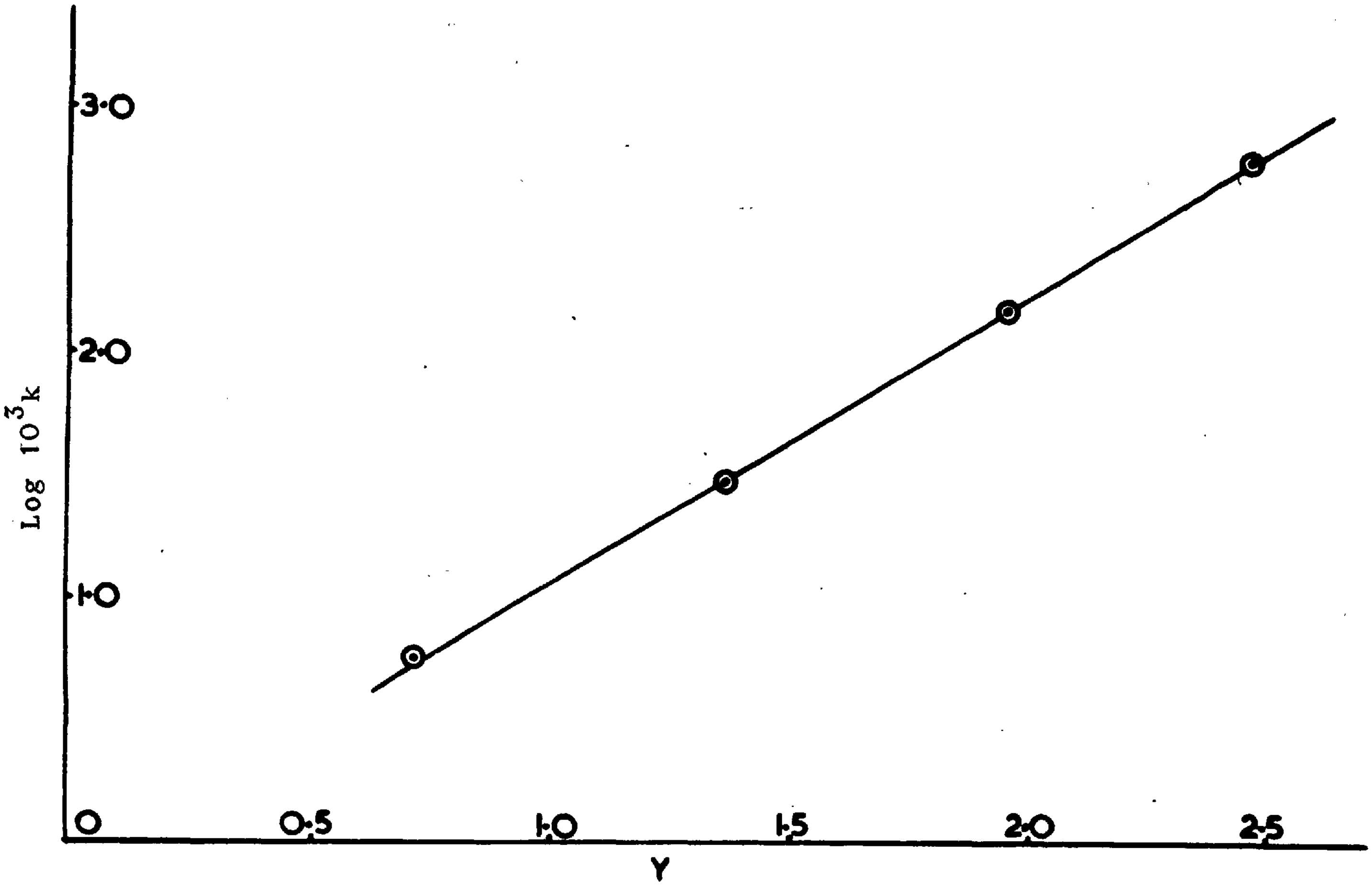


Fig. 1. Rates of hydrolysis of cinnamyl chloride in aqueous dioxan as a function of Y.

TABLE II

Solvolysis and Isomerization of 1-Phenylallyl Chloride in Aqueous Dioxan. The Effect of Solvent Ionizing Power. Chloride Concn., ca. 5 x 10^{-5}M. Temp., 30.0°C.

Dioxan (% v/v)	Solvolysis (%)	k_t ($min.^{-1}$)	k_r ($min.^{-1}$)	k_s ($min.^{-1}$)	ROH (%)
70	45.0	1.023	0.563	0.460	70.4
75	43.3	0.412	0.233	0.179	71.0
80	43.4	0.169	0.0957	0.0733	70.0
85	41.5	0.0510	0.0298	0.0212	70.6
90	36.1	0.00971	0.00621	0.00350	66.6

k_t, k_r, k_s, are rate constants for the total reaction, for isomeric rearrangement and for solvolysis respectively.

% ROH is the percentage of the solvolysis product consisting of 1-phenylallyl alcohol.

TABLE IIa (*)

Solvolysis and Isomerization of 1-Phenylallyl Chloride in Aqueous Dioxan at 30.0°C.

Dioxan (% v/v)	Solvolysis (%)	k_t (min.$^{-1}$)	k_r (min.$^{-1}$)	k_s (min.$^{-1}$)	
80	44.6	0.181	0.101	0.080	(a)
85	35.4	0.0494	0.0319	0.0175	(b)
85	39.2	0.0635	0.0393	0.0242	(a)

(a) Titration technique

(b) Spectrophotometric technique

(*) Results due to Valkanas

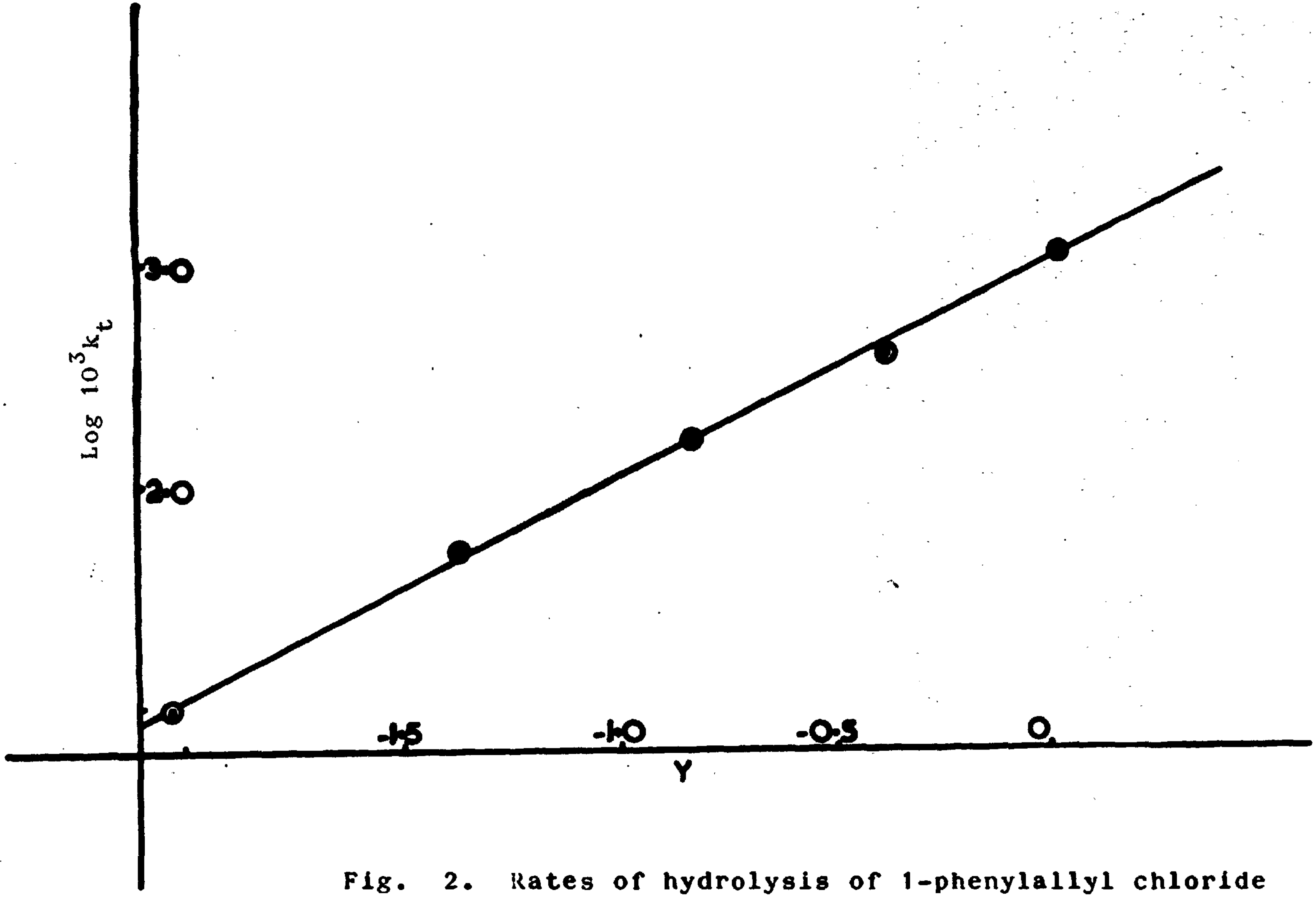


Fig. 2. Rates of hydrolysis of 1-phenylallyl chloride in aqueous dioxan as a function of Y.

The Effect of Added Base

The variation in the observed hydrolysis product ratio in the case of cinnamyl chloride suggested the possibility of a competing bimolecular displacement reaction (S_N2) between the cinnamyl chloride and water yielding cinnamyl alcohol only and increasing in importance with diminishing solvent ionizing power. In order to investigate further the possibility of bimolecular nucleophilic displacement in the hydrolysis of cinnamyl chloride, the effect of base on the rate of reaction and product ratio was studied. This was in accordance with the criterion of Catchpole and Hughes (12) who pointed out that an S_N2 mechanism can only be excluded when it can be shown that the compound substituted is insensitive to substituting agents which are more strongly basic than the solvent molecule.

Vernon had previously shown (54) that in 50% aqueous ethanol, the addition of sodium hydroxide in 0.015M concentration increased the rate of hydrolysis of cinnamyl chloride by about 10%, an amount that he considered negligible. Table (III) shows the results obtained by carrying out the solvolysis in 50% aqueous dioxan in the presence of varying concentrations of sodium hydroxide. It can be seen that sodium hydroxide decreases the rate of hydrolysis just as it does for tert-butyl nitrate, benzhydryl bromide and other substances (4) thought to undergo solvolysis by the S_N1 mechanism. However, it will be observed from Table (III) that the product ratio is dependent on the concentration of sodium hydroxide. The variation is consistent with the idea that some cinnamyl alcohol is formed as a result of a bimolecular reaction involving hydroxide ions and occurring after the rate-determining step. The effect of added base on the hydrolysis of cinnamyl chloride was not examined by Valkanas.

TABLE III

Solvolysis of Cinnamyl Chloride in 50% Aqueous Dioxan. The Effect of Sodium Hydroxide. Chloride Concn., 3.52 x 10^{-5}M. Temp., 30.0°C.

NaOH (m/l)	k'_s (min.$^{-1}$)	Product Composition (% ROH)
0.000	0.0316	54.2
0.117	0.0302	50.3
0.234	0.0239	46.8
0.467	0.0144	42.2

Salt Effects

The hydrolysis of both chlorides was carried out in the presence of lithium salts chosen because of their high solubility in organic solvents. Because of the low nucleophilicity of perchlorate ions and the known instability of alkyl perchlorates, it was convenient to use lithium perchlorate in order to ascertain the effect of increase in the ionic strength of the medium. Table (IV) shows the expected rate increase for the hydrolysis of cinnamyl chloride, due to the effective increase in the ionizing power of the medium. The increase is of the order of magnitude predicted by the theoretical treatment of Bateman, Church, Hughes, Ingold and Taher (3) for a pure ionic strength effect. The corresponding rate enhancement for the secondary chloride is shown in Table (V). Valkanas did not examine the effect of ionic strength variation for either chloride in aqueous media.

Although bromide ions are considerably more nucleophilic than perchlorate ions, the increase in the rate of hydrolysis of cinnamyl chloride caused by lithium bromide in 0.1M concentration was found to be identical with the increase caused by lithium perchlorate at the same concentration. Addition of lithium chloride allows the well-known mass-law retardation to be observed acting in the opposite manner to the ionic strength effect. In the case of cinnamyl chloride, a net decrease in the rate of solvolysis occurs compared to the rate in the absence of salt. This result is in complete desagreement with the effect of chloride ions reported by Valkanas. He found that chloride and bromide ions both increased the rate of hydrolysis of cinnamyl chloride to a similar extent. The rate was found to be doubled by a salt concentration of about 0.22M.

The overall rate of reaction of 1-phenylallyl chloride is almost unaffected by added chloride ions in 70 - 90% aqueous dioxan mixtures, but the proportion of isomeric rearrangement is quite considerably increased, particularly in the medium containing the least water. Thus, compared with the effect of perchlorate ions at a similar concentration, chloride ions cause a considerable decrease in the rate of hydrolysis. The results are shown in Tables (IV) and (V).

The ratio of the hydrolysis products obtained from cinnamyl chloride is virtually unaffected by all the salts tried at 0.1M concentration. Very high concentrations of lithium chloride, however, appear to result in the formation of a higher proportion of the primary alcohol. This finding disagrees with the result reported by Valkanas. He found that lithium chloride and lithium bromide in 0.3M concentration increased the percentage of secondary solvolysis product from 67.0 to 74.1 and 77.3 respectively.

The effect of salts on the hydrolysis product ratio is also slight for the case of 1-phenylallyl chloride. Perchlorate ions very slightly decreased the amount of secondary alcohol while chloride ions appeared to cause a slight increase.

TABLE IV

Solvolysis of Cinnamyl Chloride in Aqueous Dioxan in the Presence of Lithium Salts. Chloride Concn., ca. 3.3 x 10^{-5}M. Temp., 30.0°C.

Dioxan (% v/v)	Kind of Salt	Salt Concn. (m/l)	k'_s (min.$^{-1}$)	ROH (%)
60	LiCl	0.1	0.00520	51.1
60	LiCl	0.5	0.00408	42.6
60	$LiClO_4$	0.5	0.0106	48.4
50	LiCl	0.1	0.0273	53.7
50	LiCl	0.5	0.0200	47.6
50	$LiClO_4$	0.1	0.0303	51.9
50	$LiClO_4$	0.5	0.0532	50.5
50	LiBr	0.1	0.0398	53.5
40	LiCl	0.1	0.152	56.6
40	LiCl	0.5	0.110	51.1
40	$LiClO_4$	0.5	0.233	54.9
30	LiCl	0.1	0.643	57.4
30	LiCl	0.5	0.508	56.4

TABLE V

Solvolysis and Isomerization of 1-Phenylallyl Chloride in Aqueous Dioxan in the Presence of Lithium Salts. Chloride Concn., ca. 5 x 10^{-5}M. Temp., 30.0°C.

Dioxan (% v/v)	Kind of Salt	Salt Concn. (m/l)	Solvolysis (%)	k_t (min.$^{-1}$)	ROH (%)
80	LiCl	0.045	39.6	0.163	70.0
80	LiCl	0.090	36.4	0.169	71.7
80	LiCl	0.180	30.8	0.172	78.1
80	$LiClO_4$	0.056	47.4	0.197	67.8
80	$LiClO_4$	0.113	47.0	0.236	69.3
80	$LiClO_4$	0.226	47.5	0.281	66.4
70	LiCl	0.180	36.4	1.039	71.1
90	LiCl	0.029	32.9	0.0132	68.3

The Racemization of (+)-1-Phenylallyl Chloride in Aqueous Dioxan

Information concerning the relative ease of racemization and solvolysis of optically active halides is of value in determining the nature of the intermediates concerned in the formation of the products of solvolysis (49, 56, 58, 59, 62). Since the chlorine atom in 1-phenylallyl chloride is attached to an asymmetric carbon atom, it was possible to prepare the compound in the optically active form and to measure its rate of racemization in 90% aqueous dioxan.

Table (VI) gives the rate constants for the racemization, in the solvent alone, and in the presence of small amounts of lithium chloride. In the absence of salt, the polarimetric rate constant, k_{pol}, exceeds the total rate constant ($k_t = k_s + k_r$) for solvolysis (k_s) and isomeric rearrangement (k_r) by about 45%. As would be expected, the effect of added chloride ions is to increase still further the disparity between k_{pol} and k_t, since recombination of an intermediate carbonium ion with a chloride ion, even in the 1- position, may result in loss of configuration.

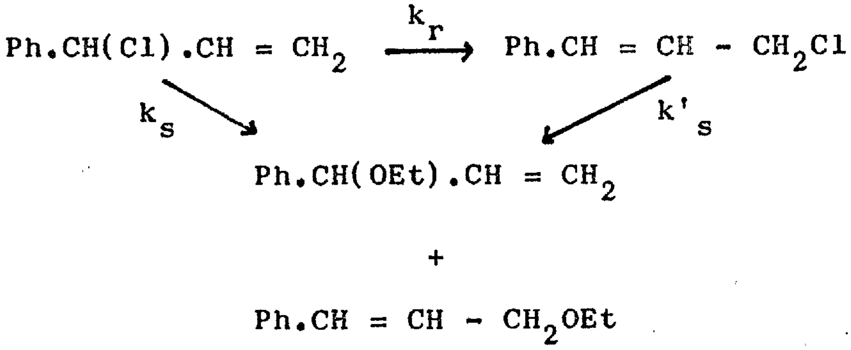
TABLE VI

Racemization of 1-Phenylallyl Chloride in 90% Aqueous Dioxan, and the Effect of Lithium Chloride. Chloride Concn., ca. 0.15M. Temp., 30.0°C.

LiCl (m/l)	k_{pol} (min.$^{-1}$)	k_t (for comparison) (min.$^{-1}$)
0.000	0.0139	0.00971
0.014	0.0175	
0.029	0.0193	0.0132

Solvolysis in Ethanol and Other Solvents

In ethanol, both 1- and 3-phenylallyl chlorides undergo solvolysis, each yielding a mixture of 1- and 3-phenylallyl ethyl ethers. As in the case of aqueous dioxan media, some cinnamyl chloride is also obtained from 1-phenylallyl chloride by isomeric rearrangement. The reaction scheme is shown below:



$$\begin{tikzcd}
\mathrm{Ph.CH(Cl).CH = CH_2} \arrow[rr, "k_r"] \arrow[dr, "k_s"'] & & \mathrm{Ph.CH = CH - CH_2Cl} \arrow[dl, "k'_s"] \\
& \mathrm{Ph.CH(OEt).CH = CH_2} & \\
& + & \\
& \mathrm{Ph.CH = CH - CH_2OEt} &
\end{tikzcd}$$

The solvolysis of both compounds was studied in a series of ethanol/cyclohexane mixtures ranging in composition from 60 - 96% ethanol v/v, the effects of added bases and salts being also determined. Rate constants were further obtained for the racemization of the secondary chloride in ethanol/cyclohexane.

The Effect of Solvent Composition

It has been observed by Kosower (40) that the energy of the charge-transfer band of 1-ethyl-4-methoxycarbonyl pyridinium iodide is very sensitive to the polarity of the solvent in which the salt was dissolved. The energy in kilocalories per mole was termed the Z value. Kosower proposed the use of Z values as empirical measures of solvent ionizing power. In Tables (VII) and (VIII) are recorded the Z values measured for ethanol/cyclohexane mixtures ranging from 98% - 60% ethanol v/v. As can be seen from the tables, the variation in Z with ethanol concentration is very small. It was thus considered that dilution of ethanol with up to 40% of its own volume of cyclohexane had little effect on the ionizing power. Any rate variation observed on varying the solvent composition would thus be largely due to a bimolecular component, the magnitude of which would be proportional to the mole-fraction of the ethanol. Rates of reaction were therefore obtained for the two chlorides in ethanol/cyclohexane mixtures, the results being shown in Tables (VII) and (VIII). It can be seen that variation in the solvent composition has a somewhat greater effect on the rate for cinnamyl than for 1-phenylallyl chloride. In both cases, log k_t varies linearly with the mole-fraction of the ethanol in the medium. However, even for the secondary chloride k_t changed by a factor of 3.65 on increasing the mole-fraction of the ethanol by a factor of 1.34. This increase is far too large to be caused by a bimolecular component. Indeed, for the secondary chloride one would expect rate increases to be determined solely by ionizing power increases (see below). Hence, it must be concluded that Z values are not satisfactory measures of solvent ionizing power in this system.

No Y values are available in the literature for mixtures of ethanol and cyclohexane. An attempt to convert the observed Z values to Y values by employing correlations based on aqueous solvents resulted in m values running into double figures.

The addition of cyclohexane appears to have a negligible effect on the ratio of 1- to 3-phenylallyl solvolysis products obtained from either isomer. In both cases, more normal ethanolysis product is obtained than would be expected from a mesomeric phenylallyl carbonium ion intermediate, the discrepancy being particularly marked in the case of the secondary chloride, where 1-phenylallyl ethyl ether constitutes about 80% of the total ethanolysis product.

The proportion of solvolysis to isomeric rearrangement for the secondary chloride is considerably higher in ethanol/cyclohexane than it is in aqueous dioxan, and it decreases as the concentration of ethanol in the mixed solvents decreases. 96% Ethanol/cyclohexane has approximately the same ionizing power as 90% aqueous dioxan, compared on the basis of Y values, but the amount of solvolysis in the former solvent is about double that in the latter. In pure methanol, the proportion of methanolysis to isomeric rearrangement is almost identical with the value in 96% ethanol/cyclohexane. Extrapolation of the aqueous dioxan results to pure water, by utilising the straight line plot of log (k_s) against Y, gives a value of about 63% hydrolysis, rather similar to the figure for alcoholysis.

In Table (VIII) are also shown rate constants for the reaction of 1-phenylallyl chloride in 22% formic acid/dioxan. This solvent has the same Y value as ethanol but has a far lower nucleophilicity. It can be seen that the principal effect of this reduction in nucleophilicity is to decrease greatly the proportion of solvolysis relative to isomeric rearrangement. The reduction in the overall rate of reaction to about half of that in ethanol is not considered to be connected with the lower nucleophilicity of the solvent. Close identity of rates cannot be expected owing to the error involved in comparing the ionizing powers of two quite different solvent systems by means of their Y values.

TABLE VII

Solvolysis of Cinnamyl Chloride in Ethanol/Cyclohexane. Chloride Concn., ca. 3.3 x 10^{-5}M.

Temp. (°C.)	Ethanol (% v/v)	Z	k'_s ($min.^{-1}$)	Product Composition (% ROEt)
50	98	79.1	0.00104	51.5
60	98	79.1	0.00285	51.6
70	98	79.1	0.00892	51.2
70	90	78.9	0.00681	52.8
70	80	78.7	0.00420	50.8
70	70	78.5	0.00276	50.0
70	60	78.3	0.00182	48.2

[R = 1-phenylallyl]

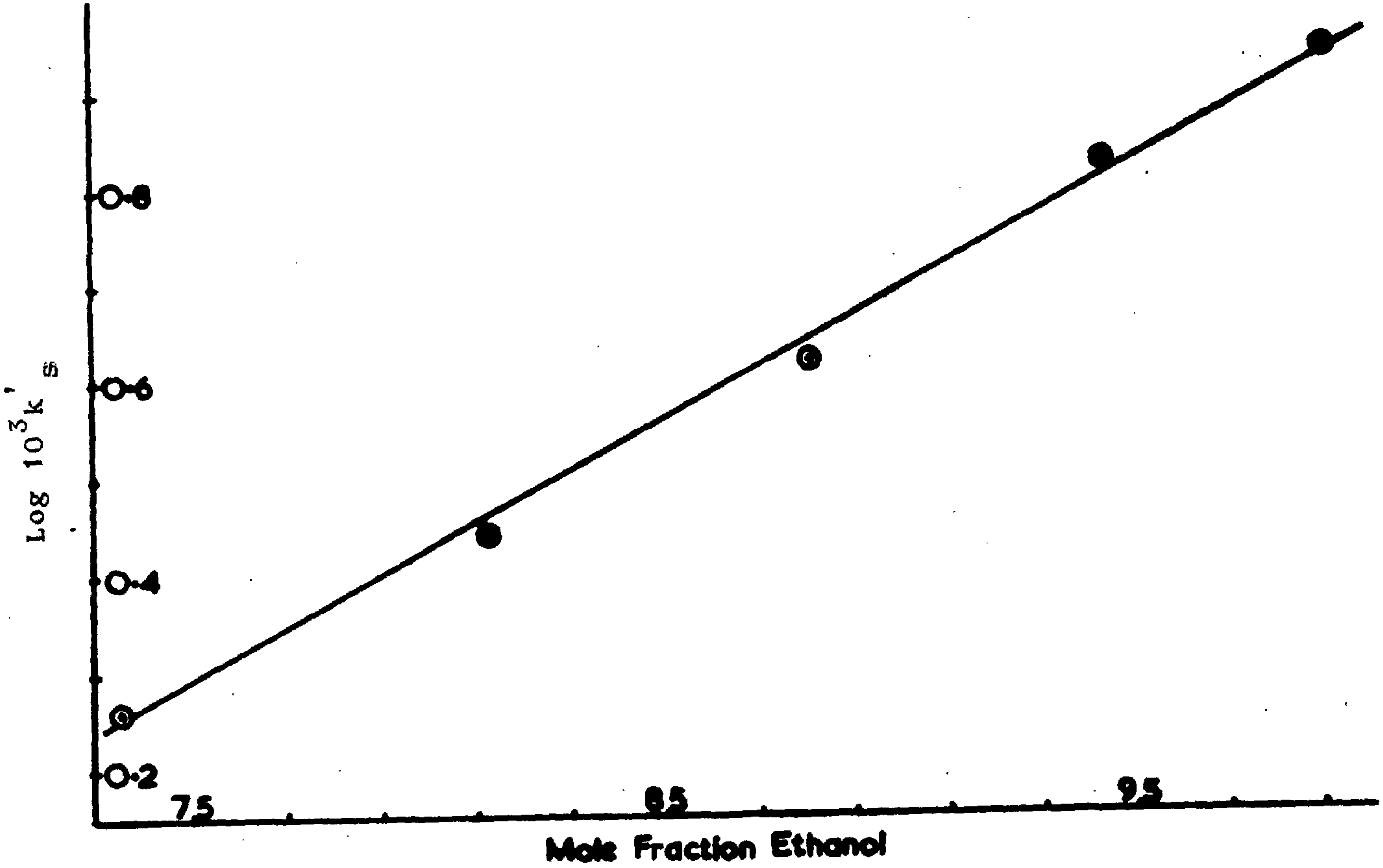


Fig. 3. Rates of solvolysis of cinnamyl chloride in ethanol/cyclohexane as a function of the mole fraction of the ethanol.

TABLE VIII

Solvolysis, Isomerization and Racemization of 1-Phenylallyl Chloride in Ethanol/Cyclohexane. Chloride Concn., ca. 5 x 10^{-5}M at 30.0°C., ca. 0.15M at 22.0°C.

Temp. (°C.)	Ethanol (% v/v)	Solvolysis (%)	k_{pol} (min.$^{-1}$)	k_t (min.$^{-1}$)	ROEt (%)
22	96		0.0274	0.0223	
22	90		0.0208	0.0184	
22	80		0.0116	0.0115	
22	70		0.00928	0.00850	
22	60		0.00624	0.00532	
30	96	69.8	0.0662	0.0566	78.3
30	90	69.2		0.0464	79.3
30	80	67.5		0.0332	82.0
30	70	67.1		0.0232	78.5
30	60	64.3		0.0155	81.4
30	22% HCOOH/ dioxan	10.6		0.0253	100
30	methanol	72.0			

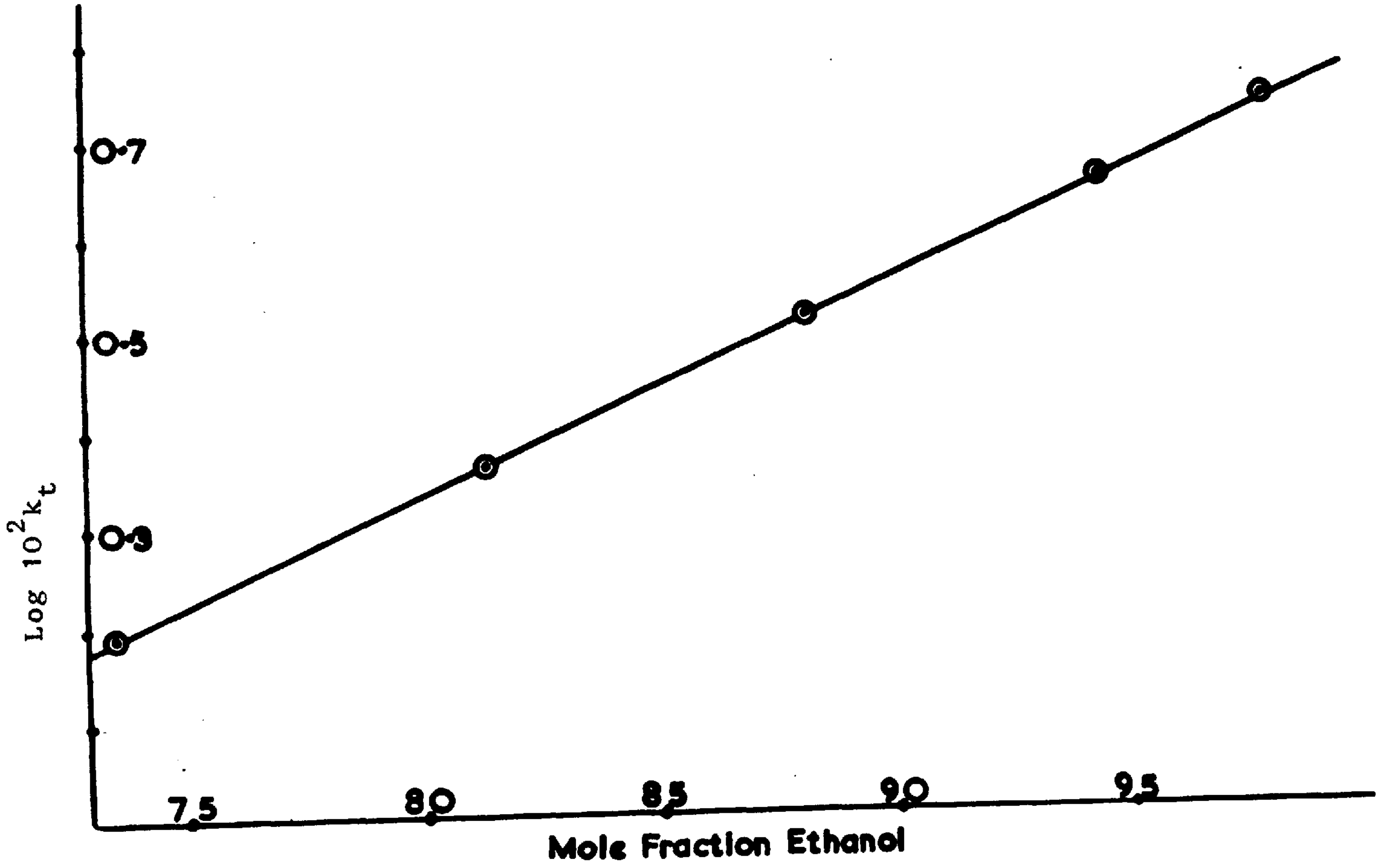


Fig. 4. Rates of solvolysis of 1-phenylallyl chloride in ethanol/cyclohexane as a function of the mole fraction of the ethanol. Temp., 30.0 C.

The Effect of Added Nucleophiles

It has been shown by Vernon (54) that ethoxide ions greatly increase the rate of ethanolysis of cinnamyl chloride when the reaction is performed using pure ethanol as the solvent. He concluded that the ethanolysis shows a tendency towards bimolecularity in that solvent. In Table (X), the rate constant for the ethanolysis of 1-phenylallyl chloride in the presence of a high concentration of sodium ethoxide is recorded. The small decrease in the overall rate is reminiscent of the cases mentioned above (page 52) where the solvolysis is thought to be unimolecular and its rate is retarded by added base. Since cinnamyl chloride reacts rapidly with ethoxide ions, it was not possible to ascertain the degrees of solvolysis and isomerization of the 1-phenylallyl chloride in the above run unless the assumption was made that the solvolysis product ratio was unaffected by the ethoxide ions save for the extra cinnamyl ethyl ether caused by bimolecular attack on the cinnamyl chloride. This assumption was made by Valkanas (50) who concluded from the final light absorption intensity that ethoxide ions slightly raised the percentage of solvolysis when used in large concentration. Valkanas, however, found that ethoxide ions in concentrations above about 0.15M substantially increased the overall rate of solvolysis, a result in complete disagreement with that obtained in the present work.

Table (X) also gives the rate constants observed for the ethanolysis of 1-phenylallyl chloride in the presence of other ions. It is noteworthy that at low and moderate concentrations, azide ions and perchlorate ions accelerate the overall reaction by virtually the same amount despite the great difference in nucleophilicity between the two species. A very similar result was observed by Valkanas using sodium perchlorate and lithium azide. Evidently the rate enhancement can be attributed solely to the increase in the ionic strength of the medium.

Perchlorate ions have little effect on the secondary-primary ratio for the products of solvolysis, but definitely cause a decrease in the amount of solvolysis with a corresponding increase in the amount of rearrangement.

Azide ions reduce the amount of ether formation even more markedly. The latter result is in agreement with the findings of Valkanas who, however, reported that sodium perchlorate increased the relative amount of ethanolysis, contrary to the observation of the present work.

Valkanas found that in ethanol, cinnamyl chloride is rapidly converted to the stable cinnamyl azide, with complete exclusion of solvolysis. Hence, it may be assumed that the only products of ethanolysis of the secondary chloride in the presence of azide ions are the two isomeric ethyl ethers and the two isomeric azides. If it is further assumed that the ratio of the two ethers is the same as that in the presence of a similar concentration of perchlorate ions, it can be calculated that the major constituent of the residue (90-100%) is cinnamyl azide.

Lithium chloride, in concentrations up to about 0.1M, increases both the rates of isomeric rearrangement (k_r) and ethanolysis (k_s); above 0.1M, k_r continues to increase slightly but k_s is not further affected. The result is, therefore, an increase in the proportion of isomeric rearrangement relative to total reaction. The increase in k_r/k_t is, however, considerably less than was observed when the solvolysis was carried out in aqueous dioxan. Catalysis by lithium chloride in the ethanolysis of 1-phenylallyl chloride has been investigated by Valkanas. His results are broadly in agreement with those of the present work with the exception that he reported linear increases in k_t, k_r, and k_s throughout the range of salt concentration 0 - 0.97M.

The rate of ethanolysis of cinnamyl chloride is increased both by perchlorate and by chloride ions, the rate enhancement being far more pronounced in the presence of the former species. The salts also increased the secondary/primary product ratio; again the effect was greater in the presence of perchlorate ions. The rate constants obtained for the chloride ion catalysis are in general agreement with those reported by Valkanas. His experiments on catalysis by sodium perchlorate were stated to yield rate constants exceeding those in the present work by a factor of ten, but on investigation it was found that an arithmetical error had been made and that there was in fact close agreement between his results and those obtained in the present work using lithium perchlorate.

TABLE IX

Solvolysis of Cinnamyl Chloride in Ethanol Containing 2% Dioxan or Cyclohexane. The Effect of Lithium Salts. Chloride Concn., ca. 3.3 x 10^{-5}M. Temp., 50.0°C.

Kind of Salt	Salt Concn. (m/l)	k'_s ($min.^{-1}$)	ROEt (%)
LiCl	0.000	0.00104	51.5
LiCl	0.254	0.00144	52.5
LiCl	0.507	0.00168	53.9
LiCl	0.760	0.00196	54.5
$LiClO_4$	0.240	0.00236	57.3
$LiClO_4$	0.480	0.00371	58.8
$LiClO_4$	0.960	0.00731	

TABLE X

Solvolysis of 1-Phenylallyl Chloride in 96% Ethanol/Cyclohexane. The Effect of Added Non-Common-Ion Salts. Chloride Concn., ca. 4 x 10^{-3}M. in the Presence of Azide Ions; Otherwise, ca. 4 x 10^{-5}M. Temp., 30.0°C.

Kind of Salt	Salt Concn. (m/l)	Solvolysis (%)	k_t ($min.^{-1}$)	ROEt (%)
		69.8	0.0566	78.3
NaOEt	0.522		0.0489	
$LiClO_4$	0.071	68.8	0.0730	76.7
$LiClO_4$	0.142	67.6	0.868	75.3
$LiClO_4$	0.282	65.1	0.134	78.3
$LiClO_4$	0.565	63.5	0.244	76.5
$LiClO_4$	1.130	57.8	0.610	79.6
NEt_4N_3	0.100	64.6	0.0923	
NEt_4N_3	0.200	35.5	0.118	
NEt_4N_3	0.400	22.2	0.158	
NEt_4N_3	0.600	16.9	0.165	

N.B. The runs containing azide ions were carried out in pure ethanol.

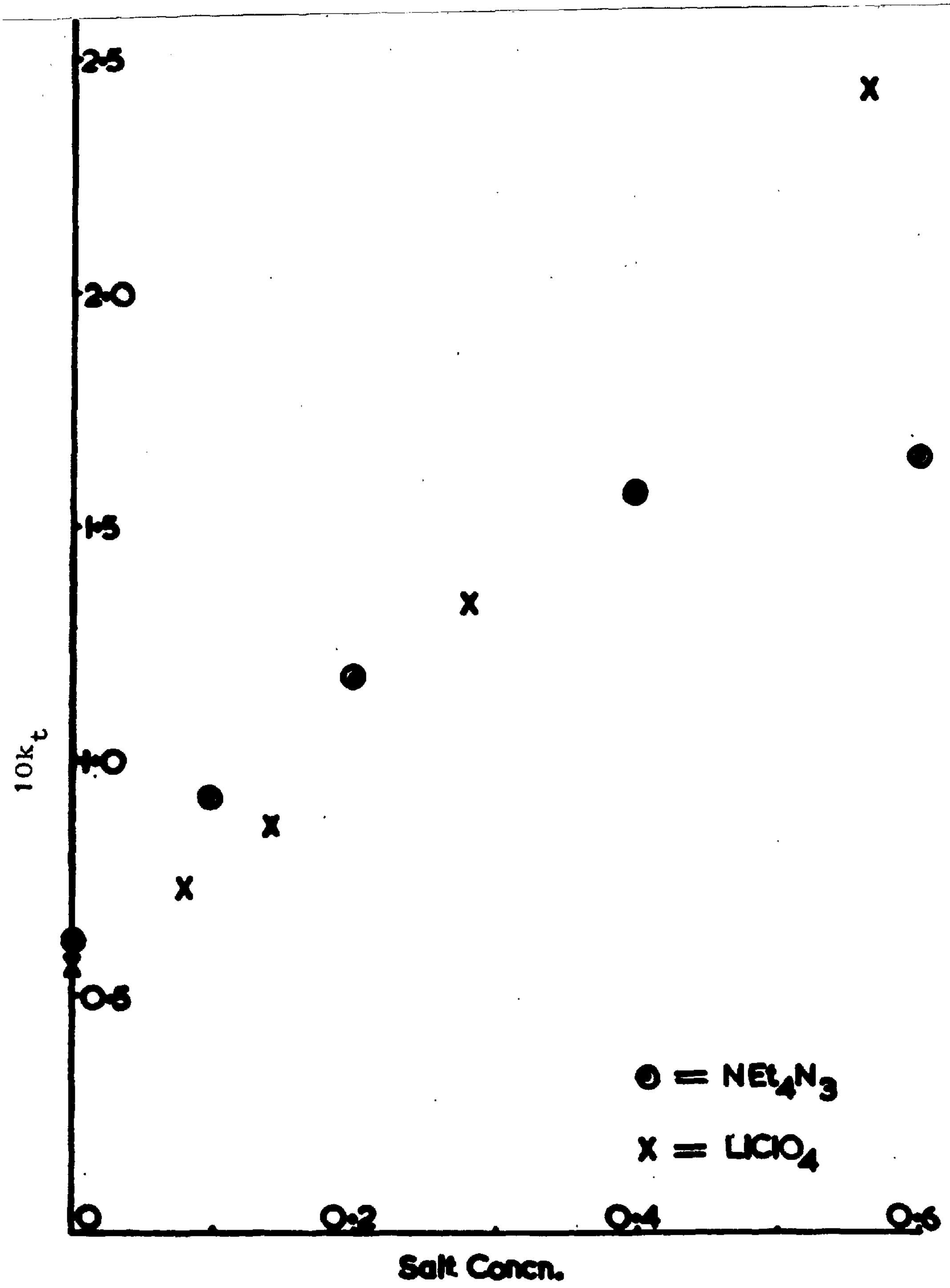


Fig. 5. Rates of reaction of 1-phenylallyl chloride in ethanol as a function of the concentration of added salts.

TABLE XI

Solvolysis of 1-Phenylallyl Chloride in 96% Ethanol/ Cyclohexane. The Effect of Added Chloride Ions. Chloride Concn., ca. 5 x 10^{-5}M. Temp., 30.0°C.

Salt Concn. (m/l)	Solvolysis (%)	k_t (min.^{-1})	ROEt (%)
0.000	69.8	0.0566	78.3
0.017	67.6	0.0587	74.9
0.034	67.4	0.0593	75.0
0.055	67.3	0.0635	74.8
0.111	67.3	0.0663	71.6
0.223	66.9	0.0683	69.4
0.334	64.2	0.0698	72.4
0.445	63.4	0.0723	70.4
0.557	61.2	0.0741	70.2

The Racemization of (+)-1-Phenylallyl Chloride in Ethanol/Cyclohexane Mixtures

The rate of racemization of optically active 1-phenylallyl chloride was measured in 96% - 60% v/v ethanol/cyclohexane. Owing to the rapidity of the reaction the runs were performed at 22°C. rather than 30°C. Additional spectrometric rate constants for the reaction of 1-phenylallyl chloride in the ethanol/cyclohexane mixtures were therefore obtained at the same temperature to allow for comparison between the two sets of rate constants. It was found - see Table (VIII) - that k_{pol} exceeded k_t in all the solvents tried and that both log (k_{pol}) and log (k_t) varied linearly with the mole-fraction of the ethanol.

DISCUSSION

The Solvolysis of Cinnamyl Chloride

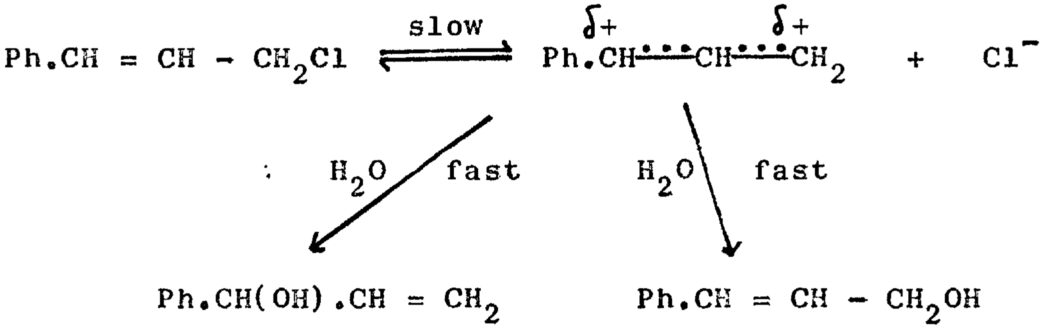
The kinetic investigations of Vernon (53, 54) of the reactions of cinnamyl chloride with absolute and aqueous ethanol have been referred to previously. The results obtained in the present work are in agreement with his general conclusion that the solvolysis is entirely unimolecular in highly ionizing aqueous media but that there is evidence of a bimolecular component in the less highly ionizing absolute ethanol. The later investigation by Valkanas (50) did not reveal the possibility of different mechanistic features in the two solvents. Valkanas considered that the solvolysis of cinnamyl chloride, both in 60% aqueous dioxan and in pure ethanol, could be represented by a single mechanism. It is unlikely that he would have reached this decision had he investigated the effect of added base in the aqueous solvent. The present work allows the conclusions of Vernon to be extended. Further details of the mechanism may be elucidated by making use of the solvolysis product ratios in the various mixtures and taking account of the effects of added nucleophiles on this ratio and on the rate of reaction.

Evidence that the solvolysis is unimolecular in 30 - 60% aqueous dioxan can be derived from the plot of log (k'_s) against Y. The m value of 1.23 indicates that the rate of solvolysis of cinnamyl chloride is at least as susceptible to the ionizing power of the medium as is the rate of solvolysis of *tert*-butyl chloride. The absence of a bimolecular component in the rate determining step is well demonstrated by the effect of hydroxide ions on the overall reaction rate. The fact that a significant rate retardation, rather than an acceleration, was observed must mean, following the theory of Doering and Zeiss (19), that orbital overlap with an hydroxide ion (or a solvent molecule) is not possible in the transition state leading to the first intermediate. The transition state must be sufficiently well stabilized by the high polarity of the solvent for it to retain a configuration near to tetrahedral at the reaction site with correspondingly little orbital available for rearward bonding.

Benfey, Hughes and Ingold (4) have discussed the rate retardation caused by hydroxide ions on a number of hydrolyses thought to occur by a unimolecular mechanism. They considered that it was due to attack by hydroxide ions on protons of the solvation shell required for ionization of the organic halide.

The salt effects are fully in agreement with a unimolecular path for the solvolysis. Strongly nucleophilic bromide ions have no effect on the rate, other than through the ionic strength increase that they cause. The effect of lithium chloride is typical of the mass-law retardation of a unimolecular solvolysis by common ion.

The product ratio data does not allow the hydrolysis to be accounted for on the basis of the simple S_N1 mechanism shown below:



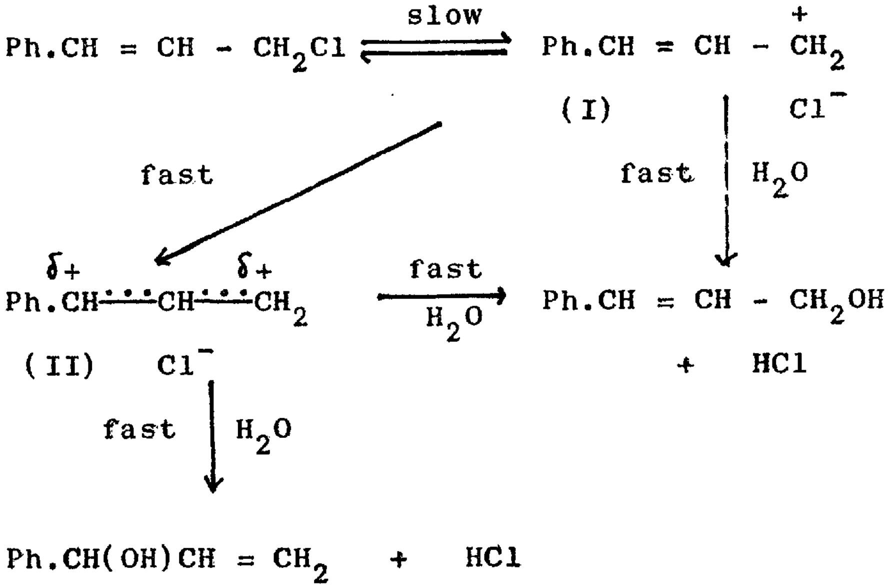
On the basis of this mechanism, one would not expect to find any variation in the product ratio under differing conditions of solvent composition. Bunton, Pocker and

Dahn (10) have studied the O^{18} exchange associated with the acid catalyzed rearrangement of 1-phenylallyl alcohol in 60% aqueous dioxan. They found that the intermediate involved in the rearrangement reacted with water about 1.4 - 1.5 times more rapidly at the 1- carbon atom than at the 3- carbon atom. Similar results were obtained by Pocker (45) in a study of the acid-catalyzed deamination of 1-phenylallylamine. In both cases, the kinetic results were most simply explained by considering that the intermediate was the mesomeric phenylallyl carbonium ion.

The most highly ionizing solvent investigated in the present work - 30% aqueous dioxan - yielded the above ratio for the hydrolysis products of cinnamyl chloride. However, as the ionizing power was decreased, so less rearrangement occurred; in 60% aqueous dioxan the two isomeric alcohols were produced in almost equal amounts.

Hydroxide ions in 50% aqueous dioxan also caused a significant decrease in the proportion of the rearranged product. It is reasonable to suppose that for a primary allylic halide in a strongly ionizing medium, hydrolysis to give the rearranged alcohol in appreciable amounts must occur through a mesomeric carbonium ion and will not involve S_N2' displacement. In the present system, the latter conclusion is supported by the absence of any evidence for S_N2 displacement. Hence, one may conclude that diminution in solvent ionizing power, or addition of base, inhibits the formation of the mesomeric ion while allowing product formation by another route.

It is proposed that the formation of an ion-pair without nucleophilic assistance is the rate determining step in highly ionizing aqueous media. In 30% aqueous dioxan, the counter ions are sufficiently well separated, before reaction with solvent occurs, for the positive charge to become completely delocalized; the products are thus obtained in the same proportions as in the reactions of a mesomeric phenylallyl carbonium ion with water. In solvents containing more dioxan, the ionizing power is less, and some reaction of the ion-pair with water can take place at a stage where the departing chloride ion is still closer to the 3- carbon atom than to the 1- carbon atom, the positive charge being effectively localized at the 3- position. The product of such a reaction is cinnamyl alcohol, and therefore the proportion of this compound in the final product mixture is higher than in the former case.



The above scheme can account for the observed salt effects. Hydroxide ions in high concentration can react with intermediate (I) at the 3- position before complete delocalization and thus increase the proportion of un-rearranged alcohol. Neither chloride nor bromide ions in 0.1M concentration have a detectable effect on the product ratio. To explain this, one must assume that relatively little 1-phenylallyl halide is produced transiently by the recombination of intermediate (II) with these ions. 1-Phenylallyl chloride is hydrolyzed rapidly and produces a much larger proportion of 1-phenylallyl alcohol than does cinnamyl chloride. Either recombination of (II) with halide ions does not occur to an extent comparable with recombination of (I), or if it does, then chiefly cinnamyl chloride or bromide is produced, in contrast to the reaction of the same intermediate with water molecules. As will be pointed out in a later chapter, return from intermediate (II) must be invoked to explain the results of hydrolysis of 1-phenylallyl chloride. In order to explain the observed product ratios one must conclude that the free phenylallyl carbonium ion is attacked by negatively charged ions to give predominantly cinnamyl compounds. Support for this idea is found in the work of Hardisson (32). He carried out a molecular orbital calculation using the self-consistent field method in order to determine the charge densities at the 1- and 3- positions of the mesomeric ion. He found that these were identical, but that the rate at which the charge density changed with the approach of an ion, i.e. the self-atom polarizability, was greater at the 3- than the 1- position. This indicated that attack should occur predominantly at the 3- position.

The ethanolysis of cinnamyl chloride must allow for some nucleophilic participation by the solvent in the rate-determining step. This was first suggested by the work of Meisenheimer and Link (44) who observed that in the presence of ethoxide ions the predominant ethanolysis product was cinnamyl ethyl ether. A mixture of isomeric ethers was formed when the solvolysis was carried out in the absence of lyate ions. Vernon (54) found that the rate of ethanolysis was greatly increased by the addition of ethoxide ions, suggesting to him the presence of a bimolecular component to the ethanolysis mechanism. However, as has been pointed out above, one cannot logically assume that a mechanism occurring in the presence of lyate ions or other strong nucleophiles also occurs in their absence. That is to say, the above results do not necessarily prove that the mechanism of the ethanolysis of cinnamyl chloride in ethanol alone involves a bimolecular component, but merely suggest it as a possibility. Confirmation of this possibility would be obtained if the ethanolysis could be carried out in a medium in which the nucleophilicity could be varied while the ionizing power was kept constant. An increase in the solvent nucleophilicity should then increase the rate of ethanolysis. Furthermore, if the unimolecular and bimolecular components were present as separate and competing mechanisms rather than as contributions to a single mechanism an increase in the proportion of the normal product should result.

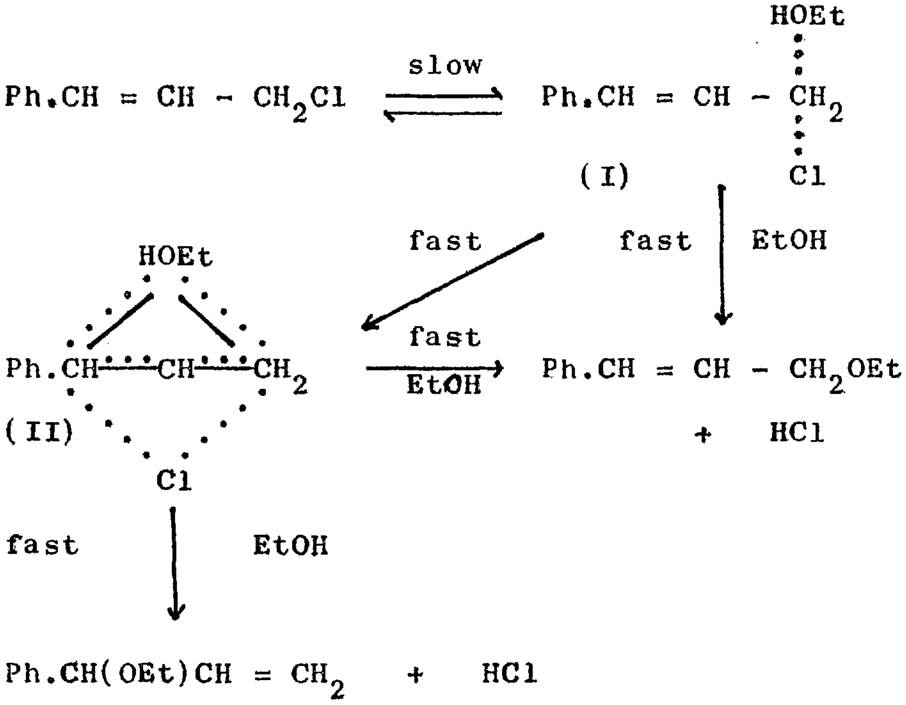
It was hoped to gather information on the above points by performing the ethanolysis in ethanol/cyclohexane mixtures. Measurements of Z values had indicated that in this solvent system the ionizing power was virtually unchanged when the proportion of ethanol was varied between 60 and 98% v/v. When the rate constants were obtained, it was apparent that the ionizing power of the medium had risen on addition of ethanol, despite the evidence of the Z values. The rate constants increased by a factor of 4.9 for an increase by a factor of only 1.7 in the molar concentration of the ethanol. Definite conclusions regarding the presence of a bimolecular component to the ethanolysis - either as part of a single mechanism, or as one of two separate mechanisms - can, therefore, not be reached. However, if one compares the rate constants for the ethanolysis of cinnamyl chloride with those for 1-phenylallyl chloride in the same solvent system, it can be seen that addition of ethanol has a rather smaller effect on the rate in the case of the latter compound. An increase in the molar concentration by a factor of 1.7 causes the rate constant to increase by a factor of 3.65, compared with 4.9 for cinnamyl chloride. It is conceivable that the greater increase in the case of cinnamyl chloride is due to some form of bimolecular nucleophilic interaction between the cinnamyl chloride and the ethanol.

The results do not allow a conclusion to be reached on the question of whether a single mechanism is operating or whether two mechanisms are in competition.

In the case of the dual mechanism, products are formed by competing S_N2 (giving cinnamyl ethyl ether) and S_N1 (giving a mixture of isomeric ethers) processes. The observed rate constants indicate that the ratio S_N2/S_N1 decreases slightly as the concentration of the ethanol increases, since the total rate increases by a factor of 4.9 and the S_N2 process cannot account for higher factor than 1.7. The proportion of 1-phenylallyl ethyl ether should therefore increase slightly with increasing ethanol concentration. This is what is, in fact, observed. An increase in the ethanol concentration from 60 - 98% v/v produces an increase of 2% in the proportion of the rearranged ether.

Alternatively, one could explain the ethanolysis by a mechanistic scheme similar to that proposed by

Streitwieser (49) for the solvolysis of crotyl chloride based on results of Catchpole and Hughes (12). The mechanism bears a strong resemblance to that proposed above for the hydrolysis, but involves a degree of nucleophilic assistance by the solvent in the formation of the first intermediate.



As in the case of hydrolysis, two intermediates are involved; the first (I) gives cinnamyl ethyl ether while the second (II) gives both isomeric ethers - probably in the same ratio as that given in the mesomeric carbonium ion. There is some nucleophilic participation by ethanol in the rate-determining step, and the formation of products from the two intermediates is such that these are formed at about equal rates. Thus reduction in ethanol concentration, as well as reduction in ionizing power, decreases the total rate of reaction but does not alter the product ratio through the change in solvent nucleophilicity. The addition of nucleophiles more powerful than ethanol makes the reaction more like an S_N2 displacement, and the formation of the second intermediate from the first becomes relatively less likely.

In his investigation of the ethanolysis of cinnamyl chloride, Valkanas arrived at a rather similar mechanism to the above (50). However, his first intermediate, stated to form normal products only, was represented as

$$\mathrm{Ph.}\overset{\delta+}{\mathrm{CH}}\overset{\cdots}{\text{—}}\mathrm{CH}\overset{\cdots}{\text{—}}\overset{\delta+}{\mathrm{CH_2}}\cdots\overset{\delta-}{\mathrm{Cl}}$$

Such an intermediate should be capable of forming rearranged products also. Furthermore, neither his first nor his second intermediate involved any nucleophilic contribution by an ethanol molecule.

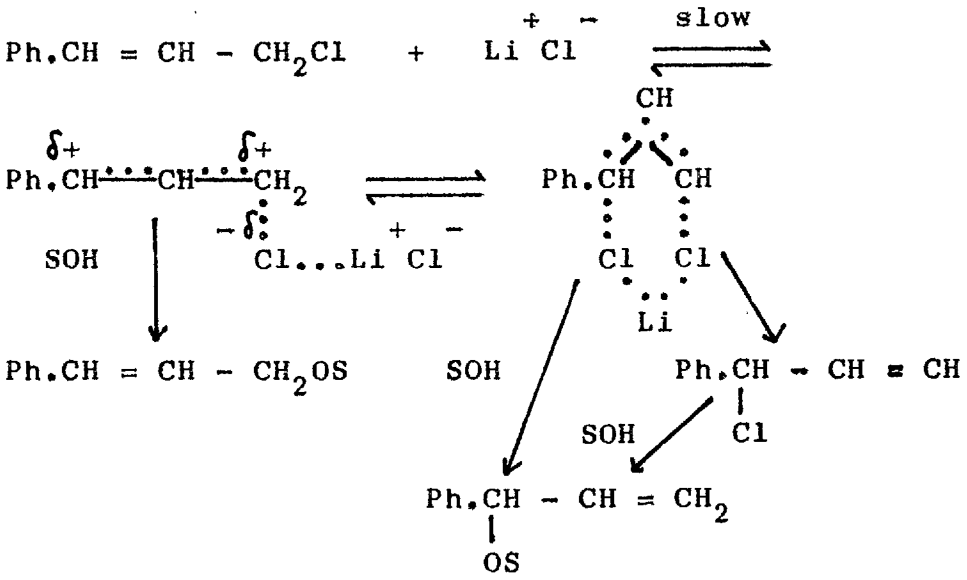
Valkanas rejected the possibility of product formation occurring via the mesomeric phenylallyl carbonium ion. His arguments were based on two principal observations.

(a) In the solvolysis reactions of cinnamyl chloride, the composition of the products was found to be greatly different from the composition of the products of solvolysis of 1-phenylallyl chloride. 1-Phenylallyl chloride gave at least 90% ordinary replacement products, but cinnamyl chloride gave 50% cinnamyl isomers under the same conditions.

(b) Azide ions in equal or higher concentrations to the organic chloride rapidly converted the cinnamyl isomer to stable cinnamyl azide with complete exclusion of solvolysis but apparently did not react with 1-phenylallyl chloride.

Although the figures quoted in (a) are in error, it is true that more secondary solvolysis product is formed from 1-phenylallyl than cinnamyl chloride. However, this observation merely proves that the solvolysis of both isomers does not proceed via one and the same intermediate. Since Valkanas had already concluded (50) that the mesomeric ion was not involved in the solvolysis of 1-phenylallyl chloride he could not infer its absence from the solvolysis of cinnamyl chloride. The observations regarding the azide ions merely indicate the availability of a different mechanistic route in the presence of strong nucleophiles and are no evidence that at least part of the solvolysis does not involve the mesomeric ion. Valkanas did not consider the possibility of concurrent S_N1 and S_N2 mechanisms for the solvolysis.

As stated in the previous chapter, the salt effects observed by Valkanas are in fairly good agreement with those of the present work as regards rate constants (not product ratios). His interpretation is therefore of interest. Catalysis by lithium chloride was thought to be strictly bimolecular since a plot of observed rate constants against lithium chloride concentration was linear. It was considered (50) that the acceleration in the solvolysis rate was too great to be accounted for by an ionic-strength effect, although no evidence on this point was quoted. The cation of the salt was considered to afford electrophilic assistance to the separation of the chlorine atom in the formation of the first intermediate. Subsequently, 1-phenylallyl chloride was formed via a six-membered ring intermediate involving a molecule of salt:



This explained the observed increase in the amount of secondary solvolysis product. In addition, the anions of salts could be involved in nucleophilic assistance to the formation of the ion-pair intermediate, the degree of the assistance depending on the nucleophilicity of the anion. This is the mechanism suggested for catalysis by azide, bromide and ethoxide ions.

The enormous rate increase caused by sodium perchlorate (erroneous) was explained as being due to a rapid equilibrium

$$R'Cl \quad + \quad ClO_4^- \quad \rightleftharpoons \quad R'ClO_4 \quad + \quad Cl^-$$

As sodium chloride is insoluble in ethanol, chloride ions are continuously removed, displacing the equilibrium to the right. This explanation is in any case unlikely since the weakly nucleophilic perchlorate ions would not be expected to achieve the rapid equilibrium as above.

While the idea of nucleophilic assistance by anions in the formation of the ion-pair intermediate is a reasonable explanation for the observed effects of azide, bromide and ethoxide ions, the schemes suggested for chloride and perchlorate catalysis are unnecessary and the following explanation is preferred.

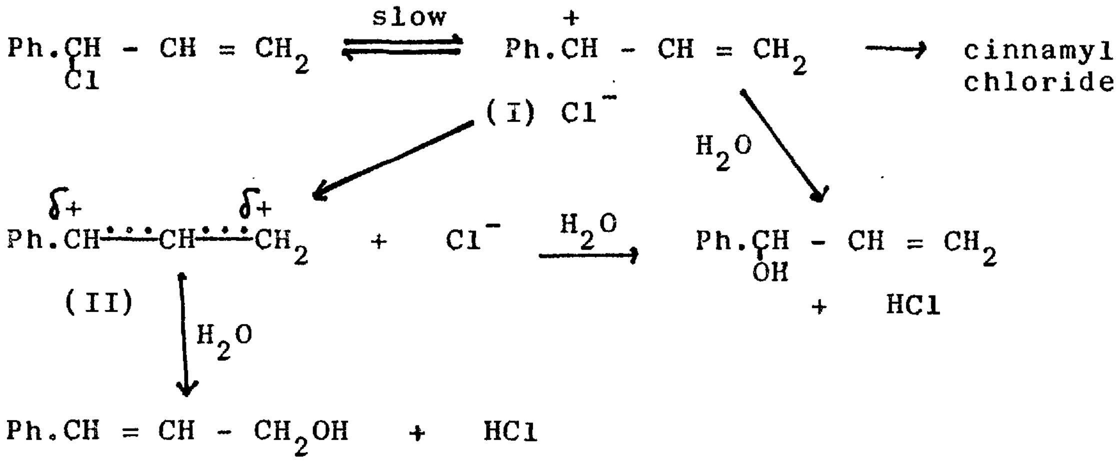
The rate increase by moderate concentrations of perchlorate ions is due to an increase in the ionic strength of the medium. Compared with the effect of perchlorate ions, chloride ions thus cause a mass-law rate depression. This is in keeping with the idea that the rate-determining step involves appreciable charge separation. Chloride ions in concentrations up to 0.25M have little effect on the product ratio, but higher concentrations slightly increase the proportion of the rearranged isomer. A far greater increase is caused by moderate and high concentrations of lithium perchlorate. It would appear that if the single mechanism is operating, the formation of the intermediate (II) is facilitated by high ionic strength, a reasonable assumption seeing that formation of (II) from (I) represents a further stage of dissociation. The dual mechanism idea requires that the proportion of the S_N1 mechanism is increased by high ionic strength.

The rate increase caused by very high concentrations of lithium perchlorate is non-linear and may be due to the initial formation of very labile cinnamyl perchlorate by an S_N2 displacement.

The Solvolysis and Isomeric Rearrangement of 1-Phenylallyl Chloride

The structural similarity of 1-phenylallyl chloride to the diphenylmethyl halides suggests that its solvolysis should occur by a similar mechanism, i.e. a unimolecular one. The sensitivity of the rate of hydrolysis in aqueous dioxan to the solvent ionizing power ($m = 0.93$), and the fact that the solvolysis of its primary isomer in aqueous dioxan has been shown to be unimolecular, is confirmation of this idea. In ethanol/cyclohexane mixtures, the ethanolysis rate is rather less sensitive to the concentration of ethanol than is the corresponding rate for cinnamyl chloride, an indication of the absence of solvent nucleophilicity as a rate-determining factor. The unimolecular nature of the ethanolysis is well demonstrated by the effect of a high concentration of ethoxide ions. A very slight decrease in the overall rate of reaction is observed, the corresponding effect for cinnamyl chloride being a vast rate increase. Identical rate enhancements were caused by highly nucleophilic azide ions and non-nucleophilic perchlorate ions, although the products were very different. This is a good indication that an ionization unassisted by the solvent is rate-determining.

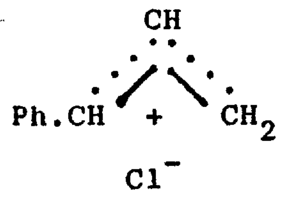
In aqueous dioxan the proportion of 1-phenylallyl alcohol produced is higher than would be expected if the mesomeric phenylallyl carbonium ion were the only intermediate. This fact, together with the occurrence of isomeric rearrangement to cinnamyl chloride to a considerable extent even in the most highly ionizing media, strongly suggests that an ion-pair is formed in the rate-determining step. As in the case of cinnamyl chloride, reaction with solvent can occur at a point where the departing chloride ion is still sufficiently close to the carbon atom whence it came to cause the positive charge to be effectively retained at that atom. The suggested scheme is shown below:



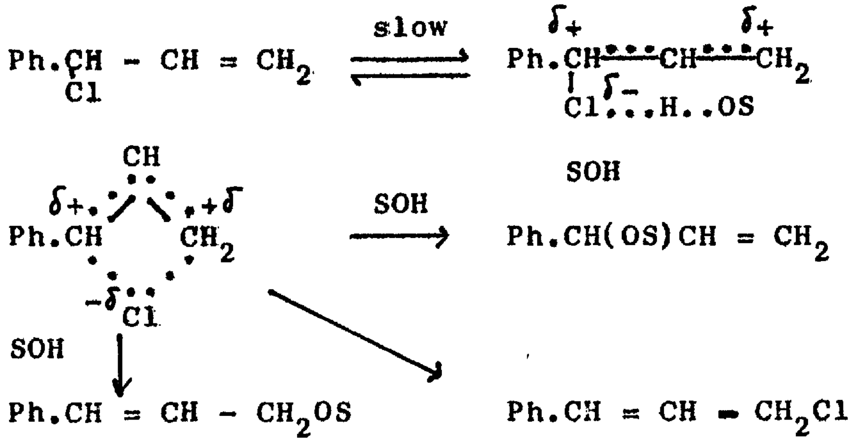
The polarimetric studies in 90% aqueous dioxan bring further evidence for the existence of the ion-pair intermediate (I). Since k_{pol} exceeds the rate constant for the overall reaction k_t, there must be considerable return from the first intermediate, the lower limit being denoted by $k_{pol} - k_t$, representing return with loss of configuration. Return from the dissociated intermediate (II) can be considered to be most unlikely in the absence of added chloride ions, bearing in mind the very low concentration (ca. 3×10^{-5}M) of the organic chloride.

The proportion of hydrolysis relative to total reaction k_s/k_t is not very greatly affected by solvent ionizing power variations. An increase in the latter which causes the overall rate to increase by a factor of 100, only increases k_s/k_t by 8.9%. This is indicative of a single rate-determining step as shown above for both the hydrolysis and the isomeric rearrangement. If the latter process were of the S_Ni' type involving very little or no charge separation, the proportion of hydrolysis should have been very greatly increased by increasing ionizing power.

The formation of cinnamyl chloride from the intermediate (I) is a process regarding which little definite information is available. Presumably a structure of the form



is involved, either as a transition state between (I) and the final product or as an intermediate. If it were present as an intermediate, it could also lead to solvolysis products. The mechanistic scheme suggested by Valkanas for the solvolysis of 1-phenylallyl chloride is shown below:



It can be seen that he considered the free phenylallyl carbonium ion to be absent from all stages of the mechanism. He stated (50) that if ionization were involved, then there were two possibilities, viz.

(1) Both solvolysis and isomeric rearrangement have the same rate-controlling step, i.e. the complete ionization of the chloride.

(2) Solvolysis and isomeric rearrangement result from two entirely different routes, one involving ionization and the other not. Both his results, and those of the present work, indicate that the above two possibilities are not in operation. However, both sets of results are adequately explained by the mechanism involving the free carbonium ion shown above.

In the presence of lithium perchlorate, the magnitude of the ratio k_s/k_t is somewhat raised, contrary to the observation of Valkanas using sodium perchlorate. This is consistent with the idea that isomerization in the absence of added chloride ions takes place chiefly or wholly from the ion-pair (I), and that dissociation of (I) to (II) is facilitated by high ionic strength. Cinnamyl alcohol can only be formed from (II) and the addition of a moderate amount of lithium perchlorate does in fact cause a very slight increase in the proportion of it in the solvolysis product mixture.

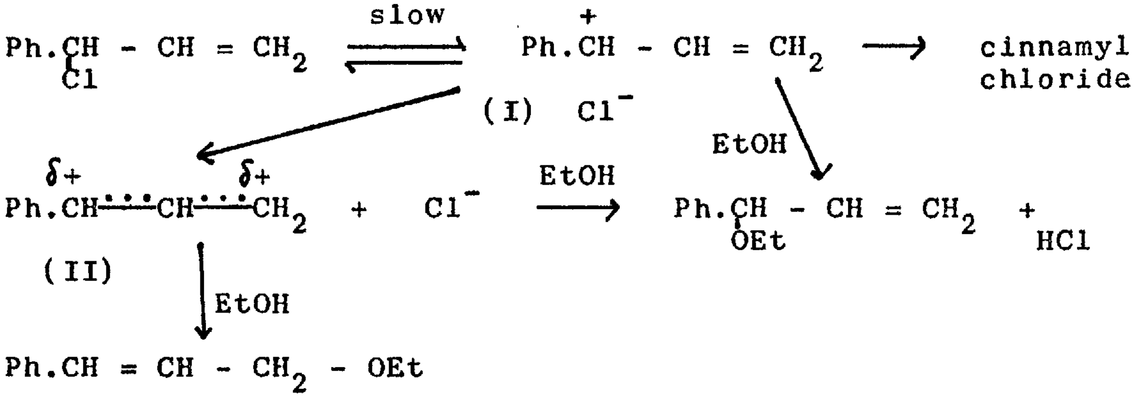
Since k_t in the presence of lithium chloride is not as high as it is in the presence of an equivalent concentration of the perchlorate, return of one or both of the intermediates to covalent chloride must occur. The percentage of isomeric rearrangement definitely increases with increasing chloride ion concentration, the effect being most marked in the mixtures containing the lowest amount of water. It therefore seems likely that the isomerization is not intramolecular in the presence of chloride ions. Evidently, these can compete with solvent molecules for intermediate (II), yielding mainly cinnamyl chloride as a result. The likelihood of the capture of (II) by chloride ions is greatest in those solvents where the concentration of the nucleophilic reagent, water, is least.

The formation of cinnamyl chloride from (II) by combination with added chloride ions can further explain the small increase in the proportion of 1-phenylallyl alcohol in their presence. Combination of (II) with chloride ions removes the only intermediate which can yield the primary alcohol, the return of (I) to covalent chloride not affecting the subsequent product formation.

The conclusion that there is a competition for the intermediate (II) between chloride ions (to give cinnamyl chloride) and water molecules (to give the primary as well as the secondary alcohol) is further supported by the data concerning the products of hydrolysis. In the solvent containing the lowest concentration of the nucleophilic reagent - 90% aqueous dioxan - chloride ions are most efficient in increasing the proportion of the secondary alcohol, a significant effect appearing at a concentration of only 0.029M. The efficiency is least for 70% aqueous dioxan where lithium chloride at a concentration of 0.18M produces a smaller effect.

These results are of interest in connection with the hydrolysis of cinnamyl chloride in the presence of chloride ions. In that case, it was found necessary to assume that 1-phenylallyl chloride was not formed transiently in appreciable amounts. This could be either because return did not take place from the mesomeric ion (II) or because it did so to give predominantly cinnamyl chloride. It is now clear that the mesomeric ion can combine with chloride ions, at least, in solvents containing up to 30% water.

The proportion of secondary to primary ethyl ether obtained on ethanolysis of 1-phenylallyl chloride exceeded that for the hydrolysis. About 80% of the total ethanolysis product was secondary in 60 - 90% ethanol/cyclohexane. Although no reliable information is available regarding the product ratio to be expected from attack of ethanol molecules on a mesomeric phenylallyl carbonium ion, there is no reason to suppose that this should have a value significantly different from that for the hydrolysis in aqueous dioxan, i.e. secondary product predominating in the ratio 1.5 : 1. One may, therefore, consider that, as in the case of the hydrolysis, two intermediates are involved, the first yielding only 1-phenylallyl ethyl ether:



The rate constant for racemization, k_{pol}, exceeded k_t, the rate constant for the overall reaction, in all the ethanol/cyclohexane mixtures and little variation in the ratio k_{pol}/k_t was observed. This is further evidence for the formation of an ion-pair intermediate in the rate-determining step. Kenyon and his co-workers (2, 33) have studied the solvolysis reactions of a number of optically active allylic chlorides and hydrogen phthalates containing simple alkyl substituents. Complete racemization was generally observed in solvents of high ionizing power, but in alcohols some inversion of configuration at the original carbon atom occurred. In all the media investigated in the present work, (+)-1-phenylallyl chloride racemized completely. Evidently, no covalent forces exist in the ion-pair intermediate (I) between the chloride ion and the organic residue, and the latter is capable of free rotation. Reaction with a solvent molecule does not cause inversion.

The effects of azide and perchlorate ions on k_t have been referred to previously. Perchlorate ions in low and moderate concentrations have little effect on the ratio k_r/k_t, but the tendency is in the opposite direction to that in aqueous dioxan and becomes significantly large when massive concentrations of the ion are used. On the basis of the above mechanism, one would expect ionic strength increases to promote ethanolysis rather than isomerization, and it is not easy to understand why the reverse is observed.

From the final ultra-violet absorption intensity, it is clear that azide ions cause the formation of more conjugated material than is found in their absence. If one makes the assumption that the ethanolysis products are formed in their usual ratio, viz. secondary predominating in the ratio 3 : 1, it appears that the residue is almost entirely cinnamyl azide and that little or no 1-phenylallyl azide is produced. If an intermediate such as (I) is postulated, one would expect this to be attacked by azide ions very readily, just as the corresponding intermediate in the solvolysis of cinnamyl chloride is attacked by hydroxide ions (see Table III). Such attack would result in the formation of stable secondary azide. The fact that azide ions are effective competitors for the intermediates is shown by the diminution in solvolysis which they cause. In order to explain the high final absorption intensities, it is necessary to assume that the composition of the solvolysis product mixture is not the same as in the absence of azide ions. There is instead a higher proportion of cinnamyl ethyl ether formed, the intermediate (I) leading to the isomer being partially removed by the azide ions.

Chloride ions increase k_t, particularly at low concentration, although less than either perchlorate or azide. It is apparent that in 96% ethanol/cyclohexane, a solvent containing a high concentration of the nucleophilic reagent, added chloride ions are less well able to effect return of intermediate (I) to the covalent state than they are in 70 - 90% aqueous dioxan. Hence, the ionic strength effect exceeds the mass-law effect and a net rate increase results.

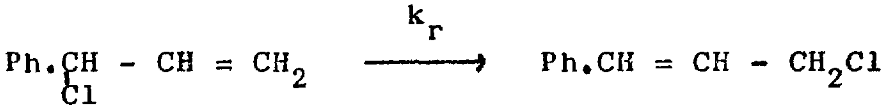
Chloride ions are also less effective in competing with the solvent for intermediate (II). The ratio k_r/k_t does increase as more chloride ions are added, but the increase is considerably less than is observed in all the aqueous media and is, in fact, not significantly greater than in the presence of an equivalent concentration of lithium perchlorate. The isomeric rearrangement is therefore seen to be predominantly intramolecular in ethanol, and occurs through the intermediate (I).

In hydroxylic solvents, the relative proportions of isomerization and solvolysis are determined principally by the nucleophilicity of the solvent. This was first suggested by the work of Young, Winstein and Goering (64) who were able to detect isomerization during the acetolysis of 1:1-dimethylallyl chloride, but not during the ethanolysis, the two solvents having similar ionizing power as shown by their Y values. In the present work, it was found that the ratio k_r/k_t had the same value as in pure ethanol when the solvolysis was performed in pure methanol, and, by extrapolation, in pure water. The three solvents may be expected to have similar nucleophilicities. When the nucleophilicity of the solvent was lowered and the ionizing power kept unchanged (as in 22% formic acid/dioxan), k_r/k_t increased considerably. Similarly, ethanol and 90% aqueous dioxan have similar Y values, but the former is more nucleophilic. Isomerization accounts for 30% of the total reaction in the former solvent and 64% in the latter. In this context, it must be understood that a nucleophilic solvent is one in which the molecules are attracted to a positive centre and are then capable of forming a stable product.

ISOMERIZATION OF 1-PHENYLALLYL CHLORIDE

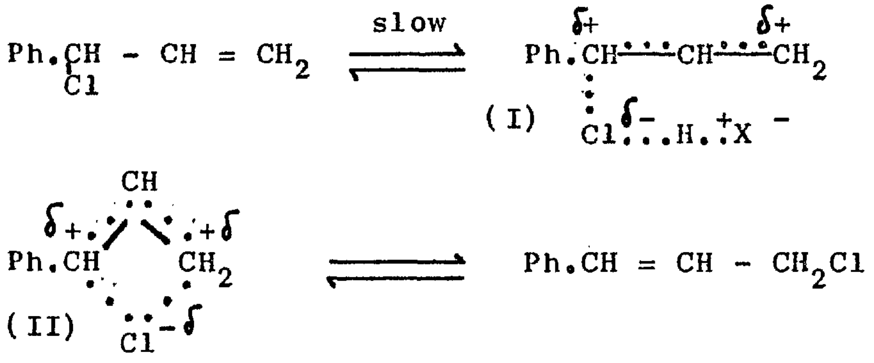
INTRODUCTION AND RESULTS

In non-hydroxylic solvents, 1-phenylallyl chloride undergoes isomeric rearrangement to cinnamyl chloride.



$$\underset{\text{Cl}}{\text{Ph.CH}} - \text{CH} = \text{CH}_2 \xrightarrow{k_r} \text{Ph.CH} = \text{CH} - \text{CH}_2\text{Cl}$$

The isomerization has been studied by Valkanas and Waight (50, 52) who found that the chloride isolated at the end of the reaction consisted entirely of the primary isomer. The isomerization was slow at room temperature in weakly polar solvents, e.g. k_r = ca. 0.29 x 10^{-4} min.$^{-1}$ in chlorobenzene at 40°C. Valkanas showed that the isomerization was catalyzed by acids, the rate being proportional to the acid concentration. It was suggested that in the presence of acids the following mechanism was in operation:



For the uncatalyzed isomerization, Valkanas proposed a similar mechanism in which the ion-pair (I) was formed without the assistance of hydrogen bonding (50). It was considered that the isomerization would be facilitated by an increase in the solvent polarity, and it was shown that the rate was far higher in N:N-dimethylformamide than in chlorobenzene. In a later paper (52) Valkanas and Waight suggested that in alcoholic media an S_Ni' reaction might be operating involving a transition state to which covalent structures such as (II) made an important contribution. No mention was made of the asymmetric ion-pair intermediate (I). Indeed, the results of Valkanas did not give much information concerning the nature of this intermediate, and there is no evidence that the non-acid-catalyzed isomerization does not proceed directly via a symmetric intermediate or transition state of the form (II).

In the present work, an attempt was made to gain further information concerning the nature of the intermediate leading to isomerization. Since (+)-1-phenylallyl chloride was available, it was possible to make a comparison between the rates of isomerization and racemization. N:N-Dimethylformamide was chosen as the solvent.

The reactions could therefore be carried out at the conveniently low temperature of 40°C.

(+)-1-Phenylallyl chloride racemizes completely as it isomerizes. The comparison of the rate constants for racemization, k_{pol}, and isomerization, k_r, is of mechanistic interest, as has been pointed out in previous chapters. In particular, if k_{pol} exceeds k_r, it is likely that an ion-pair intermediate is involved leading to either cinnamyl chloride or 1-phenylallyl chloride. The rate of racemization of the chloride was determined under similar conditions of temperature and concentration to the isomerization, and k_{pol} was, in fact, found to exceed k_r, as can be seen from Tables (XII) and (XIII).

Increase in the ionic strength of the medium, using sodium perchlorate, was found to cause an increase in the rate of isomeric rearrangement, a linear dependence of k_r on the salt concentration being observed.

Chloride ions were found to affect both k_r and k_{pol}. The variation in k_r with the concentration of lithium chloride was linear; the rate increase was somewhat greater than that due to an equivalent concentration of sodium perchlorate. The variation in k_{pol} with added chloride ions was more complicated. In solutions containing up to 0.055M lithium chloride, the rate increased linearly and very steeply. The second order rate constant for the chloride ion catalysis was 0.0131 l.mole^{-1} min.$^{-1}$, as compared with a figure of 0.00147 l.mole^{-1} min.$^{-1}$ for the isomerization. At concentrations of chloride ion greater than the above figure, the rate increase was less steep, although the plot of k_{pol} against lithium chloride concentration remained linear, at least as far as 0.25M, the highest chloride concentration investigated. For this region, the second order rate constant was 0.00680 l.mole^{-1} min.$^{-1}$

TABLE XII

Isomeric Rearrangement of 1-Phenylallyl Chloride in NN-Dimethylformamide. The Effect of Added Salts. Chloride Concn., ca. 0.15M. Temp., 40.0°C.

Kind of Salt	Salt Concn. (m/l)	k_r (min.$^{-1}$)
——	——	0.000398
LiCl	0.0993	0.000544
LiCl	0.159	0.000780
$NaClO_4$	0.071	0.000479
$NaClO_4$	0.142	0.000590
$NaClO_4$	0.212	0.000665

TABLE XIII

Racemization of (+)-1-Phenylallyl Chloride in N:N-Dimethylformamide. The Effect of Added Chloride Ions. Chloride Concn., ca. 0.15M., Temp., 40.0°C.

LiCl (m/l)	k_{pol} (min.$^{-1}$)
0.000	0.000460
0.0141	0.000647
0.0365	0.000975
0.0640	0.00129
0.108	0.00160
0.144	0.00184
0.180	0.00209
0.216	0.00231
0.245	0.00256

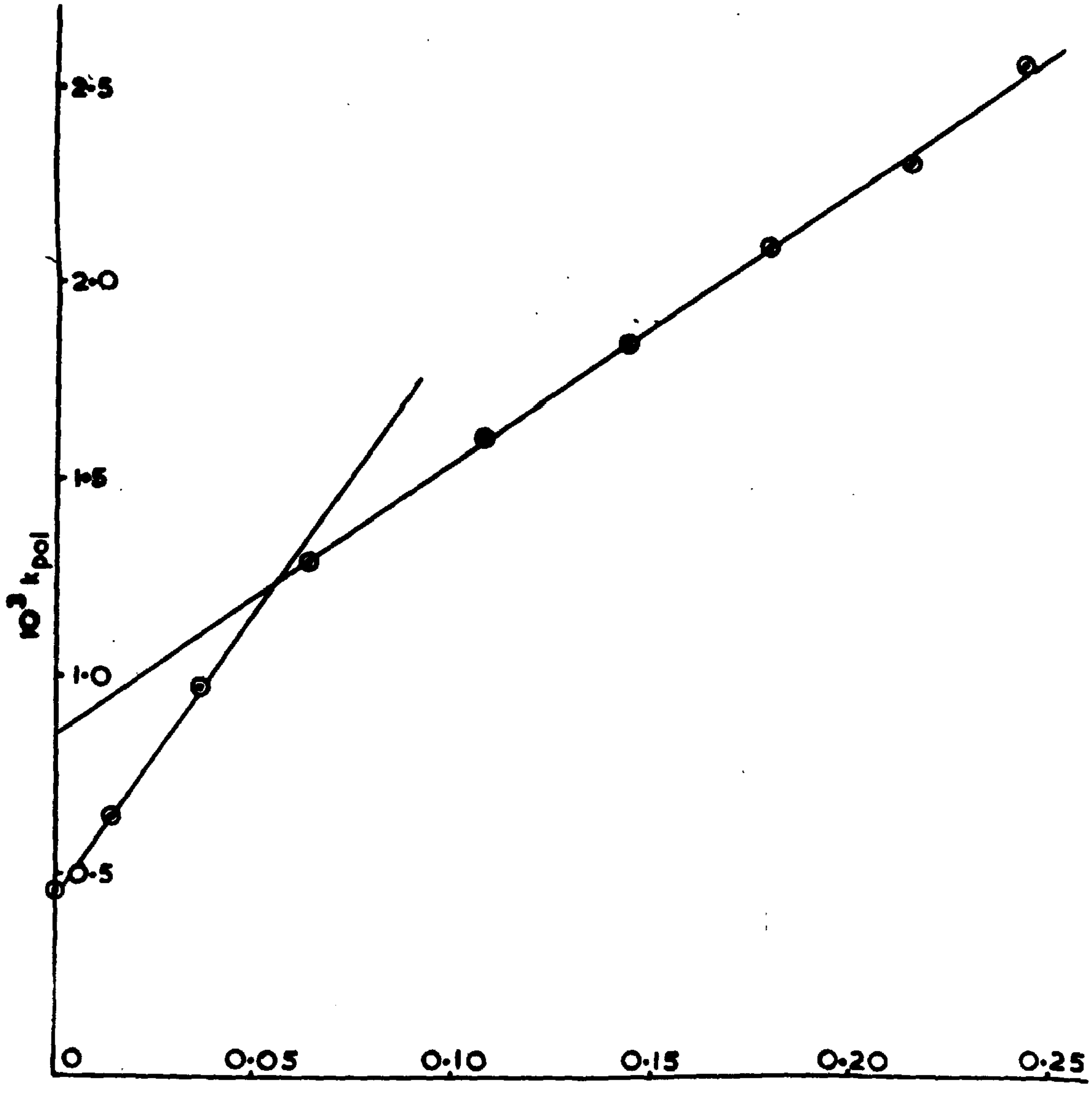


Fig. 6. Rates of racemization of (+)-1-phenylallyl chloride as a function of the concentration of added lithium chloride.

DISCUSSION

The results obtained in the present work indicate that an intermediate must be involved in the isomerization which can return to starting material as well as giving cinnamyl chloride, i.e. an ion-pair.

The ratio $(k_{pol} - k_r)/k_r$ compares the loss of configuration at the 1- carbon atom with rearrangement to cinnamyl chloride and has values of 0.58 and 0.68 at 30.0°C. for ethanol and 90% aqueous dioxan respectively. In dimethylformamide this ratio is 0.15. It appears that if the intermediate involved in the racemization-rearrangement returns to 1-phenylallyl chloride more rapidly than it forms cinnamyl chloride, then it does so more often than not to produce the original structure. Furthermore, it appears that the intermediate is more likely to lose configuration in strongly ionizing media, such as ethanol or aqueous dioxan, than in dimethylformamide.

Valkanas and Waight have previously observed that the rate of isomerization of 1-phenylallyl chloride in dimethylformamide increases linearly with the concentration of added lithium chloride (50, 52). The first order rate constants for the isomerization can be fitted by an equation of the form

$$k = a + b\,[MX]$$

where MX is the added salt, For sodium perchlorate catalysis b is 1.25×10^{-3} l. mole^{-1} min.$^{-1}$ This is slightly smaller than the value for lithium chloride. If one assumes a similar ionic strength effect for the two salts, the slightly greater value or b in the case of lithium chloride could be ascribed to an S_N2' displacement.

The increase in k_{pol} caused by lithium chloride is very large and is unlikely to be due to an ionic strength effect alone. If an S_N2' displacement is postulated for the rearrangement, then an S_N2 displacement must be an important factor in the racemization. The two straight lines in figure 6 can then be explained as follows:

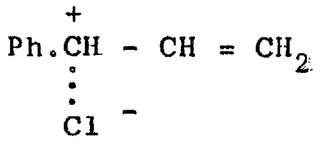
$$R^{*}Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^{*+} \quad Cl^{-} \xrightarrow{k_2} RCl \text{ (racemic)}$$

$$R^{*+} \quad Cl^{-} \xrightarrow[Cl^{-}]{k_3} RCl \text{ (racemic)}$$

$$R^{*}Cl \xrightarrow[Cl^{-}]{k_4} RCl\ \text{(racemic)}$$

We assume that initially k_{-1} is greater than k_2. The addition of chloride ions will provide a second path for the formation of racemic product from the ion-pair intermediate. At a certain chloride ion concentration - denoted by the intersection of the two straight lines - the rate of return to starting material will be equal to the rate of racemization, i.e. $k_{-1} = k_2 + k_3[Cl^-]$. Higher chloride ion concentrations can then no longer increase k_{pol} by reaction with the ion-pair. The subsequent lower increase in k_{pol} is due to an S_N2 displacement with rate constant k_4.

The above explanation of the racemization involves an asymmetric ion-pair intermediate which can be written as



$$\underset{\substack{\vdots \\ Cl^{-}}}{Ph.\overset{+}{C}H} - CH = CH_2$$

It may be expected that this intermediate is also formed in the first step of the isomerization.

Attempts were made to measure the rate of exchange of 1-phenylallyl chloride with isotopically labelled chloride ions present in low concentration. Preliminary experiments by Valkanas (50) indicated that at high chloride ion concentrations the exchange was bimolecular. In the present work, experimental difficulties did not permit useful results to be obtained. An account of the method adopted for the tracer measurements is given in the Experimental Section.

EXPERIMENTAL SECTION

Materials

Cinnamyl Alcohol

Commercial cinnamyl alcohol was recrystallized four times from ether-pentane. It had λmax. 2510 Å (ε 18,180) /‾lit. λmax. 2510 Å (ε 17,900) (28)_7.

Cinnamyl Chloride

A solution of thionyl chloride (8 ml.) in dry ether (25 ml.), was added dropwise to a stirred solution of cinnamyl alcohol (13.4 g., 0.1 mole) in pyridine (8 ml.), maintained at 0°C. Stirring was continued for one hour after the addition. The ether layer was washed with saturated aqueous sodium bicarbonate solution until neutral and dried over magnesium sulphate. After evaporation of the ether, the product was twice distilled, a centre portion being retained. The sample used had b.p. 51-53°/ 0.1 mm., n_D^{25} 1.5815, λmax. 2530 Å (ε 19,300) /‾lit. λmax. 2530 Å (ε 20,000) (50)_7.

Cinnamyl Ethyl Ether

Cinnamyl chloride (15.2 ml., 0.1 mole) was added to a 2N solution of sodium ethoxide in ethanol (200 ml.). The mixture was boiled under reflux for one hour, added to water (200 ml.), and extracted with ether. The ethereal extracts were dried over potassium carbonate and evaporated. After two fractional distillations, the product had b.p. 127°/15 mm., λmax. 2530 Å (ϵ 17,800). The infra-red spectrum showed no evidence for the presence of traces of the secondary isomer, and the purity of the product was confirmed by the gas-liquid chromatogram (Pye Argon Chromatograph, Column: 10% Geigy AD264 on Celite) which showed a single peak.

1-Phenylallyl Alcohol

A solution of acrolein (134 ml.), in anhydrous ether (200 ml.), was added dropwise to a well-stirred solution of phenyl magnesium bromide - prepared from bromobenzene (314 g., 2 moles) and magnesium (48 g.) - in ether (600 ml.) maintained at -10°. Stirring was continued for two hours after the addition, and the complex was then decomposed with ice-cold saturated aqueous ammonium chloride solution (1500 ml.). The ether layer was separated, washed with water, dried over sodium sulphate and potassium carbonate and evaporated. After three fractional distillations, the product had b.p. 101-102°/10 mm., n_D^{16} 1.5465, λmax. 2520 Å (ε 724). Although this product was sufficiently pure for conversion to the chloride, further purification was necessary in order to ascertain the precise extinction coefficient. For this purpose, the alcohol was converted to the hydrogen phthalate (28).

1-Phenylallyl Hydrogen Phthalate

The alcohol (87 g.) was added to a suspension of phthalic anhydride (96 g.) in dry pyridine (58 g.). The mixture was stirred for four hours at 50. The resulting syrupy clear solution was diluted with ether (200 ml.), washed several times with ice-cold 2N hydrochloric acid, and concentrated. The resulting semi-solid mass was triturated with a large volume of ice and dilute acid, and after being allowed to stand for a short time, yielded solid material (140 g.), m.p. 61-70°. It was dried and recrystallized three times from carbon disulphide-hexane to m.p. 73° [lit. m.p. 73-74°(21)].

The hydrogen phthalate was reconverted to the alcohol as follows:

A solution of lithium aluminium hydride (13.75 g.), in anhydrous ether (720 ml.), was added dropwise to a stirred solution of the hydrogen phthalate (51 g.), in anhydrous ether (800 ml.), at -10°. The mixture was then stirred at 0° for one hour after which it was decomposed by addition of saturated aqueous ammonium chloride solution (350 ml.). The ether layer was washed with water, dried over potassium carbonate, and evaporated. The product was fractionally distilled, and the fraction (16 g.) boiling at 96 /6.5 mm. was collected. It had n_D^{26} 1.5385, λmax. 2520 Å (ε 178) [lit. n_D^{25} 1.5386, λmax. 2520 Å (ε 187) (28)].

1-Phenylallyl Chloride

This compound was prepared by the method of Valkanas and Waight (52). 1-Phenylallyl alcohol (13.4 g., 0.1 mole) was added to a solution of triethylamine (13 g.), in dry alcohol-free chloroform (150 ml.). The mixture was cooled to -10° and a solution of thionyl chloride (13.1 g.) in chloroform (10 ml.) was added dropwise. The addition lasted twenty-five minutes during which time the reaction mixture was stirred vigorously. The stirring was continued for ten minutes after the completion of the addition. The solution was then quickly washed with ice-cold water, saturated aqueous sodium bicarbonate solution (three times), and water again. It was dried over anhydrous magnesium sulphate (two hours). The chloroform was evaporated under oil-pump vacuum (CO_2 trap), and the crude chloride, consisting of a mixture of 1- and 3-phenylallyl chlorides, was subjected to rapid fractional distillation three times, the higher boiling fractions being discarded on each occasion. The boiling points, refractive indices, and ultra-violet light absorption intensities of samples prepared at different times showed only slight variations. The purest sample obtained had b.p. 35-36°/0.15 mm., n_D^{22} 1.5410, λmax. 2530 Å (ε 602) representing 98.0% 1-phenylallyl chloride. Samples prepared from the unpurified alcohol had specific extinction coefficients ($E_{1\ cm.}^{1\%}$) ranging from 60 to 90 (ca. 4 to 6% cinnamyl chloride) [lit. n_D^{22} 1.5420, λmax. 2530 Å (ε 1900) (52)]. The chloride could be kept in a stoppered tube under liquid nitrogen for several weeks without undergoing appreciable rearrangement.

(+)-1-Phenylallyl Chloride

The optically active chloride was prepared in the above manner from (-)-1-phenylallyl alcohol. It had $[\alpha]_D^{23}$ +14.85° and contained 2.8% cinnamyl chloride. The alcohol was resolved by the method of Duveen and Kenyon (1, 21).

1-Phenylallyl hydrogen phthalate (71 g.), prepared from the alcohol as above, was dissolved in acetone (260 ml.). Quinidine (81 g.) was added to the warm solution. The resulting clear solution was allowed to stand, and bulky masses of solid were precipitated on cooling. After four recrystallizations from methyl acetate and working up of all the mother liquors, optically pure material was obtained. It had m.p. 124°, $[\alpha]_D^{23}$ +146.6° [lit. m.p. 124°, $[\alpha]_D$ +128.9° (28)].

The quinidine salt was covered with acetone and decomposed with a slight excess of cold dilute hydrochloric acid. The solution was extracted with ether, and the ethereal extracts washed with water, dried over magnesium sulphate, and evaporated. The residue, (+)-1-phenylallyl hydrogen phthalate, was a light yellow viscous oil. It had $[\alpha]_D^{23}$ +41.5° [lit. $[\alpha]_D^{23}$ +51.3° (28)].

Solvents

Chloroform

Reagent grade chloroform was freed from ethanol by being shaken three times with concentrated sulphuric acid followed by several washings with water. It was dried over potassium carbonate (twenty-four hours), and distilled from Union Carbide Type 4A molecular sieves, the first and last fractions being discarded.

N:N-Dimethylformamide

The purification procedure described by Smith, Fainberg and Winstein (48) was adopted. N:N-Dimethylformamide was allowed to stand for two days over calcium hydride. It was then decanted free of solid and subjected to a stream of dry nitrogen for twenty-four hours. The solvent was further purified by being passed through a column packed with molecular sieves, and distilled, b.p. 58°/24 mm.

Dioxan

Dioxan was boiled under reflux with small lumps of sodium (20 g./litre). After six hours it was distilled from the unreacted sodium through a one foot Dufton column. This process was once repeated and yielded a dry product of satisfactory transparency at 2530 Å for use in the kinetic measurements.

Ethanol

Burnett Absolute Alcohol was further dehydrated with magnesium ethoxide following the method of Lund and Bjerrum described by Vogel (55). It was distilled, the first few ml. being discarded.

Formic Acid

The low boiling constituents in commercial formic acid were removed by distillation through a column packed with Fenske helices. The residual acid (b.p. $>$ 99) was allowed to stand for three days over boric anhydride (80 g./litre), then decanted free of solid material and distilled from a further quantity of fresh boric anhydride. It had b.p. 30-31°/50 mm.

Pyridine and Triethylamine

These amines were dried by being boiled under reflux over barium oxide followed by distillation. The process was repeated. The amines were stored over molecular sieves.

Water

Distilled water was boiled over potassium permanganate and redistilled. Before use, it was de-ionized by being passed through a column packed with a mixture of cation and anion exchange resins.

Salts

Chlorides and Perchlorates

Commercial anhydrous lithium chloride was kept for several hours at 100° under reduced pressure (0.2 mm.), and subsequently handled in a dry-box. For use in aqueous media, it was used in aqueous solution (ca. 3M) standardized by titration with silver nitrate solution. Lithium perchlorate crystals were dehydrated similarly, but the infra-red spectrum (nujol mull) showed the presence of traces of water even after prolonged heating of the salt at 300°. For this reason sodium perchlorate was used where extremely dry reaction conditions were required. The sodium salt could be completely dehydrated by being heated under vacuum at 100°, and had the additional advantage of being only mildly hygroscopic. It could therefore be handled safely outside the dry-box.

Tetraethylammonium Azide

Tetraethylammonium bromide (63 g.), in ethanol (220 ml.), containing water (18 ml.), was shaken for twenty-four hours with freshly prepared silver oxide (80 g.) in ethanol (300 ml.), and filtered. The filtrate, which was shown to be free of bromide ions, was acidified to brom-thymol blue with ethereal hydrazoic acid prepared by the method given in Inorganic Syntheses (25). The solvent was removed under vacuum, and the resulting moist solid (ca. 40 g.) was twice dissolved in a mixture of chloroform and acetone (1:1) and reprecipitated by addition of ether. It was then dried under reduced pressure (0.2 mm.). The infra-red spectrum (potassium chloride disc) showed only very slight hydroxyl absorption.

All attempts to prepare reasonably pure, dry lithium azide were unsuccessful. Valkanas (50) prepared the salt by the neutralization of hydrazoic acid with lithium hydroxide in aqueous solution. Water was removed by evaporation and the salt was then dissolved in absolute alcohol which was subsequently evaporated off, this treatment being repeated three times. On repetition of the procedure of Valkanas, it was found that extensive hydrolysis of the salt had occurred, the product obtained giving an alkaline reaction to litmus and showing strong hydroxyl absorption in the I.R. Gray and Waddington (29) described the preparation of anhydrous lithium azide by the precipitation of the salt from aqueous solution with ethanol. This could not be repeated in the present work; it was in fact shown that lithium azide was extremely soluble in ethanol.

Kinetics

Measurement of Reaction Rates

Reactions were followed by observing the increase or decrease in absorption intensity of the medium at 2530 Å associated with the formation or the disappearance of the styrene chromophore. The method is due to Braude and Gore (6).

The following procedure was adopted for cases where the reaction mixture contained no additional light absorbing materials and where temperatures did not exceed 50°. The reaction medium (2.40 ml.) was allowed to equilibrate in a 1 cm. path-length stoppered quartz spectroscopic cell which was placed in the thermostatted cell compartment of a Beckman D.U. spectrophotometer. 0.010 ml. of a stock solution of the organic chloride (concentration ca. 0.125 g./l.) in cyclohexane or dioxan was added by means of a micrometer syringe and the contents of the cell thoroughly mixed. The optical density of the mixture at 2530 Å was noted immediately and taken as E_0.

Some reactions, e.g. those in N:N-dimethylformamide and in the presence of azide ions, or those requiring temperatures in excess of 50°, could not be performed with the reaction medium contained in the spectroscopic cell. In such cases, the runs were carried out in long-necked reaction vessels heated in a thermostatically controlled water bath. The reaction medium was allowed to equilibrate in the flask, and a weighed quantity of the chloride contained in a short specimen tube was then dropped in. The flask was shaken vigorously. 1.00 ml. samples were withdrawn immediately by means of a micro-pipette and diluted into cold cyclohexane to quench the reaction and give solutions of convenient absorption intensity.

First order rate constants (in min.^{-1}) were calculated from the expression:

$$k = (2.303/t) \log_{10} (E_0 - E_\infty)/(E_t - E_\infty)$$

where t is the time in minutes, and E_t and E_∞ are the optical densities after t minutes and at the end of the reaction (about nine half-lives) respectively.

Determination of the Degree of Solvolysis

A weighed quantity (ca. 0.05 g.) of 1-phenylallyl chloride contained in a short specimen tube was dropped into the reaction medium (25 ml.) contained in a long-necked reaction vessel, and maintained at the required temperature. After about nine half-lives, 5 ml. samples were removed and added to pentane (25 ml.) in a separating funnel. The pentane solution was shaken twice with conductivity water (2 x 10 ml.), and the aqueous extracts were titrated with standard (0.01M) sodium hydroxide solution, methyl red being used as the indicator. When azide ions were present, the indicator used was bromthymol blue. Where acid-alkali titration was inapplicable, e.g. where the solvolysis medium was formic acid, the aqueous extracts were analysed for chloride ion with silver nitrate, using the Volhard procedure. Recovery of hydrochloric acid from the reaction medium by the above extraction technique was shown to be better than 99%. Trial experiments were performed in which cinnamyl chloride alone was subjected to the extraction technique. No acid or chloride ions were detected.

For the solvolysis of cinnamyl chloride, the ratio of 1-phenylallyl to cinnamyl solvolysis product, r, is given by the expression:

$$r = k_1/k_3 = (\mathcal{E}_3 C_o - E_\infty)/(E_\infty - \mathcal{E}_1 C_o)$$

where k_1 and k_3 are the rate constants for the formation of the 1- and 3-phenylallyl solvolysis products respectively, C_o is the initial concentration (in mole/litre), and $\mathcal{E}_1$ and $\mathcal{E}_3$ are the molecular extinction coefficients at 2530 Å for the pure 1- and 3-phenylallyl solvolysis products.

The concentrations of the two solvolysis products (in mole/litre) obtained from 1-phenylallyl chloride were obtained as follows:

$$\begin{array}{llllllll} RCl & \longrightarrow & R'Cl & + & ROS & + & R'OS \\ a\ m/l & & b\ m/l & & c\ m/l & & d\ m/l \end{array}$$

$$E_{\infty} = \mathcal{E}_{R'Cl}.b + \mathcal{E}_{ROS}.c + \mathcal{E}_{R'OS}.d \qquad (1)$$

$$a = b + c + d \qquad (2)$$

$$T = c + d \qquad (3)$$

Solving the three simultaneous equations for c and d, we have:

$$d = \frac{E_{\infty} + T(\varepsilon_{R'Cl} - \varepsilon_{ROS}) - \varepsilon_{R'Cl} . a}{\varepsilon_{R'OS} - \varepsilon_{ROS}}$$

$$c = T - d$$

where a, b, c, d, are the concentrations in moles/litre of the starting material and the three products as indicated above, T is the concentration of the liberated acid, and ε_{ROS}, $\varepsilon_{R'OS}$, and $\varepsilon_{R'Cl}$ are the molecular extinction coefficients of the pure secondary and primary solvolysis products and of pure cinnamyl chloride respectively.

The overall rate constant k_t is given by the sum of the rate constants for the formation of the various products, i.e.

$$k_t = k_{R'Cl} + k_{ROS} + k_{R'OS}$$

$k_{R'Cl}$, k_{ROS} and $k_{R'OS}$ can be obtained by multiplying k_t by the concentrations of RCl, ROS and R'OS respectively, the concentrations being expressed as percentages of starting material.

Measurement of Polarimetric Rates

Runs in NN-dimethylformamide and 90% aqueous dioxan were carried out with the reaction mixture contained in the polarimeter tube. Those in ethanol at 22° were performed similarly. The mixture was prepared quickly at room temperature (ca. 20°), at a concentration of ca. 0.14M, and introduced by means of a narrow pipette into a 20 cm. polarimeter tube of about 2 ml. total capacity. The tube was provided with a metal outer jacket through which water at the required temperature was kept constantly circulating. After temperature equilibration (30 minutes at 40°, 10 minutes at 30°, 1 minute at 22°), the rotation was measured and taken as α_0. Further measurements were made at appropriate intervals. In between measurements, the tube, contained in a polythene bag, was kept immersed in the water thermostat.

Rotations were measured at 5893 Å on a Hilger and Watts Microptic photoelectric polarimeter. On this instrument, rotations could be read accurately to better than ± 0.002°.

The above technique could not be used for ethanolic solutions at 30° owing to the far higher rate of reaction under these conditions. A procedure similar to the one described for spectroscopic rate measurements was adopted. The organic chloride, contained in a short specimen tube, was placed into the reaction medium maintained at 30° in a long-necked reaction vessel. The vessel was shaken and a sample (0.10 ml.) was withdrawn immediately and diluted into a measured volume of ice-cold cyclohexane. Further samples were withdrawn and quenched at one minute intervals. The rotations of the cyclohexane solutions were measured at 3030 Å on a Rudolph Spectro-polarimeter.* This wave-length was used because the rotations were too small to be measured at 5893 Å owing to the increased dilution.

First order polarimetric rate constants were calculated from the expression

$$k_{pol} = (2.303/t) \log_{10} (\alpha_0/\alpha_t)$$

where t is the time in minutes and α_t is the rotation at that time.

Measurement of Z Values

Solutions of 1-ethyl-4-methoxycarbonylpyridinium iodide were prepared by weighing out 0.07g. quantities of the salt and dissolving them in 50 ml. of the ethanol/cyclohexane mixture. The resulting solutions had optical

* Courtesy of Prof. W. Klyne and Miss J. Jackson

densities of the order of 0.8-0.9 when contained in 1 cm. spectroscopic cells. The wave-lengths of maximum absorption for the various ethanol/cyclohexane mixtures were as follows:

Ethanol (% v/v)	$\lambda_{max.}$ (Å)
98	3620
90	3625
80	3635
70	3645
60	3655

Z values were calculated from the expression:

$$Z = h\bar{\nu} = 2.859 \times 10^5/\lambda_{max.}$$

Tracer Measurements

As isomerization to cinnamyl chloride occurs during the exchange reaction, it is necessary to distinguish between activity incorporated in the 1- and in the 3-positions. It was considered that if the composition of the organic chloride mixture in an aliquot of the reaction solution could be changed, without causing isomerization, then measurement of the activity of both mixtures and of their composition would yield a pair of simultaneous equations from which the activity at each position could be calculated for each aliquot. It was found that if a solution of the isomeric chlorides in dimethylformamide was shaken with its own volume of petrol (b.p. 60° - 80°), the secondary isomer was extracted preferentially, a change in composition of about 12% overall being achieved. The following procedure was therefore adopted.

The required volume of a standard solution of $LiCl^{36}$ in methanol was evaporated in a stream of nitrogen and the resulting solid dried by heating at 100°/0.5 mm. It was then dissolved in dimethylformamide to give the required concentration, and the reaction vessel was immersed in a thermostat at 40.0°. A weighed quantity of the organic chloride was then introduced to give a concentration of about 1 g./100 ml. A 5 ml. aliquot was withdrawn immediately and others at appropriate intervals. 1 ml. was added to a 10 cm. column containing Amberlite IRA-401, a strongly basic anion exchange resin, in the acetate form. The column was eluted with benzene. 0.1 ml. was diluted to 10 ml. with cyclohexane and its light absorption at 2530 Å subsequently measured. A further 1 ml. was set aside for subsequent hydrolysis in aqueous ethanol and titration of the liberated acid. The remaining solution (ca. 2.5 ml.) was shaken with an equal volume of petrol and spun on a hand centrifuge to assist the separation of the two layers. The upper (petrol) layer was then removed with a fine pipette and the remaining solution treated as above. The separation of the inorganic chloride on the column lasted about one hour during which time about 15 ml. of solution were collected. Separate columns were used for each aliquot and trial experiments showed that the retention of chloride ions under these conditions was 100%. Benzene was removed from the eluate by evaporation on a water pump at room temperature. 0.4 ml. quantities of the remaining solution were counted in nickel planchettes using a Geiger-Muller tube shielded in a lead castle.

The principal experimental difficulty in the above procedure lay in obtaining accurate activity readings. It is considered likely that anomalous results may have been due to the incomplete removal of benzene from the sample to be counted. Substitution of a more volatile solvent, e.g. acetone may lead to better results.

Examples of Kinetic Runs

(1) Hydrolysis of Cinnamyl Chloride

Concn. 4.983×10^{-4} g./100 ml.

Medium 60% Aqueous dioxan

Temp. 30.0°C.

Time (min.)	E	$10^3 k$ (min.$^{-1}$)
0	0.610	
15	0.583	5.743
80	0.489	5.774
110	0.458	5.774
154	0.420	5.651
180	0.402	5.617
210	0.382	5.691
240	0.367	5.664
1600	0.283	

k_{mean} 5.689×10^{-3} min.$^{-1}$

ROH (%) 51.2

(2) Hydrolysis of Cinnamyl Chloride

Concn. 4.475×10^{-4} g./100 ml.

Medium 50% Aqueous dioxan containing $LiClO_4$ (0.1M)

Temp. 30.0°C.

Time (min.)	E	10^2k (min.$^{-1}$)
0	0.537	
2	0.514	4.067
5	0.485	3.880
8	0.460	3.788
11	0.433	3.958
14	0.394	3.905
17	0.377	3.911
20	0.360	3.988
26	0.348	3.940
130	0.242	

k_{mean} 3.931×10^{-2} min.$^{-1}$

ROH (%) 51.0

(3) Ethanolysis of 1-Phenylallyl Chloride

Concn. 6.46×10^{-4} g./100 ml.

Medium 80% Ethanol/Cyclohexane

Temp. 30.0°C.

E_o 0.040, Sample contains 96.16% 1-phenylallyl chloride

Time (min.)	E	10^2k_t (min.$^{-1}$)
0	0.063	
2	0.082	3.027
5	0.112	3.302
7	0.130	3.332
9	0.147	3.355
11	0.162	3.338
14	0.183	3.332
17	0.202	3.289
20	0.218	3.307
25	0.244	3.303
33	0.278	3.337
37	0.290	3.297
42	0.305	3.315
135	0.0385	

k_{mean} 3.319×10^{-2} min.$^{-1}$

(4) Formolysis of 1-Phenylallyl Chloride

Concn. 2.80×10^{-2} g./100 ml.

Medium 22% Formic acid/Dioxan

Temp. 30.0°C.

$E^{1\%}_{1 cm.}$ 51.0, Sample contains 97.05% 1-phenylallyl chloride

1 ml. samples diluted to 10 ml. with cyclohexane

Absorption measured in 2 mm. cells

Time min.	sec.	E	10^2k_t (min.$^{-1}$)
0	0	0.042	
1	20	0.065	3.040
2	36	0.080	2.596
3	52	0.095	2.472
5	15	0.112	2.452
6	55	0.131	2.407
9	45	0.174	2.648
15	15	0.228	2.534
23	45	0.308	2.581
29	45	0.349	2.527
188	0	0.623	

k_{mean} 2.527×10^{-2} min.$^{-1}$

(5) Hydrolysis of 1-Phenylallyl Chloride

(Polarimetric run)

Concn.	2.244 g./100 ml.
Medium	90% Aqueous dioxan containing LiCl (0.014M)
Temp.	30.0°C.

Solvent blank + 0.070°

Time (min.)	α	$10^2 k_{pol}$ (min.$^{-1}$)
0	0.693	
5	0.640	1.774
10	0.600	1.608
15	0.551	1.722
20	0.511	1.705
25	0.469	1.782
30	0.439	1.745
35	0.403	1.788
40	0.369	1.834
45	0.345	1.818
1080	0.070	

k_{mean} 1.753×10^{-2} min.$^{-1}$

Example of the Determination of the Degree of Solvolysis of 1-Phenylallyl Chloride

1-Phenylallyl chloride (0.4805 g.) was dissolved in 80% aqueous dioxan (25 ml.). After 25 minutes at 30.0°, 2 x 5 ml. samples were withdrawn. Each sample was added to pentane (25 ml.) contained in a separating funnel, and the pentane solutions were extracted with water (2 x 10 ml.). The aqueous extracts were then analysed for hydrogen ions by titration with standard sodium hydroxide solution (1.482 x N/100).

Burette readings

2.	2.780 ml.	2.	4.660 ml.
1.	0.880 ml.	1.	2.780 ml.
	1.900 ml.		1.880 ml.

$$\text{Normality of reaction mixture} = \frac{1.89 \times 1.482}{5 \times 100}$$

Chloride contained 6.6% cinnamyl chloride.

Therefore degree of solvolysis = 47.5%

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