eight more times in the same manner, after which the ether was dried over anhydrous magnesium sulfate and the toluenesulfonate precipitated with pentane. Recrystallization from Skellysolve B gave 6.2 g. of material, m.p. 80.5–81.3°, acetolysis rate constant $(1.16 \pm 0.01) \times 10^{-6}$ sec.$^{-1}$ in 0.01 M solution at 50.0°. An ether solution (125 ml.) of this purified material (5.5 g.) was then subjected to nine more washes with 200-ml. portions of distilled water. Isolation of the solid and one recrystallization from Skellysolve B yielded 4.7 g. of material, m.p. 80.5–81.3°, acetolysis rate constant $(1.17 \pm 0.01) \times 10^{-6}$ sec.$^{-1}$ in 0.01 M solution at 50.0°.

Salts.—Lithium bromobenzenesulfonate and lithium perchlorate were prepared and handled in anhydrous acetic acid as described previously.[6e,9] Solutions of lithium acetate and lithium toluenesulfonate in anhydrous acetic acid were prepared as described previously[9] from lithium carbonate and toluenesulfonic acid.

Solutions of lithium toluenesulfonate were also prepared from solid material prepared as follows. To a solution of 18.5 g. (0.25 mole) of lithium carbonate in 600 ml. of acetic acid were added 95.1 g. (0.50 mole) of recrystallized p-toluenesulfonic acid monohydrate and 77 g. (0.75 mole) of pure acetic anhydride, and the mixture was heated overnight. Upon cooling, crystalline lithium toluenesulfonate separated. This product was recrystallized three times from acetic acid and dried for two days at 2 mm. and 140° over potassium hydroxide to yield 65 g. (73%) of salt.

Anal. Calcd. for $C_7H_7O_3SLi$: C, 47.20; H, 3.96; S, 18.00. Found: C, 46.94; H, 3.90; S, 17.57.

Tetra-n-butylammonium perchlorate was prepared by the method of Darwish[30] and Smith.[31] Two recrystallizations from an ethyl acetate–pentane mixture yielded material, m.p. 212–212.5° [reported[30,32] 213–213.5°, 213° and also[19] 203–204°.

(30) D. Darwish, Thesis, U.C.L.A., 1958.

(31) S. Smith, Thesis, U.C.L.A., 1959.

(32) M. B. Reynolds and C. A. Kraus, THIS JOURNAL, 70, 1709 (1948).

Anal. Calcd. for $C_{16}H_{36}O_4NCl$: C, 56.20; H, 10.61. Found: C, 56.47; H, 10.50.

Tetra-n-butylammonium acetate containing one mole of acetic acid of crystallization was prepared according to a method devised by Smith.[31] Five recrystallizations from ethyl acetate yielded material, m.p. 116.5–117.5°, equivalent weight by titration with perchloric acid in acetic acid solvent, 358 (calcd. 361.6).

Tetrabutylammonium toluenesulfonate was prepared as follows. To 53.4 g. (0.145 mole) of tetra-n-butylammonium iodide in 200 ml. of ethanol and 150 ml. of water was added excess freshly prepared silver oxide. The mixture was stirred until the supernatant liquid gave a negative test for iodide ion. After filtration and careful neutralization of the solution with toluenesulfonic acid monohydrate, the solvent was removed under reduced pressure to give 52 g. (87%) of crude material, m.p. 68–72°. The product was crystallized at low temperatures from ethyl acetate, yielding 35 g. of salt, m.p. 72–73°. Three more recrystallizations from ethyl acetate, followed by drying at 1.5 mm. over phosphorus pentoxide for several days, gave 28 g. of hygroscopic material, m.p. 73.5–74.5° (sealed tube).

Anal. Calcd. for $C_{22}H_{43}O_3NS$: C, 66.78; H, 10.48; S, 7.75. Found: C, 66.58; H, 10.51; S, 7.57.

Kinetic Procedure.—Anhydrous acetic acid designed to contain 0.01 M acetic anhydride was prepared in the usual way from reagent grade solvent. Karl Fischer titration on the final dried solvent always showed less than 0.002% water. Checks of the water content from time to time never showed more than a negligible increase in the percentage of water over periods of many months.

The titration methods and the rate measurements have been amply described.[9,33]

(33) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, 70, 821 (1948).

Intermediates and Transition States in Reactions of Allylic and Homoallylic Systems. II. Factors Affecting the Distribution of Products from Allylic Carbonium Ions

BY RICHARD A. SNEEN AND ARNOLD M. ROSENBERG

The distributions of products arising on methanolysis of the isomeric α-phenyl-γ-methyl- and α-methyl-γ-phenylallyl p-nitrobenzoates have been determined by a combination of kinetic and ultraviolet spectrophotometric techniques and were found to be identical; of the ethereal products each ester furnished 39% of α-phenyl-γ-methylallyl methyl ether and 61% of α-methyl-γ-phenylallyl methyl ether. Substitution of a p-methyl group into the phenyl ring of the γ-phenyl ester had no discernible effect on the product distribution; α-methyl-γ-p-tolylallyl p-nitrobenzoate underwent methanolysis to furnish the corresponding solvolysis products of which α-p-tolyl-γ-methylallyl methyl ether constituted 37.5 $\pm$ 1.5%. However when the solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate was conducted in 60 per cent. aqueous dioxane, α-phenyl-γ-methylallyl alcohol constituted only ca. 16% of the solvolysis product mixture.

Introduction

The first paper in this series[1] described the uncatalyzed first-order solvolysis of α-phenyl-γ-methyl- (RX) and α-methyl-γ-phenylallyl p-nitrobenzoate (R'X) in aqueous dioxane.[2] The former compound was found to be the more reactive by a factor of ca. 300 and to furnish, in addition to solvolysis products, the isomeric α-methyl-γ-phenylallyl p-nitrobenzoate. These results were interpreted in terms of a scheme involving an ion pair intermediate, common to the reactions of both allylic esters.

(1) R. A. Sneen, *J. Am. Chem. Soc.*, 82, 4261 (1960).

(2) In this as well as in the accompanying paper, the symbols RX and R'X will always refer to α-phenyl-γ-methyl- and α-methyl-γ-phenylallyl p-nitrobenzoate, respectively.
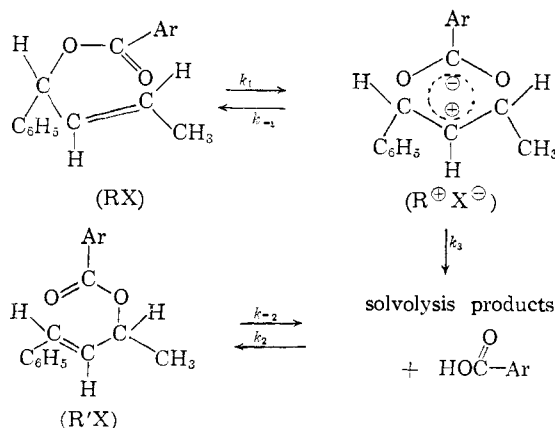
The present work is a continuation of these earlier experiments and was undertaken with a view toward unravelling the details of the solvolysis steps (summarized as k_3) of the reaction scheme and, if possible, the number and kinds of intermediate species capable of giving rise directly to solvolysis product. In particular we were interested in tracing down the factors which influence the rates of nucleophilic attack on the cationic centers in an unsymmetric allylic ion. We here describe the product distributions resulting from the solvolysis of the isomeric phenylmethylallyl p-nitrobenzoates under conditions of varying solvent (methanol and aqueous dioxane) and charge distribution in the ion (phenyl and p-tolylmethylallyl p-nitrobenzoates). In an accompanying paper[3] we describe the effect on product distribution of varied nucleophilic charge type (neutral solvents and azide ion), establish conclusively the existence of the intimate ion pair ($R^\ominus\ X^\ominus$) as a true intermediate in these solvolysis reactions, and provide evidence that neither solvent nor azide ion is capable of attacking this intimate ion pair at a rate commensurate with its rate of dissociation (or further ionization).

Results

A complicating feature we expected to encounter in the course of determining the product distributions resulting from the solvolyses of the isomeric allylic esters was the presumed instability of the less stable solvolysis product, ROS, under the conditions of its formation. In an attempt to obviate this difficulty, we carried out our initial solvolysis studies in anhydrous methanol in which, it was (mistakenly) assumed, the solvolysis products would be relatively more stable (with respect to the corresponding esters) than in the aqueous dioxane solvent systems used previously.[1] The kinetic results in methanol are recorded in Table I and are compared with selected results from earlier

TABLE I

RATES OF SOLVOLYSIS OF SOME ALLYL p-NITROBENZOATES IN METHANOL AND IN AQUEOUS DIOXIDE

Allyl p-nitro-benzoate	[ROpNB] $\times 10^2$	Solvent[a]	Temp., °C.	k, sec.$^{-1}$ $\times 10^5$	Infinity,[b] %
α-Phenyl-γ-methyl-	2.17	Methanol	35.0	8.38 ± 0.14	72.6
	2.27	60% D:W	25.0	7.07 ± .15	61.5
α-Methyl-γ-phenyl-	1.90	Methanol	65.0	1.51 ± .03	96.7
	2.27	60% D:W	50.0	0.619 ± .016	..
α-Methyl-γ-p-tolyl	1.74	Methanol	65.0	12.7 ± .3	97.6
		60% D:W	50.0	5.10 ± .06	..

[a] 60% D:W = 60 volume per cent. aqueous dioxane; data in this solvent taken from ref. 1. [b] Percentage of theoretical acid liberated after ten half-lives.

work in aqueous dioxane.[1] Solvolyses in methanol followed the pattern established in aqueous dioxane: α-phenyl-γ-methylallyl p-nitrobenzoate proved to be more reactive than its allylic isomer by a factor similar to that in aqueous dioxane, and it furnished rearranged ester in addition to solvolysis products, the extent of rearrangement being somewhat less (27%) than in 60% aqueous dioxane (39%); further, the rate enhancement effected by p-methyl substitution into α-methyl-γ-phenylallyl p-nitrobenzoate was nearly the same in

(3) R. A. Sneen and A. M. Rosenberg, J. Am. Chem. Soc., 83, 900 (1961).

methanol at 65° (8.4) as in 60% aqueous dioxane at 50° (8.25).

Analysis for reaction products resulting from solvolysis of the allyl esters involved the coupling of titrimetric and ultraviolet spectrophotometric techniques. Ultraviolet spectrophotometry appeared to be the obvious method for differentiating between the weakly absorbing unconjugated α-aryl products and the intensely absorbing conjugated γ-aryl products.[4] Since the p-nitrobenzoyl chromophore absorbs intensely in the region of the ultraviolet spectrum characteristic of the solvolysis products, it had to be removed before ultraviolet analysis. This involved the removal of not only p-nitrobenzoic acid but also, in the solvolyses of the α-aryl-γ-methylallyl p-nitrobenzoates, the removal of the acyl portion of the rearranged ester. This was accomplished by the hydroxide ion-catalyzed hydrolysis of the ester in the reaction mixture,[5] a reaction which proceeds via acyl–oxygen cleavage to produce the unrearranged alcohol. p-Nitrobenzoic acid was extracted from the resulting solution in the form of its salt by a process shown by control experiments to be quantitative. The resulting solution was then quantitatively diluted with methanol and analyzed by ultraviolet spectrophotometry at the wave length of maximum absorption.[6]

The resulting spectra are assumed to measure the combined concentrations of α-methyl-γ-arylallyl methyl ether (or alcohol in aqueous dioxone) resulting from solvolysis, and α-methyl-γ-arylallyl alcohol, obtained by saponification, since the absorption of unconjugated derivatives under these conditions is negligible.[7] Further, since the concentration of rearranged ester, and therefore of conjugated alcohol, are known from titration data, the concentrations of the isomeric methyl ethers, the solvolysis products, can be calculated.

Each step of this procedure was cross-checked for both precision and accuracy and the details of these control experiments are described in the Experimental. Incidentally, the absence of phenylbutadiene among the solvolysis products is established by the absence of any detectable absorption in the ultraviolet spectra at 280 mμ.[8]

Our first experiments were carried out with α-phenyl-γ-methylallyl p-nitrobenzoate. The ester was allowed to solvolyze in methanol at 35.0° under kinetic conditions for 10 half-lives (>99.9% reaction). The usual extraction procedure and ultra-

(4) E. A. Braude, E. R. H. Jones and E. S. Stern, J. Chem. Soc., 1087 (1947).

(5) Control experiments, described in the Experimental, established that all saponifications were carried out under conditions where the esters are stable to alkyl–oxygen fission.

(6) λ_{max} 252 mμ for phenylmethylallyl compounds and λ_{max} 256 mμ for p-tolylmethylallyl compounds.

(7) Attempts to prepare a pure sample of α-phenyl-γ-methylallyl alcohol for an accurate determination of its absorbance were unsuccessful; the product was always contaminated with small amounts of the much more intensely absorbing allylic isomer. Braude[4] has reported that, at the wave length of its maximum absorption, λ_{max} 251 mμ, α-methyl-γ-phenylallyl alcohol has ε 19,500 in ethanol and the isomeric α-phenyl-γ-methylallyl alcohol has ε 450. Probably some of the absorption observed with the latter compound was due to trace amounts of the more stable isomer. In any case, neglect of the absorbance of the α-phenyl isomer introduces into our calculations an error of, at most, less than 2.5%.

(8) Phenylbutadiene[4] has λ_{max} 280 mμ, ε 28,300.

TABLE II

PRODUCT DISTRIBUTIONS FROM UNBUFFERED SOLVOLYSES IN METHANOL AND AQUEOUS DIOXANE

Allyl p-nitro-benzoate	[ROpNB] $\times 10^3$	Solvent	Temp., °C.	Half-lives	Infinity,[d] %	ROMe,[e]%
α-Phenyl-γ-methyl	2.17	Methanol	35.0	10	72.6	34.3
				20	74.8	28.9
	1.89	60% D:W[a]	25.0	10	59.3	16.5
				20	60.0	15.1
	1.88	Methanol	{35.0	10[b]	99.3	99.7
			65.0}	20[c]	100.4	98.9
α-Methyl-γ-phenyl	2.28	Methanol	65.0	9.4	96.6	99.2
	1.90			12.5	96.7	(100)[f,g]
α-Methyl-γ-p-tolyl	1.74	Methanol	65.1	15.9	97.5	(100)[f,h]

[a] 60% D:W = 60 volume per cent. aqueous dioxane. [b] Ten half-lives of α-phenyl ester at 35.0° and 10 half-lives of γ-phenyl ester at 65.0°. [c] Ten half-lives of α-phenyl ester at 35.0° and 20 half-lives of γ-phenyl ester at 65.0°. [d] Percentage of theoretical acid liberated. [e] Percentage of α-aryl ether among solvolysis products: [α-ether/(α-ether + γ-ether)] × 100. [f] Assumed 100% and used to calculate extinction coefficient. [g] ϵ 1.86$_5$ × 10⁴. [h] ϵ 2.09$_4$ × 10.⁴

violet analysis described above indicated the reaction products to consist of 27.4% rearranged ester, 24.9% α-phenyl-γ-methylallyl methyl ether (ROMe) and 47.7% α-methyl-γ-phenylallyl methyl ether (R'OMe). Of the solvolysis products (excluding rearranged ester) the α-phenylallyl ether (ROMe) constituted 34.3%. The analysis was repeated after 20 half-lives of reaction, when it was found that the percentage of α-ether in the solvolysis products had dropped to 28.9%. Thus the α-ether is isomerized under the reaction conditions into the more stable γ-ether. This problem is intensified when the solvolysis is conducted under more vigorous conditions with the slower solvolyzing γ-aryl esters. Indeed, the isomerization was found to be essentially complete after 9.4 half-lives of reaction of γ-phenyl-α-methylallyl p-nitrobenzoate.[9] This conclusion was confirmed by an experiment in which α-phenyl-γ-methylallyl p-nitrobenzoate was allowed to react for 10 half-lives of reaction at 35° and the resulting reaction mixture was then transferred to a 65° bath and aliquots were allowed to react at this temperature for 10 and 20 half-lives of solvolysis of the γ-phenyl ester. Ultraviolet analysis of these solutions indicated the presence of 99.7% and 98.9% of α-methyl-γ-phenylallyl methyl ether, respectively.[10] These data are assembled in Table II.

Table II also records the product results of the methanolysis of α-methyl-γ-p-tolylallyl p-nitrobenzoate and the solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate in 60% aqueous dioxane. In this latter solvent, of course, the solvolysis products are alcohols. In contrast to the methanolysis results, the composition of the isomeric products in aqueous dioxane was constant, within experimental error, between 10 and 20 half-lives. This result suggests that α-phenyl-γ-methylallyl alcohol is more stable to acid-catalyzed rearrange-

(9) One can calculate that there should be less than 1% of the α-ether present at equilibrium.[1]

(10) Since authentic α-methyl-γ-phenylallyl methyl ether, prepared by the method of Kenyon,[11] was difficult to purify, the extinction coefficient of this ether was calculated from the absorption spectrum resulting from solvolysis of highly purified α-methyl-γ-phenylallyl p-nitrobenzoate, assuming quantitative conversion of this ester to the γ-phenyl ether. It was calculated to be ε 1.86₅ × 10⁴. Analyses of the spectra resulting from solvolysis of the α-phenyl methyl ester for 10 and 20 half-lives of the γ-phenyl ester provide a good internal check on this value (see Table II).

(11) J. Kenyon, S. M. Partridge and H. Phillips, J. Chem. Soc., 207 (1937).

ment (with respect to the α-phenyl ester) in aqueous dioxane than is the α-phenyl methyl ether (with respect to the ester) in methanol.

The data of Table II permit an accurate evaluation of the kinetically-controlled product distribution from the solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate in aqueous dioxane and suggest that an approximate distribution of the products from methanolysis of this ester can be calculated by extrapolation of the data at 10 and 20 half-lives (ca. 39% α-phenyl ether). However we wished, for several reasons, to establish that a similar product distribution results from both allylic isomeric esters. Accordingly we undertook to carry out these solvolyses under buffered conditions in order to slow down the acid-catalyzed isomerization of the initially formed products.

The first buffer tried, sodium phenoxide, was found to be too nucleophilic with the result that the esters reacted by a non-carbonium ion process, the first step of which involved acyl–oxygen cleavage of the p-nitrobenzoate ester, followed by a very interesting sequence of reactions which culminated in the formation of dimethyl ether by a reaction of the type labeled B_{Al}^2 by Ingold.[12] This series of reactions is discussed in detail elsewhere.[13]

Sodium acetate proved to be a satisfactory buffer for all of the systems investigated in this work, although even this relatively weak nucleophile attacked the carbonyl groups of the slower-solvolyzing esters to some extent.

The data for the runs carried out in the presence of sodium acetate are found in Table III. It is immediately apparent from these data that sodium acetate has effectively quenched any isomerization of the initially formed products of solvolysis, even in the case of the slowest solvolyzing ester, α-methyl-γ-phenylallyl p-nitrobenzoate. Further it can be seen that in the case of the rapidly solvolyzing α-phenyl ester, the presence of sodium acetate has negligible effect on either the rate of reaction or the amount of the theoretical acid liberated after ten half-lives. Thus one can conclude that, with this ester, acetate ion does not compete with solvent for carbonium ion, nor does acetate ion attack the carbonyl group of the ester at a rate comparable with ionization. (Further, the magni-

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., pp. 765 et seq.

(13) R. A. Sneen and A. M. Rosenberg, J. Org. Chem., in press.

TABLE III
PRODUCT DISTRIBUTIONS FROM BUFFERED SOLVOLYSES IN METHANOL AT 65.0°

Allyl p-nitrobenzoate	[ROpNB] X 10³	[NaOAc] X 10³	k, sec.$^{-1}$ X 10⁶	Half-lives	Infinity,[a] %	α-Ether,[b] %
α-Phenyl-γ-methyl	2.17	..	8.38 ± 0.14[d]	10	72.6	34.3
	1.87	1.80	8.45 ± .14[d]	10	74.0	39.1
α-Methyl-γ-phenyl	1.90	..	1.51 ± .03	12.5	96.6	..
	1.90	1.86	1.66 ± .06	>10	83.6	36.9
	1.91	1.88	1.68 ± .03	>10	83.5	34.8
	1.86	5.45	2.07 ± .08	8.2	65.4	38.7
				18	64.0	39.5
α-Methyl-γ-p-tolyl	1.74	..	12.7 ± .3	15.9	97.8	..
	1.77	1.85	13.5 ± .3	16.9	97.2	37.5[e]
				30.9	96.6	

[a] Percentage of theoretical acid liberated. [b] Percentage of α-aryl ether among solvolysis products: [α-ether/(α-ether + γ-ether)] X 100. [e] ± 1.5; limits defined by extreme assumptions that acid unaccounted for (2.8%) is either in the form of α-aryl products (36.0%) or γ-aryl products (39.0%). [d] Temperature, 35.0°.

tude of the salt effect of sodium acetate at this concentration is shown to be negligible.)

With the slower solvolyzing α-methyl-γ-phenyl-allyl ester, however, an acyl–oxygen cleavage reaction must be invoked to explain both the rate enhancement as well as the decreased formation of acid. The measured rate of reaction is, presumably, the sum of the ordinary first-order solvolysis reaction and a second order acetate- or methoxide-catalyzed process, either of which would result in the destruction of starting material without a concomitant production of acid.[14]

Since the acetate-catalyzed cleavage reaction proceeds by acyl–oxygen fission, the ultraviolet data have been treated assuming that methanolysis of α-methyl-γ-phenylallyl p-nitrobenzoate furnished unrearranged α-methyl-γ-phenylallyl alcohol in an amount equal to the discrepancy between the observed infinity titer and 100%.

Discussion

The problem of identifying the factors responsible for the distribution of products which result when an allylic or homoallylic carbonium ion is attacked by nucleophilic agents has been a puzzling one. Some of the more interesting features of this problem are dramatically evident in the reactions of the cyclocholesteryl cation[15]; this ion on methanolysis furnishes 90 ± 2% of 6β-cyclocholesteryl methyl ether and 10 ± 2% of the homoallylic cholesteryl methyl ether. Since the cyclic 6β-derivative is some 9 kcal. less stable than its isomer,[16] product stability is not an important factor in determining their rates of formation. Nor can steric effects of any normal kind be of significance in determining product ratios since the transition states for formation of the axial 6β-derivatives are certainly the more sterically hindered, being flanked by the C₉-angular methyl group.

It occurred to us that the position of attack in resonating carbonium ions by nucleophiles may be

largely a function of the charge distribution in the ion, an idea first advanced by Hammond.[17] Although the distribution of charge in the cyclocholesteryl cation is not known with certainty it may be concentrated heavily at the C₆-position.[18] Further support for this point of view is lent by the results of studies[19] of the solvolyses of a series of unsymmetrically substituted allylic chlorides under limiting conditions; whereas the silver oxide-catalyzed hydrolysis of α-methylallyl chloride furnishes 33% of the primary isomeric alcohol, α,α-dimethylallyl chloride under the same conditions furnishes only 15% of the corresponding primary isomer.

The homologous phenylmethyl- and p-tolylmethylallyl carbonium ions appeared to be suitable systems in which to test the importance of charge distribution in determining the rates of product formation. In the event that the introduction of a p-methyl group significantly affects the product distribution, the importance of charge distribution in the intermediate ion is established. In the event that this substitution does not affect product distributions, either or both of two consequences must follow: either charge distribution in the ion is unimportant in determining product distributions or substitution of a p-methyl group into the phenylmethylallyl carbonium ion affects both positive centers similarly. Experimentally it was found that *p-methyl substitution had no detectable effect on the distribution of products of methanolysis* (see Table III). Since evidence presented in the accompanying paper suggests that charge distribution in the ion *is* of importance in determining the rate of reaction with nucleophiles,[20] it is our feeling that this insensitivity of product distribution to p-methyl substitution is a result of the second alternative listed above; namely, that p-methyl substitution affects the electronic distribution at both allylic centers similarly. Substantiating evidence for this view comes from two related sources: first the effects of p-methyl substitution on the rates of solvolysis of α-phenyl-γ-methyl-(10.4) and α-methyl-γ-phenylallyl p-nitrobenzoate (8.6) are appreciable but similar; and second, the ratio of

(14) It is easily shown that either of these processes requires the existence of quantitative relationships among the observed acid titer at infinite time, the rate enhancement (after empirical correction for salt effects), the ultraviolet spectral data and the concentration of sodium acetate. It was found that all of the data obtained in the run at 5.42 X 10⁻³ M sodium acetate conform to predictions from the data at lower acetate concentrations.

(15) E. M. Kosower and S. Winstein, J. Am. Chem. Soc., 78, 4347 (1956).

(16) S. Winstein and E. M. Kosower, ibid., 81, 4399 (1959).

(17) G. S. Hammond, ibid., 77, 334 (1955).

(18) M. Simonetta and S. Winstein, ibid., 76, 18 (1954).

(19) R. H. DeWolfe and W. G. Young, Chem. Revs., 56, 794 (1956).

(20) Azide ion competes with solvent for the p-tolylmethylallyl carbonium ion more than three times as effectively as it does for the phenylmethylallyl carbonium ion.²

rates of formation of α-phenyl-γ-methyl- and α-methyl-γ-phenylallyl p-nitrobenzoate from the allylic ion pair (60/40) is similar to the corresponding ratio of rates from the p-tolylmethylallyl p-nitrobenzoate ion pair (53/47).[21] All of these lines of reasoning point to the conclusion that the corresponding transition states resemble very closely the ionic intermediates and that reactions of these ionic intermediates take place *via* very fast, exothermic, unselective processes. Finally, the observation that methanolysis of α-methyl-γ-phenylallyl p-nitrobenzoate furnished a distribution of solvolysis products different from that of solvolysis of this ester in 60% aqueous dioxane is not surprising in view of the similar variations in product distributions accompanying change in solvent in other allylic[19] and homoallylic[15] systems. However, at present there appears to be no simple explanation for these variations which are presumably associated with solvation effects.

Experimental

Materials.—The preparation of the allylic alcohols and p-nitrobenzoate esters has been described previously.[1,11,22] An improved recrystallization procedure for the phenylmethylallyl esters was developed using pentane–carbon disulfide mixtures which furnished α-phenyl-γ-methylallyl-p-nitrobenzoate, m.p. 99.5–100.5° (lit.[1] 96.5–98°), and α-methyl-γ-phenylallyl p-nitrobenzoate, m.p. 59–60° (lit.[1] 59°).

Rate Measurements.—The procedure used for runs in aqueous dioxane has already been described.[1] Kinetic runs in methanol were similar. Technical grade methanol was purified by refluxing for 2 hours over magnesium turnings and was then distilled.[23] In general, weighed samples of an ester and, in some cases, sodium acetate (J. T. Baker analyzed) were placed in a volumetric flask and dissolved to 100 ml. of solution with methanol. For kinetic runs at 25 and 35°, these volumetric flasks were placed in a constant temperature bath. The runs at 50 and 65° were conducted in sealed glass ampoules. Portions of the reaction mixture were divided among seventeen glass ampoules, sealed under nitrogen and introduced into a constant temperature bath. In all cases 5-ml. aliquots were removed at appropriate time intervals, quenched in 10 ml. of commercial grade acetone and titrated to the phenolphthalein end-point with *ca.* 2.0 × 10⁻² M aqueous sodium hydroxide, previously standardized against potassium acid phthalate. In all cases a blank was determined on the solvent–quench system. Nearly all of the runs for which rate data are reported are averages of from eight to fifteen separate kinetic points. The precision within a run was usually about 2–3% and separate runs under identical conditions gave results reproducible well within their combined experimental uncertainties. Wherever product distribution calculations required both kinetic and ultraviolet measurements, aliquots of the same reaction mixture were used to obtain both types of data.

Spectral Measurements.—All ultraviolet spectral measurements were made using a Cary, model 10-11M, recording spectrophotometer. Absorbancy readings were recorded. The maximum absorbancy readings were usually in the 0.3 to 0.7 region. Slit widths were determined by the needs of the instrument when the sensitivity was set at zero and never exceeded 0.1 mm. Matched, fused, 1-cm. quartz cells were used and temperature was maintained by flowing tap water. Solutions of pure compounds in methanol were prepared for ultraviolet analysis by weighing known quantities of the compounds into methanol and diluting quantitatively with methanol to the appropriate

(21) Because of the experimental uncertainties in the kinetic method used to evaluate these rate ratios the differences between the two systems may not be real.

(22) J. Kenyon, S. M. Partridge and H. Phillips, *J. Chem. Soc.*, 85 (1936).

(23) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 360.

concentration. p-Nitrobenzoic acid had λ_{max} 257 mμ, ε 1.1₈ × 10⁴; α-phenyl-γ-methylallyl p-nitrobenzoate had λ_{max} 258 mμ, ε 1.6₄ × 10⁴; α-methyl-γ-phenylallyl alcohol had λ_{max} 251 mμ, ε 1.81₈ × 10⁴.

Ultraviolet analysis of the solvolysis product mixtures was preceded by the removal from the reaction mixtures of all forms of the p-nitrobenzoyl group. In those cases in which α-methyl-γ-phenylallyl p-nitrobenzoate is a reaction product the procedure was as follows: a 5-ml. aliquot of the reaction mixture was transferred to a 60-ml., short-stemmed separatory funnel which contained 5 ml. of water and 5 ml. of a 0.04 M alcoholic potassium hydroxide solution. The funnel was shaken and the mixture allowed to stand for 3 hr. After this time 25 ml. of water was added and the resulting solution was extracted four times with 10-ml. portions of ether. The combined ethereal layers were then extracted five times with 10-ml. portions of aqueous 0.04 M potassium hydroxide and diluted quantitatively with methanol to the appropriate final concentrations. In those cases where the reaction mixture to be analyzed contained no p-nitrobenzoate ester, the procedure was the same except that no time was allowed for saponification.

Analysis for products of solvolysis in aqueous dioxane was similar, the only difference being in the composition of the saponification mixture; a 5-ml. aliquot was diluted with 5 ml. of alcoholic 0.04 M potassium hydroxide, 3 ml. of water and 2 ml. of absolute ethanol.

Saponification of α-methyl-γ-phenylallyl p-nitrobenzoate at room temperature under the conditions of the above procedure proved to have a half-life of *ca.* 990 seconds. Since the saponification mixtures (for both methanolysis and aqueous dioxane solvolysis) are considerably poorer ionizing solvents than is 60% aqueous dioxane,[24] the fact that the half-life for solvolysis of α-methyl-γ-phenylallyl p-nitrobenzoate in this latter solvent at 25°, is $t^1/_2$ = 800 hr. establishes that solvolysis of this ester under saponification conditions is negligible.

That the extraction procedure described above was quantitative is established indirectly by the general con-

TABLE IV

METHANOLYSIS OF 2.17 × 10⁻² M α-PHENYL-γ-METHYL-ALLYL p-NITROBENZOATE AT 35.0°

Titrimetric data

Titrant + 2.068 × 10⁻² M potassium hydroxide; blank (solvent + quench): 0.314 ml. titrant; theoretical infinity titer: 5.249 ml. titrant.

Time, sec.	Titrant, ml.	k, sec.⁻¹ × 10⁵
0	0.760	..
2066	1.284	8.23
2862	1.452	8.08
3832	1.662	8.16
4729	1.858	8.37
6038	2.095	8.39
7076	2.280	8.50
10089	2.700	8.53
14959	3.181	8.52
18643	3.470	8.80ᵃ
10 half-lives	4.122	..
20 half-lives	4.238	..

Av. 8.38 ± 0.14

% of theory = (4.122 − 0.314)/5.249 × 100 = 72.6%

Ultraviolet dataᵇ

Time, half-lives	Wave length, mμ	Absorbancy, A ᶜ
10	252	1.51
20	252	1.57

ᵃ Deleted in calculating rate. ᵇ Obtained by subjecting a 5-ml. aliquot of reaction mixture to the usual extraction procedure and diluting with methanol to a total volume of 1 l. ᶜ Absorbancy, $A = \epsilon lc$, where l is the length of the cell in cm., c is the concentration in moles/l. and ε the extinction coefficient.

(24) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 78, 2770 (1956).

sistency of all of the data presented in this paper. In addition, p-nitrobenzoic acid was separately shown by ultraviolet analysis to be completely removed from a methanolic solution by the extraction procedure. It was further established that the non-acidic solvolysis products of α-methyl-γ-phenylallyl p-nitrobenzoate (under unbuffered conditions in 60% aqueous dioxane) are quantitatively retained in the organic phase during the extraction procedure since, after dilution with methanol, the ultraviolet absorbance of the products was within 1% of that calculated from the separately determined absorbancy of pure authentic α-methyl-γ-phenylallyl alcohol. Actually the extinction coefficients of α-methyl-γ-phenylallyl methyl ether (ϵ 1.86$_5$ × 10^4) and of α-methyl-γ-p-tolylallyl methyl ether (ϵ 2.09$_4$ × 10^4, λ_{max} 255 mμ) were calculated from the spectra obtained from infinity samples of the methanolysis products of the corresponding p-nitrobenzoate esters (see Table II).

The ultraviolet data for α-methyl-γ-p-tolylallyl alcohol were obtained by saponification of the corresponding p-nitrobenzoate, followed by the usual extraction procedure: λ_{max} 255 mμ ϵ 2.05$_2$ × 10.^{4}

The data from a typical run are summarized in Table IV.

Calculations.—The data of Table IV will serve to illustrate the method used in calculating the product distributions reported in this work. The percentage of the theoretical acid liberated at 10 half-lives defines the concentration of rearranged ester; thus [R'X] = [R'OH] = 0.274 × 2.17 × 10^{-2}M. The absorbancy, A, was determined

after dilution of the reaction mixture by a factor of 200 and is assumed to measure the combined concentrations of γ-aryl derivatives R'OMe and R'OH (produced on saponification of R'X) with extinction coefficients $\epsilon_{R'OMe}$ = 1.86$_5$ × 10^4 and $\epsilon_{R'OH}$ = 1.83$_2$ × 10^4, respectively. Then

$$A = [R'OH]\,\epsilon_{R'OH} + [R'OMe]\,\epsilon_{R'OMe}$$

At ten half-lives

$$A = 1.51 = \frac{0.274 \times 2.17 \times 10^{-2}}{200} \times 1.832 \times 10^4 +$$
$$[R'OMe] \times 1.865 \times 10^4$$

and [R'OMe] = 5.177 × 10^{-5}. Therefore the concentration of γ-ether before dilution equals 200 × 5.177 × 10^{-5} = 1.035 × 10^{-2}M.

By difference, the concentration of α-phenyl ether is calculated to be 5.40 × 10^{-3}M. Thus the products of solvolysis at 10 half-lives consist of 27.4% rearranged ester (R'X), 47.7% γ-phenyl ether (R'OMe) and 24.9% α-phenyl ether (ROMe); and of the solvolysis products, α-phenyl ether constitutes 24.9/(24.9 + 47.7) × 100 = 34.3%.

Intermediates and Transition States in Reactions of Allylic and Homoallylic Systems. III. Reactions of Intimate Ion Pairs

By Richard A. Sneen and Arnold M. Rosenberg

Solvolyses of α-phenyl-γ-methyl-, α-methyl-γ-phenyl- and α-methyl-γ-p-tolylallyl p-nitrobenzoate have been carried out in methanol and in 60 volume per cent. aqueous dioxane in the presence of varying concentrations of sodium azide, conditions under which alkyl azides are formed by carbonium ion processes. The presence of sodium azide was found to have essentially no effect on the total rate of reaction nor did it depress significantly the amount of rearranged ester produced during the solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate.[1,2] Most of the alkyl azide arises at the expense of allyl ethers (in methanol) or alcohols (in aqueous dioxane). It is concluded that, for the most part, azide ion enters the reaction scheme only at a later stage than those which determine the rate of reaction and the amount of rearrangement products. It is shown that, both in methanol and in aqueous dioxane, only one of the two possible allylic azides is produced in measureable amounts; the α-methyl-γ-arylallyl azides are formed to the exclusion of their allylic isomers. An argument is developed which establishes definitely an ion pair as an intermediate in these solvolysis reactions. The reactivity of this ion pair intermediate was investigated and it is shown that neither solvent nor azide ion is capable of attacking it at a rate commensurate with its rate of dissociation.

Introduction

The first two papers in this series[1,2] have reported the results of an investigation into the solvolytic behavior of an isomeric pair of allylic esters, α-phenyl-γ-methylallyl- and α-methyl-γ-phenylallyl p-nitrobenzoate. The first paper dealt mainly with a study of the rates of reaction of the isomeric esters whereas the second paper reported the results of a study of the product ratios obtained when each ester undergoes solvolysis. Both kinetic and product data were determined under conditions of varying solvent (methanol and aqueous dioxane) and of varying substitution (phenyl- and p-tolylmethylallyl p-nitrobenzoates).

In an attempt to identify further of the mechanistic details of the processes involved in these solvolytic reactions we initiated a series of experiments in which solvolyses were conducted in the presence of the highly nucleophilic azide ion, a technique first used to advantage in the elucidation of reaction mechanisms by the University

College school.[3] The results of these experiments, which constitute the work described in the present paper, establish conclusively the existence of an intimate ion pair as a discrete intermediate in these solvolysis reactions and provide evidence that neither solvent nor azide ion is capable of attacking this species at a rate commensurate with its rate of dissociation.

The esters investigated in this work were the isomeric α-phenyl-γ-methyl- and α-methyl-γ-phenylallyl p-nitrobenzoates as well as α-methyl-γ-p-tolylallyl p-nitrobenzoate. Each of these esters was allowed to solvolyze in the presence of varying concentrations of azide ion under conditions otherwise identical with those described in the two previous papers of this series.[1,2] The presence of azide ion in the solvolyzing mixture altered the course of these solvolyses by providing an alternate route of reaction for the destruction of ester, the formation of alkyl azides; and the incursion of this reaction affected not only the stoichiometry

(1) R. A. Sneen, J. Am. Chem. Soc., **82**, 4261 (1960).
(2) R. A. Sneen and A. M. Rosenberg, ibid., **83**, 895 (1961).
(3) See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., pp. 353 et seq.