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 ($\epsilon$ 1.86$_5$ × 10$^4$) and of α-methyl-γ-*p*-tolylallyl methyl ether ($\epsilon$ 2.09$_4$ × 10$^4$, $\lambda_{max}$ 255 m$\mu$) 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: $\lambda_{max}$ 255 m$\mu$ $\epsilon$ 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%.

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# 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.*

TABLE I

KINETICS AND PRODUCTS OF THE SOLVOLYSES OF SOME ALLYL p-NITROBENZOATES IN THE PRESENCE OF SODIUM AZIDE

| Allyl p-nitro-benzoate | Solvent[a] | [ROp·NB] × 10² | [NaN₃] | Temp., °C. | k, sec.⁻¹ × 10⁵ | Half-lives | Acid,[b] % | Ester,[c] % | Azide,[d] % | α-Aryl solv., prdts.,[e] % | α-Azide,[f] % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| α-Phenyl-γ-methyl | MeOH | 1.87 | ...[i] | 35.0 | 8.45 ± 0.14[i] | 10 | 74.0 | 26.0 | .. | 39.1 | ... |
| | MeOH | 1.87 | 0.0770 | 35.0 | 9.47 ± .28 | 12.5 | 68.4 | 24.8 | 6.8 | 34.6 | −0.6 |
| | | | | | | 22.5 | | | | 32.6 | −2.1 |
| | MeOH | 1.84 | .154 | 35.0 | 10.0 ± .1 | 10 | 61.9 | 21.6 | 16.5 | 33.0 | 1.8 |
| | | | | | | 24.6 | | | | 31.3 | 0.4 |
| | MeOH | 1.86 | .290 | 35.0 | 11.1 ± .5 | 11.3 | 54.6 | 22.2 | 23.2 | 30.1 | 2.4 |
| | D:W | 1.89 | .... | 25.0 | 7.3 ± .6[i] | 10 | 59.2 | 40.7 | .. | 16.5 | ... |
| | D:W | 1.68 | 0.153 | 25.0 | 6.9 ± .8 | 10 | 34.1 | 32.6 | 33.3 | .. | ... |
| | D:W | 1.68 | .153 | 25.0 | 7.84 ± .42 | 7.6 | 32.9 | 34.4 | 32.7 | 7.9 | 0.0 |
| | D:W | 1.61 | .448 | 25.0 | 6.69 ± .15 | 10 | 19.5 | 28.9 | 51.6 | −3.4 | −5.5 |
| α-Methyl-γ-phenyl | MeOH | 1.90 | .... | 65.0 | 1.66 ± .06[i] | .. | .. | .. | .. | .. | ... |
| | MeOH | 1.77 | 0.077 | 65.0 | 2.03 ± .12 | 12.4 | 64.4 | .. | 35.6[g] | 25.0 | −0.1 |
| | | | | | | 17.5 | | | | 23.4 | −1.7 |
| α-Methyl-γ-p-tolyl | MeOH | 1.74 | .... | 65.1 | 12.7 ± .3[i] | 15.9 | 97.5 | .. | .. | .. | ... |
| | MeOH | 1.48 | 0.291 | 65.1 | 17.7 ± 1.0 | 18.8 | 33.9 | .. | 66.1 | 13.2 | 2.0 |
| | | | | | | 43.1 | 33.8 | | 66.2 | | |
| | MeOH | 1.78 | .0403 | 65.0 | ..........[h] | 10.0 | 76.6 | .. | 23.4 | .. | ... |
| | MeOH | 1.79 | .0498 | 65.0 | ..........[h] | 10.0 | 72.0 | .. | 28.0 | .. | ... |
| | MeOH | 1.80 | .0749 | 65.0 | ..........[h] | 10.0 | 64.0 | .. | 36.0 | .. | ... |
| | MeOH | 1.79 | .149 | 65.0 | ..........[h] | 10.0 | 51.2 | .. | 48.8 | .. | ... |

[a] D-W 60 volume per cent. aqueous dioxane. [b] Percentage of theoretical acid liberated. [c] Percentage of rearranged ester. [d] Percentage of alkyl azide formed. [e] Percentage of solvolysis products (excluding rearranged ester) in α-aryl form = ([ROS] + [RN₃])/([ROS] + [RN₃] + [R'OS] + [R'N₃]) × 100. [f] Percentage of initial ester calculated to be in form of α-aryl-γ-methylallyl azide = [RN₃]/[ROpNB]ᵢ. [g] Since acyl–oxygen cleavage by azide ion is involved in this run this quantity does not necessarily measure the percentage of alkyl azides. [h] No kinetic data were obtained for these four runs. Data taken from ref. 2. [i] [NaOAc] = 1.80 × 10⁻² M.

of the reactions but also, to a lesser extent, the kinetic behavior. The pertinent kinetic and product distribution data are recorded in Table I.

The kinetics of reaction were followed, as previously described,[1] by titration of the liberated p-nitrobenzoic acid. With all three esters, the percentage of the theoretical acid liberated at infinity (≥10 half-lives) was less than in the control runs without added azide ion. In the case of the γ-aryl-α-methylallyl esters this decrease in infinity titer is presumed a measure of the amount of alkyl azide produced. With α-phenyl-γ-methylallyl p-nitrobenzoate, however, a compound whose solvolyses in methanol and aqueous dioxane have been shown to be accompanied by a non-acid-producing rearrangement, it was desirable to determine whether the alkyl azide formation, associated with the lowered infinity titers, had occurred at the expense of rearranged ester. Accordingly infinity solutions were subjected to quantitative saponification. The base consumed during this process is assumed to measure the concentration of rearranged ester present in the solvolysis reaction mixture. The amount of alkyl azides formed was then determined by difference.

Rate constants were calculated using the experimental rather than the theoretical infinity titer, a procedure which can be shown to evaluate the sum of the rates of all concurrent processes for the destruction of starting material. The rate constants of Table I therefore measure the sum of the rates of formation of solvolysis products (ethers or alcohols), alkyl azides and, with the α-phenyl ester, rearranged ester.

Product analyses were carried out as described in the accompanying paper,[2] using a combination of titrimetric and ultraviolet spectrophotometric techniques. Aliquots of the reaction mixture were subjected to basic saponification conditions, where necessary, to solubilize all p-nitrobenzoyl groups. After basic extraction of p-nitrobenzoic acid, the resulting solutions were quantitatively diluted with methanol for ultraviolet analysis. The extinction coefficients of the γ-aryl-α-methylallyl azides have not been measured directly. However in view of the fact that the corresponding alcohols and methyl ethers have coefficients identical within 2%,[2] we have assumed the α-methyl-γ-arylallyl azide to have an extinction coefficient equal to that of the corresponding methyl ether (in methanolysis runs) or alcohol (aqueous dioxane runs).[4] The data of the penultimate column in Table I, which represent the percentage of the total solvolysis product (excluding rearranged ester) in the α-aryl form, have been calculated on this basis.

The data of the last column of Table I have been calculated assuming that the ratios of isomeric ethereal or alcoholic solvolysis products are unchanged by the presence of azide ion. These ratios were reported in the preceding paper.[2] Justification for this assumption will be found in the discussion section of this paper.

The rate data of Table I make it apparent that the rate-determining step in the solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate remains es-

(4) Further justification for this assumption is provided by the fact that benzhydryl azide, prepared in situ by the solvolysis of benzhydryl chloride in aqueous dioxane containing sodium azide, was found to have ε 567 at λmax 258 mμ. Since 2-octyl azide is reported[5] to have ε ~10 at λ 258 mμ, the absorption due to the phenyl rings of benzhydryl azide is within 6% of that found for benzhydrol (ε 527, λmax 258 mμ).

(5) P. A. Levene and A. Rothen, J. Chem. Phys., 5, 985 (1937).

sentially unchanged in the presence of azide ion; thus, although the reaction products are dramatically altered in the presence of this salt, the total rate of reaction is nearly independent of the azide concentration in aqueous dioxane and shows only a small positive salt effect in methanol. Apparently, azide becomes involved only subsequent to the rate-determining step of the reaction.

With the slower-solvolyzing $\alpha$-methyl-$\gamma$-phenylallyl $p$-nitrobenzoate however, it is equally apparent that a modest concentration of azide ion significantly accelerates the rate of reaction. It is presumed that this rate enhancement reflects the incursion of a second-order acyl–oxygen cleavage reaction involving either azide or methoxide ion, a reaction analogous to the acetate-catalyzed reaction observed with this same ester.[2] Consistent with the proposed mechanism is the low infinity titer. No further attempts were made to clarify the details of this reaction but the available data serve as a useful control experiment (see below).

In the case of $\alpha$-methyl-$\gamma$-$p$-tolylallyl $p$-nitrobenzoate, intermediate in solvolytic reactivity between the methylphenylallyl esters, it appears that the azide-catalyzed acyl–oxygen fission reaction is of negligible importance. This conclusion follows from the fact that, at comparable concentrations of sodium azide (0.29 $M$), the rate enhancement observed with the $p$-tolyl ester (39.5%) is similar to that observed with $\alpha$-phenyl-$\gamma$-methylallyl $p$-nitrobenzoate (30.5%). Further, if it is assumed that the rate of the azide-catalyzed acyl–oxygen cleavage reaction is identical for $\alpha$-methyl-$\gamma$-phenyl- and $\alpha$-methyl-$\gamma$-$p$-tolylallyl $p$-nitrobenzoate, it can be calculated that greater than 90% of the amount of azide reported in Table I to arise from the $p$-tolyl ester does so by the usual solvolytic mechanism. This conclusion will be of importance in the discussion.

In the accompanying paper[2] it was shown that the initially-formed methanolysis products could be stabilized by the buffering action of sodium acetate. From the data of Table I it is apparent that this function is also served by sodium azide[6] since the product distributions are constant with time.[7]

## Discussion

It will be convenient to discuss the results of this work in two sections; the first will deal with product distributions and the second will discuss the kinetic implications.

**Product Distributions.**—In the preceding paper[1] we reported the results of a series of experiments designed to isolate the factors which determine the point of attack of a nucleophilic agent on an allylic carbonium ion. It was found there that the carbonium ion, produced on methanolysis of either $\alpha$-phenyl-$\gamma$-methylallyl $p$-nitrobenzoate or its allylic isomer, furnished 39% of $\alpha$-phenyl-$\gamma$-methylallyl methyl ether. Substitution of a $p$-methyl group into the phenyl ring of the solvolyzing ester was

found to have no detectable effect on the product distribution, 37.5 $\pm$ 1.5% of the corresponding $\alpha$-$p$-tolyl-$\gamma$-methylallyl methyl ether being produced. A change in solvent, however, did effect a change in product distribution; only 16% of $\alpha$-phenyl-$\gamma$-methylallyl alcohol was formed on solvolysis of the corresponding ester in 60% aqueous dioxane. Further, a kinetic argument, developed in the first paper of this series,[1] suggested that the $p$-nitrobenzoate anion attacks this carbonium ion to furnish 53–60% of $\alpha$-phenyl-$\gamma$-methylallyl $p$-nitrobenzoate although this result is admittedly open to a large experimental uncertainty.

It seemed of interest, therefore, to measure the distribution of allylic products arising when the phenylmethylallyl carbonium ion is attacked by another negatively-charged nucleophile, azide ion, which is known to be a linear species[8] and which could only with difficulty adopt the pseudo-six-membered ring geometry assumed to exist in the $p$-nitrobenzoate ion-pair. We were also interested in determining the effect, if any, exerted by the solvating medium on the reaction between the allylic carbonium ion and azide; $i.e.$, we were looking for evidence of specific solvation.

From the data of the last two columns of Table I it can be seen that, within the limits of experimental error, azide ion appears to attack the arylmethylallyl carbonium ions to furnish exclusively $\alpha$-methyl-$\gamma$-arylallyl azides, both in methanol and aqueous dioxane.[7] It thus appears that the nature of the anion as well as the nature of the nucleophilic solvent can dramatically alter the product distributions in these systems. It is also apparent that no evidence of specific solvation was found.[8a]

A further comparison from the present work which has mechanistic implications is the enhanced ability of azide ion to compete with methanol for the presumably more stable $p$-tolylmethylallyl carbonium ion than for the unsubstituted phenylmethylallyl ion, a phenomenon similar to that observed in the benzhydryl and $p,p'$-dimethylbenzhydryl systems by Bateman, Hughes and Ingold.[3] This fact emerges from the data of Table I where it can be seen that, at a comparable concentration of sodium azide (0.29 $M$), alkyl azide constituted 66% of the total solvolysis product mixture from the methanolysis of $\alpha$-methyl-$\gamma$-$p$-tolylallyl $p$-nitrobenzoate, but only 30% of the solvolysis product (excluding rearranged ester) from $\alpha$-phenyl-$\gamma$-methylallyl $p$-nitrobenzoate. This selectivity is presumably associated with the greater stability of the $p$-methyl-stabilized carbonium ion. In view of the fact that the product distribution resulting on methanolysis of $\alpha$-phenyl-$\gamma$-methylallyl $p$-nitrobenzoate was found to be unchanged by $p$-methyl

(6) Hydrazoic acid is reported to have $pKa = 4.70$–4.78; C. A. West, *J. Chem. Soc.*, **77**, 705 (1900).

(7) It is, of course, conceivable that the $\alpha$-aryl-$\gamma$-methylallyl azides, which we have made no attempt to isolate, are extremely unstable under the reaction conditions and react as rapidly as they are formed. In view of the stability of the $\alpha$-methyl-$\gamma$-arylallyl azides, however (note constancy of infinity titers), this possibility seems remote.

(8) See L. Pauling, "The Nature of the Chemical Bond," third edition, Cornell University Press, Ithaca, N. Y., 1960, p. 271.

(8a) NOTE ADDED IN PROOF.—A recent communication by A. Gagneux, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **82**, 5956 (1960), reports the facile rearrangement of some allylic azides by a non-ionic, intramolecular pathway and thus makes apparent the reason for the nearly exclusive formation of the $\alpha$-methyl-$\gamma$-arylallyl azides observed in the present work; the less stable $\alpha$-aryl-$\gamma$-methylallyl azides may be formed initially but, if so, rearrange rapidly to the more stable $\gamma$-aryl isomers. The azide product distributions reported in this work thus reflect equilibrium compositions rather than relative rates of formation of the isomeric pairs of azides. Compare this conclusion with ref. 7.

substitution,[2] we conclude that the effect of the *p*-methyl group on electron distribution in the carbonium ion is considerable, but similar at both allylic centers.

It is also of interest to note that azide ion competes more effectively with solvent for the phenylmethylallyl carbonium ion in aqueous dioxane than it does in methanol.

**Kinetic Implications.**—Implicit in the interpretation which we have placed on the solvolytic behavior of the arylmethylallyl *p*-nitrobenzoates is the assumption that an intimate ion pair serves as an intermediate in the formation of both solvolysis product and rearranged ester. Most authors appear to favor the view that solvolyses of allylic systems, which in general furnish both rearrangement and solvolysis products, proceed *via* common ion pairs[9] although an alternative scheme, first advanced by de la Mare and Vernon,[10] has never been rigorously disproved. These authors postulated that rearrangement and solvolysis are the results of the simultaneous operation of two distinct reactions, a so-called SNi' rearrangement reaction and an SN1 ionization reaction; thus no common ion pair intermediate is required by their scheme.

The case for the common intermediate scheme has been argued very effectively by Winstein and Robinson.[9] They point out that, in a number of systems, the sensitivity of the rearrangement process to ionizing power of the solvent approaches that of the solvolysis process, a result difficult to rationalize on the basis of separate rearrangement and solvolysis processes.[11]

However, up to the present there appears to have been no completely convincing evidence that ion pairs can serve as common intermediates for both rearrangement and solvolysis products. In our opinion the results reported in this paper furnish this evidence.

The observation that the total rate of reaction of the allylic esters is essentially independent of the concentration of azide ion (except for a small positive salt effect in methanol) whereas the products are greatly altered in the presence of this salt leads to the conclusion that azide ion becomes involved in the reaction scheme only after the rate-determining step. Of greater interest for our present purposes, however, is the slight decrease in the amount of rearranged ester formed, on either methanolysis or hydrolysis of α-phenyl-γ-methylallyl *p*-nitrobenzoate, with increasing azide ion concentration; in aqueous dioxane the effect is definitely outside the limits of experimental error.

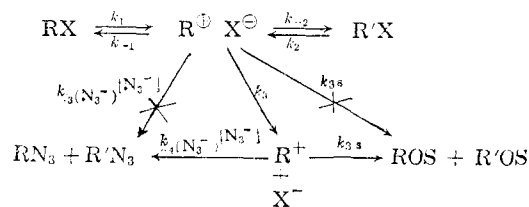The decrease in the amount of rearranged ester,

at a given salt concentration, however, is in all cases quite small compared with the amount of alkyl azide formed; thus only a small fraction of the alkyl azide (if any) can be formed at the expense of rearranged ester. One concludes that, for the most part, azide ion enters the reaction scheme only at a later stage than that which determines the amount of rearrangement products.

However, the small but unmistakable decrease in the amount of rearranged ester formed with increasing azide ion concentration remains to be explained. Two simple explanations seem tenable; and it will be shown that either is consistent *only* with a scheme involving an ion pair intermediate.

First, this decreased ester formation may result simply from the attack by azide ion on a species, presumably the intimate ion pair, present in limited supply.[13] Alternatively the decrease in rearranged ester may have its cause in the change in the ionic atmosphere of the reaction medium effected by the presence of the ionic salt. Such a change would direct a reactive intermediate, present in limited supply, toward a more ionic reaction pathway (dissociation) at the expense of a less ionic pathway (rearrangement).

Consider these results however in terms of a reaction scheme requiring two separate processes for solvolysis and rearrangement. The rates of these presumed separate reactions can be calculated easily from the data of Table I. In aqueous dioxane, although the total rate of reaction is essentially constant with changing azide ion concentration, the sum of the rates of the non-rearrangement processes is *increased* by *ca.* 10% by 0.448 *M* sodium azide, while the rate of rearrangement is *decreased* by *ca.* 35%. Since from previous work it is known that both the solvolysis and rearrangement products are formed *via* highly ionic transition states, it would seem impossible to reconcile these different salt effects with any scheme not involving a common intermediate.

On the basis of the work described in this paper it is possible to particularize further the scheme of reactions involved in the solvolyses of the isomeric α-aryl-γ-methylallyl *p*-nitrobenzoate (RX) and α-methyl-γ-arylallyl *p*-nitrobenzoate (R'X). An expanded scheme, which summarizes all the facts known about these systems at present, is

(9) See, *e.g.*, S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

(10) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 2504 (1954).

(11) A related argument in favor of the common intermediate scheme, which does not appear to have been made in print, depends on the fact that, of all published examples of reactions of the sort under discussion, only one does not produce rearrangement and solvolysis products at comparable rates, *viz.*, ethanolysis of α,α-dimethylallyl chloride. The more general behavior, dual product formation, has been observed with a wide variety of leaving groups, solvents and alkyl substrates.[12] This lack of sensitivity to reaction conditions is difficult to rationalize in terms of a scheme which requires the product-determining steps to be identical with the high energy rate-determining steps.

(12) See ref. 1 for references.

(13) An interesting extension of this idea is suggested by the fact that the effectiveness of sodium azide in decreasing the amount of rearranged ester appears to be greatest at low concentrations of the salt; *i.e.*, the depression of the amount of ester formed may approach a limit. This behavior is strongly reminiscent of effects observed by the Winstein school,[14] especially in the solvent acetic acid, and which were interpreted by these authors as evidence for the existence of a second type of ion pair, a so-called solvent-separated ion pair, capable of being attacked by nucleophilic agents. We have initiated a series of experiments to determine whether any such solvent-separated ion pairs can be detected in the reactions of the arylmethylallyl *p*-nitrobenzoates.

(14) See S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956), and later papers in this series.
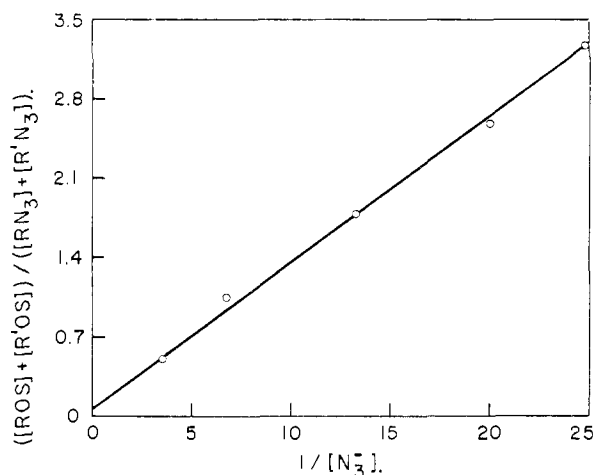
Fig. 1.—Plot of ratio of total ether to total azide products vs. the reciprocal of the azide ion concentration for the methanolysis of α-methyl-γ-p-tolylallyl p-nitrobenzoate.

We have already shown that attack by azide ion on the ion pair, the reaction labeled $k_{3(N_3^-)}{}^{[N_3^-]}$ is of negligible importance in this system. It remains for us to establish that solvent attack on $R^\oplus$ $X^\ominus$, the reaction labeled $k_{3s}$, cannot compete with dissociation (labeled $k_3$) as a route of reaction for the ion-pair.

Using the rate constants defined above, assuming $k_{3(N_3^-)} = 0$, and making the usual steady-state approximations the following equation is readily derived

$$\frac{[ROS] + [R'OS]}{[RN_3] + [R'N_3]} = \frac{k_{3s} + \dfrac{k_3 k_{4s}}{k_{4s} + k_{4(N_3^-)}{}^{[N_3^-]}}}{\dfrac{k_3 k_{3(N_3^-)}{}^{[N_3^-]}}{k_{4s} + k_{4(N_3^-)}{}^{[N_3^-]}}}$$

On rearrangement, this furnishes

$$\frac{ROS] + [R'OS]}{[RN_3] + [R'N_3]} = \frac{k_{4s}(k_{3s} + k_3)}{k_3 k_{4(N_3^-)}} \times \frac{1}{[N_3^-]} + \frac{k_{3s}}{k_3}$$

If the assumed mechanism is correct it is obvious that a plot of the ratio of total solvolysis product to total alkyl azide vs. the reciprocal of the azide ion concentration should result in a straight line, whose intercept is $k_{3s}/k_3$. Such a plot for the data of the methanolysis of α-methyl-γ-p-tolylallyl p-nitrobenzoate is given in Fig. 1. It is apparent that the intercept is experimentally indistinguishable from zero. We therefore conclude that $k_{3s} \sim 0$, and that solvent is incapable of attacking the intimate ion pair at a rate commensurate with its rate of dissociation.[15-17]

(15) A referee has called to our attention the work of G. Kohnstam and B. Shillaker who demonstrated that if the hydrolysis of dichlorodi-phenylmethane in aqueous acetone proceeds via ion-pairs "only the fully developed carbonium ion reacts with water and with anions"; J. Chem. Soc., 1915 (1959).

(16) This conclusion, incidentally, justifies the assumption made earlier; namely, that the ratio of isomeric ethereal or alcoholic solvolysis products formed in the presence of azide ion. This follows since both of these types of products arise from the same intermediate, the dissociated carbonium ion.

(17) A similar plot of the data for the solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate in aqueous dioxane also yields an intercept indistinguishable from zero. The data for the methanolysis of this ester, because of problems of azide solubility and reactivity, proved to be too imprecise to treat in this manner.

## Experimental

Materials.—Most of the materials used in this work have been described.[1,2] Sodium azide (Fisher, purified) was twice recrystallized from water and dried in vacuo. Analysis for hydrogen indicated the presence of less than 0.03% water.

Rate and Spectral Measurements.—Most of these techniques have been described.[1,2] Rate constants were calculated from the usual first-order expression using experimental rather than theoretical infinity titers.

The determination of the amount of rearranged ester formed on solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate in the presence of sodium azide involved the quantitative saponification of the reaction mixture resulting from solvolysis: a 5-ml. aliquot of the reaction mixture was placed in a 50-ml. glass-stoppered erlenmeyer flask containing 5 ml. of water and 5 ml. of 0.0400 M alcoholic potassium hydroxide. After 3 hours, the excess base was back titrated with ca. 0.02 M standard acid. The necessary control experiments have already been described.[2]

The experimental data from a typical run are recorded in Table II.

### TABLE II

SOLVOLYSIS OF 1.68 × 10⁻² M α-PHENYL-γ-METHYLALLYL p-NITROBENZOATE AT 35.0° IN 60 VOLUME PER CENT AQUEOUS DIOXANE CONTAINING 0.153 M SODIUM AZIDE

Titrimetric data: titrant: $1.73_4 \times 10^{-2} M$ potassium hydroxide; blank (solvent + quench): 0.177 ml.; theoretical infinity titer: 4.835 ml.

| Time, sec. | Titrant, ml. | $k$, sec.$^{-1}$ × 10⁵ |
|---|---|---|
| 0 | 0.756 | ... |
| 603 | .810 | 9.0[a] |
| 1860 | .900 | 8.3 |
| 2400 | .945 | 8.6 |
| 8830 | 1.259 | 7.8 |
| 9370 | 1.280 | 7.8 |
| 13800 | 1.434 | 8.0 |
| 14500 | 1.460 | 8.2 |
| 17100 | 1.475 | 7.2 |
| 17700 | 1.465 | 6.9 |
| ∞ (9 half-lives) | 1.751 | .. |
| ∞ (9 half-lives) | 1.760 | .. |
| ∞ (18 half-lives) | 1.799 | .. |

Av. 7.8 ± 0.4

% of theory (1.756 − 0.177)/4.835 × 100 = 32.9%

| Ultraviolet data[b] | | | Saponification data[d] | |
|---|---|---|---|---|
| Time, half-lives | Wave length, mμ | Absorbancy, A[c] | Time, half-lives | Titrant, ml. |
| 7.6 | 252 | 0.583 | 7.6 | 8.068 |
| 16.8 | 252 | 0.587 | 7.6 | 8.071 |

[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 2.5 l. [c] Absorbancy, $A = \epsilon lc$, where $l$ is the length of the cell in cm., $c$ is the concentration in moles/l. and $\epsilon$ the extinction coefficient. [d] A 5-ml. aliquot of the reacted solution was saponified with 5 ml. of an alcoholic potassium hydroxide solution and back titrated with 2.09 × 10⁻² M hydrochloric acid. The blank titer of 5 ml. of solvent and 5 ml. of the potassium hydroxide solution was 10.760 ml.

The determination of the extinction coefficients of benzhydrol and of benzhydryl azide[4] involved the solvolysis in 60 volume per cent. aqueous dioxane of benzhydryl chloride (Eastman Kodak Co. white label), both in the absence of sodium azide and in the presence of 0.400 M salt. The latter reaction was found by titration to produce 32.7% benzhydrol and 67.1% benzhydryl azide. Infinity solutions of each of these reaction mixtures were subjected to the usual extraction procedure,[2] and diluted quantitatively with ethyl ether for ultraviolet analysis. The spectra were qualitatively indistinguishable.

Calculations.—The experiment described in Table II will illustrate the methods used in calculating the new features of this work. From the saponification data of Table II it is apparent that, after saponification, a 5-ml. aliquot of the reacted solution had liberated $(10.760 - 8.070) \times 0.0209 = 0.0562$ mmole of acid. The concentration of acid in the reaction mixture is, accordingly, $0.0112\ M$. The concentration of liberated acid can be equated to the combined concentrations of alcoholic solvolysis products and rearranged ester present in the solvolysis reaction mixture: $[HX] = [ROH] + [R'OH] + [R'X]$, and the concentration of rearranged ester can then be calculated to be $[R'X] = 0.0112 - (0.329)(0.0168) = 0.0057\ M$. The total concentration of alkyl azide is then given by difference: $[RN_3] + [R'N_3] = [RX]_i - [R'X] - [ROH] - [R'OH] = 0.0168 - 0.0057 - 0.0055 = 0.0056\ M$. Thus the solvolysis mixture is found to consist of 34.4% rearranged ester $(R'X)$, 32.7% alkyl azides and 32.9% alcohols.

By the methods described in the preceding paper,[3] the ultraviolet data can be shown to require that, of the solvolysis products (alcohols and azides), 7.9% are in the $\gamma$-aryl-$\gamma$-methylallyl form: $(\%_{ROH} + \%_{RN_3})/(\%_{R'OH} + \%_{ROH} + \%_{RN_3} + \%_{R'N_3}) = 0.079$. This equation can be solved for the percentage of $\alpha$-phenyl-$\gamma$-methylallyl azide $(\%_{RN_3})$, provided it is assumed that the ratio of allylic alcohols is unaffected by the presence of azide ion; $i.e.$, that $\%_{ROH}/(\%_{ROH} + \%_{R'OH}) = 0.158$, the value reported in the accompanying paper. Then $(32.9 \times 0.158 + \%_{RN_3})/(32.9 + 32.7) = 0.079$, and $\%_{RN_3} = \pm 0.0$.

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE, BRYN MAWR, PENNA.]

# The Bromination of Biphenyl and Benzene in 50% Aqueous Acetic Acid[1]

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The kinetics of bromination of biphenyl and benzene in 50% by volume aqueous acetic acid in the presence of an excess of bromide ion has been found to have the same characteristic features as the bromination of naphthalene.[3] Relative rates of bromination of these compounds, as well as some partial rate factors, have been established.

The bromination of naphthalene by bromine in 50% by volume aqueous acetic acid, in the presence of an excess of bromide ion, is first-order in bromine and in naphthalene, and the brominating species is molecular bromine.[3] This kinetic behavior differs from bromination in glacial acetic acid or other non-polar solvents, where the order with respect to bromine is usually higher than one, although the brominating entity is the same.[4] In order to test the generality of the kinetic form observed in 50% aqueous acetic acid, as well as the suitability of the reaction for a comparison of the reactivities of different aromatic compounds with various theoretical parameters, two other compounds, biphenyl and benzene, were subjected to a similar kinetic study. The results are reported below.

## Experimental

Materials.—All inorganic materials and the glacial acetic acid were as described before.[3] The purified acetic acid had a m.p. of at least 16.4°. Runs made with different batches of solvent gave identical results. One lot of acetic acid (for a series of runs with benzene) was first purified in the usual way with chromic oxide and was then treated with a small amount of bromine, followed by treatment with an excess of silver acetate and distillation. This acid melted at 16.3°, but the kinetic results did not change. Biphenyl (Distillation Products) was recrystallized three times from ethanol and melted at 69.5–70.3° (cor.). Benzene (J. T. Baker reagent grade), purified with concentrated sulfuric acid and twice distilled, boiled at 80.0° over a range of less than 0.1° and was stored in a brown bottle over sodium wire.

Kinetic Determinations.—The preparation of stock solutions and the kinetic runs in the bromination of biphenyl were carried out exactly as described previously for naphthalene.[3] All stock solutions were made up at the tempera-

(1) Kinetics of Aromatic Halogenation. VIII.

(2) Post-doctorate Fellow, 1958–1959.

(3) E. Berliner and M. C. Beckett, J. Am. Chem. Soc., **79**, 1425 (1957).

(4) (a) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, J. Chem. Soc., 276 (1943); P. W. Robertson, ibid., 1267 (1954); (b) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, Chapter 9.

tures at which runs were conducted. All runs were conducted at least in duplicate, and the data in Table II, except those under heading A, are average values of duplicate runs. Duplicate runs usually agreed within less than 2%. In the bromination of benzene, a solution of all reagents except the bromine was similarly prepared from appropriate stock solutions in a 100-ml. volumetric flask, into which the benzene had originally been either weighed out or added from a calibrated pipet. To 90 ml. of this solution was then added 10 ml. of the bromine stock solution, which also contained some of the bromide. After thorough mixing, approximately 12-ml. samples were poured carefully into eight 16–150 mm. Pyrex test-tubes which had previously been constricted at one end. The narrow portions of the tubes were carefully dried with absorbent paper and, after sealing, the tubes were placed in the thermostat. About 30 min. was allowed for the tubes to reach the reaction temperature and for the attainment of equilibrium between dissolved bromine and the bromine in the small air space above the solution. After appropriate time intervals, 10-ml. samples were withdrawn from the opened tubes with a pipet and the residual bromine determined in the usual way, using a microburet. Blank runs were conducted in the same way, except that the benzene was omitted. Sometimes a kinetic run went extremely fast, and this was usually attributed to minute amounts of carbon deposits which had formed during the sealing of the tubes; such runs were discarded. Benzene was always used in excess, and rate constants for the over-all brominations and the blank reactions were obtained from first-order plots, which were calculated by the method of least squares. The least square slopes had errors which were rarely greater than 2%. Final second-order rate constants for the bromination of benzene were calculated by subtracting the pseudo-first-order rate constants of the blank reactions from those of the over-all reactions and dividing by the excess of benzene used. The errors for both the bromination of biphenyl and of benzene, quoted in the text, are the probable errors obtained from the least square calculations.

The Blank Reaction in the Bromination of Biphenyl.—Although rate constants calculated by the integrated form of the second-order rate equation were usually good and internally consistent, discrepancies were noted when the concentration of biphenyl was reduced to about 0.002 $M$ and the reaction became very slow. In these cases rate constants were about 30% higher than those with the concentration of biphenyl at about 0.01 $M$. Under these conditions the loss of bromine through a blank reaction was not negligible. It was possible to determine approximate first-order rate con-