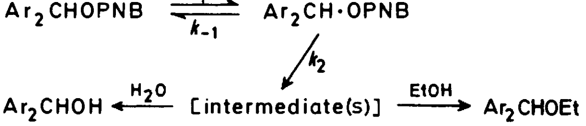
An Approach towards Identification of Product Precursors in the Solvolyses of Diarylmethyl *p*-Nitrobenzoates in Ethanol–Water Solvents [1]

By **Duncan J. McLennan** * and **Peter L. Martin**, Department of Chemistry, University of Auckland, Auckland, New Zealand

The product ratios, ether : alcohol, for the solvolyses of the title compounds in ethanol–water solvent mixtures have been measured, and have been compared with ratios of the same products generated from the reactions of the corresponding diaryldiazomethanes in the same solvents. The ratios are similar although not always identical, and disparities are ascribed to solvation differences. The question of ' selectivities ' of intermediates towards ethanol and water is addressed, and it is concluded that product ratios can be used as selectivity measures only when a single intermediate yields stable products. The present results thus throw little light on the reality or otherwise of stability–selectivity relationships in the present series. Internal return is suggested as an important component in the unassisted solvolysis of the esters.

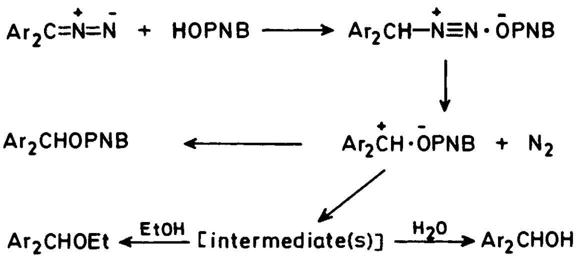
THERE are two principal ways of providing information pertinent to the reactivity–selectivity principle (RSP).[2] One is to derive kinetic selectivity parameters for the reactions in question by comparing their rate responses to substituent or environmental change with rate or equilibrium behaviour of a model reaction. This approach is exemplified in the preceding paper. A second method is to generate an intermediate in an environment where two or more reagents can compete to form stable products. Analysis of the product mixture then affords a measure of selectivity of the intermediate.[3] This method is also a powerful tool for the identification of intermediates: if two or more potential precursors of a reactive intermediate yield the same selectivities towards a given pair of reagents a common intermediate is strongly implied.[4]

In the preceding paper on the solvolysis of diarylmethyl *p*-nitrobenzoates in aqueous ethanol we were left with two alternatives as to mechanisms. One was that unassisted ionization (a k_c process) is the rate-limiting step, in which case the RSP does not apply. The second alternative was that internal return of the tight ion pair occurred, so that further unassisted reaction of the ion pair becomes the rate-limiting step. If this is so, the apparent lack of dependence of selectivity upon reactivity can be rationalized in terms of competition between steps whose behaviour is in accordance with the RSP. The principal aim of the present work is to distinguish between the alternatives.



SCHEME 1

To this end we compare ether : alcohol product ratios from solvolyses of $Ar_2CHOPNB$ substrates in ethanol–water mixtures (Scheme 1; $k_{-1} \ll k_2$ for a k_c process whilst $k_{-1} \gg k_2$ for an internal return mechanism) with products arising from the reactions of the corresponding diaryldiazomethanes with HOPNB in the same solvents. A mechanism of minimal detail for this process is shown in Scheme 2.[5-8] Evidence in ref. 9 suggests that the tight ion pair is immune to solvent attack, whilst Diaz and Winstein argue that the diazonium ion is too short-lived to suffer nucleophilic attack.[6] If the intermediate or spectrum of intermediates responsible for product formation in Scheme 1 is identical to that in Scheme 2, it is expected that the same ether : alcohol ratio will be obtained. A subsidiary task is therefore to identify the intermediate(s). Product studies of other reactions in ethanol–water [10-13] and ethanol–trifluoroethanol [14-17] mixtures, particularly with regard to substrate alteration and variation in solvent composition, provide a background to this aspect of the work.



SCHEME 2

RESULTS

Diphenylmethyl *p*-nitrobenzoates were solvolysed in EtOH–H_2O solvent mixtures at 100 °C for times corresponding to more than ten half-lives. Reaction mixtures were buffered with an excess of pyridine, and the ether: alcohol product ratios were insensitive to pyridine concentration. Under these conditions no ether to alcohol interconversion was observed. Product ratios were evaluated from quantitative g.l.c. measurements using internal standards. Temperature changes over a 25 °C range had little effect on the product ratios. Other systems behave similarly.[11,13] Diarylmethyl ethyl ethers and alcohols were the only products observed except in the case of solvolysis of $(p\text{-}ClC_6H_4)_2CHOPNB$, the slowest reacting substrate. Some 2—3% $(p\text{-}ClC_6H_4)_2C{=}O$ was obtained here, with check experiments revealing that it arose from decomposition of the ether product, hence the product ratio was accordingly

TABLE 1

Ether : alcohol product ratios for reactions of diarylmethyl derivatives in ethanol–water solvent mixtures

Product precursor	T/°C	$[Ar_2CHOEt]/[Ar_2CHOH]$ in solvent				
		90E	80E	70E	60E	50E
Ph_2CHCl	25	6.05	3.21	2.17	1.48	1.13
$(p\text{-}MeC_6H_4)_2CHOPNB$	60	8.47	5.05	3.53	2.68	2.16
$Ph_2CHOPNB$	100		3.09	2.03	1.49	1.16
$(p\text{-}ClC_6H_4)_2CHOPNB$	100		2.39 [a]	1.84 [b]	1.41	1.13
$Ph_2CHODNB$	100		2.70	1.91	1.54	1.17
$Ph_2CHOPNB$ [c]	100		3.30	2.46	2.36	2.04
$(p\text{-}MeC_6H_4)_2CN_2\text{–}HOPNB$	25	5.49	4.81	4.14	3.23	2.62
$Ph_2CN_2\text{–}HOPNB$	25		2.71	2.29	1.64	1.31
$(p\text{-}ClC_6H_4)_2CN_2\text{–}HOPNB$	25	4.84	2.52	1.80	1.45	1.21
$Ph_2CN_2\text{–}HOPNB$ [c,d]	25		3.11	2.03	1.46	1.08

[a] Ratio = 2.36 at 125 °C. [b] Ratio = 1.78 at 125 °C. [c] Solvent contains 50% acetone (v/v). [d] Ratios independent of temperature.

corrected. Rappoport *et al.*[15] have reported a similar result pertaining to the solvolysis of $(p\text{-}ClC_6H_4)_2CHCl$ in ethanol–trifluoroethanol solvents. Diphenylmethyl chloride was solvolysed at 25 °C and the products were analysed as above.

The reaction of diaryldiazomethanes with HOPNB in the aqueous ethanolic solvents were allowed to proceed to completion at 25 °C and the ether : alcohol product ratio was determined as above. Some ketone, $Ar_2C{=}O$, was detected in all product mixtures but was discovered to result from impurities in the Ar_2CN_2 starting materials. The amount of HOPNB remaining in the product mixture was assayed spectrophotometrically and compared with the quantity originally introduced, so that the amount of $Ar_2CHOPNB$ ester could be estimated. In calculating the percentage ester formed the original Ar_2CN_2 concentration was corrected for the small amount of ketone present. In no case did the ester solvolyse to a detectable extent under the reaction conditions. Product ratios are temperature-independent.[1]

Ether : alcohol product ratios are shown in Table 1. In the case of Ph_2CHCl the results agree closely with those of Karton and Pross.[10] The results for $Ph_2CHOPNB$ are discordant with respect to those of Harris *et al.*[11a] We found that if our ratios were derived simply by comparing g.l.c. peak heights we could bring our results into line with those of Harris; however, we preferred to employ peak areas relative to that of an internal standard as a method of estimation. Replicate experiments suggested that the product ratios in Table 1 were in error by no more than 3%, with the majority yielding uncertainties of less than 2%.

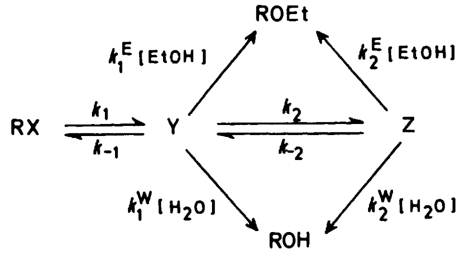
The percentage ester formed in the Ar_2CN_2–HOPNB reaction as a function of solvent composition is shown in Table 2. The comparative amount of ester is seen to decrease with increasing solvent polarity; another group has reported likewise.[18]

DISCUSSION

Leaving Group Effects.—It has become customary to discuss selectivities of substrates and/or intermediates generated from them towards a pair of nucleophilic solvent components as say k_E/k_W ratios in the case of ethanol and water, where k_E/k_W is given by equation (1). We will follow this procedure to ensure consistency, but it is necessary to point out that k_E/k_W ratios so evaluated

$$k_E/k_W = [Ar_2CHOEt][H_2O]/[Ar_2CHOH][EtOH] \quad (1)$$

are not necessarily true selectivity measures. Consider a case where two intermediates Y and Z suffer competition between ethanol and water to form ether and alcohol (Scheme 3). Steady-state analysis reveals that k_E/k_W, as defined by equation (1), is given by equation (2). Thus the 'selectivity' is in general a function of the solvent composition and most of the rate constants in the system,



SCHEME 3

$$\frac{k_E}{k_W} = \frac{k_1^E(k_{-2} + k_2^W[H_2O]) + k_2^E(k_2 + k_1^E[EtOH])}{k_1^W(k_{-2} + k_2^E[EtOH]) + k_2^W(k_2 + k_1^W[H_2O])} \quad (2)$$

and is in no way a simple selectivity measure. In the limit where $k_1^E[EtOH]$ and $k_1^W[H_2O] \gg k_2$, and $k_2^E[EtOH]$ and $k_2^W[H_2O] \gg k_{-2}$, k_E/k_W is simply k_1^E/k_1^W, since only one intermediate, Y, will be involved. Similarly if Z is the sole intermediate from which products arise, $k_E/k_W = k_2^E/k_2^W$. But if intermediate interconversion is competitive with solvent capture the general expression must apply.

TABLE 2

Percentage ester [a] formed in the reactions of Ar_2CN_2 with HOPNB in aqueous ethanol at 25 °C

Substrate	% Ester in solvent					
	100E	90E	80E	70E	60E	50E
$(p\text{-}MeC_6H_4)_2CN_2$	53.6		37.2	31.4	26.8	22.3
Ph_2CN_2	65.2		53.2	49.8	46.2	41.5
$(p\text{-}ClC_6H_4)_2CN_2$	57.8	55.7	52.2	50.0	44.2	42.1

[a] % Ester = $100[\text{ester}]/[Ar_2CN_2]_0$, with $[Ar_2CN_2]_0$ being corrected as described in text.

Harris and his co-workers have discussed selectivities in terms of an expression which, when applied to Scheme 3, assumes the form of equation (3).[11a,b] Here, f_y and f_z

$$k_E/k_W = f_y(k_1^E/k_1^W) + f_z(k_2^E/k_2^W) \qquad (3)$$

are the respective fractions of the intermediate in forms Y and Z. It is, however, incorrect to argue on the basis of equation (3) either explicitly or implicitly since evaluation of the f_y and f_z fractions in terms of the rate constants in Scheme 3 yields an expression for k_E/k_W that in no way resembles equation (2). We contend therefore that attempts to identify intermediates in solvolysis from k_E/k_W values in cases where more than one intermediate is involved yield conclusions of dubious validity. And if one cannot even identify the important product precursors in instances of plurality, it is certainly not in order to use measured k_E/k_W values to discuss selectivity–stability relationships. Ritchie has considered the question of plural intermediates with reference to competition between external (salt) nucleophiles and the solvent,[11c] and his results reinforce this conclusion.

TABLE 3

Leaving group effect in the reactions of diarylmethyl derivatives in ethanol–water solvent mixtures

Product precursor	T/°C	k_E/k_W [a] in solvent 90E	80E	70E	60E	50E
Ph_2CHBr [b]	25	3.34	3.69	4.13		
Ph_2CHCl	25	2.16	2.60	3.02	3.20	3.76
$Ph_2CHOPNB$	100		2.25	2.82	3.22	3.79
$Ph_2CHODNB$	100		2.18	2.64	3.33	3.79
Ph_2CN_2–HOPNB	25		2.19	2.95	3.54	4.24
$(p\text{-}ClC_6H_4)_2CHCl$ [b]	25	2.03	2.41	2.75	3.1 [c]	3.5 [c]
$(p\text{-}ClC_6H_4)_2CHOPNB$	100		1.92	2.47	3.04	3.66
$(p\text{-}ClC_6H_4)_2CN_2$–HOPNB	25	1.73	2.02	2.50	3.13	3.92
$(p\text{-}MeC_6H_4)_2CHOPNB$	100	3.05	4.10	4.91	5.79	7.00
$(p\text{-}MeC_6H_4)_2CN_2$–HOPNB	25	1.97	3.90	5.76	6.98	8.49

[a] Defined by equation (1). [b] From ref. 10. [c] Extrapolated from linear log (k_E/k_W) *versus* $Y(Bu^tCl)$ plot.

A second caveat must be made, even for cases where only one intermediate yields stable products. This applies to the use of molar concentrations of solvent components in equation (1). The practice would be in order were ethanol and water completely unassociated over the entire spectrum of solvent composition, or were the fractions of ethanol and water molecules with free lone pairs available for nucleophilic attack constant over the solvent range, but neither of these conditions are fulfilled for ethanol and water.[19] The region of maximum structural change in ethanol–water mixtures is *ca.* 20% mole fraction ethanol,[19,20] which corresponds to 50% v/v ethanol. As the 90E–50E range is commonly used, here and elsewhere for solubility reasons, it follows that the molar ratio of components is a most imprecise tool for measuring the relative availability of nucleophilic ethanol and water molecules. The identification of k_E/k_W as an ethanol : water nucleophilicity ratio is therefore also open to serious doubt even when only one intermediate is attacked; the ratio so evaluated is just as likely to be a function of the availability of free ethanol *versus* water lone pairs [21] as an intrinsic nucleophilicity ratio.

Allied to these sources of uncertainty is the complexity arising from the fate of solvent-separated ion pairs in mixed solvents. Each of $R^+{\cdot}EtOH{\cdot}X^-$ and $R^+{\cdot}OH_2{\cdot}X^-$ could reasonably form products by at least three pathways, one involving frontside attack by the separating molecule and two involving backside attack by the two solvent components. Addition of this level of complexity to Scheme 3 for instance produces a situation which in our view defies even simple qualitative analysis. Finally, the practice of relating ' selectivities ', no matter how defined, to intrinsic stabilities of carbocations is not without its dangers. A gas-phase stability order can possibly be reversed in solution if solvation forces are sufficiently strong [23] and apparent breakdowns in selectivity–stability relationships [2a] may reflect nothing more than differential solvation effects.

With these remarks in mind we proceed to discuss our results insofar as this is possible.

Table 3 lists k_E/k_W values as a function of leaving group identity in a variety of solvent mixtures, and some generalizations can be made. In the more polar solvents (60E and 50E), Ph_2CHCl, $Ph_2CHOPNB$, and $Ph_2CHODNB$ yield virtually the same k_E/k_W value, notwithstanding the temperature difference. It is likely then that the principal if not the only product precursor is the free solvated carbocation, since the identity of the departing anion is of no consequence. This is as expected; increasingly complete dissociation of ion pair intermediates should occur in more polar solvents. A straight-line extrapolation of the Ph_2CHBr results of Karton and Pross [10] into 60E and 50E yields k_E/k_W values that are significantly higher, a surprising result. Perhaps k_E/k_W for this substrate passes through a maximum as the solvent becomes more aqueous, a not unprecedented situation.[12] The *p*-chloro-substituted chloride and *p*-nitrobenzoate also appear to share the same product precursor in 60E and 50E, and again the free carbocation is indicated. In less polar solvents a divergence between the chlorides and nitrobenzoates is indicated. This means that at least part of the reaction products are derived from an intermediate with which the leaving group is associated, and ion pairs are implicated. This is again as expected since the carbocation in the less polar solvents must derive extra stabilization from the anion. We decline to comment on the trend in k_E/k_W with increasing solvent polarity for a given substrate for reasons given above. However, since the free carbocation is clearly the product precursor in 50E it is safe to remark in this instance that the trend in k_E/k_W of *p*-Me > *p*-H > *p*-Cl is a selectivity–stability order.

We now consider the ester hydrolyses in juxtaposition with the Ar_2CN_2–HOPNB reactions. For a given ring substituent these yield substantially similar k_E/k_W values in the more ethanolic solvents (but note the crossover for the *p*-methyl compounds in 90E). We can therefore speculate that the two reactions share to a good extent a spectrum of common intermediates, in which ion pairs are obviously of importance. It can also be stated with reasonable confidence that more ion pair return to covalent substrate occurs during solvolysis in the less polar solvents. Evidence for this is the increase in the proportion of ester obtained in the Ar_2CN_2–HOPNB reactions as solvent polarity decreases (Table 2). Other comparisons can be invoked to support the above proposals,[6,8,9] and most important of these is a comparison of return to carbocation capture, *i.e.* estimation of the partitioning ratio of the tight ion pair. While these comparisons are a little equivocal in that a necessary assumption is that ^{18}O equilibration involves an ion pair having equivalent oxygens,[6] the present work suggests, no more equivocally, that the spectrum of intermediates leading to solvolysis products is essentially identical to that in the Ar_2CN_2–HOPNB system. This does not necessarily mean that the intermediate involved in ^{18}O equilibration itself yields solvolysis products, since these can conceivably arise from more dissociated species.[9,24]

TABLE 4

Solvent effect in the reactions of diphenylmethyl derivatives in ethanol–water solvent mixtures

		k_E/k_W [b] in solvent			
Product precursor [a]	% Acetone	80E	70E	60E	50E
$Ph_2CHOPNB$	0	2.25	2.82	3.22	3.79
$Ph_2CHOPNB$	50	2.67	3.42	5.10	6.61
Ph_2CN_2–HOPNB	0	2.19	2.95	3.54	4.24
Ph_2CN_2–HOPNB	50	2.52	2.82	3.15	3.50

[a] Ester solvolyses at 100 °C, Ph_2CN_2 decompositions at 25 °C; the latter values are temperature independent. [b] Defined by equation (1).

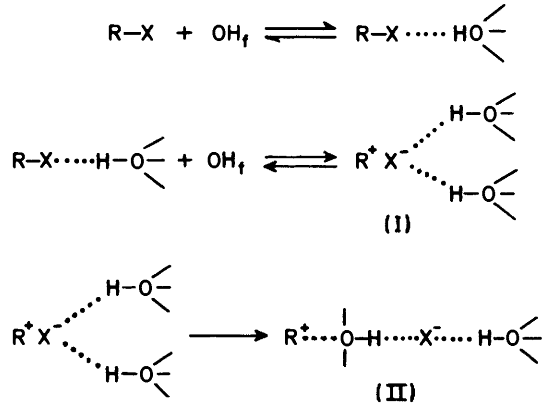
The observation that ion pair return is a necessary component in these solvolyses has implications of importance in interpreting the results in the preceding paper. Of the alternatives given there, only one was consistent with the operation of the reactivity–selectivity principle, and it is therefore satisfying that this required an increasing incidence of internal return in less polar solvents, as found in the present work.

Several other conclusions can be reached from these results. The proposed diazonium ion pair intermediate seems not to be a solvolysis product precursor except perhaps for the $(p\text{-}MeC_6H_4)_2CN_2$–HOPNB reaction in 90E, where it or the corresponding nitrogen-separated ion pair[25] could be invoked to explain the low ' selectivity '. Another possibility is that the instability of the diazonium ion pair in solvents of low polarity leads to its more rapid decomposition and loss of nitrogen, with the result that the diarylmethyl *p*-nitrobenzoate ion pairs are generated and solvolysed within the solvation shell of their immediate precursor. There is no evidence for nucleophilic solvent assistance in the solvolyses. None is expected in the Ar_2CN_2–HOPNB reactions and the essential similarity of these and the solvolyses rules out the possibility in the latter. We speculated in the preceding paper that solvent assistance might marginally affect the rate of solvolysis of $(p\text{-}ClC_6H_4)_2CHOPNB$ in 80E and 70E; the present results allow this view to be laid to rest. In the more polar solvents the Ar_2CN_2–HOPNB reaction clearly yields solvolysis products from precursors(s) other than the free carbocation that has been suggested for the ester solvolysis. The results give no indication as to what these might be.

Cosolvent Effects.—We consider the results in Table 4 pertaining to the addition of acetone to various ethanol–water solvents. Our previous studies in this area utilized ethanol–water mixtures in solvents containing 50% acetone, and the discrepancy between k_E/k_W values in the $Ph_2CHOPNB$ solvolysis and the Ph_2CN_2–HOPNB reaction led us to propose that nucleophilic solvent assistance provided an additional pathway to products in the former.[1] While this suggestion is not disqualified by any of the work described herein, realisation of the inherent complexity of the systems under examination give us less confidence in its veracity. For instance, k_E/k_W is larger for the solvolysis than for the diazoalkane reaction when the solvent contains acetone, but the order is reversed in acetone-free solvents, especially in the more aqueous regions. Again it is not unreasonable to assume that the two reactions have differing solvational requirements, and it follows that the addition of acetone may have a differential effect on the two reactions even though the intermediates may be intrinsically identical. We make no attempt to speculate on how acetone influences k_E/k_W ratios in either case, but point out that added basic cosolvents should, in Symonds' terminology, scavenge free hydroxy-groups and thereby cause an increase in the concentration of nucleophilic lone pairs. The fact that the consequences of this are different for the $Ar_2CHOPNB$ solvolyses and the Ar_2CN_2–HOPNB reactions could reflect initial state solvational requirements, in that HOPNB in the latter systems will be more tightly locked into the solvent structure than the carboxy-moiety in the esters. It may therefore be significant that just as the addition of acetone has the greatest differential effect in the more strongly solvating polar solvent region, so is the discrepancy between the k_E/k_W values for the solvolyses and the Ar_2CN_2–HOPNB reactions greatest in the more aqueous of the acetone-free solvents.

Conclusion.—We conclude that k_E/k_W values have little to do with selectivity of intermediates in the general case. The reactions of Ar_2CHOPNB esters and of Ar_2CN_2 with HOPNB appear to produce a substantially common set of intermediates, and as one of these in the latter process allows return to covalent ester we suggest that internal return is a component of the solvolysis reaction. This in turn means that the apparent lack of adherence of the rate responses in solvolysis to the reactivity–selectivity principle (preceding paper) is a consequence of the multistep mechanism and, most importantly, of two of the individual reactions in this mechanism behaving in accordance with the principle but in opposition. It is of importance to delineate those substrate structures that mark the onset of nucleophilic solvent assistance in solvolysis, and the present work allows the conclusion that diphenylmethyl cations are sufficiently stable in solution to require no detectable solvent assistance in their formative process.

Except for reproducing the conventional Winstein schemes [26] for unassisted solvolysis in Schemes 1 and 2 we have not been particularly explicit about the identity of the ion pair intermediates. The Winstein intimate ion pair is an obvious candidate for the species that is partitioned between internal return and further dissociation to produce precursors of solvolysis products. There is no evidence that the first-formed ion pair is attacked by solvent [9, 24] and one rationalization would be that some overlap between the empty *p*-orbital on carbon and orbitals of the associated anion remains, even though the forces of attraction are predominantly electrostatic. Why then should such a species be an intermediate rather than a transition state or a virtual intermediate? Jencks and Sinnott have also raised this question.[17] The answer may lie in the idea that lone pairs on the anion may not be fully available for bonding to carbon, being bonded instead to free lone hydroxy-groups of the solvent which provide electrophilic assistance to ionization. The solvolysis mechanism proposed by Symonds [21] is pertinent in this regard (Scheme 4). The initial hydrogen bond to the covalent substrate is justifiable if the leaving group contains an electronegative oxygen (benzoate or sulphonate), and intimate ion pair formation (I) is seen to involve electrophilic attack by a free hydroxy. Internal return is simply the expulsion of this species. Formation of the looser solvent-separated ion pair (II) can be depicted in a number of ways. As shown above, we envisage a rotation of the solvated anion in concert with the breaking of a hydrogen bond to one of the oxygens, which makes available a free lone pair capable of co-ordinating (perhaps with imperfect orbital overlap, which is reasonable considering the geometric relationship of the empty *p*- and the filled sp^3-orbitals) with the electron-deficient carbon. Alternatively we could invoke the idea that the scavenging of free hydroxy-groups in the first two steps will increase the likelihood than an external free lone pair will be available to associate with carbon. As depicted in (II), the stability of the intermediate will be enhanced if concurrent lone pair co-ordination and hydrogen bonding can occur. In this way potential barriers between solvated substrate and (I), and between (I) and (II) can be envisaged; it is not so easy to understand why there should be a barrier between substrate and intimate ion pair in the unelaborated Winstein process. Intermediate (II) is now capable of suffering nucleophilic attack on the frontside by either the intervening solvent molecule if it is substantially free from the bulk solvent structure (*i.e.* with two free lone pairs on the oxygen) or by an external free lone pair, and on the backside by other external free lone pairs. All these processes involve the breaking of hydrogen bonds in some way, and small energy barriers between intermediate species can be rationalized. Solvent assistance in what has been termed the S_N2 (intermediate) mechanism [27] simply involves the use of a free lone pair at the backside to stabilize or delocalize the developing positive change in systems where internal stabilization is not readily available.



SCHEME 4

The description above is speculation but it allows rationalization of several cloudy aspects of the basic Winstein scheme by focusing attention on the properties of the solvent. The simple mechanism in Scheme 1 does not give any indication of why an intimate ion pair should not immediately collapse to covalent product, of the restraints on the intervening solvent molecule in a solvent-separated ion pair that allow the species a life sufficiently long to suffer external attack from the rear in competition with internal frontside collapse, and of the nature of the energy barriers between various intermediate species.

Bimolecular (S_N2) solvolyses [28] could well be viewed in the same light, except that the discrete intermediates would be absent. It is thus important to realise that multiple equilibria involving the solvent will accompany any substitution process in solution and it is therefore not surprising that curved Arrhenius plots should be observed.[21,29] Recent attempts to rationalize this behaviour on the basis of an internal return mechanism for *all* solvolyses [30] are thus seen to be oversimplifications at best and wrong at worst, especially as the alternative presented is a ' unitary ' mechanism of an unspecified nature, expected to yield linear Arrhenius plots.[30] The above discussion reveals that there is no such thing as a unitary, or one-step, mechanism for nucleophilic substitution of any sort.

EXPERIMENTAL

Diarylmethyl *p*-nitrobenzoate esters were prepared as previously described.[31] Hydrazones of benzophenone, *pp'*-dichlorobenzophenone, and *pp'*-dimethylbenzophenone were prepared by a published method [32] and were converted into the corresponding diaryldiazomethanes by oxidation with mercury(II) oxide.[33] The diaryldiazomethanes exhibited m.p.s and u.v.–visible absorption maxima in agreement with literature values.[34] G.l.c. analysis revealed that the corresponding benzophenones were contaminants to the extent of no more than 3%; the proportion increased the longer the hydrazone–HgO suspension was stirred. Diphenylmethanol and bis-(*p*-chlorophenyl)methanol were commercial products and were recrystallized from n-hexane. The Grignard reaction between *p*-MeC$_6$H$_4$MgBr and *p*-MeC$_6$H$_4$CHO was used to prepare di-(*p*-tolyl)methanol. The ethyl ethers of the three alcohols were prepared by refluxing the alcohol (0.016 mol) in dry ethanol (50 ml) in the presence of concentrated HCl (5 ml) for 2 h. The solutions were extracted with ether and the oils remaining after solvent removal were chromatographed on alumina. T.l.c., g.l.c., and n.m.r. established the purity and identity of the oils, but attempted vacuum distillation caused decomposition. The ethers were stable for long periods only when stored in the dark, in ethanolic solution, at 0 °C.

Ester solvolysis was performed by sealing solutions of the appropriate ester in ethanol–water solvent mixtures containing pyridine in glass ampoules under nitrogen. The ampoules were left in a thermostat bath for a time corresponding to 10—15 half-lives.[31] The more reactive diphenylmethyl chloride was solvolysed by dissolving a sample in dry ethanol and placing the solution in one arm of a Y-tube. An appropriate volume of aqueous pyridine buffer was placed in the other arm, and the assembly was allowed to attain thermal equilibrium. The solutions were then rapidly mixed and were left in the thermostat bath for 10—15 half-lives.[35] The decomposition of the diaryldiazomethanes was effected by mixing an ethanolic solution of Ar$_2$CN$_2$ (*ca.* 0.02 mol l^{-1}) with the appropriate volume of water containing a slight excess of *p*-nitrobenzoic acid. Reactions were allowed to proceed at thermostat temperature until the colour had disappeared.

In all cases product analysis was initiated by extraction of solutions with ether, which was washed with saturated NaHCO$_3$ solution. Recoveries were >98% as revealed by check experiments. The dried ether extract was then concentrated, an accurately measured acetone solution containing a known amount of internal standard was added, and g.l.c. analysis was performed. Check experiments showed that ether extraction was essential with the *p*-tolyl and phenyl derivatives; direct injection of reaction mixtures was accompanied by significant conversion of the alcohol into the ether. Other check experiments are discussed in the Results section.

G.l.c. analyses were performed on a Varian 1532-2B instrument (flame ionization detector) equipped with a Disc integrator. The stationary phase was OV17 (3% on DMCS-treated Chromosorb W; column length 3 m). The following are the column temperatures and internal standards for each product pair: (*p*-MeC$_6$H$_4$)$_2$CHOEt/(*p* MeC$_6$H$_4$)$_2$CHOH: 180 °C, *p*-chlorobenzophenone; Ph$_2$CHOEt–Ph$_2$CHOH: 120 °C, fluorene; (*p*-ClC$_6$H$_4$)$_2$CHOEt/(*p*-ClC$_6$H$_4$)$_2$CHOH: 194 °C, *pp'*-dimethylbenzophenone. The detector responses of each of the six products relative to the relevant internal standard were evaluated by analysing several synthetic samples containing various amounts of the pure product and standard. The responses were linear with respect to concentration. In no case was the molar response of an ether equal to that for the corresponding alcohol. The relevant benzophenones were calibrated in a like manner. Under the above conditions all components of each reaction mixture were clearly separated. No ethyl *p*-nitrobenzoate was ever detected.

In selected cases runs were independently replicated, and product ratios were reproducible to within 3%. Repeated injections of extract from a given reaction mixture gave ratios in agreement within 1%.

We gratefully acknowledge discussions on the work in this and the preceding paper with Drs. M. H. Abraham and A. Pross.

[1/1951 *Received, 17th December, 1981*]

Note added in proof: Since the submission of this paper there has appeared a solvolysis mechanism for tertiary substrates that explicitly takes solvent involvement into account in considering the question of curved Arrhenius plots: M. J. Blandamer, J. Burgess, P. P. Duce, M. C. R. Symonds, R. E. Robertson, and J. W. M. Scott, *J. Chem. Res.* 1982 (*s*), 130.

REFERENCES

[1] Preliminary communication, D. J. McLennan and P. L. Martin, *Tetrahedron Lett.*, 1973, 4215.

[2] (*a*) A. Pross, *Adv. Phys. Org. Chem.*, 1977, **14**, 69; (*b*) C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755; (*c*) *Tetrahedron*, 1980, **36**, 3461; (*d*) B. Giese, *Angew. Chem. Int. Edn. Engl.*, 1977, **16**, 125; (*e*) D. J. McLennan, *Tetrahedron*, 1978, **34**, 2331.

[3] R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Am. Chem. Soc.*, 1966, **88**, 2594; D. J. Raber, J. M. Harris, R. E. Hall, and P. von R. Schleyer, *ibid.*, 1971, **93**, 4821.

[4] R. Huisgen and R. Knorr, *Tetrahedron Lett.*, 1963, 1017 provide a classic case.

[5] R. A. More O'Ferrall, *Adv. Phys. Org. Chem.*, 1967, **5**, 331.

[6] A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, 1966, **88**, 1318.

[7] E. H. White and C. A. Elliger, *J. Am. Chem. Soc.*, 1967, **89**, 165.

[8] E. R. Stedronsky, J. Gal, R. A. More O'Ferrall, and S. I. Miller, *J. Am. Chem. Soc.*, 1968, **90**, 993; R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *ibid.*, 1964, **86**, 5553.

[9] H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, 1964, **86**, 120; H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, 1963, **85**, 3059; H. L. Goering and H. Hopf, *ibid.*, 1971, **93**, 1224. See also H. Maskill, J. T. Thompson, and A. A. Wilson, *J. Chem. Soc., Chem. Commun.*, 1981, 1239.

[10] Y. Karton and A. Pross, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1860, and earlier papers in the series.

[11] (*a*) J. M. Harris, D. C. Clark, A. Becker, and J. F. Fagan, *J. Am. Chem. Soc.*, 1974, **96**, 4478; (*b*) J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *ibid.*, p. 4484; (*c*) C. D. Ritchie, *ibid.*, 1971, **93**, 7324.

[12] H. Aronovitch and A. Pross, *J. Chem. Soc., Perkin Trans. 2*, 1978, 540.

[13] P. R. Luton and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1979, 646; Y. Karton and A. Pross, *ibid.*, 1978, 595.

[14] D. A. da Roza, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, 1973, **95**, 7003; T. Ando and S. I. Tsukamoto, *Tetrahedron Lett.*, 1977, 2775.

[15] Z. Rappoport, H. Ben-Yacov, and J. Kaspi, *J. Org. Chem.*, 1978, **43**, 3678.

[16] J. Kaspi and Z. Rappoport, *J. Am. Chem. Soc.*, 1980, **102**, 3829.

[17] M. L. Sinnott and W. P. Jencks, *J. Am. Chem. Soc.*, 1980, **102**, 2026.

[18] A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc. B*, 1968, 631.

[19] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1; M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, 1975, **4**, 55; M. J. Blandamer, *Adv. Phys. Org. Chem.*, 1977, **14**, 204.

[20] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, 1965, **87**, 1541.

[21] M. C. R. Symonds, *J. Chem. Soc., Chem. Commun.*, 1978, 418; *Acc. Chem. Res.*, 1981, **14**, 179.

[22] For discussion of the relative nucleophilicities of ethanol and water see P. E. Petersen, D. W. Vidrine, F. J. Waller, P. M. Hendricks, S. Magaha, and B. Stevens, *J. Am. Chem. Soc.*, 1977, **99**, 7968; S. P. McManus, *J. Org. Chem.*, 1981, **46**, 635.

[23] A. Pross, *J. Am. Chem. Soc.*, 1976, **98**, 776; W. L. Jorgensen, *ibid.*, 1977, **99**, 280, 4274.

[24] B. L. Murr and M. F. Donnelly, *J. Am. Chem. Soc.*, 1970, **92**, 6686, 6688.

[25] R. A. Moss, *Acc. Chem. Res.*, 1974, **7**, 421.

[26] S. Winstein, B. Appel, R. Baker, and A. Diaz, Chem. Soc. Spec. Publ., 1965, No. 19, p. 109.

[27] T. W. Bentley and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1976, **98**, 7658; T. W. Bentley, C. T. Bowen, D. H. Morten, and P. von R. Schleyer, *ibid.*, 1981, **103**, 5466.

[28] D. J. McLennan, *Acc. Chem. Res.*, 1976, **9**, 281.

[29] R. E. Robertson, *Prog. Phys. Org. Chem.*, 1967, **4**, 213.

[30] M. J. Blandamer, R. E. Robertson, J. M. W. Scott, and A. Vrielink, *J. Am. Chem. Soc.*, 1980, **102**, 2585; M. J. Blandamer, J .Burgess, P. P. Duce, R. E. Robertson, and J. M. W. Scott, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1157.

[31] D. J. McLennan and P. L. Martin, *Aust. J. Chem.*, 1979, **32**, 2361.

[32] T. Curtius and F. Rauterberg, *J. prakt. Chem.*, 1891, **44**, 194.

[33] H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, 1916, **49**, 1932.

[34] D. Bethell and J. D. Callister, *J. Chem. Soc.*, 1963, 3801.

[35] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.