Reactivity–Selectivity Relationships. Part 9.[1] Identification of Solvolytic Intermediates in the Solvolysis of Substituted Benzyl Derivatives

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The selectivity of substituted benzyl derivatives toward ethanol and water during solvolysis was examined. The results provide a detailed description of the solvolytic intermediates formed during solvolysis. p-Chlorobenzyl and benzyl derivatives are found to undergo product formation via intimate ion pairs, p-methylbenzyl derivatives via intimate ion pairs at low solvent polarity but through increasing proportion of solvent separated ion pairs as the polarity of the medium is increased, and p-methoxybenzyl chloride predominantly through solvent separated ion pairs. A leaving group effect on selectivity is proposed as a new diagnostic tool for the identification of solvent separated ion pairs. Application of this tool leads to conclusions identical to those we obtain based on the study of solvent effects on selectivity.

OVER recent years considerable study has been devoted to the solvolytic mechanism of substituted benzyl derivatives.[2] Much of this interest has stemmed from the border line nature of these solvolyses, so that assignment to either S_N1 or S_N2 processes has been particularly difficult.[3–5] Recently Thornton [2a] has presented a detailed analysis of the mechanistic possibilities associated with the benzyl system and attempted to integrate seemingly conflicting results reported by a variety of different workers.[2] Thornton concluded that most of the data could be accommodated by a central or ' loose ' S_N2 type transition state.[2a] For the p-methoxy-

analysis is based on application of the reactivity–selectivity principle (r.s.p.).[6] Application of the principle is of particular utility in the study of short lived intermediates such as ion pairs, carbenes, free radicals, and electrophilic species.[6a]

This work covers the effect of solvent changes, ring substituent, leaving group, and temperature on substrate selectivity toward the competing nucleophiles, ethanol and water, and presents the mechanistic conclusions the data provide. We believe that the present work illustrates that the study of selectivity and application of the r.s.p. together provide a most powerful

TABLE 1

Selectivity [a] of p-substituted benzyl derivatives in aqueous ethanol solutions (50—95%) at 75°

Substrate	% Ethanol (v/v)					
	50	60	70	80	90	95
p-Chlorobenzy chloride	3.23 ± 0.11	2.98 ± 0.06	2.67 ± 0.11	2.33 ± 0.10	1.86 ± 0.07	1.67 ± 0.08
Benzyl chloride [b]	3.33 ± 0.11	3.09 ± 0.16	2.87 ± 0.10	2.45 ± 0.13	2.17 ± 0.06	1.86 ± 0.06
p-Methylbenzyl chloride	2.00 ± 0.06	1.96 ± 0.07	2.07 ± 0.03	2.07 ± 0.04	2.05 ± 0.09	1.91 ± 0.05
p-Methoxybenzyl chloride [c]	3.81 ± 0.06	3.24 ± 0.12	2.78 ± 0.10	2.46 ± 0.12	2.15 ± 0.13	2.22 ± 0.19
Benzyl bromide	3.61 ± 0.09	3.30 ± 0.06	2.95 ± 0.05	2.56 ± 0.01	2.12 ± 0.04	1.80 ± 0.06
p-Methylbenzyl bromide	2.61 ± 0.15	2.61 ± 0.15	2.50 ± 0.10	2.39 ± 0.10	2.15 ± 0.14	1.99 ± 0.10

[a] Selectivity defined as k_E/k_W and determined by g.l.c. in the presence of excess pyridine. Error values are standard deviations. [b] Data from ref. 5. [c] Selectivity values for p-methoxybenzyl chloride were obtained in aqueous 85, 91, and 94% ethanol as 2.28, 2.27, and 2.22 respectively

benzyl system reacting with azide ion, an ion pair ' sandwich ' was postulated [2a] to account for the chlorine kinetic isotope effect results reported by Graczyk and Taylor.[2c]

While these studies provided considerable information concerning the transition states in the solvolysis of substituted benzyl derivatives, little insight was obtained into the nature of the solvolytic intermediates formed *after* the transition state, and which are responsible for product formation through reaction with solvent.

In this work we have attempted to clarify this problem by the study of the selectivity of the solvolytic species formed during the aqueous ethanolysis of p-substituted benzyl chlorides and bromides. Our

tool for the study of transient intermediates in solvolytic reactions.

RESULTS AND DISCUSSION

The selectivity of *para*-substituted benzyl halides towards ethanol and water in aqueous 50—95% ethanol are listed in Table 1. Selectivity is defined as k_E/k_W [7] where k_E and k_W are the specific first-order rate constants for reaction of a given substrate with ethanol and with water, respectively. Thus the selectivity values indicate the ability of the given substrate to differentiate between

[1] Part 8, H. Aronovitch and A. Pross, *Tetrahedron Letters*, 1977, 2729.

[2] (a) M. P. Friedberger and E. R. Thornton, *J. Amer. Chem. Soc.*, 1976, 98, 2861; (b) J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, 1962, 84, 2763; (c) D. G. Graczyk and J. W. Taylor, *J. Amer. Chem. Soc.*, 1974, 96, 3255; (d) R. A. Sneen, *Accounts Chem. Res.*, 1973, 6, 46; (e) V. F. Raaen, T. Juhlke, F. J. Brown, and C. J. Collins, *J. Amer. Chem. Soc.*, 1974, 96, 5928.

[3] For reviews on the S_N1—S_N2 borderline area see (a) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in ' Ions and Ion Pairs in Organic Reactions ' ed. M. Szwarc, Wiley, New York, 1974, vol. 2; (b) J. M. Harris, *Progr. Phys. Org. Chem.*, 1974, 11, 89; (c) D. J. McLennan, *Accounts Chem. Res.*, 1976, 9, 281.

[4] T. W. Bentley and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1976, 98, 7658.

[5] A. Pross, H. Aronovitch, and R. Koren, *J.C.S. Perkin II*, 1978, 197.

[6] For reviews see (a) A. Pross, *Adv. Phys. Org. Chem.*, 1977, 14, 69; (b) B. Giese, *Angew. Chem. Internat. Edn.*, 1977, 16, 125.

[7] J. M. Harris, D. C. Clark, A. Becker, and J. F. Fagan, *J. Amer. Chem. Soc.*, 1974, 96, 4478.

the two competing nucleophiles. Selectivity values were obtained using equation (1) where [R–OEt] and

$$k_E/k_W = [\text{R–OEt}][\text{H}_2\text{O}]/[\text{R–OH}][\text{EtOH}] \quad (1)$$

[R–OH] are the concentrations of the substituted benzyl ether and alcohol products. The [R–OEt]/[R–OH] ratios were established by analytical g.l.c.

A plot of the logarithm of selectivity against solvent ionizing power (Y values) is particularly revealing and enables the solvolytic intermediates present during solvolyses to be identified.

Effect of Substituent.—The effect of *para*-substitution on the selectivity of benzyl chlorides in aqueous 50—95% ethanol is shown in Figures 1 and 2. It is apparent that benzyl and p-chlorobenzyl chlorides (Figure 1)
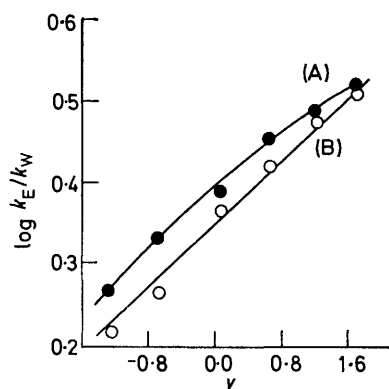

FIGURE 1 Plot of selectivity (log k_E/k_W) against Y values for (A) benzyl chloride and (B) p-chlorobenzyl chloride in aqueous ethanol
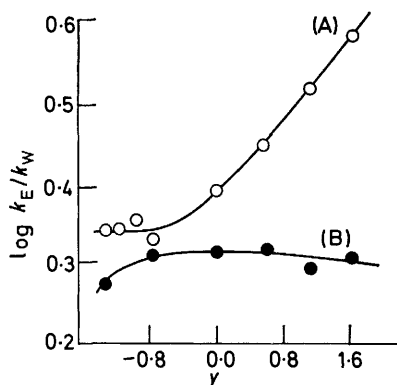

FIGURE 2 Plot of selectivity (log k_E/k_W) against Y values for (A) p-methoxybenzyl chloride and (B) p-methylbenzyl chloride in aqueous ethanol

exhibit similar behaviour giving close to linear plots of selectivity against Y values, by analogy with the behaviour exhibited by octyl [5] and diphenylmethyl [8,9] derivatives. All these substrates show a gradual increase in substrate selectivity as the proportion of water in the binary aqueous ethanol mixture increases. In another Part,[9] the linear increase in selectivity as a function of solvent ionizing power was attributed to changes in the relative nucleophilicity of ethanol and

[8] Y. Karton and A. Pross, *J.C.S. Perkin II*, 1977, 1860.

water. This conclusion was based on the fact that a range of model compounds followed this pattern of behaviour.[5,8,9] In other words, as the aqueous component of the solution increases, ethanol exhibits greater nucleophilicity relative to water, resulting in enhanced selectivity values.
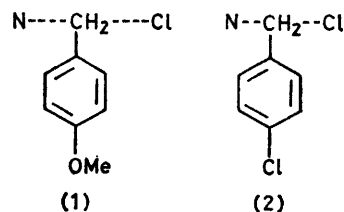
p-Methyl- and p-methoxy-benzyl chlorides, however, show decidedly different behaviour (Figure 2). Both deviate considerably from the ' normal ' response exhibited by the substrates mentioned previously. This deviation is presumably due to some additional effect which operates for these two substrates. We propose therefore that benzyl and p-chlorobenzyl chlorides, which conform to the ' normal ' behaviour pattern, undergo product formation from just one solvolytic species in each case. The anomalous behaviour exhibited by p-methyl- and p-methoxy-benzyl chlorides may then be attributed to product formation from at least *two* solvolytic intermediates. The change in the quasi-equilibrium between these intermediates as the solvent composition changes is presumed to be responsible for this different pattern. This is because the observed selectivity is determined by the selectivity of each individual species as well as the proportion of product formation from that species.

The question which needs to be answered is then which solvolytic species is involved in product formation from p-chlorobenzyl and benzyl chlorides and which species are formed during the aqueous ethanolysis of p-methyl- and p-methoxy-benzyl chlorides.

We believe the behaviour of the benzyl system may be understood in terms of a truncated form of the Winstein solvolysis Scheme. The possibility of significant product

$$\text{RX} \rightleftharpoons \text{R}^+\text{X}^- \rightleftharpoons \text{R}^+||\text{X}^-$$

SCHEME
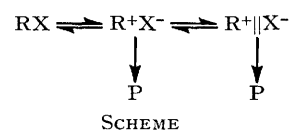
formation from nucleophilic attack on neutral substrate may be eliminated by the following argument. For an S_N2 process the selectivity order of a series of substituted benzyl chlorides is expected to *increase* in the order p-CH$_3$O $< p$-Me $< p$-H $< p$-Cl. This is because for an electron-releasing substituent such as p-MeO a ' loose ' transition state (1) is expected compared to the corres-

ponding transition state for an electron-withdrawing substituent such as p-Cl (2). This expectation is anticipated theoretically on the basis of Thornton's rules [10] since the substituent change for an S_N2 reaction

[9] Y. Karton and A. Pross, *J.C.S., Perkin II*, 1978, 595.
[10] E. R. Thornton *J. Amer. Chem. Soc.*, 1967, **89**, 2915.

constitutes a perturbation *perpendicular* to the reaction co-ordinate. Experimental verification for this prediction has also been obtained.[11] Now a ' loose ' transition state implies low selectivity since the interaction between substrate and nucleophile is as yet weak. In such circumstances the substrate will exhibit low discriminating ability. On the other hand, for a ' tight ' transition state in which substrate and nucleophile are more strongly associated, greater selectivity will result.

For an S_N1 process however, product formation takes place *after* the rate-determining step, as a result of nucleophilic attack on the ion pair intermediate. Here the substituent effect represents a perturbation *parallel* to the reaction co-ordinate. In this case stabilisation of the ion pair species is expected to *enhance* ion pair selectivity. There is experimental support for this belief. Karton and Pross [8] found that for a group of substituted diphenylmethyl derivatives (a classic S_N1 case), selectivity decreases along the series p-Me > H > p-Cl > p,p'-Cl$_2$. In other words, more stable ion pairs are more selective. This is the *opposite* order anticipated for a concerted S_N2 process and provides a simple means of differentiating between these two possibilities.

Examination of substrate selectivity in aqueous 95% ethanol (the least polar medium in which a converted process is most facilitated) shows the selectivity order which *decreases* for more electron-attracting substituents, *i.e.* p-MeO > p-Me > H > p-Cl. This is analogous to the diphenylmethyl case and suggests that product formation occurs as a result of solvent attack on an ion pair species. Electron-releasing substituents, which stabilise the ion pairs, result in an increase in selectivity toward the competing nucleophiles. In other words, the rate-determining step in which solvent attacks to form a nucleophilically solvated ion pair appears to be quite distinct from the product-determining step, in which a molecule of solvent, *other* than the one responsible for ion pair formation, is likely to lead to product formation.*

If we examine the graph for p-methylbenzyl chloride (Figure 2) it appears that at high solvent ionizing power some factor intervenes which *reduces* the selectivity below the value anticipated as a result of the solvent effect alone. This is explained in terms of some dissociation of intimate ion pairs to solvent separated ion pairs. Solvent separated ion pairs are known to exhibit low selectivity values.[7,9,12] This is due to the fact that during front side attack in the solvent separated ion pair, water is more nucleophilic than ethanol, *i.e.* $k_W > k_E$. Therefore as a result of some front side

attack, the solvent separated ion pair exhibits reduced k_E/k_W values. As a consequence, in more polar mixtures, which promote greater substrate dissociation, p-methylbenzyl chloride shows little change in selectivity. The ' normal ' increase in selectivity, expected as a result of the solvent effect is compensated for by the reduction in selectivity due to increasing formation of solvent separated ion pairs. For the p-methoxy-derivative, where greater dissociation to solvent separated ion pairs occurs due to the more powerful electron-releasing substituent, constant selectivity results in solutions of low polarity, while the ' normal ' increase is observed at higher polarity ($Y > -0.4$). This suggests that at Y values < -0.4, p-methoxybenzyl chloride responds in the same manner as the p-methyl derivative, *i.e.* both intimate and solvent separated ion pairs are formed. At higher Y values, product formation occurs almost entirely from the solvent separated ion pair so that only the ' normal ' increase due to the solvent effect is observed. In summary, the selectivity data indicate that p-chlorobenzyl and benzyl chlorides undergo predominant product formation from nucleophilically solvated intimate ion pairs, that p-methylbenzyl chloride undergoes product formation from both intimate and solvent separated ion pairs, and that p-methoxybenzyl chloride undergoes product formation from both intimate and solvent separated ion pairs at low ionizing power but exclusively through the solvent separated ion pair at high ionizing power.

Effect of Leaving Group.—The study of the effect of a change in leaving group on substrate selectivity offers strong support for the conclusions stated above as well as providing a new diagnostic tool for the identification of solvent separated ion pairs in solvolytic reactions.
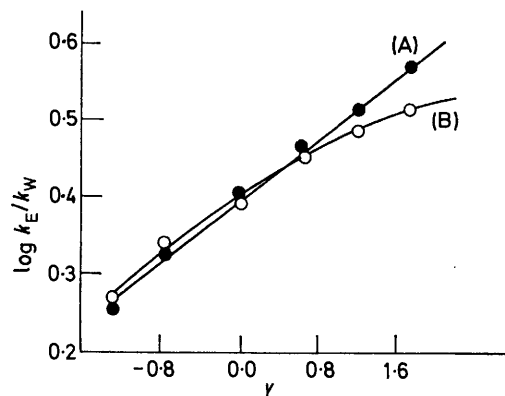

FIGURE 3   Plot of selectivity (log k_E/k_W) against Y values for (A) benzyl bromide and (B) benzyl chloride in aqueous ethanol

A plot of selectivity against solvent ionizing power for benzyl bromide and chloride is illustrated in Figure 3. With the exception of aqueous 50 and possibly 60% ethanol, it appears that there is no significant effect of

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* The concerted S_N2 and the stepwise S_N1 process have been distinguished here by assuming that the former is susceptible to perpendicular substituent effects while the latter is influenced by parallel effects. This change from perpendicular to parallel substituent control is in fact a gradual one. Therefore it is conceivable that an S_N2 type process with only very weak nucleophilic assistance could also result in a dominant perpendicular effect. Operationally however this borderline situation is also best considered as S_N1 since the nucleophilic assistance is then unlikely to be kinetically measurable.

[11] (a) E. C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, 1968, **90**, 6447; (b) C. G. Swain, T. Rees, and L. J. Taylor, *J. Org. Chem.*, 1963, **28**, 2903.
[12] A. Pross, *Tetrahedron Letters*, 1975, 637.

leaving group on substrate selectivity. This is analogous to octyl and 1-methylheptyl derivatives,[5] but in contrast to 1- and 2-adamantyl [9] and diphenylmethyl [8] derivatives which exhibit a clear leaving group dependence on selectivity. The apparent conclusion is that product formation from back side nucleophilic attack on intimate ion pairs is leaving group independent while attack on the solvent separated ion pair is leaving group dependent.
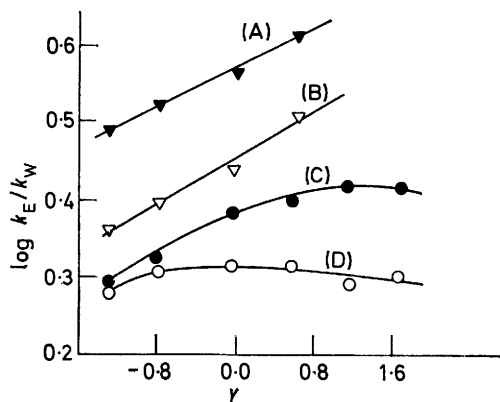

FIGURE 4 Plot of selectivity (log k_E/k_W) against Y values for (A) diphenylmethyl bromide, (B) diphenylmethyl chloride, (C) p-methylbenzyl bromide and (D) p-methylbenzyl chloride in aqueous ethanol. Data for diphenylmethyl derivatives from ref. 8

This may be stated as a rule. *The observation of a leaving group effect on selectivity during the aqueous ethanolysis of a particular substrate indicates at least partial product formation from the solvent separated ion pair.* This behaviour presumably stems from the possibility of front side attack in the solvent separated ion pair. Since in such a process, leaving group and incoming nucleophile interact directly, the dependence of substrate selectivity on leaving group is not unexpected. Application of this diagnostic tool toward benzyl and diphenyl-methyl derivatives leads to conclusions identical to those arrived at based on the solvent effect on selectivity. Thus p-methylbenzyl chloride and bromide which exhibit similar selectivity in aqueous 95% ethanol (Y —1.3) show increasingly dissimilar selectivity as the ionizing power increases (Figure 4). Accordingly, this suggests that the intervention of solvent separated ion pairs increases constantly with an increase in solvent ionizing power. This is consistent with our earlier conclusion based on the effect of solvent polarity on selectivity.

The slight but significant difference between the

selectivity exhibited by benzyl chloride and bromide in aqueous 50 and 60% ethanol (Figure 3) suggests that at high polarity, there is already some product formation *via* the solvent separated ion pair even in the un-substituted substrate. The slight curvature for benzyl chloride at high ionizing power also supports this inter-pretation (Figures 1 and 3).

The leaving group behaviour for the diphenylmethyl system is also consistent with the above picture (Figure 4). There is a large difference between the selectivity of diphenylmethyl chloride and bromide. This points to attack on the solvent separated ion pair. The fact that the selectivity difference is approximately constant throughout the entire polarity range studied, suggests that no other significant product-determining step takes place. Were either intimate ion pair of free cation involved to any significant extent the two plots for diphenylmethyl chloride and bromide would be expected to converge either at the low polarity end (implicating the intimate ion pair) or the high polarity end (implicating the free ion). The ' normal ' linear increase in selectivity with solvent polarity further reinforces the view that product formation from one intermediate only is indicated.

One point requires clarification. For all those sub-strates undergoing solvolysis *via* solvent separated ion pairs, the bromide invariably exhibits higher selectivity than the corresponding chloride. We believe this is due to the greater hydrogen bonding ability of chloride ion compared with bromide ion. Thus in the competitive attack of solvent from the back side and the front side (3), greater hydrogen bonding ability of the leaving

$$S\text{—}O \quad R\text{---}O\text{—}H\text{---}X$$
$$\quad |\qquad\quad |$$
$$\quad H\qquad\quad S$$
$$(3)$$
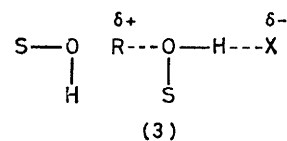
group will enhance the nucleophilicity of that solvent molecule separating the cation from the anion. As a result front side attack is relatively favoured leading to reduced selectivity values for chlorides compared with bromides.

Effect of Added Acetone.—We have studied the effect of solvent composition on selectivity by the addition of acetone to fixed aqueous ethanol mixtures. Data for p-methylbenzyl and the previously reported [5] benzyl chloride in aqueous 50 and 95% ethanol are presented in Table 2 and illustrated in Figures 5 and 6. In

TABLE 2

Selectivity [a] of p-methylbenzyl and benzyl chlorides in aqueous 50 and 95% ethanol–acetone [b] mixtures at 75°

Substrate	Aqueous % ethanol (v/v)	% Acetone (v/v) [b]			
		20	40	60	80
Benzyl chloride	50	2.88 ± 0.05	2.59 ± 0.03	2.18 ± 0.08	1.79 ± 0.03
	95	1.73 ± 0.03	1.56 ± 0.02	1.35 ± 0.04	
p-Methylbenzyl	50	1.87 ± 0.03	1.90 ± 0.04	1.90 ± 0.04	1.79 ± 0.06
chloride	95	1.64 ± 0.02	1.52 ± 0.05	1.36 ± 0.07	

[a] Selectivity defined as k_E/k_W and determined by g.l.c. in the presence of excess pyridine. Error values are standard deviations.
[b] Solutions made up by mixing x ml of either aqueous 50 or 95% ethanol and (100 — x) ml acetone by volume.

general the effect of the addition of acetone mirrors the effect observed on changing the composition of the aqueous ethanol mixture. Thus addition of acetone to a solution of benzyl chloride in aqueous 50 and 95% ethanol (Figure 5) brings about a decrease in substrate
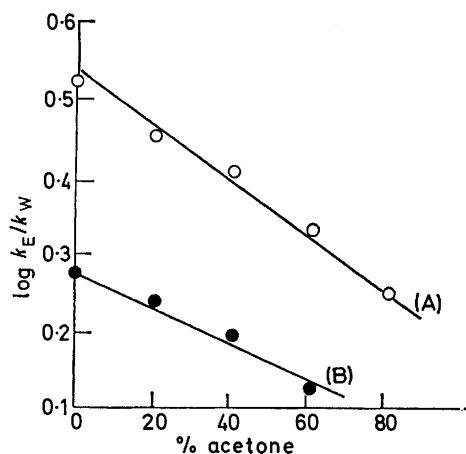

FIGURE 5   Plot of selectivity (log k_E/k_W) against % acetone for benzyl chloride in (A) aqueous 50% ethanol and (B) aqueous 95% ethanol
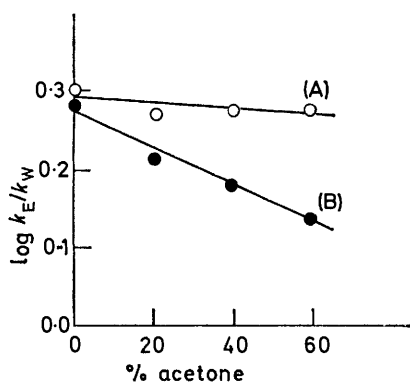

FIGURE 6   Plot of selectivity (log k_E/k_W) against % acetone for p-methylbenzyl chloride in (A) aqueous 50% ethanol and (B) aqueous 95% ethanol

selectivity in analogy to octyl [5] and diphenylmethyl substrates.[8] Due to the similar response of these substrates we conclude that the effect is primarily a solvent

addition of acetone (in analogy with benzyl, diphenylmethyl, and octyl derivatives), the response of selectivity toward acetone is very small for aqueous 50% ethanol. We believe this behaviour mirrors the response of p-methylbenzyl chloride to variations in the aqueous ethanol composition (Figure 2). The addition of acetone brings about the ' normal ' reduction of selectivity due to the solvent effect, which is largely cancelled out by the perturbation in the intimate ion pair–solvent separated ion pair quasi-equilibrium. Greater product formation takes place from the more selective intimate ion pair. In aqueous 95% ethanol this compensation phenomenon does not occur since only the intimate ion pair is implicated in this less polar mixture (confirmed by the leaving group effect criterion).

Effect of Temperature.—The effect of temperature on the selectivity of p-methyldiphenylmethyl chloride in aqueous 50 and 95% ethanol was determined. The data as well as the previously reported data for benzyl chloride [5] are listed in Table 3. There appears to be a general tendency for selectivity to decrease as the temperature increases. This is not unexpected in view of the relationship (2) between selectivity and temperature. The absence of a significant effect for benzyl

$$\log k_E/k_W = -\Delta\Delta H^{\ddagger}/2.303RT + \text{constant} \quad (2)$$

chloride in aqueous 95% ethanol implies a small $\Delta\Delta H^{\ddagger}$ value. As we have stated, it is noteworthy that for benzyl chloride in aqueous 50% ethanol a substantial temperature dependence exists.

This suggests that for substrates exhibiting significant selectivity, a greater temperature dependence is obtained, due to the greater $\Delta\Delta H^{\ddagger}$ values. The overall conclusion however is that temperature effects on selectivity are not of great significance. Certainly, in these systems there is no evidence for an isoselective point such as has been noted by Giese.[6b,13]

Conclusions.—The application of selectivity studies to identification of reaction intermediates such as carbenes, is well known. However, use of this tool in solvolytic studies has been very scant. We believe that this technique has considerable potential in solving some of the outstanding problems in this area. This particular

TABLE 3

Effect of temperature on selectivity [a] of benzyl and p-methylbenzyl chloride in aqueous 50 and 95% ethanol

Substrate	Aqueous % ethanol (v/v)	Temperature (°C)			
		75	100	120	140
Benzyl chloride	50	3.33 ± 0.11	3.03 ± 0.05	2.73 ± 0.04	2.61 ± 0.02
	95	1.86 ± 0.06	1.86 ± 0.07	1.98 ± 0.06	1.86 ± 0.03
p-Methylbenzyl	50	2.00 ± 0.06	1.80 ± 0.02	1.73 ± 0.01	1.67 ± 0.03
chloride	95	1.91 ± 0.05	1.79 ± 0.05	1.70 ± 0.08	1.70 ± 0.02

[a] Selectivity defined as k_E/k_W and determined by g.l.c. in the presence of excess pyridine.   Error values are standard deviations.

effect whereby the addition of acetone increases the relative nucleophilicity of water in comparison to ethanol. The behaviour of p-methylbenzyl chloride is of interest (Figure 6). Whereas in aqueous 95% ethanol a drop in selectivity occurs following the

work demonstrates the reaction intermediates present in benzyl solvolysis. In addition, a new selectivity criterion for the identification of solvent separated ion pairs in solvolytic reactions is reported.

[13] B. Giese, *Angew. Chem. Internat. Edn.*, 1976, **15**, 174.

EXPERIMENTAL

Materials.—Alkyl halides were commercially available and were distilled prior to use. *p*-Methoxybenzyl chloride was prepared from the alcohol and thionyl chloride, b.p. 58—59° at 0.1 mmHg (lit.,[14] 83—84° at 2 mmHg), and found to be pure by n.m.r. and i.r. spectra. Pyridine was stored over KOH and distilled prior to use.

Product Determination.—Reactions were performed in pressure tubes containing substrate (0.01M), pyridine as base (0.013M), and solvent (5 ml). Pyridine concentrations of up to 0.06M were found to have no influence on the selectivity data. Reactions were conducted in thermo-statted oil baths (± 0.05 °C) for 10—20 half-lives. For all materials, product ratios were established as stable under

the reaction conditions. Product ratios were determined by g.l.c. on a 1.5 m $\times$ 1/4 in column packed with 3% Carbowax 20 M on 60—70 mesh Chromasorb WAW DMCS. Response factors of alcohol and ether products were measured using standard mixtures. Ether standards were prepared from the corresponding halide and sodium ethoxide in ethanol. All gave satisfactory n.m.r. spectra after distillation. Selectivity data are the average of between two and four determinations with a least duplicate runs. An error of up to 5% is estimated for product ratios though standard deviations generally amounted to less than this.

[14] ' Handbook of Chemistry and Physics ', ed., R. C, Weast, CRC Press, Cleveland, 1976.