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REACTIVITY-SELECTIVITY RELATIONSHIPS. VIII.[1]

AN UNUSUAL SOLVENT EFFECT ON SELECTIVITY IN THE SOLVOLYSIS OF BENZYL DERIVATIVES

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In earlier papers of this series we studied the effect of solvent on the selectivity of alkyl derivatives during solvolysis, toward the competing nucleophiles ethanol and water. This study included octyl halides and arenesulphonates,[2] benzyl chloride[2], 1- and 2- adamantyl derivatives[1] and a series of substituted benzhydryl halides.[3] With the exception of adamantyl derivatives these substrates all showed k_E/k_W values greater than 1,[4] and a plot of log k_E/k_W against solvent ionizing power gave linear correlations of essentially identical slopes. The similarity in the response toward solvent changes for such mechanistically distinct model substrates led us to conclude that the changes in selectivity could be attributed in all cases to changes in the relative nucleophilicity of ethanol and water as a function of solvent composition.[1]

This paper concerns itself with the examination of the response of selectivity to changes in solvent polarity for a series of substituted benzyl derivatives. The selectivity data are listed in the Table and are illustrated in Figs. 1 and 2.

While the behavior exhibited by p-chlorobenzyl chloride is identical to that shown by benzyl chloride and the previously reported series of substituted benzhydryl derivatives,[3] it is apparent that p-methylbenzyl and p-methoxybenzyl derivatives are anomalous. Neither give linear correlations. Also in contrast to benzhydryl derivatives in which a Hammett correlation resulted from a plot of selectivity against σ^+ at all solvent compositions, no such correlation occurs for benzyl derivatives.

We believe this deviation from the normal pattern may be utilized as a mechanistic tool. The results suggest that an additional effect takes place which superimposes itself on the usual linear increase in selectivity as solvent polarity is increased. Whereas the "normal" behavior re-

Table. Selectivity[a] values of p-substituted benzyl derivatives during solvolysis in aqueous ethanol at 75°.

	% ethanol (v/v)					
Substituent	50	60	70	80	90	95
H[b]	3.33	3.09	2.87	2.45	2.17	1.86
Cl	3.23	2.98	2.67	2.33	1.86	1.67
CH_3	2.00	1.96	2.07	2.07	2.05	1.91
CH_3O[c]	3.81	3.24	2.78	2.46	2.15	2.22

[a] Selectivity defined as k_E/k_W and determined by g.l.c. in the presence of excess lutidine or pyridine.[2a] Error is estimated as ± 5%.

[b] Data from ref. 2a.

[c] Selectivity values obtained in 85, 92 and 94% aqueous ethanol were 2.28, 2.27 and 2.22, respectively.

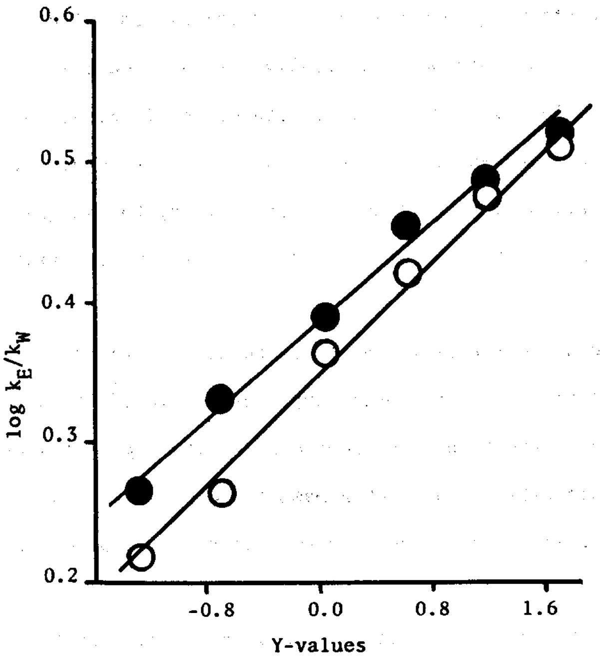

Fig. 1: Plot of log k_E/k_W against Y values for ●, benzyl, and ○, p-chlorobenzyl chlorides.

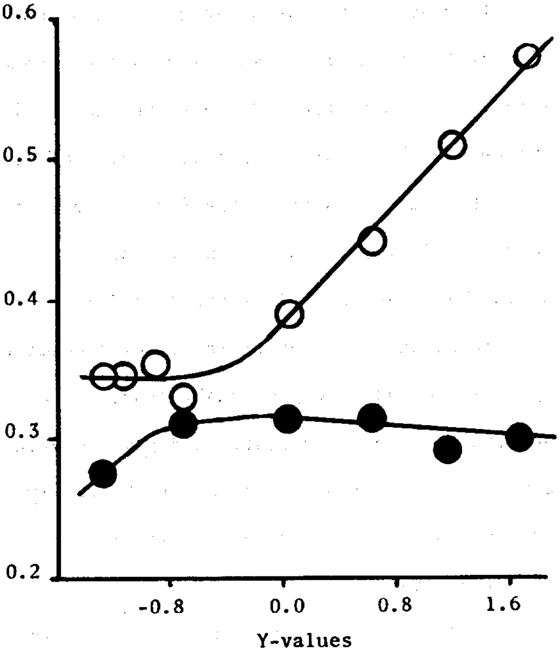

Fig. 2: Plot of log k_E/k_W against Y values for ○, p-methoxybenzyl, and ●, p-methylbenzyl chlorides.

sults from product formation from a single solvolytic species, the change in solvent polarity appears to perturb the system for p-methylbenzyl and p-methoxybenzyl chlorides by varying the nature of the product determining step. This may be understood in terms of the Winstein solvolysis[6] scheme:

$$\begin{tikzcd}
RX \arrow[r, shift left] \arrow[d] & R^+X^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & R^+||X^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & R^+ \arrow[l, shift left] \arrow[d] \\
P & P & P & P
\end{tikzcd}$$

Thus if at least two solvolytic intermediates are formed during the solvolysis of p-methylbenzyl and p-methoxybenzyl derivatives then a shift in the quasi-equilibrium as a result of a change in solvent polarity will change the relative proportion of the species undergoing product formation. Since these species are likely to exhibit different selectivities this perturbation will induce a change in selectivity superimposed onto the "normal" increase in selectivity which occurs.

Inspection of Figs. 1 & 2 shows that the perturbation which operates on p-methylbenzyl chloride acts so as to decrease the observed selectivity below its anticipated value. We believe this to indicate increasing attack on the solvent separated ion pair in more polar mixtures. This is because solvent separated ion pairs are established as exhibiting low k_E/k_W values due to some front side attack (for which k_W is actually greater than k_E). This interpretation is consistent with the increased electron releasing ability of the CH_3- group which is expected to favor greater dissociation before product formation occurs. p-Chlorobenzyl chloride and benzyl chloride are therefore indicated as undergoing product formation from R^+X^-, which represents the nucleophilically solvated intimate ion pair.[7] Consistent with this, p-chlorobenzyl chloride is less selective than benzyl chloride in accordance with the reactivity selectivity principle,[8] since electron withdrawing Cl is expected to destabilize the ion pair species.[9] For p-methoxybenzyl chloride there also appears to be a shift in the quasi-equilibrium toward solvent separated ion pairs. However, at Y values greater than ca. -0.4 the "normal" increase in selectivity reappears indicating product formation from one species only – in this case the solvent separated ion pair. The increased electron donating ability of the CH_3O– group is presumably responsible for the greater degree of dissociation that takes place in this substrated compared to the p-methylbenzyl derivative, for which both intimate and solvent separated ion pairs are still present in the more polar media.

Thus we conclude that selectivity studies in solvolytic reactions may provide information concerning solvolytic species not readily available by other means. Further study on the benzyl system which encompasses more extensive solvent studies and the effect of different leaving groups is in progress.

References and Notes

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9. While the plots for both benzyl and *p*-chlorobenzyl chlorides have been treated as linear, there appears to be slight curvature leading to lower selectivity at large Y values. This is more readily discernible for benzyl chloride and suggest that even for these two substrates, that a small contribution from the solvent separated ion pair may contribute to product formation in the more aqueous solutions.