Reactivity–Selectivity Relationships. Part 12.[1] Intermediates formed in the Solvolysis of Substituted Benzyl Derivatives. The Importance of HOMO–LUMO Interactions in determining Selectivity

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The intermediates undergoing nucleophilic attack during the solvolysis of a series of substituted benzyl derivatives in aqueous ethanol are examined in the presence of *m*-chloroaniline. Conclusions are based on the measurement of substrate selectivity towards the competing nucleophiles, ethanol and *m*-chloroaniline and the application of perturbation molecular orbital (PMO) theory. The results suggest that *p*-chlorobenzyl, benzyl, and *p*-methyl benzyl chlorides undergo nucleophilic attack on intimate ion pairs while *p*-methoxybenzyl chloride undergoes attack on solvent separated ion pairs. These conclusions are in accord with a previous study on benzyl derivatives utilizing ethanol and water as competing nucleophiles. The importance of HOMO–LUMO interactions in determining substrate selectivity in nucleophilic substitution reactions, using two dissimilar nucleophiles, is confirmed.

THE reaction mechanism for the nucleophilic substitution reaction of benzyl derivatives has attracted considerable attention in recent years.[2-10] Much of the interest has stemmed from the borderline nature of the process, making a precise mechanistic assignment particularly difficult. In addition, the problem has been exacerbated by what appears to be conflicting results obtained from studies based on kinetic isotope effect (k.i.e.) data.[3-7]

A key difficulty with the k.i.e. data is that they may be influenced by a number of parameters in addition to the degree of carbon-leaving group bond breaking in the transition state. These include the possibility of ion pair return which may be variable, the possibility of changes in the rate-determining step brought about through the use of different substituents and attacking nucleophiles, and the possibility that solvation of the leaving group (for chlorine k.i.e. studies) in the transition state may affect the k.i.e. values.[11,12] It is apparent, therefore, that interpretation of k.i.e. data in support of a unique mechanism is far from straightforward.

In an earlier Part,[2] the intermediates formed during the solvolysis of a number of substituted benzyl derivatives were studied using the tool of selectivity. Specifically, the selectivity of the benzyl derivatives toward competing nucleophiles, ethanol and water, as a function of (a) substituent, (b) leaving group, and (c) solvent composition suggested that *p*-chlorobenzyl and benzyl chlorides undergo product formation *via* attack on intimate ion pairs, *p*-methylbenzyl chloride reacts *via* both intimate and solvent separated ion pairs, while *p*-methoxybenzyl chloride reacts through solvent separated ion pairs (Scheme).

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

SCHEME

In view of the controversy surrounding the benzyl system, we decided to examine the same series of benzyl derivatives toward a different pair of competing nucleophiles, *m*-chloroaniline and ethanol, and to compare the results with conclusions reached in the previous report.[2] Hopefully this would reaffirm those conclusions regarding the benzyl system as well as to place the use of selectivity, as a mechanistic tool in substitution reactions, on a firmer basis.

RESULTS AND DISCUSSION

The use of the competitive nucleophiles, ethanol, and *m*-chloroaniline, with a substrate, RX, results in reaction (1). In order to make use of this reaction as a mechanistic

$$RX \xrightarrow[m\text{-}ClC_6H_4NH_2]{EtOH} RNHC_6H_4Cl + ROEt \qquad (1)$$

tool during solvolysis, it is necessary that the tool be applied to a number of standard models whose mechanisms are relatively well understood. In a previous publication the selectivity of octyl halides toward these two nucleophiles was studied.[1] Large selectivity values were observed, ranging from 184 for octyl brosylate to 1 670 to octyl iodide in 50% aqueous ethanol. This represents the S_N2 end of the solvolytic spectrum, where attack on the neutral substrate is expected. However, for comparison purposes, an S_N1 standard is also necessary. We have therefore examined the selectivities of 1- and 2-adamantyl derivatives toward the competing nucleophiles, *m*-chloroaniline and ethanol, in aqueous ethanol. The data are listed in Table 1.

Selectivity of Adamantyl Derivatives.—Selectivity values were obtained using equation (2), where k_N and

$$\begin{aligned}\text{Selectivity} &= k_N/k_E \\ &= \frac{[N\text{-adamantyl-}m\text{-chloroaniline}][\text{ethanol}]}{[\text{adamantyl ether ether}][m\text{-chloroaniline}]} \qquad (2)\end{aligned}$$

k_E are the rate constants of the substrates in their reactions with *m*-chloroaniline and ethanol, respectively.

The data in Table 1 indicate that adamantyl derivatives exhibit very low selectivity toward *m*-chloroaniline and ethanol (values range between 1.5 and 22.1). This contrasts with the large values observed for octyl derivatives. Since adamantyl derivatives are established as undergoing product formation predominantly through solvent separated ion pairs,[13] the low selectivity values observed may assist in the identification of solvent separated ion pairs in other systems. The low values indicate that, contrary to back-side attack, where *m*-chloroaniline is substantially more nucleophilic than ethanol, *m*-chloroaniline is only slightly more effective a nucleophile, during front-side attack from within the solvent separated ion pair. This is probably due to the greater tendency for the more acidic ethanol molecules to interpose themselves between cation and anion during the formation of the solvent separated ion pair. Being more acidic the ethanol molecules may stabilize the ion pair through a more effective hydrogen bond to the anion. Thus the greater nucleophilic character of a nitrogen compared with an oxygen atom is largely cancelled out by the more acidic nature of the ethanol molecules.

TABLE 1

Selectivity[a] of 1- and 2-adamantyl derivatives toward *m*-chloroaniline and ethanol in 60—80% aqueous ethanol

Substrate	% Ethanol (v/v) 60	70	80
2-Adamantyl bromide[b]	8.0	16.8	22.1
2-Adamantyl 4-nitrobenzenesulphonate[c]	6.2	10.7	9.6
2-Adamantyl 4-methylbenzenesulphonate	5.8	10.7	8.9
1-Adamantyl bromide[b]	1.8	1.9	1.8
1-Adamantyl chloride[b]	*d*	1.7	1.5

[a] Selectivity defined as k_N/k_E and evaluated using equation (2). Error is estimated as ±5%. [b] Data obtained at 100°. [c] Data obtained at 75°. [d] Measurement unreliable due to the formation of a precipitate during the reaction.

This view is reinforced by the difference in the selectivity data for 1- and 2-adamantyl systems. Whereas 1-adamantyl derivatives show selectivity values below 2 (Table 1), the corresponding values for 2-adamantyl derivatives range between 6 and 22. This may be understood by noting that, whereas for 1-adamantyl systems *only* front-side attack is possible, due to the bridgehead carbon, the 2-adamantyl system can undergo some inversion through back-side attack leading to higher selectivity values. Indeed, the occurrence of some back-side attack in 2-adamantyl derivatives has been observed by study of the optical purity of solvolytic products[14] obtained from 2-adamantyl solvolysis. It should be pointed out that evidence of back-side attack in 2-adamantyl derivatives in no way implies an S_N2 type reaction in such systems. On the contrary, extensive work by Schleyer and his co-workers[13] suggest that the 2-adamantyl system undergoes no significant nucleophilic assistance during rate-determining ion pair formation. It would seem that the back-side attack only occurs after formation of solvent separated ion pairs. Examination of models shows that such attack is sterically more accessible at the ion pair stage when the carbon undergoing attack is essentially sp^2 hybridized than on the neutral substrate when the particular carbon atom is sp^3.

Selectivity of Benzyl Derivatives.—Having examined the adamantyl system, we can now assess the results observed for a series of benzyl chlorides. Selectivity data for *p*-Cl-, H-, *p*-CH$_3$-, and *p*-CH$_3$O-substituted benzyl chlorides are listed in Table 2. A plot of log k_N/k_E against solvent ionizing power (*Y* values) is shown in Figure 1.

The most apparent result is that while *p*-chlorobenzyl, benzyl, and *p*-methylbenzyl chlorides show large selectivities (600—2 500), *p*-methoxybenzyl chloride shows very low selectivity by comparison (14—22). This is clearly seen in Figure 1 where the first three substrates are grouped together, while *p*-methoxybenzyl chloride lies well apart from the rest (there is a discontinuity in the selectivity scale). This result in itself, suggests that whereas the former group (*p*-Cl, H, *p*-CH$_3$) are mechanistically similar, *p*-methoxybenzyl chloride is mechanistically distinct. We are led to conclude, therefore, that for this substrate product formation results from attack on solvent separated ion pairs since the low selectivity values observed are very similar in magnitude to the results obtained for adamantyl derivatives (between 1 and 22). Further inspection shows that the selectivity values more closely resemble the 2- than the 1-adamantyl system. This suggests that *p*-methoxybenzyl chloride may undergo some back-side attack on the solvent separated ion pair in the same way that was suggested for the 2-adamantyl system.

TABLE 2

Selectivity[a] of substituted benzyl derivatives toward *m*-chloroaniline and ethanol in aqueous ethanol at 75°

Substrate	% Ethanol (v/v) 50	60	70	80	95
p-Chlorobenzyl chloride	2 460	2 030	1 710	1 110	1 015
Benzyl chloride[b]	1 440	1 250	1 130	1 080	835
p-Methylbenzyl chloride	680	615	695	695	725
p-Methoxybenzyl chloride	22	19	17	14	14
Benzyl bromide[b]	3 780	2 470	2 300	2 025	1 475

[a] Selectivity defined as k_N/k_E and evaluated using equation (2). Error is estimated as ±5%. [b] Data from ref. 1.

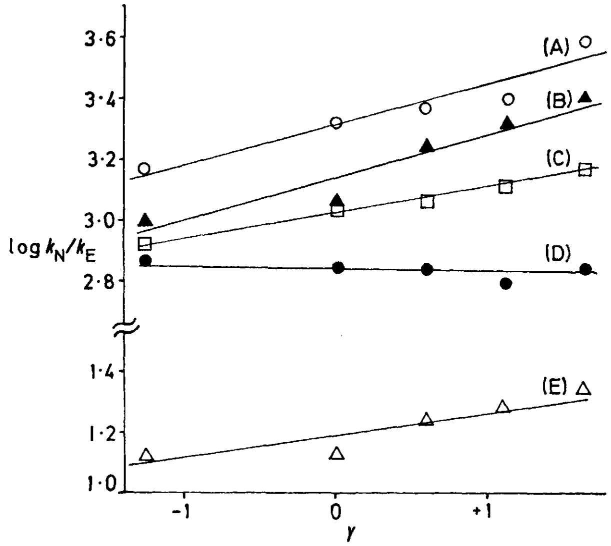

FIGURE 1 Plot of selectivity (log k_N/k_E) against *Y* values for (A) benzyl bromide, (B) *p*-chlorobenzyl chloride, (C) benzyl chloride, (D) *p*-methylbenzyl chloride, (E) *p*-methoxybenzyl chloride

An intriguing result that we noted in this and previously obtained data [1] is the fact that benzyl derivatives are, in general, substantially *more* selective than octyl derivatives. For example, in 50% ethanol, benzyl chloride shows a selectivity of 1 440 whereas octyl chloride shows a corresponding value of 640. This result is surprising at first sight, because transition states for benzyl solvolysis are considered to be ' looser ' than those for a primary substrate such as octyl derivatives. In other words, the carbon–nucleophile bond for benzyl solvolysis is expected to be *longer* than for octyl solvolysis. Now a greater carbon–nucleophile bond distance would imply lower selectivity since interaction between the nucleophile and the substrate is as yet low. This is precisely the opposite behaviour to that we observe experimentally. We believe this unexpected result suggests that nucleophilic attack takes place on intimate ion pairs and may be explained using perturbation molecular orbital (PMO) theory.[15]

In an earlier publication [1] we noted that a dominant influence on the selectivity of a substrate towards two nucleophiles attacking through different atoms, *e.g.* *m*-choroaniline and ethanol, is the difference in the HOMO–LUMO gap for the two nucleophiles. As the gap increases (through a raising of the electrophile LUMO, generally the $\sigma_{C-X}{}^*$ orbital) the selectivity decreases since the differential stabilization resulting from the HOMO–LUMO gap for the two nucleophiles decreases. Thus the selectivity is expected to be closely related to the stabilizing interaction, SE, for each nucleophile between the nucleophile HOMO and the electrophile LUMO, as shown in equation (3). β is the resonance

$$\mathrm{SE} = \beta^2/\Delta E \qquad (3)$$

integral associated with the two orbitals and ΔE is the energy difference between the two orbitals. The difference in the stabilization energy for each of the two nucleophiles, as given by equation (4), should be proportional to the observed selectivity. The subscripts N and

$$\mathrm{SE}_\mathrm{N} - \mathrm{SE}_\mathrm{O} = \beta_\mathrm{N}{}^2/\Delta E_\mathrm{N} - \beta_\mathrm{O}{}^2/\Delta E_\mathrm{O} \qquad (4)$$

O refer to the amine and alcohol nucleophiles, respectively. The greater this differential stabilization, for a particular substrate, the greater the observed selectivity of that substrate.

Now the lower the energy of the substrate LUMO the greater the differential stabilization [equation (4)] and hence also the observed selectivity. This implies that in the benzyl system, the HOMOs of the two nucleophiles interact with a *particularly low-lying substrate LUMO.* This may be seen in Figure 2. For a low-lying LUMO, the differential stabilization is greater since $\Delta E_\mathrm{N}/\Delta E_\mathrm{O} \ll 1$. For a high lying LUMO, $\Delta E_\mathrm{N}/\Delta E_\mathrm{O} \approx 1$ and correspondingly low selectivity is anticipated.

If benzyl substrates exhibit higher selectivity than octyl ones due to a lower-lying LUMO the question arises: why is the LUMO associated with the benzyl derivative lower in energy than the corresponding one for the octyl derivative?

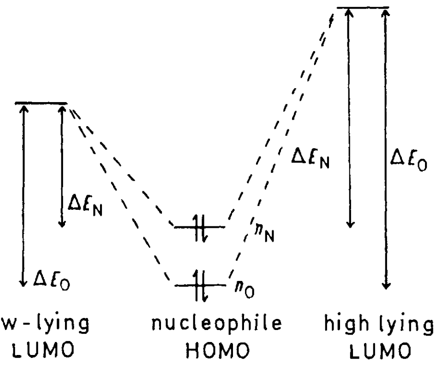

FIGURE 2 PMO Diagram showing the interaction of the two nucleophile lone pair orbitals, n_N and n_O, with a low-lying and a high-lying LUMO

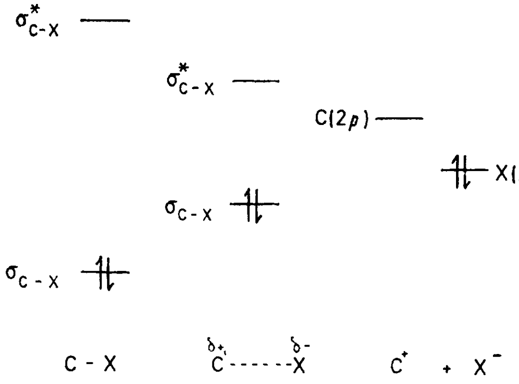

FIGURE 3 Schematic diagram showing the effect of C–X bond breaking on the energies of the σ_{C-X} and $\sigma_{C-X}{}^*$ orbitals

We believe the reason is that in the benzyl system, nucleophilic attack takes place on an intimate ion pair with a more extended carbon–leaving group bond than in the octyl system. Examination of Figure 3 clarifies this point. The relevant orbitals associated with the C–X bond are the σ and σ* orbitals. As the bond is extended the σ* orbital drops in energy while the σ orbital rises in energy. Once separation into ions is achieved a carbon 2*p* orbital and a X^- lone pair orbital result. The key point is that the $\sigma_{C-X}{}^*$ orbital, the substrate LUMO, *drops in energy as the bond is extended.* The high selectivity of benzyl derivatives, compared with octyl derivatives, therefore, suggests that the transition state for benzyl derivatives contains a ' looser ' carbon–leaving group bond than that for octyl derivatives. This ' looseness ' of the transition state in benzyl derivatives has been noted previously [16] and may be accounted for using Thornton's rules.[17] It appears, therefore, that the ' looseness ' affects the selectivity of benzyl derivatives in opposing ways. The ' looseness ' of the nucleophile–carbon bond tends to decrease selectivity (due to less interaction between nucleophile and substrate) while the ion pair nature of the carbon–leaving group bond tends to increase selectivity (due to a lowering in the energy of the substrate LUMO). The enhanced selectivities of benzyl derivatives compared with octyl derivatives suggests that the latter effect is dominant.

While we have explained the high selectivity of benzyl derivatives in terms of nucleophilic attack on intimate ion pairs, the possibility of attack on the neutral substrate cannot be dismissed. This is because evidence for a transition state with substantial bond breaking in the carbon–leaving group bond does not really reveal whether attack took place on an ion pair or whether the bond extends during the period between attack on the neutral substrate and formation of the transition state. In principle both processes could lead to the same kind of transition state. However, we favour the view that nucleophilic attack on the *p*-Cl-, H-, and *p*-CH_3-substituted benzyl chlorides takes place on intimate ion pairs rather than on neutral substrate. This is because *p*-methoxybenzyl chloride was concluded to react *via* solvent separated ion pairs. Since one would expect some mechanistic continuity in the behaviour of a series of benzyl derivatives, it seems less likely to us that *p*-Cl-, H-, and *p*-CH_3-substituted benzyl derivatives would react through the neutral substrate while *p*-methoxybenzyl chloride would react through solvent separated ion pairs. A more reasonable process would appear to be attack on intimate ion pairs for the former group while the more reactive *p*-methoxybenzyl derivative undergoes greater dissociation (to solvent separated ion pairs) before product formation occurs. The fact that *p*-methylbenzyl chloride appears to react to a slight extent through solvent separated ion pairs in the more aqueous solvent mixtures (see following discussion) lends further support to this view. However, while this possibility does appear to us more likely, the results cannot be considered unambiguous on this score.

The data in Table 2 show that the selectivity for the mechanistically related group *p*-Cl-, H-, and *p*-CH_3-substituted benzyl chlorides increases in the order *p*-$CH_3 < H <$ *p*-Cl. In other words electron-withdrawing substituents appear to enhance substrate selectivity. In a previous publication [18] we have noted that for two nucleophiles, attacking through identical atoms (*e.g.* ethanol and water) ion pair reactivity and selectivity are related. That is, reactive ion pairs are less selective than unreactive ones. For two dissimilar nucleophiles, such as *m*-chloroaniline and ethanol, reacting through different atoms, reactivity and selectivity are quite unrelated, even for a series of octyl derivatives. For the series of benzyl derivatives however, the principle appears to hold: *p*-chlorobenzyl chloride is both the least reactive and the most selective of the benzyl substrates studied, in their reaction with *m*-chloroaniline and ethanol. However, it seems clear that this correspondence is fortuitous and is unrelated to changes in transition state structure, the parameter responsible for bringing about the inverse relationship between reactivity and selectivity. Again the changes in selectivity appear to result from changes in specific orbital interactions between substrate and nucleophile. Electron donors on the benzene ring are found to raise all substrate orbitals by either a shielding process or by orbital interaction, while electron acceptors do the reverse.[19] Clearly, such behaviour is likely to affect the magnitude of the energy gap [equation (3)] between the nucleophile HOMO and substrate LUMO, leading to reduced selectivity for the *p*-CH_3 derivative where the gap increases, and enhanced selectivity for the *p*-Cl substrate where the gap decreases.

Effect of Solvent Ionizing Power.—Examination of Figure 1 indicates that with the exception of *p*-methylbenzyl chloride all substrates studied show a definite increase in selectivity as solvent ionizing power (Y values) is increased. This behaviour was noted also for octyl and 1-methylheptyl derivatives,[1] and was attributed to changes in the relative nucleophilicity of *m*-chloroaniline and ethanol as a function of solvent composition. In more aqueous mixtures, values of k_N/k_E appear to increase. Similar trends have been noted for the competitive reaction of ethanol and water.[20] In that system, an increase in solvent ionizing power was also found to lead to an increase in selectivity. In a previous publication,[20] it has been suggested that departures from a pattern, in which increasing solvent ionizing power leads to increasing selectivity, is indicative of a gradual shift from one solvolytic intermediate to another. The plot in Figure 1 suggests this is the case for *p*-methylbenzyl chloride, where an increase in solvent ionizing power may be seen to bring about a levelling off (or even a slight decrease) in the observed selectivity. The levelling off appears to be outside the bounds of experimental error. We attribute this behaviour to a slight, but increasing degree of nucleophilic attack on solvent separated ion pair intermediates superimposed on the major pathway of nucleophilic attack on intimate ion pairs. An increasing degree of product formation from solvent separated ion pairs is possible as the solvent ionizing power increases, favouring attack on a more dissociated species. Since solvent separated ion pairs show relatively low selectivity, the normal increase in selectivity as the solvent ionizing power increases, is cancelled out. The data in a similar way suggest that in the aqueous ethanol *m*-chloroaniline medium, *p*-methoxybenzyl, benzyl, and *p*-chlorobenzyl chlorides react predominantly through one solvolytic species, though the experimental uncertainty as manifested by the poor linear correlation, does not preclude a small contribution of a second species to the observed selectivity.

Conclusions.—The selectivity of a series of benzyl derivatives toward *m*-chloroaniline and ethanol in aqueous ethanol, reported here, suggests that *p*-methoxybenzyl chloride undergoes product formation through collapse of solvent separated ion pairs, while *p*-chlorobenzyl, benzyl, and *p*-methylbenzyl chlorides react through intimate ion pairs (though attack on neutral substrate has not been entirely ruled out). In more aqueous mixtures, *p*-methylbenzyl chloride reacts, in addition, to a slight extent *via* solvent separated ion pairs. These results are remarkably similar to conclusions based on the corresponding study in which competing nucleophiles, ethanol and water were employed.[2] The fact that in that study intimate ion pairs were implicated for *p*-Cl-, H-, and *p*-CH$_3$-substituted benzyl chlorides might be seen as further confirmation that ion pairs are involved in the reaction with *m*-chloroaniline and ethanol. However, caution is required in reaching such a conclusion. This is because it is conceivable that *m*-chloroaniline, a relatively strong nucleophile, may shift the point of attack to a less dissociated species than the intimate ion pair, *i.e.* the neutral substrate, making the analogy an uncertain one. The weight of evidence does in fact suggest that with powerful anionic nucleophiles (*e.g.* thiolate or azide ions) that attack on neutral substrate does occur.[3,4b]

Finally, it is of interest to briefly compare our conclusions with the k.i.e. studies on the benzyl system. Our results support conclusions reached by Hill and Fry [3] and Taylor *et al.*[4] who reported that *p*-methoxybenzyl chloride undergoes hydrolysis *via* ion pair intermediates but disagree with Collins *et al.*[6] who concluded that an $S_{\mathrm{N}}2$ process is involved. Our data also agree with Hill and Fry's contention [3] that the other benzyl derivatives undergo dissociation to ion pairs during solvolysis before reacting with solvent to form products. However, constant sulphur isotope effects observed by Friedberger and Thornton [5] in the hydrolysis of substituted benzylmethylsulphonium tosylates (including the *p*-methoxy derivative) are difficult to reconcile with our findings. Also, their results contrast with ^{14}C k.i.e. data obtained by Ando *et al.*,[21] where small variations in structure produce measurable changes in the ^{14}C k.i.e. values. We are led therefore to conclude that at the present stage of understanding k.i.e. data should be interpreted with caution as a tool in elucidating reaction mechanisms in substitution reactions, and that additional probes be employed in such studies.

EXPERIMENTAL

Materials.—Adamantyl bromides were commercially available. 1-Adamantyl chloride was prepared from adamantan-1-ol and thionyl chloride.[22] 2-Adamantyl arenesulphonates were prepared from adamantan-2-ol and the corresponding arenesulphonyl chloride.[23] Benzyl 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.,[24] 83—84° at 2 mmHg). All compounds were found to be pure by i.r. and n.m.r. spectra. Lutidine was distilled and stored over KOH or molecular sieves. *m*-Chloroaniline was distilled prior to use. Analytical grade absolute ethanol was stored over molecular sieves and used directly.

Product Determination.—Reactions were performed in pressure tubes containing substrate (0.01M), *m*-chloroaniline (0.2M), and aqueous ethanol (5 ml). Reactions were conducted in thermostatted oil-baths (±0.05 °C) for 10 half-lives. Products were established as stable under the reaction conditions. The possibility of reaction in the g.l.c. injection port was eliminated by injecting reaction mixtures at zero time. No products were detected. The possibility of the formation of the alkylammonium salt so as to render product ratios insignificant was eliminated through the addition of excess of lutidine to the reacted mixtures. No difference in product ratios was detected. The formation of alcohol products resulting from attack of water was observed in all cases, though alcohol concentrations were not estimated. Product ratios were established using response calibrated g.l.c. on a 1/4 in × 1.5 m column packed with 5% SF-96 on Anakrom ABS. Results are the average of at least 3 determinations on at least duplicate runs. An error of up to 5% is estimated in product ratios.

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