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# AMBIDENT NEIGHBOURING GROUPS, II. THE EFFECTS OF SUBSTITUENTS ON ANCHIMERISM BY URETHANE FUNCTIONS

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We have shown (1) that the urethane group can be a very powerful internal nucleophile in the presence of base, leading to what we have called (1) $N^-$-5 ring closures. We now report the response of such closures to substituent variation, using β-chloroethyl-N-arylurethanes (I) as substrates, and also report the response to the substituent variation of urethano O-5 closures, this time using β-bromoethyl-N-arylurethanes as substrates —the variation in leaving group between the systems used to explore the $N^-$5 and the O-5 closures being dictated by experimental convenience with regard to rate measurements.

Table I summarizes the behaviour of the appropriately substituted urethane under O-5 closure conditions.

The reaction concerned is as follows.

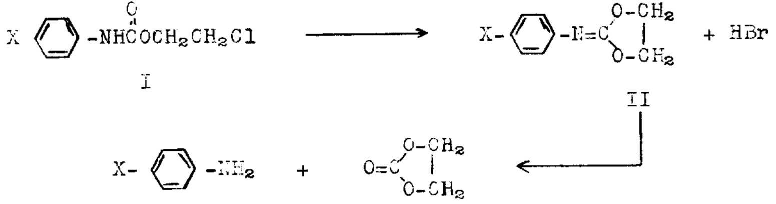


Table I

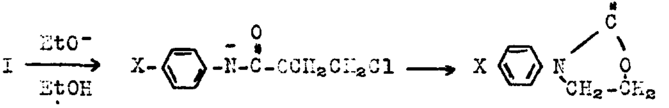
Rates of cyclization of β-bromoethyl-N-(p-substituted-phenyl)-urethanes in 80% aqueous ethanol

| X (in I) | $10^5k_1$, sec.$^{-1}$ (50°C) | $10^4k_1$, sec.$^{-1}$, (75°C) | $\Delta H^{\pm}$ (kcal./mole) | $\Delta S^{\pm}$ e.u. |
|---|---|---|---|---|
| $OC_2H_5$ | 3.70 | 4.59 | 21.7 | -11.6 |
| $CH_3$ | 3.51 | 4.56 | 22.3 | -10.2 |
| H | 2.52 | 3.32 | 22.4 | -10.4 |
| Cl | 1.61 | 2.16 | 22.6 | -10.7 |
| $NO_2$ | 0.40 | 0.62 | 23.8 | - 9.7 |

These data correspond to a Hammett $\rho$ of -0.88, the $\rho\sigma$ plot being given a least squares fit, with $r$ = -.992, and s = 0.18.

We have prepared the aryliminodioxolanes (II) by another route (2) and have shown that they, as well as ethylene carbonate, decompose under the solvolysis conditions — the former compounds yielding the corresponding arylamine, and ethylene carbonate, which in turn yields ethylene glycol. We have also established that the products formed by $N^-$-5 closure, i.e. the N-aryloxazolidones (III) do not decompose under the solvolysis conditions. We have obtained quantitative yields of the arylamines from the solvolyses of compounds of type I and have thus established the O-5 pattern of closure. The entropies of activation (while essentially constant, mean -10.5 ± 0.5, as befitting a reaction series with the substituent variation so remote from the reaction site) are substantially negative and thus correspond to the mechanism we suggest. (3)

The reactions in ethanol, in the presence of ethoxide ion, follow a different pattern, the products being N-aryloxazolidones (4). Table 2 summarizes the rate data obtained in the $N^-$-5 closures.



(III)

Table 2

Rates of $N^-$-5 closures with Substituted Urethanochlorides (I)

| X | $10^4k(0°C)$<br>$l.mole^{-1}sec.^{-1}$ | $10^2k(25°C)$<br>$l.mole^{-1}sec.^{-1}$ | $\Delta H^{\pm}$<br>kcal/mole | $\Delta S^{\pm}$<br>(e.u) |
|---|---|---|---|---|
| $NC_2$ | 232 | 123 | 25.1 | +16.0 |
| Cl | 25.2 | 15.1 | 25.9 | +24.5 |
| HQ | 8.14 | 4.57 | 25.4 | +20.7 |
| $CH_3$ | 5.37 | 3.03 | 25.5 | +20.0 |
| $OC_2H_5$ | 4.14 | 2.33 | 25.5 | +19.4 |

These data when plotted (using a least squares treatment) show a $\rho$ of +1.72 ( $r$ = 0.996, S = 0.19). These base induced reactions follow a second-order rate equation unlike the reactions of the sulphonamido halides reported by us recently (6). The $\rho$ values for the two neighbouring groups differ in sign and the $\Delta S^{\pm}$ data are appreciably more positive in the present case.

The prediction (6) that the presence of base would increase the neighbouring group potencies of certain complex groups has been amply confirmed (7). Our data now permit the division of such groups as show this base-induced potentiation into two classes; (the categories referring to reactions in the presence of base): the first, groups whose acidities are many orders of magnitude greater than the solvents employed in their study (e.g. the sulphonamido (5) and phenol (8) groups; for such groups, $\rho$ will be negative, $\Delta S^{\pm}$ close to zero (or negative (9) ) and the kinetic pattern first-order. The second (and perhaps more general class) involves such groups as the arylamido, ureido and urethano wherein the behaviour will be that discussed here (as exemplified with the urethano group), and where, for the reactions studied, $\rho$ will be positive, $\Delta S^{\pm}$ markedly positive and the rate-dependence second-order.

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3. See L.L.Schaleger and F.A. Long, pp. 17 et seq., in ''Advances in Physical Organic Chemistry'', Ed. V.Gold, Academic Press, N.Y., 1963.

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7. See Scott, Glick and Winstein (*loc.cit.*) and pertinent references therein.

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9. One can calculate the thermodynamic data involved in the cyclization of 4-p-hydroxyphenyl-1butyl-p-bromobenzene sulphonate in t-butyl alcohol in the presence of potassium t-butoxide from the kinetic data reported by Baird and Winstein, loc.cit. The thermodynamic data are $E^{\ddagger}$ 18.9 kcals. per mole, $\Delta H^{\ddagger}$ 18.3 kilocals. per mole and $\Delta S^{\ddagger}$ -17.1 e.u. .