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# NEIGHBOURING-GROUP PARTICIPATION BY SULPHINYL-OXYGEN. INFLUENCE OF DIPOLAR APROTIC SOLVENTS ON THE RATES OF SOLVOLYSIS OF CHLOROALKYLSULPHOXIDES

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In previous researches (1) we measured the rates of solvolysis in 80%-aqueous ethanol of tertiary β-, γ-, and δ-chloroalkylsulphoxides (I) $Ph-SO-(CH_2)_n-C(R'R'')Cl$ ($R' = R'' = CH_3$; $n = 1, 2, 3$). All the compounds examined reacted faster than the corresponding sulphides and sulphones (up to a maximum of 200 and 1000 times, respectively), indicating the existence of neighbouring-group participation by sulphinyl-oxygen, apparently in the order γ > β > δ.*

Nevertheless, the rates of solvolysis of the γ- and of the δ-derivatives were relatively slow in comparison with that of the β-derivative (table 1) (5-, 6-, and 4-membered cyclic transition states or intermediates, respectively), and the sequence found did not seem to give a correct picture of the SO-group participation.

The rates of solvolysis have now been measured in dimethylformammide (DMF) and sulpholane. The study has also been extended to the tertiary ε-derivative [(I), $n = 4$] and to some secondary [(I), $R' = H$, $R'' - CH_3$] and

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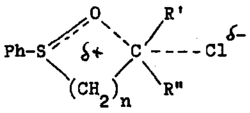
* The rate constant of the γ-derivative previously found ($k_1 = 193 \times 10^{-5}\ sec^{-1}$) turned out to be $160 \times 10^{-5}\ sec^{-1}$, i.e. equal to that of the β-derivative (table 1).

primary [(I), R' = R" = H] derivatives.

In mixtures containing 20% water (a molar fraction equivalent to 0.41 and 0.57 in DMF and sulpholane, respectively) the reaction rates follow the order $\delta > \gamma > \beta > \varepsilon \leqslant$ t-But-Cl (table 1), i.e. the maximum of reactivity is observed for a 6-membered cyclic transition state or intermediate [(II), n = 3]. With the same chain lenght, the rates decrease passing from the primary to the secondary, and tertiary derivatives (table 2).



(II)

The relative and absolute rates depend largely on the composition of the solvent; by increasing the molar fraction of water the sequence shown is substantially modified and approaches that found in aqueous ethanol (c.f. table 2). This behaviour is understandable if one bears in mind the influence exerted by dipolar aprotic solvents on nucleophilic substitutions, and also takes into account the different solvation of the SO group according to its own steric environment and to the solvent.

Solvation of anions by dipolar aprotic solvents is poor, as the positive charge of these solvents, not the negative, is surrounded by large groups. Since large, polarisable transition states are solvated similarly by protic and dipolar aprotic solvents, the result is that bimolecular nucleophilic substitutions by anions are very much accelerated in the latter solvents (2).

On the other hand these solvents are not very effective in promoting unimolecular nucleophilic substitutions, because in this case solvation of the leaving group assumes an important role (2).

Sulphinyl-oxygen is strongly hydrogen-bonded in protic solvents, but it is to be assumed that it is poorly solvated in dipolar aprotic solvents, because of the same steric factors which oppose the solvation of anions. Bearing in mind that anchimeric assistance by a neighbouring-group in solvolytic reactions can be likened to an intramolecular $SN_2$ substitution, one may expect a general increase in SO-group participation in passing from protic to dipolar aprotic solvents. This is apparent from the experimental results (tables 1, 2). A further result is that in dipolar aprotic solvents the rates of solvolysis should reflect the extent of participation more correctly than is the case in protic solvents; for interaction of sulphinyl-oxygen with the solvent, which interaction also depends on the steric environment of the SO-group, opposes interaction with cationic carbon. A typical example is that of the tertiary β-derivative [(I), n = 1], which is sterically comparable to neopentyl-phenyl-sulphoxide, and in which the (poorly solvated) SO-group can interact similarly with the centre of reaction in protic and dipolar aprotic solvents (table 1).

Table 2 shows the rates of solvolysis of the tertiary, secondary and primary γ-derivatives [(I), n = 2], and of t-butyl-chloride in 80%-, 50%- and 30%-aqueous DMF (v/v). Clearly there is present in the tertiary and, to a lesser extent, in the secondary derivatives a mechanism of direct $SN_1$ solvolysis, competing with the assisted reaction, which tends to prevail for high percentages of water. The sensitivity of the substrate to variations of the solvents is an inverse function of the extent of participation. This is highest in the primary derivative, and the anchimeric acceleration of solvolysis in aqueous DMF is not noticeably lowered even for a molar fraction of water equal to 0.87. This behaviour is analogous to that already found (4) in intermolecular $SN_2$ substitutions by anions in aqueous dipolar aprotic solvents.

The sulphides and sulphones corresponding to the sulphoxides (I) do not undergo appreciable variations in the rates of hydrolysis (relative and absolute) in passing from aqueous ethanol to 80%-aqueous sulpholane (table 3). This is to be expected for sulphones, in which participation does not take place, and also for sulphides, where the sulphur atom may provide assistance, but is poorly solvated even in protic solvents.

The solvolysis reactions were followed conductometrically at least up to 90%-conversion, first-order constants being derived by Guggenheim's method. In some cases the rates were checked by titrimetric measurements. The principal products of hydrolysis of the chloro-sulphoxides, -sulphides and -sulphones in the various solvents are, in each case, the hydroxy-derivatives.

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## TABLE 1

Rates of solvolysis of $Ph-SO-(CH_2)_n-C(CH_3)_2Cl$ (a) at 35.0° ($k_1 \times 10^5$ $sec^{-1}$)

| n | 80%-DMF (v/v) | 80%-sulpholane (v/v) | 80%-ethanol (v/v) (b) |
|---|---|---|---|
| 1 (β) | 23.8 | 82 | 160 |
| 2 (γ) | 150 | 238 | 160 |
| 3 (δ) | 315 | 830 | 37.1 |
| 4 (ε) (c) | 0.37 | 5.6 | 4.4 |
| $(CH_3)_3C-Cl$ | 1.5 | 5.1 | 5.9 |

(a) From the parent hydroxy-sulphoxides [ref. (1)] and anhydrous hydrochloric acid (2 equiv.) in chloroform solution; (b) see also ref. (1); (c) hydroxy-sulphoxide: $N_D^{20°}$ = 1.5302.

## TABLE 2

Rates of solvolysis of $Ph-SO-CH_2-CH_2-C(R'R'')Cl$ (a) at 35.0° ($k_1 \times 10^5$ $sec^{-1}$)

| R' | R" | 80%-DMF | 50%-DMF | 30%-DMF | 80%-ethanol |
|---|---|---|---|---|---|
| H | H (b) | 612 | 506 | 422 | 27.2 |
| $CH_3$ | H (c) | 337 | 755 | 978 | 36.8 |
| $CH_3$ | $CH_3$ | 150 | 736 | 1010 | 160 |
| $(CH_3)_3C-Cl$ | | 1.5 | 134 | 632 | 5.9 |

(a) From the parent hydroxy-sulphoxides and anhydrous hydrochloric acid (2 equiv.) in chloroform solution; (b) $N_D^{20°}$ = 1.5710 (crude); hydroxy--sulphoxide: b.p. = 146-148°/0.06 mm., $N_D^{20°}$ = 1.5821; (c) hydroxy-sulphoxide: b.p. = 152°/0.06 mm; $N_D^{20°}$ = 1.5683.

TABLE 3

Rates of solvolysis of $Ph\text{-}X\text{-}(CH_2)_n\text{-}C(CH_3)_2Cl$ at 35.0° ($k_1 \times 10^5$ $sec^{-1}$)

| n | | X = S | | X = $SO_2$ | |
|---|---|---|---|---|---|
| | | 80%-sulpholane | 80%-ethanol | 80%-sulpholane | 80%-ethanol |
| 1 | (β) | 97.8 | 125 (a) | 0.20 | 0.15 (a) |
| 2 | (γ) | 0.46 | 0.87 (a) | 0.57 | 0.54 (a) |
| 3 | (δ) | 1.26 | 2.36 (a) | 0.99 | 0.99 (a) |
| 4 | (ε) | 3.90 | 4.07 (b) | 3.13 | 2.84 (c) |

(a) See ref. (1); (b) b.p. 106-108°/1.2 mm., $n_D^{20°} = 1.5496$; (c) $n_D^{20°} =$ = 1.5280 (crude).

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