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CATHODIC CLEAVAGE OF SOME CYCLIC SULPHONES

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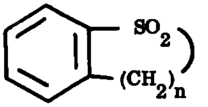
It is known[1,2] that electrochemical cleavage of unsubstituted aryl alkyl sulphones takes place according to the scheme

$$ArSO_2R + 2\ e^- + H^+ \longrightarrow ArSO_2^- + RH$$

at a mercury cathode in the potential range below -2 V (vs. SCE). Horner and Neumann[1] have suggested that the stability of the radical initially formed determines which bond is cleaved. The above cleavage mode has been shown to be valid for alkyl-, amino-, alkoxy-, and halophenyl methyl sulphones.[2] Only with strongly electron-attracting substituents does the cleavage take place across the aryl-sulphur bond.[3]

It was thought to be of interest to study the cathodic cleavage of the cyclic sulphones (**1**-**3**). If the cleavage were to take place between the sulphonyl group and the neighbouring methylene group, which appeared probable in view of earlier work,[1,2] o-alkylbenzenesulphinate ions would have been obtained. It has now been demonstrated that the main product in all three cases is the sulphinate ion of structure $C_6H_5(CH_2)_nSO_2^-$, i.e., the cleavage takes place between the aromatic ring and the sulphonyl group. The reductions were performed in DMF with tetraethylammonium perchlorate as supporting electrolyte.

The reason for this remarkable ring opening mode, which contrasts the behaviour of open-chain aryl alkyl sulphones, is being sought at present. It may be a consequence either



1: n = 2
2: n = 3
3: n = 4

of the vibrational pattern of the cyclic compounds or of the detailed mechanism of electron transfer at the mercury cathode. The polarographic half-wave potentials of (1-3) are about 0.2 V more negative than that of phenyl methyl sulphone.

Experimental. 50 ml of a 0.2 M solution of the appropriate sulphone in DMF, also being 0.5 M in tetraethylammonium perchlorate, were electrolysed in a divided cell with mercury cathode area 15 cm^2 at a constant current density of 10 mA/cm^2. A glass-encapsulated magnetic stirrer bar was used. The cathode potential, monitored with a SCE, remained constant at -2.45 V until very nearly the calculated amount of charge, 2 F/mole, had been introduced. The potential then suddenly decreased to -2.70 V and the cathode surface became black. At this moment the electrolysis was stopped. The sulphinate in the catholyte was converted into the corresponding benzyl sulphone[1] which was identified by NMR. In this way the structure was unequivocally proved. The yields of main product were at least 50 %. Smaller amounts (10 - 20 %) of other compounds, probably the o-alkylbenzene sulphinate derivatives, were also found.

References

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