CCCCXII.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part III. A Decomposition of Dialkylsulphones.*

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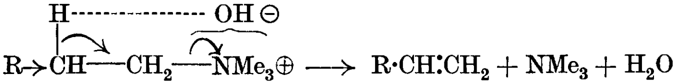
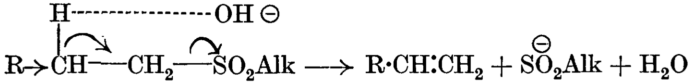
The mechanism advanced in Part I (Hanhart and Ingold, J., 1927, 997) for the decomposition of quaternary ammonium hydroxides into olefins, tertiary amines, and water suggests that dialkylsulphones (Alk·SO_2·Alk′) should be capable of a similar decomposition, since the dipole in the sulphone group (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525; Sugden, this vol., p. 263) would be expected to induce incipient ionisation in the β-protons of each alkyl group in sufficient degree to facilitate their union with a suitable protonacceptor. The products would be an olefin and an alkylsulphinic acid (*A*). Indeed the suggested analogy between



$$\begin{array}{l} H\text{--------------------}OH^{\ominus} \\ R{\to}CH{-}CH_2{-}NMe_3{\oplus} \longrightarrow R{\cdot}CH{:}CH_2 + NMe_3 + H_2O \end{array}$$

and



$$\begin{array}{l} H\text{--------------------}OH^{\ominus} \\ R{\to}CH{-}CH_2{-}SO_2Alk \longrightarrow R{\cdot}CH{:}CH_2 + \overset{\ominus}{S}O_2Alk + H_2O \end{array}$$

is complete except in two respects. The first of these is that, whereas the quaternary ammonium compound can supply its own proton-seeking anions (hydroxide), the sulphone cannot; wherefore alkali would have to be added in the latter case (*B*). The second is that the electron-affinity of $\cdot SO_2Alk$ is weaker than that of $\cdot NMe_3$ (Ingold, Ingold, and Shaw, J., 1927, 813); wherefore the effect of R→ in inhibiting the reaction (compare Parts I and II) should work more powerfully in the case of the sulphones (*C*). Otherwise we should expect most of the features which characterise the reaction of the quaternary hydroxides to apply without change to that of the sulphones, as, for instance, the rule regarding the preferential elimination of ethylene (*D*).

We have examined the action of alkali on three typical sulphones and have established the following facts :

(1) The expected decomposition of diethylsulphone occurs, the products being ethylene and ethanesulphinic acid (compare *A*). Alkali is necessary to the decomposition (compare *B*).

(2) *Ethyl-*n*-octylsulphone* similarly decomposes, giving ethylene and *n*-octanesulphinic acid, but no detectable quantity of *n*-octene or ethanesulphinic acid. This illustrates the ethylene rule (compare *D*).

(3) In contrast with the fission of trimethyl-*n*-octylammonium hydroxide, which yields some 75% of *n*-octene (compare Part II), di-*n*-octylsulphone is not decomposed at all under the conditions of reaction mentioned under (1) and (2); so that, when each β-proton is protected by the electron-source action of a *n*-hexyl group (R in the formulæ), the fission of the sulphone is inhibited completely (compare *C*).

EXPERIMENTAL.

Decomposition of Diethylsulphone.—Diethylsulphone (4 g., m. p. 71°, prepared from diethyl sulphide by oxidation with permanganate, and crystallised from alcohol) was mixed with ground potassium hydroxide (15 g.) and a little water, and the melt heated in a metal-bath at 200° until the vigorous evolution of gas ceased; the whole apparatus was then swept out with a current of nitrogen. The gases were passed first through dilute hydrochloric acid (two flasks), then through liquid bromine (two flasks), and finally into an aspirator. The gas in this was proved to be free from ethane or other hydrocarbon. The hydrochloric acid solution was tested for ethyl alcohol by distilling it and treating the first portion of the distillate with *p*-nitrobenzoyl chloride and alkali; no ethyl *p*-nitrobenzoate was obtained. Thus it appears that possible hydrolysis to ethyl alcohol and ethanesulphinic acid does not correspond with the products, and that, if ethanesulphinic acid is formed in any manner, it does not break down to ethane and sulphurous acid under the conditions of the experiment. The contents of the traps containing bromine were mixed with ice, decolorised with sulphur dioxide, and made alkaline with sodium carbonate. The heavy oil was partly run off and partly extracted with ligroin, and then distilled, 3·7 g., b. p. 129—131°, being obtained. Its b. p. and analysis (Found : C, 12·4; H, 2·2. Calc. : C, 12·8; H, 2·1%) identify it as ethylene dibromide. The alkaline residue was mixed with water and dilute hydrochloric acid, during which process the odour of hydrogen sulphide was noticed, and then exactly neutralised with sodium carbonate and evaporated to dryness. The residue was extracted with alcohol, which removed sodium ethanesulphinate and traces of inorganic salts; and the latter were finally eliminated by complete evaporation of the alcohol and re-extraction of the sulphinate with the same solvent, from which it crystallised on concentration (yield, 60%). From the sodium salt (2·3 g.), barium ethanesulphinate was prepared by precipitation with barium iodide in alcoholic solution (Found : Ba, 42·4; C, 14·7; H, 3·1. Calc. : Ba, 42·5; C, 14·8; H, 3·1%).

Decomposition of Ethyl-n-*octylsulphone*.—Sodium (1·2 g.) was dissolved in a solution of ethyl mercaptan (3·1 g.) in ether and the ether evaporated. The residue was heated on the steam-bath for 5 hours with an alcoholic solution of *n*-octyl bromide (10 g.) and the product was poured into a large volume of water and extracted with ether. The ethyl *n*-octyl sulphide, b. p. 102—103°/11 mm., was run with rapid stirring into nitric acid, and the product poured on ice; a rapidly solidifying oil was then precipitated. On crystallisation from ligroin this yielded *ethyl*-n-*octylsulphone* as platelets, m. p. 68°. On one occasion the product obtained by oxidation with nitric acid remained largely liquid; it was therefore treated with powdered potassium permanganate in glacial acetic acid and the same crystalline sulphone, m. p. 68°, was obtained (Found : C, 58·4; H, 10·9. $C_{10}H_{22}O_2S$ requires C, 58·3; H, 10·7%).

The method of decomposition was that already described for diethylsulphone and the reaction again took place smoothly at 200°;

the bath, however, was raised to 270° at the end of the process. The absence of appreciable amounts of ethane, octane, ethyl alcohol, and octyl alcohol was demonstrated. Octene, which would have collected mainly in the hydrochloric acid traps, was also absent, and the bromine solution, on being worked up for bromohydrocarbons, yielded only ethylene dibromide (b. p. 129—131°. Found: C, 13·3; H, 2·4%). The alkaline residues on acidification had an odour of hydrogen sulphide, and, following the procedure described above, sodium *n*-octanesulphinate was isolated in 70% yield. The corresponding *ferric* salt was obtained by precipitation with ferric chloride in the presence of dilute hydrochloric acid (Found: Fe, 9·6. $C_{24}H_{51}O_6S_3Fe$ requires Fe, 9·5%).

Stability of Di-n-*octylsulphone.*—A portion (180 c.c.) of a solution of potassium hydroxide (17 g.) in ethyl alcohol (450 c.c.) was saturated with hydrogen sulphide and added to the remainder. *n*-Octyl bromide (20 g.) was added and the mixture was kept at the ordinary temperature for 2 days, heated for 2 hours on the steam-bath, poured into a large volume of water, and extracted with ether. The di-*n*-octyl sulphide (compare Möslinger, *Annalen*, 1877, **185**, 59), b. p. 180°/10 mm., was treated (10 g.) with nitric acid (50 c.c., *d* 1·49). The oil which was precipitated by the addition of water partly solidified on keeping, and probably consisted of a mixture of di-*n*-octyl sulphoxide and di-*n*-octylsulphone. On treatment with powdered potassium permanganate in glacial acetic acid, it yielded *di*-n-*octylsulphone*, which was isolated by adding water and passing sulphur dioxide, and was purified by crystallisation from ligroin, from which it separated in platelets, m. p. 76° (Found: C, 65·9; H, 12·0. $C_{16}H_{34}O_2S$ requires C, 66·2; H, 11·8%).

On treatment with alkali under the conditions of the previous experiments, no decomposition took place, and some unchanged sulphone collected in the first trap containing hydrochloric acid. The sulphone was therefore heated for 2 hours under reflux with 90% potassium hydroxide; again no evidence of decomposition was observed and, on cooling, the original sulphone was recovered in almost the theoretical quantity.

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