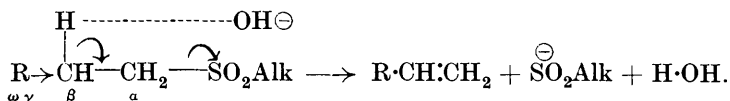


CCCVI.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part IV. Further Experiments on the Olefinic Degradation of Sulphones.*

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THE observations recorded in Parts I and II (Hanhart and Ingold, J., 1927, 997; Ingold and Vass, J., 1928, 3125) relating to the mechanism of the decomposition of quaternary ammonium hydroxides led us to anticipate that sulphones in the presence of alkali would exhibit an analogous degradation; and in Part III (J., 1928, 3127) we were able to show that diethylsulphone and ethyl-*n*-octylsulphone, when heated with concentrated aqueous potassium hydroxide, passed smoothly into the expected products, namely, ethylene and an alkylsulphinic acid.

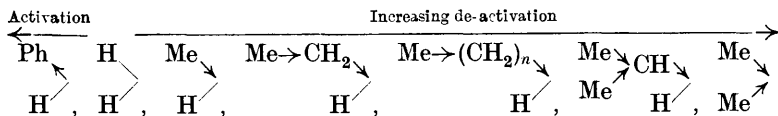
On the other hand, di-*n*-octylsulphone, when subjected to the same conditions, remained unaltered. This result, also, was not entirely unexpected, because, according to the mechanism which follows from the suggested analogy with the Hofmann degradation, the electron-repulsion due to the  $C_\gamma$ - $C_\omega$  part of each alkyl group in the sulphone will exert a protective action, reducing the incipient ionisation of the corresponding  $\beta$ -hydrogen atoms against the contrary effect of the electron-attracting sulphone dipole; and, according to the theory, these  $\beta$ -protons are the focus of the attack by the alkaline anion:



In the decomposition of ammonium hydroxides an analogous protective effect of the  $C_\gamma$ - $C_\omega$  parts of the alkyl groups is discernible (Parts I and II, *loc. cit.*); but it is opposed in all cases by the powerful electron-attraction of the ammonium pole, and does not in any known instance cause a complete disappearance of the reaction leading to an olefin, a tertiary amine and water. That the electron-affinity of  $\cdot\text{SO}_2\text{R}$  is considerably smaller than that of  $\cdot\text{NR}_3^\oplus$  has been shown (Ingold, Ingold, and Shaw, J., 1927, 84) by observations on the relative *m*-orienting powers of such groups in aromatic substitution.

Utilising the data in Parts I and II relating to the decomposition of quaternary ammonium hydroxides, it is possible to arrange a

series of alkyl groups in the order of the ease of their elimination as olefins in this reaction. The series  $\beta$ -phenylethyl > ethyl, *isopropyl*, *sec.*-butyl > *n*-propyl > *n*-butyl > *n*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl > *iso*amyl > *isobutyl*, which has been experimentally established in this way, is in agreement with the order in which the groups, which are in each case attached to the  $\beta$ -carbon atom of the alkyl radical, are expected on theoretical grounds to increase or decrease the incipient ionisation of the  $\beta$ -hydrogen atom attached by the hydroxide ion :



This correspondence with theoretical anticipation suggests that the sequence of alkyl radicals should not only apply to the degradation of quaternary ammonium hydroxides, but should also represent the ease of elimination of radicals as olefins in the new degradation of sulphones.

On this view, the difference of behaviour between diethylsulphone and dioctylsulphone must mean that, for the conditions used, there is some point between ethyl and *n*-octyl in the above series of radicals such that all sulphones,  $R'_2SO_2$ , containing radicals,  $R'$ , occurring to the left of this point undergo the degradation, whilst all sulphones,  $R''_2SO_2$ , possessing radicals,  $R''$ , occurring to the right of it do so only slightly or not at all. The same should be true for the unsymmetrical sulphones,  $R'GSO_2$  and  $R''GSO_2$  respectively, where  $G$  is a group, such as phenyl, incapable of elimination as an olefin. Sulphones having the constitution  $R'R''SO_2$  should undergo degradation to  $R''SO_2H$  and the olefin corresponding to  $R'$ . Sulphones of the form  $R'R'SO_2$ , where the  $R'$ 's are different, should yield a greater proportion of that olefin which corresponds to the  $R'$  occupying a position more to the left in the series. The last two statements embody as much as is correct of the rule, well-known in its application to quaternary ammonium hydroxides, relating to the preferential elimination of ethylene; the degradation of ethyl- $\beta$ -phenylethylsulphone should, for instance, proceed in the sense contrary to that indicated by the rule in its simplest form.

Illustrations of most of these points are contained in the following experimental record. Phenyl- $\beta$ -phenylethylsulphone yielded styrene almost quantitatively, together with sulphur dioxide and benzene, the products into which benzenesulphinic acid would decompose under the conditions used. Diethylsulphone, *diiso*-

propylsulphone and di-*n*-propylsulphone passed smoothly into the corresponding olefins and sulphinic acids, although in the last case the decomposition was distinctly slower than in the first two. We infer that any sulphone containing a  $\beta$ -phenylethyl or any  $\alpha$ -benzylalkyl, or ethyl, or any  $\alpha$ -methylalkyl, or propyl, or any  $\alpha$ -ethylalkyl group would exhibit the degradation. With di-*n*-butylsulphone, on the other hand, the reaction was so slow that under our conditions the products were formed in traces only. Not only di-*n*-octylsulphone, but also diisomyrsulphone and diisobutylsulphone, remained unaltered. Ethylisomyrsulphone, as well as ethyl-*n*-octylsulphone, underwent smooth degradation to ethylene and the appropriate aliphatic sulphinic acid. Ethyl-*n*-propylsulphone gave ethylene and propane- $\alpha$ -sulphinic acid as the principal products.

#### EXPERIMENTAL.

*Ethyl-n-propylsulphone*.—Ethyl *n*-propyl sulphide (Strömholm, *Ber.*, 1900, **33**, 830), b. p. 114—117°, was stirred for 16 hours at the ordinary temperature with a small excess of 3% aqueous potassium permanganate. The solution was heated on the steam-bath for  $\frac{1}{2}$  hour, treated with sulphur dioxide to dissolve oxides of manganese, acidified with sulphuric acid (Congo-red), partly evaporated, basified with ammonia, and evaporated to a small bulk. The residue was mixed with absolute alcohol and filtered, the salts were washed with a further quantity of alcohol, and the combined filtrates concentrated and finally evaporated to dryness in a vacuum. The residue was extracted with a small amount of alcohol, and the solution completely distilled under diminished pressure. The *ethyl-n-propylsulphone* obtained was again distilled and finally purified by partial freezing; it formed large plates, m. p. 25°, b. p. 142—143°/23 mm. (Found: C, 44.3; H, 8.6.  $C_5H_{12}O_2S$  requires C, 44.1; H, 8.8%). The decomposition with potassium hydroxide was carried out as described in Part III for diethylsulphone. The oil obtained by passage of the gases through bromine (yield, 73%, calculated as ethylene bromide) boiled almost completely at 130—131° (Found: C, 13.4; H, 2.4. Ethylene bromide requires b. p. 130°; C, 12.8; H, 2.1%), but the temperature rose to 135° at the end of the distillation. The alkaline residue was dissolved in water and neutralised with sulphuric acid, and the solution evaporated to dryness. The residue was extracted with boiling alcohol, the solution completely evaporated, and the extraction repeated with a small quantity of hot absolute alcohol. The *silver* salt of propane- $\alpha$ -sulphinic acid was obtained by addition of silver nitrate to a warm aqueous solution of the salt obtained from the last extraction.

Crystallisation from hot water yielded minute pearly leaflets (Found : C, 16.6; H, 3.3.  $C_3H_7O_2S$ Ag requires C, 16.7; H, 3.25%). Yield, 69%.

*Diisopropylsulphone*.—The decomposition of this substance, m. p. 35–36° (Beckmann, *J. pr. Chem.*, 1878, **17**, 459), yielded propylene, which was isolated as propylene bromide, b. p. 140–141°, in 78% yield (Found : C, 18.0; H, 3.05. Calc. : C, 17.8; H, 3.0%), and propane- $\beta$ -sulphinic acid, which was separated as its *silver* salt (yield, 72%) (Found : C, 16.5; H, 3.4.  $C_3H_7O_2S$ Ag requires C, 16.7; H, 3.25%).

*Di-n-propylsulphone*.—Spring and Wissenger (*Ber.*, 1883, **16**, 329; compare Wissenger, *Bull. Soc. chim.*, 1887, **48**, 111) prepared this substance from the sulphoxide; we obtained it directly from the sulphide by the method illustrated above. Under the conditions of the preceding experiments, 32%, m. p. 29°, was recovered unaltered. Propylene bromide, b. p. 140–141°, was isolated in 50% yield, and silver propane- $\alpha$ -sulphinate in 41% yield.

*Ethylisoamylsulphone* (m. p. 15°; Beckmann, *J. pr. Chem.*, 1878, **17**, 450).—The ethylene bromide (yield, 75%) boiled completely at 130–131° (Found : C, 12.6; H, 2.2%). The *silver* salt of isopentanesulphinic acid was obtained as a minute crystalline precipitate (Found : C, 24.4; H, 4.7.  $C_5H_{11}O_2S$ Ag requires C, 24.7; H, 4.5%).

*Phenyl- $\beta$ -phenylethylsulphone* (m. p. 57–58°; Posner, *Ber.*, 1905, **38**, 651).—The mixture of liquid hydrocarbons was dried with fused calcium chloride and treated with bromine, delivered through a fine capillary, until just coloured, after which the benzene, b. p. 80° (yield, 76%), was separated from the styrene dibromide, m. p. and mixed m. p. 73–74° (yield, 86%), by distillation. Benzene-sulphinic acid could not be found in the alkaline residue from the decomposition.

The behaviour of the other sulphones examined was as stated in the introduction.

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