8. *Degradation of Quaternary Ammonium Salts. Part V. Molecular Rearrangement in Related Sulphur Compounds.*

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Previous work (J., 1930, 2107, 2119) has shown that the rearrangement

$$Ph{\cdot}CO{\cdot}CH_2{\cdot}N(CH_2Ph)Me_2Br \xrightarrow{\text{Alkali}} Ph{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}NMe_2$$

is a general reaction, and the attempt has now been made to realise similar migrations with certain sulphur compounds :

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}S(CH_2Ph)MeBr \longrightarrow Ph{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}SMe} \quad \text{(A)}$$

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2Ph \longrightarrow Ph{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}SO_2Na} \quad \text{(B)}$$

$$\mathrm{Ph{\cdot}SO_2{\cdot}CH_2{\cdot}N(CH_2Ph)Me_2Br \longrightarrow Ph{\cdot}SO_2{\cdot}CH(CH_2Ph){\cdot}NMe_2} \quad \text{(C)}$$

The reaction (A) proceeded smoothly, and the product was converted, by methylation and reduction, into benzylacetophenone, in order to confirm the structure assigned to it. Attempted synthesis by the process

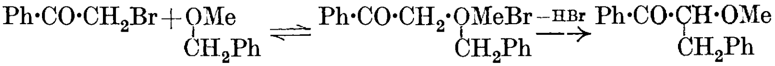
$$\mathrm{Ph{\cdot}CO{\cdot}CHBr{\cdot}CH_2Ph \xrightarrow{NaSMe} Ph{\cdot}CO{\cdot}CH(SMe){\cdot}CH_2Ph}$$

led only to replacement of the bromine atom by hydrogen, a surprising result in view of the ready preparation of phenacyl benzyl sulphide from phenacyl bromide and sodium benzyl mercaptide (Wahl, *Ber.*, 1922, **55**, 1454).

The second scheme (B) was suggested by the fact that the positively charged sulphone sulphur atom simulates in several respects the behaviour of an "-onium" atom. In particular there may be cited the observations of Fenton and Ingold (J., 1928, 3127; 1929, 2338; 1930, 705) that the Hofmann degradation of quaternary ammonium bases finds a parallel in the "olefinic" decomposition of sulphones by alkali. In case (B) above, mild treatment with alkali left the sulphone unaltered, and more drastic conditions led to hydrolysis to benzoic acid and benzylmethylsulphone. No trace of the expected sulphinic acid, or of its possible decomposition product, benzylacetophenone, could be detected. In order to obtain alkaline conditions without possibility of hydrolysis, the sulphone was heated with a strong tertiary base (benzyldimethylamine) at 190°, but with no better result.

Case (C) was suggested by the fact that the sulphonyl group, like carbonyl, confers reactivity upon an adjacent methylene radical, the presence of such a reactive methylene group being considered a condition of the rearrangement. Unfortunately, the required initial material could not be obtained, for bromomethylphenylsulphone would not under any conditions combine with benzyldimethylamine. This unexpected inertness of the halogen atom was further exemplified by the observation that the bromo-sulphone would not react with piperidine.

In the hope of extending reaction (A) to the case in which the sulphur atom is replaced by oxygen, benzyl methyl ether and bromoacetophenone were heated in presence of calcium carbonate, but no evidence could be obtained of reaction according to the scheme



$$\mathrm{Ph{\cdot}CO{\cdot}CH_2Br} + \underset{\mathrm{CH_2Ph}}{\mathrm{OMe}} \rightleftharpoons \mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}}\underset{\mathrm{CH_2Ph}}{\mathrm{OMeBr}} \xrightarrow{-\mathrm{HBr}} \mathrm{Ph{\cdot}CO{\cdot}}\underset{\mathrm{CH_2Ph}}{\mathrm{CH}}\mathrm{{\cdot}OMe}$$

EXPERIMENTAL.

Benzyl Methyl Sulphide.—Benzyl chloride was refluxed with an alcoholic solution of potassium hydrogen sulphide (3—4 mols.) on the water-bath for 4 hours, a 20% excess of caustic soda solution was added, followed, gradually, by a slight excess of methyl sulphate, the whole was refluxed for 3 hours, and the product isolated by dilution with water and extraction with ether. Benzyl methyl sulphide was obtained as a water-clear liquid of powerful, horse-radish odour, b. p. 206—210°/751 mm. Obermeyer (*Ber.*, 1887, **20**, 2926) gives b. p. 195—198°. On account of this discrepancy in boiling point, the identity of the benzyl methyl sulphide was confirmed by conversion into the sulphone by means of hydrogen peroxide in glacial acetic acid (compare Gilman and Beaber, *J. Amer. Chem. Soc.*, 1925, **47**, 1451). Benzylmethylsulphone was obtained in large plates, m. p. 125—127° (Fromm and de Seixas Palma, *Ber.*, 1906, **39**, 3315, give m. p. 127°).

Phenacylbenzylmethylsulphonium bromide, prepared from benzyl methyl sulphide and ω-bromoacetophenone in cold benzene, separated over a long period of time in masses of long fine needles, m. p. 113—115° (decomp.) (Found: Br, 23·6. $C_{16}H_{17}OSBr$ requires Br, 23·7%). The *picrate* formed masses of fine, yellow, prismatic needles, m. p. 115—117°, from methyl alcohol (Found: $C_6H_2O_7N_3'$, 47·2. $C_{16}H_{17}OS{\cdot}C_6H_2O_7N_3$ requires $C_6H_2O_7N_3'$, 47·0%).

ω-Benzyl-ω-methylthiolacetophenone was obtained by heating the foregoing bromide with an excess of methyl-alcoholic sodium methoxide solution for 3 hours. The product was isolated by dilution with water and extraction with ether; it crystallised from aqueous methyl alcohol in laminæ, m. p. 55—56° (Found: S, 12·2. $C_{16}H_{16}OS$ requires S, 12·5%). An attempt to synthesise this compound from ω-bromo-ω-benzylacetophenone and sodium methyl mercaptide in alcoholic solution led to the formation of benzylacetophenone, m. p. and mixed m. p. 70—72°. To establish the constitution of the rearrangement product, equimolecular quantities of the latter and methyl sulphate were refluxed for 6 hours in benzene solution. The oily sulphonium salt was reduced with zinc dust and dilute sulphuric acid, and the solution, on extraction with ether, yielded benzylacetophenone, m. p. and mixed m. p. 70—72°; semicarbazone, m. p. and mixed m. p. 141—143°.

Phenacylbenzylsulphone.—Phenacyl benzyl sulphide was prepared from sodium benzyl mercaptide and ω-bromoacetophenone in alcoholic solution (Wahl, *loc. cit.*); it separated slowly and after being washed with water crystallised from alcohol in irregular plates, m. p. 87—89° (Wahl describes needles, m. p. 89°). The sulphide was heated in glacial acetic acid on the water-bath for 3 hours with a 50% excess of 30% hydrogen peroxide solution. The sulphone, which separated when the mixture was poured into water, crystallised from aqueous methyl alcohol in leaflets, m. p. 111—113°, as found by Wahl, who used potassium permanganate as oxidising agent. By treatment of phenacyl benzyl sulphide with hydrogen peroxide in the *cold*, Wahl obtained the sulphoxide.

Attempted Degradation of Phenacylbenzylsulphone.—The sulphone was refluxed with an excess of methyl-alcoholic sodium methoxide solution for 3 hours, and was then recovered unchanged in almost quantitative yield. (Wahl, *loc. cit.*, refluxed phenacylbenzylsulphone with 20% alcoholic potassium hydroxide solution for several hours and obtained benzylmethylsulphone and benzoic acid.) Phenacylbenzylsulphone was heated with methyl-alcoholic sodium methoxide solution for 5 hours at 120—140°. From the solution, long prismatic needles of benzylmethylsulphone, m. p. and mixed m. p. 125—127°, were obtained. The filtrate, after dilution with water, was extracted with ether. The extract yielded benzoic acid, m. p. and mixed m. p. 119—121°, to sodium bicarbonate solution, but no unchanged phenacylbenzylsulphone to caustic soda solution. No trace of any rearrangement product was obtained, benzylacetophenone, in particular, being looked for. After phenacylbenzylsulphone had been refluxed with benzyldimethylamine for 3 hours, the only isolable substance was some unchanged initial material.

Bromomethylphenylsulphone.—In attempts to prepare this compound as described by Otto (*J. pr. Chem.*, 1889, **40**, 541) by bromination in the cold of phenylsulphonacetic acid, obtained from sodium benzenesulphinate and chloroacetic acid, only the dibromo-compound was obtained and not a mixture of the mono- and disubstituted compounds as stated by Otto. An attempt to convert the dibromomethylphenylsulphone into the monobromo-compound by refluxing the former for 7 days with alcoholic sodium ethoxide solution (2 mols.), as described for the dichloro-compound by Otto and Engelhardt (*Ber.*, 1888, **21**, 656), resulted in a 33% yield of the monobromomethylphenylsulphone, m. p. 48—50° (Otto gives m. p. 46—48°). Bromomethylphenylsulphone was also obtained by heating methylene bromide and sodium benzenesulphinate in alcoholic solution as described by Otto (*loc. cit.*). The latter gives no experimental details, but it was found that no reaction occurred on refluxing for 4 hours, whereas on heating for 6 hours at 120—140°, a moderate yield of bromomethylphenylsulphone was obtained.

It was found impossible to combine bromomethylphenylsulphone with benzyldimethylamine under any conditions whatsoever, nor would it react on refluxing with undiluted piperidine for 2 hours.

Action of Bromoacetophenone on Benzyl Methyl Ether.—Equivalent quantities of ω-bromoacetophenone and benzyl methyl ether were refluxed, after the addition of a moderate excess of calcium carbonate, first in dry toluene for 5 hours and in a later experiment in dry xylene for 6 hours, but no evidence of rearrangement was obtained, the benzyl methyl ether being recovered unchanged.

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