125. p-*Methylthiobenzenesulphonyl Chloride and Related Compounds.*

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Thioanisole with chlorosulphonic acid gave the *p*-sulphonyl chloride which was a useful intermediate for the preparation of *p*-derivatives containing sulphur in both groups.

We have shown (previous paper) that thioanisole undergoes the Friedel–Crafts reaction to give *p*-methylthioacetophenone, and we now report the successful introduction of the sulphonyl chloride group—also into the *p*-position. The resulting p-*methylthiobenzenesulphonyl chloride* (I) was utilised for the preparation of *p-methylthio- and* thence p-*methylsulphonylbenzenesulphonamide* and also of p-*methylthiobenzenesulphinic acid* (II). The last compound (as the sodium salt) was converted by methyl iodide into p-*methylsulphonylthioanisole* (III) which was also obtained by methylation of *p*-methylsulphonylthiophenol, in turn prepared from *p*-methylsulphonylaniline (*p*-aminophenyl methyl sulphone) by the diazo-reaction. These results confirm the structure of (I). p-*Bismethylsulphonylbenzene* was readily obtained by oxidation of (III).

The production of (III) from (II) is an example of the well-known method of synthesis of sulphones, $\mathrm{R{\cdot}SO_2R'}$, whereby an alkali or silver sulphinate, $\mathrm{R{\cdot}SO_2M}$, is treated with a reactive halide, R′Hal. Steinkopf (Houben's "Methoden der Org. Chem.", 1930, Vol. 3, 1325) consequently postulates the structure of a sulphinic acid as either $\mathrm{R{\cdot}\underset{O\,/\!\!/\;\;\backslash\,O}{S}{\cdot}H}$ or $\mathrm{R{\cdot}\underset{\overset{\|}{O}}{S}{\cdot}OH}$. This dual mode of representing the structure appears to be quite unnecessary especially as the sulphinate ion is undoubtedly $\mathrm{R{\cdot}\overbrace{S(O){\cdot}O}^{\ominus}}$. The group introduced would be co-ordinated either to sulphur (as is usually the case) or to oxygen, and would parallel the alkylation of ethyl acetoacetate.

Todd and Shriner (*J. Amer. Chem. Soc.*, 1934, **56**, 1382) have shown that the activating effect of the methylsulphonyl group on halogen is not nearly so great as that of the nitro-group in the reaction with alcoholic sodium ethoxide. We have confirmed this in the behaviour of *p*-chlorophenyl methyl sulphone towards sodium disulphide. Reaction proceeded much less readily than with *p*-chloronitrobenzene, and under the reaction conditions used we obtained only 4 : *4′-bismethylsulphonyldiphenyl sulphide*; a careful search for any disulphide failed to reveal more than a trace. This sulphide was characterised further by oxidation to the *trisulphone*.

Experimental.

p-*Methylthiobenzenesulphonyl Chloride.*—Chlorosulphonic acid (25 g.) was added dropwise with stirring to a solution of thioanisole (5 g.) in chloroform (20 c.c.) at such a rate that the temperature did not exceed 5°. After the intital evolution of hydrogen chloride had subsided the mixture was stirred at room temperature, and further evolution of hydrogen chloride occurred. The mixture was then poured with vigorous stirring on crushed ice (100 g.), and the chloroform layer (*A*) subsequently separated, wasted with a little ice-cold water, and dried (Na_2SO_4). Evaporation gave a viscous oil which solidified when kept. Crystallisation of this solid, m. p. 42—43°, from benzene–ligroin gave colourless prisms of the *sulphonyl chloride* (7·5 g.), m. p. 44—45° (Found : C, 38·1; H, 3·4. $C_7H_7O_2ClS_2$ requires C, 37·7; H, 3·2%).

When the chloroform solution (*A*) was treated with ammonium carbonate (10 g.), the mixture evaporated to dryness on the steam-bath, and the crystalline residue washed repeatedly with cold water, p-*methylthiobenzenesulphonamide* remained insoluble. It separated from alcohol in colourless prisms (6·5 g.), m. p. 164—165° (Found : C, 41·4; H, 4·4; S, 32·4. $C_7H_9O_2NS_2$ requires C, 41·4; H, 4·4; S, 31·7%).

This amide was oxidised by 30% hydrogen peroxide in acetic acid at 100° to p-*methylsulphonylbenzenesulphonamide*, colourless prisms from alcohol, m. p. 236° (Found : S, 27·4. $C_7H_9O_4NS_2$ requires S, 27·2%).

p-*Methylthiobenzenesulphinic Acid.*—Finely powdered *p*-methylthiobenzenesulphonyl chloride (5 g.) was shaken with a solution of sodium sulphite heptahydrate (7 g.) in water (30 c.c.), the mixture being kept slightly alkaline (phenolphthalein) by addition of 50% sodium hydroxide. After 2 hours a little insoluble matter was removed and the filtrate kept overnight in the refrigerator. The crystalline inorganic matter was filtered off and washed with a little ice-cold water, and the combined filtrate and washings were acidified (Congo-red) with 60% sulphuric acid. Colourless needles separated; crystallisation from dilute alcohol gave the *sulphinic acid* (3·5 g.), m. p. 91—92° (Found : C, 44·5; H, 3·9. $C_7H_8O_2S_2$ requires C, 44·7; H, 4·25%).

p-*Methylsulphonylthioanisole.*—(*a*) *p*-Methylsulphonylaniline hydrochloride (Goldberg and Besly, *J.*, 1945, 568) (8·3 g.) was diazotised with sodium nitrite (2·8 g.) in N-hydrochloric acid (40 c.c.) and then treated with sodium acetate trihydrate (5·2 g.). This solution was then added gradually with stirring to potassium ethyl xanthate (12 g.) in water (28 c.c.) at 70—80° and maintained at this temperature for 1½ hours. The solid product, combined with the ethereal extract of the aqueous filtrate, was refluxed with alcohol (80 c.c.) containing potassium hydroxide (4·6 g.) and glucose (4·6 g.), and the alcohol removed by distillation. Dilute sulphuric acid precipitated a solid product, together with some oil, when added to the residue. The solid, after drying on porous earthenware, crystallised from acetic acid in nearly colourless plates, and was 4 : *4'-bismethylsulphonyldiphenyl disulphide* (4 g.), m. p. 188° (Found: C, 44·4; H, 3·9. $C_{14}H_{14}O_4S_4$ requires C, 44·9; H, 3·7%). The disulphide was also obtained by oxidation of the oil (free thiol) with ferric chloride in acetic acid. Methylation of the thiol with methyl sulphate in 2N-sodium hydroxide first below 10° and then at 95° gave p-*methylsulphonylthioanisole*, colourless prisms from alcohol, m. p. 98—99° (Found: C, 47·9; H, 5·2. $C_8H_{10}O_2S_2$ requires C, 47·5; H, 5·0%).

(*b*) *p*-Methylthiobenzenesulphinic acid (2 g.) was neutralised with 2N-sodium hydroxide and alcohol (5 c.c.), and methyl iodide (2 c.c.) added. The mixture was refluxed for 14 hours and volatile products distilled. Cooling and addition of water precipitated the compound (1·5 g.), which when crystallised from alcohol had m. p. and mixed m. p. 98—99°.

p-*Bismethylsulphonylbenzene.*—*p*-Methylsulphonylthioanisole (1·5 g.) in acetic acid (10 c.c.) was heated with 30% hydrogen peroxide (8 c.c.) at 100° for ½ hour. Colourless plates of the *disulphone* (1 g.) separated on cooling; these had m. p. 256° after crystallisation from alcohol (Found: C, 41·0; H, 4·3. $C_8H_{10}O_4S_2$ requires C, 41·0; H, 4·3%).

4 : *4'-Bismethylsulphonyldiphenyl Sulphone.*—*p*-Chlorophenyl methyl sulphone, prepared from sodium *p*-chlorobenzenesulphinate and methyl iodide (as above), crystallised from alcohol in colourless needles, m. p. 96° (Miller and Smiles, *J.*, 1925, **127**, 224, give m. p. 96°, whilst Purgotti, *Chem. Abs.*, 1919, **13**, 2515, gives m. p. 57—58°).

This sulphone (10 g.) was added to sodium disulphide, made by heating crystalline sodium sulphide (11 g.) with sulphur (1·5 g.) until a clear solution resulted, and the mixture kept at 150—160° (bath temp.) for 20 hours. The mass was treated with warm water and the insoluble solid crystallised from acetic acid. 4 : *4'-Bismethylsulphonyldiphenyl sulphide* (6 g.) formed small, colourless, shining plates, m. p. 196—197° (Found: C, 49·0; H, 4·2. $C_{14}H_{14}O_4S_3$ requires C, 49·1; H, 4·1%). No reaction occurred below 140°.

Oxidation with 30% hydrogen peroxide in acetic acid at 100° for ½ hour gave the crystalline *trisulphone*, which did not melt below 308°, and was insoluble in the usual common solvents (Found: C, 44·6; H, 3·9; S, 25·4. $C_{14}H_{14}O_6S_3$ requires C, 44·9; H, 3·8; S, 25·7%).

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