The Oxidation of Alkyl Sulphides.

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Oxidation of saturated alkyl sulphides with chromic acid in pyridine and with manganese dioxide in light petroleum afforded the corresponding sulphoxides. Allyl sulphoxide has also been obtained by oxidation of allyl sulphide with manganese dioxide in light petroleum.

Oxidation of sulphides to sulphoxides and sulphones can be brought about by many reagents, including 30% hydrogen peroxide in acetic acid (Gazdar and Smiles, *J.*, 1908, **93**, 1834), nitric acid or potassium permanganate (Beckmann, *J. pr. Chem.*, 1878, **17**, 441), chromic acid (Knoll, *ibid.*, 1926, **113**, 40), and perbenzoic acid (Lewin, *ibid.*, 1928, **118**, 282). The state of oxidation achieved depends largely on reaction conditions, though mixtures of sulphoxides and sulphones are often obtained (Berg, *J.*, 1949, 1991). Chromic acid in acetic acid, alone, appears to be specific for oxidation to the sulphoxide (Knoll, *loc. cit.*). Yields are poor in the direct oxidation of unsaturated sulphides with these mentioned reagents (Price and Gillis, *J. Amer. Chem. Soc.*, 1953, **75**, 4750), presumably owing to concurrent oxidation at the centre of unsaturation. Indirect methods, involving dehydrohalogenation of β-halogeno-sulphones, offer a more satisfactory route to αβ-unsaturated sulphones, the intermediate halogeno-sulphones being readily available in good yield by oxidation of the corresponding sulphides (Price and Morita, *ibid.*, p. 4747).

The successful oxidation of unsaturated alcohols by chromic acid in pyridine (Poos, Arth, Beyler, and Sarett, *ibid.*, p. 422), and manganese dioxide in light petroleum (Ball, Goodwin, and Morton, *Biochem. J.*, 1948, **42**, 516; Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094) prompted investigation of their use with unsaturated aliphatic sulphides. Preliminary experiments were conducted with saturated aliphatic sulphides. In no case studied did oxidation proceed beyond the sulphoxide.

Under Poos, Arth, Beyler, and Sarett's conditions (*loc. cit.*), di-*n*-butyl sulphide and chromic acid in pyridine at room temperature gave di-*n*-butyl sulphoxide in 49% yield without trace of the sulphone. Use of a large excess of reagent both at room temperature and at 100° also gave only the sulphoxide. Di-*n*-butyl sulphoxide so obtained was characterised by its known physical constants and by conversion into toluene-*p*-sulphonyldi-*n*-butylsulphilimine $Bu^n_2S{:}N{\cdot}SO_2{\cdot}C_6H_4Me$-*p* by condensation with toluene-*p*-sulphonamide by use of phosphoric oxide in chloroform (cf. Tarbell and Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2939). The product was identical (m. p. and mixed m. p.) with that obtained from the sulphide and chloramine-T (cf. Mann and Pope, *J.*, 1922, 1052).

Similar oxidation of dibenzyl sulphide gave dibenzyl sulphoxide in 70% yield after 5 days at room temperature.

Similar oxidations of diallyl sulphide proved abortive. Products containing sulphur were isolated in only minute amounts, insufficient for identification. Although in all experiments difficulties were encountered with emulsions, our failure to isolate either product or starting material could not be attributed to this cause, but much allyl sulphide was lost through co-distillation with the extraction solvents. These difficulties were largely overcome by the use of manganese dioxide in light petroleum.

Oxidation of di-*n*-butyl sulphide with activated manganese dioxide in light petroleum gave the sulphoxide exclusively; reaction was slow at room temperature, but a yield of 71% was obtained after 85 hr. Dibenzyl sulphoxide was obtained, similarly, in 74% yield after 72 hr. at room temperature. Little, if any, acceleration was observed at higher temperatures. The method is suitable for oxidation of diallyl sulphide which, after 76 hr., gave diallyl sulphoxide in 13% yield. Longer reaction times (7 days) and higher temperatures failed to improve the yield. The only aromatic sulphide examined, 2 : 2′ : 4 : 4′-tetranitrodiphenyl sulphide, was not oxidised by manganese dioxide, but was recovered quantitatively.

EXPERIMENTAL

Oxidations with Chromic Acid in Pyridine.—(a) *Di-*n*-butyl sulphoxide.* Chromic acid (18·5 g.) was added during 1 hr., with stirring, to di-*n*-butyl sulphide (5·5 g.) in pyridine (180 ml.). Next morning the mixture was poured into water (1 l.) and extracted with ether, and the extract dried (Na_2SO_4) and evaporated. Distillation gave di-*n*-butyl sulphoxide (3 g., 49%) as a colourless liquid, which crystallised only under anhydrous conditions m. p. 31—32° (lit., m. p. 32°).

On exposure to air the crystals rapidly absorb moisture and liquefy, a process which is reversed on dehydration.

(b) *Dibenzyl sulphoxide.* Chromic acid (6·2 g.) was added during 1 hr. with stirring to dibenzyl sulphide (1·25 g.) in pyridine (60 ml.). After 5 days the mixture was poured into water (500 ml.) and extracted with benzene, and the extract dried (Na_2SO_4) and evaporated, to give dibenzyl sulphoxide (0·95 g., 71%), m. p. 133—134° (from light petroleum). Bohme (*Ber.*, 1937, **70**, 383) gives m. p. 134—135°.

Oxidations with Manganese Dioxide in Light Petroleum.—Manganese dioxide was prepared by precipitation from manganese sulphate and potassium permanganate as described by Ball, Goodwin, and Morton (*loc. cit.*). Light petroleum (b. p. 40—60°) was sodium-dried.

(a) *Di-*n*-butyl sulphoxide.* Di-*n*-butyl sulphide (1·2 g.) in light petroleum (120 ml.) was shaken continuously with manganese dioxide (12·7 g.) for 85 hr. Filtration and evaporation gave a small quantity of di-*n*-butyl sulphoxide. The bulk of product was isolated by continuous extraction of the manganese dioxide with benzene, which after evaporation and distillation gave di-*n*-butyl sulphoxide (0·97 g., 71%) as an oil, crystallising under anhydrous conditions (m. p. 31—32°).

(b) *Dibenzyl sulphoxide.* Dibenzyl sulphide (0·74 g.) in light petroleum (75 ml.) was shaken continuously with manganese dioxide (7·5 g.) for 72 hr. Filtration and evaporation gave only traces of unchanged sulphide. The product was isolated by continuous extraction of the manganese dioxide with chloroform, which on evaporation gave dibenzyl sulphoxide (0·5 g., 74%), m. p. 133—134° (from light petroleum).

(c) *Diallyl sulphoxide.* Diallyl sulphide (2·5 g.) in light petroleum (70 ml.) was shaken continuously with manganese dioxide (37·5 g.) for 76 hr. Filtration and evaporation gave a small quantity of unchanged sulphide. The product, isolated as in (*b*), was a brownish-red liquid (1·28 g., 45%), which on distillation yielded diallyl sulphoxide (0·36 g., 13%), b. p. 100—110° (bath)/3 mm., $n_D^{17\cdot5}$ 1·5117, $d_{17\cdot5}^{17\cdot5}$ 1·034. Lewin (*loc. cit.*) gives n_D^{20} 1·5115, d_4^{20} 1·0261.

Toluene-p-*sulphonyldi*-n-*butylsulphilimine.*—(a) *From di-*n*-butyl sulphide.* Di-*n*-butyl sulphide (0·68 g.) was shaken vigorously with cold saturated aqueous chloramine-T (1·36 g.). The solid which rapidly separated was filtered off after 1 hr. and recrystallised from benzene–light petroleum, to yield the *sulphilimine* in colourless needles, m. p. 77·5—78° (Found: S, 19·5. $C_{15}H_{25}O_2NS$ requires S, 20·3%).

(b) *From di*-n-*butyl sulphoxide.* Di-*n*-butyl sulphoxide (0·55 g.) and toluene-*p*-sulphonamide (0·56 g.) were refluxed with phosphoric oxide (0·35 g.) in chloroform (4 ml.) for 30 min. Phosphoric oxide (0·35 g.) was then added and refluxing continued for a further 30 min. The solution was decanted from the sludge whilst still hot, cooled, and washed with sodium hydroxide solution (10%). Evaporation of the chloroform gave the sulphilimine in colourless needles, m. p. 77·5—78° (from benzene–light petroleum), alone or mixed with a specimen prepared as described under (a).

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