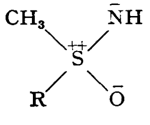
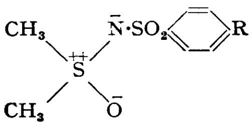
425. *Dimethylsulphoximine.*

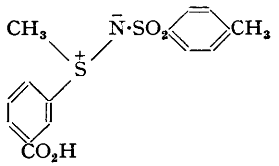
By H. R. Bentley and J. K. Whitehead.

Oxidation of dimethylsulphintoluene-*p*-sulphonylimine (VI) with permanganate followed by acid hydrolysis gives dimethylsulphoximine (I; R = CH_3). The toxic factor from nitrogen trichloride-treated proteins is considered to be a member of this new class of sulphur compounds.

The toxic factor ($C_5H_{12}O_3N_2S$) from nitrogen trichloride-treated proteins is derived from methionine by the addition to the sulphur atom of one atom each of nitrogen, oxygen, and hydrogen (Bentley, McDermott, Pace, Whitehead, and Moran, *Nature*, 1950, **165**, 150). In order to account for its considerable stability the molecule is represented formally as [I; R = $\cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$] which is stabilised by resonance in the same manner as a sulphone. This serves in particular to explain the considerably increased resistance to acid hydrolysis of (I) compared with the sulphilimines $R_2S \rightarrow NR'$ (Mann and Pope, *J.*, 1922, **121**, 1052; Tarbell and Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2939), where resonance stabilisation of this type cannot occur.

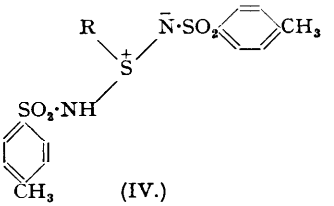

(I.)


(II.)


(III.)

Compounds of the type (I) have not previously been described although it is logical to expect them to arise by oxidation of sulphilimines. The name " sulphoximine " is adopted for the class of compound; * the toxic factor from nitrogen trichloride-treated proteins may be designated " methionine-sulphoximine."

The present communication describes the synthesis of dimethylsulphoximine (I; R = CH_3).*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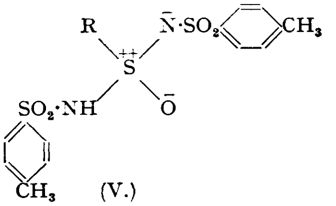
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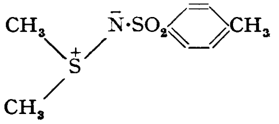
(VI.)

Clark, Kenyon, and Phillips (*J.*, 1927, 188) attempted the oxidation of (III) with perhydrol but obtained only toluene-*p*-sulphonamide and the corresponding sulphone. The compounds (IV; R = C_6H_5, C_2H_5), which are stable to hydrogen peroxide, can be oxidised to (V; R = C_6H_5, C_2H_5) by means of alkaline permanganate (*idem, ibid.*, 1930, 1225). In the present case, dimethylsulphintoluene-*p*-sulphonylimine (toluene-*p*-sulphondimethylsulphidimide) (VI) is found to be oxidised by means of neutral or alkaline permanganate to toluene-*p*-sulphondimethylsulphoximide (II; R = CH_3); prolonged treatment with permanganate oxidises the methyl group of the toluene radical giving *p*-carboxybenzenesulphondimethylsulphoximide (II; R = CO_2H).

With concentrated sulphuric acid at room temperature overnight or on the steam-bath after 5 minutes, (II; R = CH_3) undergoes hydrolysis yielding (I; R = CH_3) as the principal product. Small quantities of dimethyl sulphone may also be formed by the second mode of hydrolysis but, if so, the amounts formed have not been sufficient for characterisation in the present case.

(I; R = CH_3) is obtained in 30—40% yield as a low-melting, hygroscopic solid. It is conveniently characterised by means of its crystalline picrate which is more easily purified than the free base.

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* The name " sulphoximine " for the class of compounds typified by (I), suggested to one of the authors (H. R. B.) by Sir Robert Robinson, is an abbreviated form of " sulphoxidimine."

EXPERIMENTAL.

Toluene-p-*sulphondimethylsulphoximide*.—A mixture of dimethylsulphintoluene-*p*-sulphonylimine (VI) (10·0 g.) in aqueous sodium hydroxide (3% w/v; 50 ml.) and potassium permanganate (10·0 g., 1·5 mols.) in hot water (50 ml.) was heated for 5 minutes on the steam-bath. The mixture was then cooled and cleared with sulphur dioxide. The white solid was collected, washed thoroughly with water, and then stirred with aqueous sodium hydrogen carbonate (50% w/v; 100 ml.), collected, washed with water, and dried. *Toluene*-p-*sulphondimethylsulphoximide* (II; R = CH_3) crystallised from water as flat colourless needles, m. p. 167—169° (8·0 g., 75%) (Found : C, 43·7; H, 5·4; N, 6·0. $C_9H_{13}O_3NS_2$ requires C, 43·7; H, 5·3; N, 5·7%).

p-*Carboxybenzenesulphondimethylsulphoximide*.—A mixture of dimethylsulphintoluene-*p*-sulphonylimine (3·0 g.) and potassium permanganate (3·9 g., 2 mols.) in water (60 ml.) was boiled for 10 minutes and the mixture then cooled and cleared with sulphur dioxide. The crude dried reaction product melted over the range 160—200° and was partly soluble with effervescence in aqueous sodium hydrogen carbonate (5% w/v; 50 ml.). The insoluble fraction crystallised from water as colourless needles, m. p. 165—167° alone or mixed with a specimen of toluene-*p*-sulphondimethylsulphoximide. Acidification of the sodium hydrogen carbonate solution gave p-*carboxybenzenesulphondimethylsulphoximide* (II; R = CO_2H) as a white precipitate. This was collected, washed with water and was obtained after crystallisation from water as colourless needles, m. p. 256° (Found : C, 39·2; H, 4·1; N, 4·9. $C_9H_{11}O_5NS_2$ requires C, 39·0; H, 4·0; N, 5·1%).

Dimethylsulphoximine.—A mixture of the toluene-*p*-sulphonyl compound (16·0 g.) and sulphuric acid (*d* 1·84; 25 ml.) was heated for 5 minutes on the steam-bath, and the mixture then cooled and diluted cautiously with water (250 ml.). The solution, neutralised with sodium hydrogen carbonate, was concentrated to small volume under diminished pressure on the steam-bath, and ethanol (250 ml.) added to the residue. The ethanol solution, filtered free from salts, was again concentrated and a further quantity of salts removed similarly, the final ethanol solution being evaporated to dryness and the dry residue extracted with hot dry benzene (2 × 100 ml.). Evaporation of benzene under diminished pressure left *dimethylsulphoximine* as a pale brown oil (2·0 g., 30%) which crystallised on cooling. Redistilled, the product was obtained as a colourless oil, b. p. 130—140° (bath temp.)/15 mm., solidifying to a crystalline solid, m. p. 52—53° (Found: C, 26·4; H, 7·5; N, 13·7. C_2H_7ONS requires C, 25·8; H, 7·5; N, 15·0%). The dry product is deliquescent.

Equimolecular amounts of the free base and picric acid in water give a *picrate*, crystallising from water as long orange-yellow needles, m. p. 182—184° (Found: C, 29·5; H, 3·1; N, 16·8. $C_2H_7ONS,C_6H_3O_7N_3$ requires C, 29·8; H, 3·1; N, 17·4%).

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