# LXXXIV.—*Some Sulphur Derivatives of Aromatic Methyl Ethers.*

By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY.

FROM the nitro-*m*-chloroanisoles previously studied (J., 1926, 542), a number of mono- and di-sulphides have been prepared. They give characteristic colours with concentrated sulphuric acid, oleum, and chlorosulphonic acid, and the monosulphides are readily converted into sulphones by treatment with hydrogen peroxide in glacial acetic acid solution.

No trisulphide is formed when sodium trisulphide reacts with 3-chloro-4- or -6-nitroanisole, the disulphide alone being produced in each case (compare Blanksma, *Rec. trav. chim.*, 1901, **20**, 144; Hodgson and Wilson, J., 1925, **127**, 440).

## EXPERIMENTAL.

2 : 2′- *and* 4 : 4′-*Diamino*-5 : 5′-*dimethoxydiphenyl Disulphides.*—The corresponding dinitro-compound (4 g.) is boiled under reflux with crystallised sodium sulphide (14 g.) and water (30 c.c.) for 3 hours and the pale brown, filtered solution is exposed to the air; the base then separates (the yield exceeds 90%).

2 : 2′-*Diamino*-5 : 5′-*dimethoxydiphenyl disulphide* crystallises from alcohol (charcoal) in pale yellow needles, m. p. 76° (Found : S, 21·2.

$C_{14}H_{16}O_2N_2S_2$ requires S, 20·8%). Concentrated sulphuric acid, oleum (20%), and chlorosulphonic acid give bluish-green colorations in the cold. Ferric chloride imparts a reddish-purple colour to the solution in alcohol. The *diacetyl* derivative crystallises from dilute acetic acid or alcohol in colourless needles, m. p. 202—203° (Found : S, 16·5. $C_{18}H_{20}O_4N_2S_2$ requires S, 16·3%). The *hydrochloride*, prepared either by passing hydrogen chloride into an alcoholic solution of the base or by dissolving the latter in warm dilute hydrochloric acid (equal parts of concentrated acid and water), separates in colourless needles; on treatment with nitrous acid, it gives 5-*methoxybenzene* 2 : 1-*diazosulphide*, which has a characteristic odour and crystallises from alcohol in long, colourless needles, m. p. 80° (Found : N, 17·3; S, 19·6. $C_7H_6ON_2S$ requires N, 16·9; S, 19·3%).

4 : 4′-*Diamino*-5 : 5′-*dimethoxydiphenyl disulphide* crystallises from alcohol (charcoal) in colourless needles, m. p. 88° (Found : N, 9·4; S, 21·1. $C_{14}H_{16}O_2N_2S_2$ requires N, 9·1; S, 20·8%). Concentrated sulphuric acid, oleum (20%), and chlorosulphonic acid give blue solutions which deepen in colour on warming and become colourless on dilution. Ferric chloride gives a red colour with the alcoholic solution. The *diacetyl* derivative crystallises from dilute acetic acid or alcohol in colourless needles, m. p. 136° (Found : S, 16·6%). The *hydrochloride* is obtained in small, colourless needles and, like its isomeride above, tends to form supersaturated solutions with hydrochloric acid, from which it crystallises with difficulty; it diazotises normally.

2 : 2′- *and* 4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenyl Sulphides*.—(*a*) The disulphide (4 g.), dissolved in warm alcohol (50 c.c.) to which sodium (0·5 g.) had previously been added, was boiled under reflux with the corresponding chloronitroanisole (5 g.) for 8 hours. The separated sulphide was washed with hot alcohol and, after removal of any unchanged chloronitroanisole by steam-distillation, crystallised from glacial acetic acid. The yields were 1·8 g. and 4 g., respectively. (*b*) By Nietzki and Bothof's method (*Ber.*, 1894, **27**, 3261) of treating the respective chloronitroanisoles with sodium monosulphide in alcoholic solution. The yields were only 4% and 11%, respectively.

[In the following descriptions the characteristic colours obtained with sulphuric acid, oleum (20%), and chlorosulphonic acid are stated in this order after the analysis in sets of three, each set referring to cold treatment, subsequent warming, and dilution with water.]

2 : 2′-*Dinitro*-5 : 5′-*dimethoxydiphenyl sulphide* was obtained in stout, yellow needles, m. p. 151° (Found : S, 9·8. $C_{14}H_{12}O_6N_2S$

requires S, 9·5%), which are almost insoluble in alcohol or benzene. Red, reddish-purple, red; brown, reddish-purple, reddish-purple; brown, green, red.

4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenyl sulphide* crystallises in colourless micro-needles, m. p. 154° (Found: S, 9·8%). Deep orange, brown, colourless; black, reddish-purple, reddish-purple; black, purple, purple.

*The Sulphones of the above Compounds.*—The sulphide (1 g.), dissolved in glacial acetic acid (20 c.c.), was treated with hydrogen peroxide (1·5 c.c.; 100 vol.) and heated on the water-bath for 2 hours. On cooling, part of the sulphone crystallised. Waldron and Reid's method (*J. Amer. Chem. Soc.*, 1923, **45**, 2399) proved unsatisfactory for the preparation of these substances.

2 : 2′-*Dinitro*-5 : 5′-*dimethoxydiphenyl sulphone* is practically insoluble in alcohol and benzene, but crystallises from glacial acetic acid in colourless needles, m. p. 182° (Found : C, 45·5. $C_{14}H_{12}O_8N_2S$ requires C, 45·6%). No colour throughout; bright green, violet, red; bluish-green, blue-black, violet.

4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenylsulphone* is similar to the above, but less soluble in glacial acetic acid, from which it crystallises in colourless micro-needles, m. p. 245—246° (Found : C, 45·4%). No colour throughout; brown, brownish-purple, brown precipitate; orange, chocolate-brown, brown precipitate.

2- *and* 4-*Nitro*-5-*methoxyphenylmethylsulphones.*—The nitromethoxy-thioether (Hodgson and Handley, *loc. cit.*) (1 g.) in glacial acetic acid (10 c.c.) was heated with hydrogen peroxide (3 c.c.; 100 vol.) for 30 mins. On dilution with water, the sulphone separated as a white, crystalline powder (yield, 1 g. in both cases).

2-*Nitro*-5-*methoxyphenylmethylsulphone* is slightly soluble in hot water, but very soluble in benzene and alcohol, from which it crystallises in colourless needles, m. p. 122° (Found: S, 13·7. $C_8H_9O_5NS$ requires S, 13·8%). Pale yellow, pale yellow, colourless; dark brown, red, yellow; lemon-yellow, reddish-brown, yellow.

4-*Nitro*-5-*methoxyphenylmethylsulphone* is less soluble than its isomeride and crystallises from alcohol in stout prisms, m. p. 130° (Found: S, 13·5%). No colour throughout; orange, purple, yellow; orange, pale yellow, colourless.

2- *and* 4-*Chloro*-5-*methoxythioanisoles.*—The methoxythioanisidine (Hodgson and Handley, *loc. cit.*) was converted by the Sandmeyer method into the chloro-compound, which was removed by steam distillation, and solidified when kept over calcium chloride.

2-*Chloro*-5-*methoxythioanisole* crystallises from light petroleum in stout, colourless needles, m. p. 41° (Found : Cl, 18·7. $C_8H_9OClS$

requires Cl, 18·8%). Pink, purple, colourless; bluish-green, green, colourless; green, bright blue, colourless.

4-*Chloro*-5-*methoxythioanisole* crystallises from light petroleum in long, silky needles, m. p. 36° (Found : Cl, 18·9%). Yellow, purple, colourless; yellow, bluish-green, colourless; yellow, green, colourless.

*The Action of Sodium Trisulphide on* 3-*Chloro*-4- *and* -6-*nitroanisoles*.—A solution of the chloronitroanisole (6 g.) in alcohol (50 c.c.) was mixed with a solution of sodium trisulphide (crystallised sodium sulphide, 3·6 g.; sulphur, 0·96 g.; water, 10 c.c.) and boiled under reflux for 4 hours. The product, after removal of unchanged chloronitroanisole by steam distillation, was crystallised from glacial acetic acid, but no trisulphide was detected, the product being the almost pure disulphide (yield, 4·1 g. and 5·0 g., respectively).

The authors desire to thank Messrs. Cole and Wilson, Ltd., and the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December* 17*th*, 1927.]