113. *The Formation of Azo-compounds from* o-*Nitrothiophenol and its Methyl Ether.*

By Charles Simons and L. G. Ratner.

o-Nitrothiophenol can be converted into azobenzene-2 : 2′-disulphinic acid (*sodium* salt) in the presence of sodium amyloxide at 130°. The methyl ether of the thiophenol under similar conditions gives a mixture of reduction products, with no oxidation of the sulphur atom.

It is well known that nitrobenzene can act as an oxidising agent in the presence of alkali; *e.g.*, *iso*eugenol is thereby converted into vanillin, the nitrobenzene being reduced to aniline with some azobenzene (E.P. 271818/9; *B.*, 1928, 360). Scholl (*Monatsh.*, 1913, **34**, 1011) discusses the intramolecular oxidation–reduction of *o*-nitrotoluene to anthranilic acid, suggesting a mechanism for the reaction and pointing out the difference between the *o*- and the *p*-isomer in their behaviour in this respect. Schönberg and Iskander (J., 1942, 90) describe the formation of 4 : 4′-azobenzaldehyde from α-(*p*-nitrobenzylthio)acetic acid and, like Scholl, postulate the formation of the enol form of the nitro-group before the reduction.

We have heated *o*-nitrothiophenol to 130° with sodium amyloxide in amyl alcohol. The resulting pink product indicated that the reaction had stopped at the azo-stage and was probably *sodium azobenzene*-2 : 2′-*disulphinate* as shown by analysis and ultra-violet absorption spectrum ($\log_{10} \varepsilon$ 4·27, 4·22, 2·27; $\lambda_{\text{max.}}$ 3270, 2250, 4650 A.). Fromm (*Ber.*, 1908, **41**, 3404) obtained *p*-nitrophenyl benzyl sulphide and *p*-nitrophenylsulphinic acid by heating dinitrodiphenyl disulphide with alkali and benzyl chloride, but Price and Twiss (J., 1910, **97**, 1175) could not get a sulphinic acid by similar means from diphenyl disulphide.

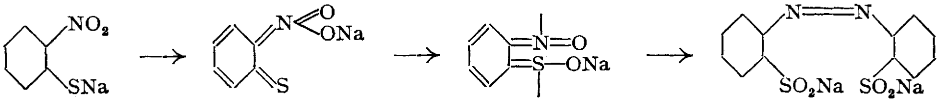
Our pink sodium salt, which is readily soluble in water, was acidified to give a pink acid, which gave two *esters* (probably dimorphous) with diazomethane ($\log_{10} \varepsilon$ 4·27, 4·28, 2·53; $\lambda_{\text{max.}}$ 2390, 3310, 4600 A.; $\log_{10} \varepsilon$ 4·26, 4·28, 2·53; $\lambda_{\text{max.}}$ 2400, 3330, 4600 A.) (cf. Cook, J., 1939, 1315). Both esters were readily hydrolysed by alkali.

Attempted reductions of the sulphinic acid to the known *o*-aminobenzenesulphinic acid (Claasz, *Annalen*, 1911, **380**, 309) failed, but the following observations were recorded. Acid reduction (zinc in acetic acid, zinc or tin and hydrochloric acid, etc.) gave colourless solutions but no substance corresponding in properties to *o*-aminobenzenesulphinic acid was isolated, owing perhaps to the ease with which the sulphinic group can be reduced to the thiophenol under such conditions. Bauer (*Annalen*, 1885, **229**, 368) attempted to reduce azobenzene-4 : 4′-disulphinic acid, finding that stannous chloride seems to give the hydrazo-compound but that sodium amalgam has no effect.

Alkaline reductions (zinc and ammonia or sodium hydroxide, sodium hyposulphite, or electrolytic) gave colourless or straw-coloured solutions, gradual acidification of which produced intense purple colours and then precipitated an orange acid, apparently different from the foregoing pink acid. Neither acid had definite characteristics. The methyl esters were rapidly hydrolysed on attempted alkaline reductions, and acid reductions gave colourless solutions from which no compound having the expected properties was isolated.

It was thought that a similar treatment of the methyl ether of *o*-nitrothiophenol with sodium amyloxide should give the corresponding azobenzenebismethylsulphone and this could be characterised by reductive fission of the azo-group to the known *o*-aminophenylmethylsulphone (Zincke and Siebert, *Ber.*, 1915, **48**, 1246). On treatment as before, a brick-red substance was obtained, which could be separated by chromatographic analysis into the red *azobenzene*-2 : 2′-*di*(*methylsulphide*) ($\log_{10} \varepsilon$ 4·35, 4·33, 4·06, 3·95; $\lambda_{\text{max.}}$ 2250, 2670, 3240, 4300 A.) (cf. Brand, *Ber.*, 1909, **42**, 3466) and the orange *azoxybenzene*-2 : 2′-*di*(*methylsulphide*) ($\log_{10} \varepsilon$ 4·45, 3·86; $\lambda_{\text{max.}}$ 2470, 3150 A.), identified by reduction to the colourless hydrazo-compound (Brand, *loc. cit.*), which was oxidised by heating in the air to the red azo-compound. Furthermore, after alkaline extraction of the aliphatic acids (formed by oxidation of the amyl alcohol) from the mother-liquors of the original reaction mixture, acid extraction gave a solution which when made alkaline afforded *o*-anisidine.

Contrary both to Scholl and to Schönberg and Iskander, enolisation of the nitro-group of the methyl ether of *o*-nitrothiophenol cannot readily occur although it may be possible for the thiophenol itself:



This would account for the exclusive formation of the azo-compound. In the case of the methyl ether, three reduction products were isolated, the azoxy-compound in the greatest yield. Furthermore, enolisation of the ether is not possible by the postulation of any intermediate compound capable of giving the compounds formed. It is known that nitrobenzene does not form an *aci*-salt and yet is capable of the oxidation of *iso*eugenol. The methyl ether may react in an analogous fashion.

EXPERIMENTAL.

o-*Nitrothiophenol*.—97 G. of di-*o*-nitrophenyl disulphide (m. p. 195°) were prepared and reduced by Claasz's methods (*Ber.*, 1912, **45**, 133, 2426) to give 60 g. of *o*-nitrothiophenol, m. p. 45°.

Dimethyl Azobenzene-2 : 2′-*disulphinate*.—12 G. of sodium were dissolved in 400 ml. of *n*-amyl alcohol under reflux, the solution heated to remove hydrogen, and cooled to 30—40°. 60 G. of *o*-nitrothiophenol were added, and the whole gently warmed in an oil-bath to 130°, whereupon a violent reaction set in and the flask was withdrawn from the bath. When the reaction had subsided it was completed by 30 mins.' heating. The mixture was cooled, filtered, and the residue washed with amyl alcohol, benzene, and finally petroleum. The crude substance (65 g.) was dissolved in hot methanol, filtered from inorganic salts, and evaporated to dryness. It recrystallised from water in spangles and was washed with methanol and ether; yield 20 g. of *sodium azobenzene*-2 : 2′-*disulphinate* (Found: C, 39·2; H, 3·1; S, 17·2; N, 7·7; Na, 11·9. $C_{12}H_8O_4N_2S_2Na_2$,MeOH requires C, 40·4; H, 3·1; S, 16·6; N, 7·3; Na, 11·9%. $C_{12}H_8O_4N_2S_2Na_2,H_2O$ requires C, 38·7; H, 2·7; S, 17·2; N, 7·5; Na, 12·4%). The aqueous mother-liquors gave a buff-coloured solid (10 g.) which was mainly inorganic but contained a trace of diazotisable material.

1 G. of this sodium salt was acidified, sucked dry on a filter, suspended in 80 ml. of acetone–ether (1 : 1), and treated with diazomethane (from 2 g. of nitrosomethylurea). The solution was evaporated to dryness, the residue dissolved in benzene, treated with alumina, and fractionally crystallised, giving 0·7 g. of red needles, sparingly soluble in ethanol, m. p. 195° from acetone (Found: C, 50·1; H, 4·5; N, 8·8; *M*, Rast, 360. $C_{14}H_{14}O_4N_2S_2$ requires C, 49·7; H, 4·2; N, 8·3%; *M*, 338), and 0·3 g. of red rhombs, m. p. 135° from ethanol (Found: C, 50·2; H, 4·3; N, 8·7%; *M*, Rast, 363).

o-*Nitrothiophenol Methyl Ether and its Reduction*.—23 G. of *o*-nitrothiophenol were dissolved in 115 ml. of 2N-sodium hydroxide and 300 ml. of water, filtered from disulphide, and shaken with 10 ml. of methyl sulphate. After standing for 30 mins., the ether was filtered off; yield 20 g., m. p. 62—63° (Brand, *loc. cit.*). 20 G. of this methyl ether were reduced as above with 4·0 g. of sodium in 150 ml. of amyl alcohol. The red substance formed was filtered off, dissolved in benzene, washed with water, and dried over sodium sulphate. The benzene solution was poured on an alumina column, which was washed with benzene until the red band had been eluted and left the orange band, which was eluted with ethanol. The red band gave 2 g. of *azobenzene*-2 : 2′-*di*(*methylsulphide*), m. p. 153—155°, from alcohol (Found: C, 61·65; H, 5·3; N, 10·0; S, 23·5. $C_{14}H_{14}N_2S_2$ requires C, 61·3; H, 5·15; N, 10·2; S, 23·4%). The orange band gave 8 g. of *azoxybenzene*-2 : 2′-*di*(*methylsulphide*) as orange needles from methanol, m. p. 78—80°, depressed by *o*-nitrothioanisole (Found: C, 57·8; H, 4·9; N, 9·8; S, 22·2. $C_{14}H_{14}ON_2S_2$ requires C, 57·9; H, 4·9; N, 9·7; S, 22·1%).

1 G. of the azoxy-compound was reduced in 50% alcohol by sodium hyposulphite to give colourless prismatic needles (from alcohol) of hydrazobenzene-2 : 2′-di(methylsulphide), m. p. 99—101°. Heated above its m. p. in air, this gave red plates, m. p. 155°, mixed m. p. with azobenzene-2 : 2′-di(methylsulphide) 155—156°. Reduction with zinc and sodium hydroxide or acetic acid gave the same hydrazo-compound.

The amyl alcoholic mother-liquors were washed with water and then alkali to remove fatty acids, and again with water. Extraction with dilute acid afforded a solution which, on being neutralised and steam-distilled, gave *o*-thioanisidine as an oil; b. p. 242°/760 mm., 134°/25 mm. Its picrate had m. p. 158° (from methanol) and, mixed with benzthiazole picrate (m. p. 169°), m. p. 148°; its acetyl derivative had m. p. 102—103°.

Attempted Preparation of o-*Aminobenzenesulphinic Acid*.—(*a*) 8 G. of sodium azobenzene-2 : 2′-disulphinate were treated with 4·5 g. of zinc, 4 g. of sodium hydroxide, and 25 ml. of water. The colourless solution was filtered, and on acidification it became purple, then pink, and finally deposited an orange-coloured acid of indefinite m. p., but giving a red solution in sodium hydroxide.

(*b*) Similar properties were shown by the product of an electrolytic reduction of 0·5 g. of the sodium salt in 10 ml. of N-sodium carbonate in a stone cell of 2 cm. diam. at 50° with a current of 5 volts and 0·8 amp., a platinum anode and a mercury cathode being used with an outer solution of 2N-sodium carbonate. (*c*) Sodium hyposulphite, sodium sulphite, sodium sulphide, titanous chloride, zinc in ammonia, and aluminium amalgam with ether (*d* 0·720), hot water, or 95% alcohol all gave the same sort of product. (*d*) Tin and hydrochloric acid with or without acetic acid gave colourless solutions not containing the required compound. (*e*) Zinc and hot glacial acetic acid gave a colourless solution from which extracts were obtained which diazotised and seemed to be of the aminothiophenol type. (*f*) Zinc and ethanolic hydrogen chloride behaved similarly. (*g*) The methyl esters, m. p. 195° and 135°, also failed to give the required product with sodium hyposulphite, or zinc with sodium hydroxide or acetic acid.

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