237. *Normal and Abnormal Reactions of the Sodium Derivatives of Aromatic Thiols with Halogenonitro-naphthalenes and -benzenes.*

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The anomalies previously described (J., 1938, 1031) have likewise been established for the reactions of the sodium salt of 4-nitronaphthalene-1-thiol with 2-bromo- and 2-iodo-1-nitronaphthalene and also with 2-bromo- and 2-iodo-1-nitrobenzene. The reactions between 2-chloro-1-nitronaphthalene and the sodium salts of benzene-, the two naphthalene-, and the two anthraquinone-thiols, however, give the normal anticipated sulphides. These results appear to support the previous tentative explanation of the anomalies.

THE anomalous reactions of the sodium salt of 4-nitronaphthalene-1-thiol with 2-chloro-1-nitronaphthalene and with 2-chloro-1-nitrobenzene to form 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide and 4-nitrophenyl 4-nitro-1-naphthyl sulphide respectively (Hodgson and Leigh, J., 1938, 1031) have been repeated with 2-bromo- and 2-iodo-1-nitronaphthalenes, and with 2-bromo- and 2-iodo-1-nitrobenzenes, and the same anomalous phenomena established, *viz.*, the formation of 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide and of 4-nitrophenyl 4-nitro-1-naphthyl sulphide respectively.

When, however, the sodium salt of benzenethiol reacts with 2-chloro-1-nitro- and 1-chloro-4-nitro-naphthalene, the normal reactions occur, *viz.*, formation of *phenyl* 1-*nitro*-2-*naphthyl sulphide* and *phenyl* 4-*nitro*-1-*naphthyl sulphide* respectively. The corresponding normal reactions with *o*- and *p*-chloronitrobenzenes are well known (Mauthner, *Ber.*, 1906, **39**, 3597; Kehrmann and Bauer, *Ber.*, 1896, **29**, 2364). Similarly the sodium salts of naphthalene-1- and -2-thiols react normally with 2-chloro-1-nitro- and 1-chloro-4-nitro-naphthalenes to give the expected sulphides. Analogous normal behaviour has likewise been found for the reactions between the sodium salts of anthraquinone-1- and -2-thiols and 2-chloro-1-nitro- and 1-chloro-4-nitro-naphthalene.

The normal reactions now recorded support the tentative explanation of the anomalies already given (*loc. cit.*) inasmuch as the absence of the restraining nitro-group in the benzenethiol, 1- and 2-naphthalenethiol, and 1- and 2-anthraquinonethiol ions formed after the initial separation of the sodium and chlorine as ions enables combination to occur between the charged aromatic residues before any electrical rearrangements can take place in the residual 1-nitronaphthyl ion from the 2-chloro-1-nitronaphthalene.

EXPERIMENTAL.

Phenyl 1-*Nitro*-2-*naphthyl Sulphide*.—Benzenethiol was prepared by the normal method from benzenesulphonic acid, its solution in aqueous alcoholic sodium hydroxide treated with the stoicheiometric amount of 2-chloro-1-nitronaphthalene, and the mixture boiled for 1 hour. After steam-distillation, the solid non-volatile residue was crystallised from 75% aqueous alcohol or 75% aqueous acetic acid, *phenyl* 1-*nitro*-2-*naphthyl sulphide* being obtained in primrose-yellow plates, m. p. 58—58·5° (Found : N, 5·1; S, 11·5. $C_{16}H_{11}O_2NS$ requires N, 5·0; S, 11·4%), soluble in acetone, acetic acid, acetic anhydride, alcohol, benzene and chloroform. It gave with cold concentrated sulphuric acid a bluish-violet colour, which turned deep blue and bluish-black on heating and reddish-violet on dilution with water.

Phenyl 4-*nitro*-1-*naphthyl sulphide*, similarly obtained from 1-chloro-4-nitronaphthalene, crystallised in silky yellow needles, m. p. 105·5—106° (Found : N, 5·1; S, 11·5%); it resembled the isomeride in solubility, and gave with cold concentrated sulphuric acid an intense port-wine colour, which became light brown on heating and yellow on dilution with water.

Preparation of Naphthalene-1- *and* -2- *and Anthraquinone*-1- *and* -2-*thiols and Condensation of their Sodium Salts with* 2-*Chloro*-1-*nitro*- *and* 1-*Chloro*-4-*nitro*-*naphthalene*.—Naphthalene- and anthraquinone-α- and -β-sulphonic acids were each fractionally crystallised twice from boiling water, the first crystalline fraction of the α-compounds and the last fraction of the β-compounds being rejected. The purified sulphonic acids were severally heated with equal weights of phosphorus pentachloride at 120—130° in an oil-bath for 1½—2 hours, the products stirred with ice, and the insoluble sulphonyl chlorides washed with water until free from hydrochloric acid and dried between filter-paper (yield, 65—70%). For conversion into the thiol, the sulphonyl chloride (5 g.) was mixed with concentrated hydrochloric acid (25 c.c.) and water (100 c.c.), treated with granulated tin (10 g.), added portionwise, and the mixture boiled under reflux for 3 hours. The isolation of naphthalene-1-thiol was effected by steam-distillation, but naphthalene-2-thiol and anthraquinone-1- and -2-thiols were separated by filtration, and any excess of tin removed by hand. A solution of each thiol (5 g.) in the minimum amount of boiling ethyl alcohol was treated with a boiling saturated solution of 2-chloro-1-nitronaphthalene (6·5 g.) or 1-chloro-4-nitronaphthalene (6·5 g.), and the mixture, after addition of 20% aqueous sodium hydroxide (10 g.), boiled under reflux for 2 hours and then kept overnight. The product was separated from the liquid while boiling and crystallised from glacial acetic acid. The colours given with cold concentrated sulphuric acid are stated after each m. p.

1-*Naphthyl* 1-*nitro*-2-*naphthyl sulphide* formed yellow crystals, m. p. 107° (depressed by the following isomeride) (dark blue) (Found : C, 72·3 H, 3·7; S, 9·9. $C_{20}H_{13}O_2NS$ requires C, 72·5; H, 3·9; S, 9·7%).

4-*Nitrodi*-1-*naphthyl sulphide* crystallised in greenish-yellow cubes, m. p. 127° (bright red, quickly turning dark brown) (Found : C, 72·4; H, 3·9; S, 9·8%).

1-*Nitrodi*-2-*naphthyl sulphide* formed brownish-yellow plates, m. p. 91° (depressed by the following isomeride) (dark green) (Found : C, 72·3; H, 3·7; S, 9·8%).

2-*Naphthyl* 4-*nitro*-1-*naphthyl sulphide* crystallised in yellow needles, m. p. 151° (red, quickly turning light brown) (Found: C, 72·5; H, 3·8; S, 9·9%).

1-*Nitro*-2-*naphthyl* 1-*anthraquinonyl sulphide* formed silvery-brown leaflets, m. p. 435° (decomp.) (greenish-yellow) (Found: C, 69·7; S, 8·0. $C_{24}H_{13}O_4NS$ requires C, 70·0; S, 7·8%).

4-*Nitro*-2-*naphthyl* 1-*anthraquinonyl sulphide* formed brown micro-plates, no m. p. (dark red) (Found: C, 69·8; S, 7·9%).

1-*Nitro*-2-*naphthyl* 2-*anthraquinonyl sulphide* formed brown micro-crystals, m. p. 384° (decomp.) (greenish-yellow) (Found: C, 69·8; S, 8·0%).

4-*Nitro*-2-*naphthyl* 2-*anthraquinonyl sulphide* crystallised in light yellowish-brown prisms, m. p. 238° (bright purple) (Found: C, 69·9; S, 7·9%).

Note on the Melting Points of the Naphthyl Anthraquinonyl Sulphides.—Rapidly heated near a naked Bunsen flame, three of the above compounds melted, but with gradual rise of temperature during 20 minutes decomposition took place in each case before the m. p. was reached. The following device was therefore adopted: A heating block at 500° was allowed to cool gradually and melting point tubes were inserted in it at temperatures near the m. p.'s of the substances, which had previously been approximately determined. The first points at which no melting occurred were thus found, and the m. p.'s recorded are 1° higher than these values.

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