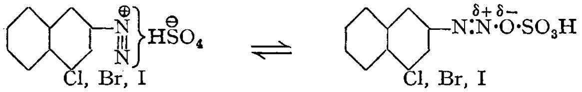
126.—*Preparation of 4-Halogeno-2-naphthols and 4-Nitro-2-naphthol, with a Note on the Resonance Structure of the Internal Diazo-oxides (Diazo-naphthols).*

By Herbert H. Hodgson and Stanley Birtwell.

4-*Chloro*-, 4-bromo-, and 4-*iodo*-2-*naphthols* are prepared from the corresponding 4-halogenonaphthalene-1 : 2-diazo-oxides (diazo-naphthols). A method is described for the rapid preparation of 4-nitro-2-naphthol. The properties of the diazo-naphthols indicate them to be resonance hybrids.

Failure to obtain the 4-halogeno-2-naphthols in satisfactory quantity from the corresponding 4-halogeno-2-naphthylamines by customary methods has revealed a noteworthy difference between the decompositions of the diazonium sulphates of 4-halogeno-2-naphthylamines and the 3-halogenoanilines in boiling aqueous sulphuric acid: the latter give almost quantitative yields of the 3-halogenophenols (Hodgson, E.P. 200,714), but the former yield only traces of the 4-halogeno-2-naphthols, the product being almost entirely 4′-halogenonaphthalene-2′ : 1-azo-4-halogeno-2-naphthol, owing to coupling of the 4-halogeno-2-naphthol with still undecomposed diazonium sulphate. Since only traces of naphthol can be isolated, the velocity of coupling must be at least equal to that of decomposition, and indicates that the 4-halogenonaphthalene-2-diazonium sulphates are not only very stable towards boiling sulphuric acid but possess high coupling power. The latter property points to a predominance of the diazo-component (right-hand side) in the equilibrium mixture, since it is only the diazo-component that can couple (cf. Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4541):

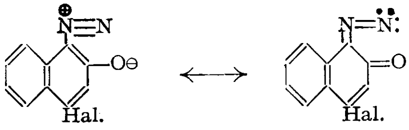


Attempts to prepare 4-halogeno-2-naphthols by treatment of 4-halogeno-2-naphthylamines with sodium bisulphite, acetone bisulphite, and sodium bisulphite and sulphur dioxide failed, and heating the 4-halogeno-2-naphthylamine with 20% hydrochloric acid under pressure (Bucherer's reaction, *J. pr. Chem.*, 1904, **69**, 49) afforded traces only of 4-halogeno-2-naphthol after 24 hours. 4-Amino-2-naphthol, prepared with difficulty (cf. Morgan and Evens, J., 1919, **115**, 1126), proved so susceptible to oxidation that manipulation was only possible in an atmosphere of carbon dioxide; the improvement effected by Ingold (J., 1923, **123**, 2066) *via* 4-nitro-2-naphthyl toluene-*p*-sulphonate involved recourse to such reducing agents as amalgamated aluminium foil in moist ether, which were obviously unsuitable for large-scale operations. Finally, the method of Morgan and Evens (*loc. cit.*), who obtained 4-nitro-2-naphthol in 58—64% yield by boiling 4-nitronaphthalene-1 : 2-diazo-oxide for 32 hours with aluminium powder and alcohol, was found to be capable of general application. 4-Chloro- and 4-bromo-naphthalene-1 : 2-diazo-oxides required 18—20 hours' boiling for complete decomposition (no further coupling with alcoholic alkaline resorcinol), the iodo-analogue only 4 hours, and naphthalene-1 : 2-diazo-oxide-4-sulphonic acid did not require aluminium powder for its decomposition (Ingold, *loc. cit.*). Shorter periods of boiling (*e.g.*, 5 hours) afforded satisfactory yields (41%) (cf. Ingold, *loc. cit.*). The tedious extraction of the naphthol with boiling water; as prescribed by Morgan and Evens (*loc. cit.*) for the isolation of 4-nitro-2-naphthol, was replaced by extraction with cold 2% aqueous sodium hydroxide (so dilute because of the sparing solubility of the sodium salts of the 4-halogeno-2-naphthols), whereby the small amount of by-product, 4 : 4′-dihalogeno-1 : 1′-azonaphthol was also extracted, as shown by the bright red colour of the solution. The latter compound was removed as a barium lake by treatment of the alkaline extract with barium chloride.

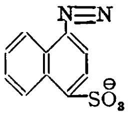
Decomposition of 4-nitronaphthalene-1 : 2-diazo-oxide by boiling alcohol and metallic copper, generated *in situ* by the action of iron filings on copper sulphate, gave a 50% yield of 4-nitro-2-naphthol in 30 minutes: this is the most convenient method for its preparation in quantity (the yield is only 38% in 12 hours when ordinary copper is used; Morgan and Evens, *loc. cit.*).

4-Chloro- and 4-bromo-naphthalene-1 : 2-diazo-oxides were decomposed more rapidly by sodium stannite, but the yields were variable and the products of inferior quality.

The Resonance Structure of the Internal Diazo-Oxides.—The difficulty of replacement of the diazo-nitrogen by hydrogen in the above diazo-naphthols is in the order of the negative inductive (–*I*) effects of their *p*-substituents, *viz.*, $NO_2 > Cl > Br > I > SO_3H$; *i.e.*, the diazo-oxide group is stabilised by the *p*-substituents in this order. Such uniformity of replacement suggests that the diazo-naphthols contain a diazonium group (I*a*), analogous cases being the diazonium sulphates and the diazo-aryl sulphonates (Saunders, "The Aromatic Diazo-Compounds," pp. 32, 39). This structure is in harmony with the solubilities of the diazo-naphthols in hot water and sparing solubilities in non-polar solvents such as light petroleum, and with their decomposition (sometimes with explosive violence) on fusion; on the other hand, their pronounced colours indicate ease of transition to a quinonoid structure (I*b*). The existence of both structures is reconciled by formulation of the diazo-naphthols as resonance hybrids (I); since only the positions of the electrons are involved in the two forms, the resonance energy would account for the stability, and the betaine (zwitter-ion) structure for the diazonium form is established for such analogous compounds as the slightly soluble and explosive diazonium sulphonates, *e.g.*, diazonaphthionic acid (II) (cf. Sidgwick, " Organic Chemistry of Nitrogen," revised by Taylor and Baker, Oxford, 1937, p. 422) :



(I*a*.) (I*b*.)



(II.)

Experimental.

Decomposition of 4-*Halogenonaphthalene*-1 : 2-*diazo-oxides by Alcohol and Aluminium Powder.*—4-*Chloro*-2-*naphthol* was obtained when 4-chloronaphthalene-1 : 2-diazo-oxide (2·0 g.) (Hodgson and Birtwell, this vol., p. 322) was boiled for 19 hours with ethyl alcohol (50 c.c.) and aluminium powder (0·75 g.), until the mixture no longer gave a blue or purple colour with alkaline resorcinol. The aluminium powder was removed by filtration and the alcohol by distillation, the tarry residue extracted with cold 2% aqueous sodium hydroxide (20 c.c.), the filtered extract diluted with an equal volume of water, and a solution of crystallised barium chloride (1·2 g.) in water (20 c.c.) added; the solution, after being heated almost to boiling, was filtered at room temperature and diluted with ice, and hydrochloric acid added to precipitate the 4-chloro-2-naphthol (1·5 g.; 84·3% yield), which crystallised from 30% aqueous alcohol (charcoal) in colourless feathery needles, m. p. 100° (Found : Cl, 19·8. $C_{10}H_7OCl$ requires Cl, 19·9%). The sodium salt was sparingly soluble in cold 10% aqueous sodium hydroxide.

4-*Chloro*-1-*benzeneazo*-2-*naphthol*, prepared from diazotised aniline and alkaline 4-chloro-2-naphthol, crystallised slowly from acetone in orange-red needles, m. p. 165° (Found : Cl, 12·5. $C_{16}H_{11}ON_2Cl$ requires 12·6%), and from chlorobenzene in crimson needles, which changed on keeping in air to the orange-red variety. The latter after fusion and solidification had m. p. 151°, but resolidified at *ca.* 155°, and remelted at 165° if the temperature was allowed to rise very slowly; the process could be repeated.

4-*Chloro*-2-*naphthyl methyl ether*, prepared from 4-chloro-2-naphthol, aqueous sodium hydroxide, and methyl sulphate, crystallised from light petroleum (charcoal) in colourless plates, m. p. 44—45° (Found : Cl, 18·3. $C_{11}H_9OCl$ requires Cl, 18·4%).

4-*Chloro*-2-*naphthyl acetate*, obtained by refluxing 4-chloro-2-naphthol with excess of acetic anhydride for 30 minutes (90—100% yield), crystallised from aqueous methyl alcohol in colourless plates, m. p. 56° (Found : Cl, 16·0. $C_{12}H_9O_2Cl$ requires Cl, 16·1%).

4-Bromo-2-naphthol, obtained by the method used for the chloro-analogue (77% yield), crystallised from aqueous methyl or ethyl alcohol (charcoal) in colourless feathery needles, m. p. 122° (Fries and Schimmelschmidt, *Annalen*, 1930, **484**, 245, give m. p. 122°) (Found : Br, 35·7. Calc. : Br, 35·8%).

4-*Bromo*-1-*benzeneazo*-2-*naphthol* crystallised from glacial acetic acid in bright red needles, m. p. 160° (Found : Br, 24·3. $C_{16}H_{11}ON_2Br$ requires Br, 24·4%), 4-*bromo*-2-*naphthyl methyl ether* from light petroleum in light colourless plates (flat parallelepipeds), m. p. 64° (Found : Br, 33·6. $C_{11}H_9OBr$ requires Br, 33·7%), and 4-*bromo*-2-*naphthyl acetate* from aqueous methyl alcohol (charcoal) in colourless plates, m. p. 61° (Found : Br, 30·1. $C_{12}H_9O_2Br$ requires Br, 30·2%).

Reduction of 4-*Chloro- and* 4-*Bromo-naphthalene*-1 : 2-*diazo-oxide by Sodium Stannite.*—The diazo-oxide (prepared from 0·1 g.-mol. of the 4-halogeno-2-nitro-1-naphthylamine) was made into a slurry with warm water (220 c.c.) and added during 20 minutes to a solution of stannous chloride crystals (40 g.) in 10% aqueous sodium hydroxide (400 c.c.) maintained at 80—90°. The mixture was heated for another 10 minutes, nitrogen being evolved, and the deep purple liquid was then filtered and rapidly acidified at 0° by addition to hydrochloric acid (250 c.c., *d* 1·16) (yield, 85—54%). Distillation in steam or superheated steam gave only 0·6—0·65 g. of 4-halogeno-2-naphthol per l., but yields exceeding 60% (on the amine taken) were obtained by distillation under ordinary pressure; vacuum distillation entailed considerable loss due to sublimation of the 4-halogeno-2-naphthol. When the excess of stannous chloride used above was diminished, a larger amount of coupled product was obtained (*i.e.*, coloured material sparingly soluble in hot aqueous sodium hydroxide).

Reduction of the above diazo-oxides in glacial acetic acid solution by stannous chloride–hydrochloric acid afforded no halogenonaphthol.

4-*Iodo*-2-*naphthol.*—4-Iodonaphthalene-1 : 2-diazo-oxide (15 g.) (Hodgson and Birtwell, *loc. cit.*) was boiled with alcohol (250 c.c.) and aluminium powder (3·75 g.); the reaction was complete in 4 hours. The product, worked up as in the case of the chloro-analogue, gave 8·0 g. (60%) of 4-*iodo*-2-*naphthol*, which, crystallised from benzene and then from aqueous ethyl alcohol (charcoal), formed colourless needles, m. p. 128·5° (Found : I, 46·8. $C_{10}H_7OI$ requires I, 47·0%).

4-*Iodo*-1-*benzeneazo*-2-*naphthol* crystallised from glacial acetic acid in red felted needles, m. p. 176° (Found : I, 33·8. $C_{16}H_{11}ON_2I$ requires I, 33·9%), 4-*iodo*-2-*naphthyl methyl ether* from light petroleum (charcoal) in plates, m. p. 67° (Found : I, 44·6. $C_{11}H_9OI$ requires I, 44·7%), and 4-*iodo*-2-*naphthyl acetate* from light petroleum in colourless plates, m. p. 59° (Found : I, 40·6. $C_{12}H_9O_2I$ requires I, 40·7%).

4-Nitronaphthalene-1 : 2-diazo-oxide (2·15 g.) was refluxed with ethyl alcohol (40 c.c.), iron filings (5 g.), and copper sulphate crystals (2·5 g.) while water (40 c.c.) was added during 30 minutes. The alcohol was then distilled off, and the 4-nitro-2-naphthol extracted from the residue by the above procedure. Yield, 1·0 g. (52%).

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