857. *The Direct Introduction of the Diazonium Group. Part VII.*[1] *The Coupling of Toluene-*p*-sulphonazide with Phenoxide Ions to Yield Diazo-oxides.*

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Toluene-*p*-sulphonazide couples with reactive phenoxide ions to yield a triazen which breaks down spontaneously to give a diazo-oxide and the sodium salt of toluene-*p*-sulphonamide. In the necessarily basic conditions the diazo-oxide couples in turn with more phenoxide ions to yield the sodium salt of the azo-dye.

Previous papers in this series have described the preparation of the diazonium salts from aromatic compounds by treatment with excess of nitrous acid or its derivatives.[1] Although these reactions have been carried out under many conditions they have all involved initial nitrosation, and subsequent conversion of the nitroso-compound into the diazonium salt. A totally different method is now described in which the two nitrogen atoms of the ultimate diazo-group are introduced simultaneously. Curtius showed that aromatic sulphonazides couple with diethyl sodiomalonate[2] and more recently Doering showed that toluene-*p*-sulphonazide would couple with cyclopentadienyllithium.[3] The resultant triazen from the latter broke down spontaneously to diazocyclopentadiene. We have found that an exactly analogous reaction occurs with the sodium salt of reactive phenols:

$$\mathrm{Ar{\cdot}SO_2{\cdot}N_3 + H{\cdot}X{\cdot}O^-Na^+ \longrightarrow Ar{\cdot}SO_2{\cdot}NH{\cdot}N{:}N{\cdot}X{\cdot}ONa \longrightarrow Ar{\cdot}SO_2{\cdot}NHNa + {}^+N_2{\cdot}X{\cdot}O^-}$$

The diazo-oxide produced couples with more sodium phenoxide to yield the sodium salt of the symmetrical azophenol:

$$\mathrm{{}^+N_2{\cdot}X{\cdot}O^- + H{\cdot}X{\cdot}ONa \longrightarrow HO{\cdot}X{\cdot}N{:}N{\cdot}X{\cdot}O^-Na^+}$$

The reaction is restricted to the more reactive phenols, *e.g.*, α- and β-naphthol, resorcinol, phloroglucinol, and 3-methoxyphenol. Towards less reactive phenols the sulphonazide behaves like an acid chloride and the sodium salts of phenol and *o*-cresol yield the

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[1] Part VI, Tedder and Theaker, *Tetrahedron*, 1959, **5**, 288.
[2] Curtius and Klavehn, *J. prakt. Chem.*, 1926, **112**, 65.
[3] Doering and De Puy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.

toluene-*p*-sulphonate and sodium azide. *m*-Cresol also yields *m*-tolyl toluene-*p*-sulphonate, but trace amounts of dye appear to be formed. The coupling of the azide with reactive phenols is of interest not only because it is a new type of electrophilic substitution involving

$$CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}N_3 + C_6H_5{\cdot}ONa \longrightarrow CH_3{\cdot}C_6H_4{\cdot}SO_3{\cdot}C_6H_5 + NaN_3$$

a stable molecular species as electrophile, but also because it provides a direct method of introducing the diazonium group into the very phenols which cannot be converted directly into diazo-oxides by treatment with nitrous acid.[4] The symmetrical azophenol dye is obtained from sodium phenoxide (1 mol.), the free phenol (1 mol.), and toluene-*p*-sulphonazide; resorcinol reacts readily with the azide in dilute aqueous alkali to give presumably 2,2′,4,4′-tetrahydroxyazobenzene. α- and β-Naphthols react only with reluctance in an aqueous medium, but rapidly in ether, from which solution the sodium salt of the azonaphthol is precipitated. It seems impossible to avoid forming some of the azophenol dye, but it is possible to isolate the 1-diazo-2-oxide from β-naphthol by adding sodium β-naphthoxide to excess of azide. When a similar isolation was attempted from α-naphthol, the diazo-oxide isolated was the 2-diazo-1-oxide and not the expected 1-diazo-4-oxide. *ortho*-Diazo-oxides couple far less readily than the *para*-isomers. Although α-naphthol couples predominantly in the 4-position, considerable amounts of *ortho*-coupling also occur.[5] Some reaction of the diazo-oxides formed with unchanged α-naphthol is unavoidable, even when excess of azide is used, and as a result the final diazo-oxide solution will be relatively rich in the less reactive *ortho*-diazo-oxide. The *ortho*-diazo-oxide is certainly much more stable and probably less soluble than the *para*-isomer, so that it is not surprising that repeated recrystallisation of the crude diazo-oxide should eventually yield the pure 2-diazo-1-oxide.

EXPERIMENTAL

2,2′-*Dihydroxy*-1,1′-*azonaphthalene*.—β-Naphthol (2·88 g.) was treated with sodium (0·23 g.) in dry ether (30 c.c.), the ether being refluxed until all the sodium had disappeared Toluene-*p*-sulphonazide (2·0 g.) in ether (20 c.c.) was added and the mixture stirred overnight. The precipitate was filtered off and washed repeatedly with ether. A solution of the dried precipitate in aqueous acetone was acidified with concentrated hydrochloric acid; the red-brown precipitate (1·22 g.) was crystallised from chloroform to yield 2,2′-*dihydroxy*-1,1′-*azonaphthalene* as dark red needles with a green lustre, m. p. 245—246° (Found: C, 75·7; H, 4·6; N, 8·9. $C_{20}H_{14}N_2O_2$ requires C, 76·4; H, 4·5; N, 8·9%.) The dye gave an intense blue colour in concentrated sulphuric acid. The acidic filtrate was bright yellow indicating the presence of uncoupled diazo-oxide. The acetone was removed under reduced pressure and the solution filtered. Resorcinol was added to the filtrate and the solution made alkaline. A deep purple colour developed, and after an hour the solution was acidified and the resultant dark brown precipitate filtered. Recrystallisation of the crude dye from aqueous ethanol gave a dark brown powder, m. p. 197—198°, which gave a red-purple colour in sulphuric acid. This product was presumed to be 2,2′,4′-trihydroxy-1-phenylazonaphthalene.

4,4′-*Dihydroxy*-1,1′-*azonaphthalene*.—α-Naphthol (2·88 g.) was treated with sodium (0·23 g.) in dry ether (30 c.c.) and then with toluene-*p*-sulphonazide (2·0 g.) in ether (20 c.c.), as in the preceding experiment. The reaction was more rapid, and after ½ hr., the blue sodium salt of the dye was filtered off. The free dye (1·22 g.) was precipitated from aqueous acetone as before; recrystallised from aqueous acetone it formed dark red-brown needles, m. p. 226—227° (Found: C, 76·1; H, 4·8; N, 8·6. Calc. for $C_{20}H_{14}N_2O_2$: C, 76·4; H, 4·5; N, 8·9%). Bigiavi and Cherchiai[6] report that 4,4′-dihydroxy-1,1′-azonaphthalene has m. p. 223°. The dye gave an intense blue colour in concentrated sulphuric acid. Unchanged diazo-oxide in the acidic filtrate was again coupled with resorcinol as before. A crude dye assumed to be 1,2′,4′-trihydroxy-2-phenylazonaphthalene was obtained.

4,4′-*Dihydroxy*-2,2′-*dimethoxyazobenzene*.—Resorcinol monomethyl ether (5 g.) was dissolved in sodium methoxide solution [from sodium (0·5 g.) and methanol (20 c.c.)]. The excess of

[4] Tedder and Theaker, *J.*, 1958, 2573.

[5] Saunders, " The Aromatic Diazocompounds and their Technical Applications," E. Arnold, London, 1949, p. 198.

[6] Bigiavi and Cherchiai, *Atti Accad. Lincei*, 1922, **31**, II, 40.

methanol was evaporated and the resulting sodium phenoxide mixture suspended in ether (100 c.c.). Toluene-*p*-sulphonazide (4·2 g.) was added and the ether refluxed for ½ hr., filtered, and then washed with dilute sodium hydroxide solution. The precipitated sodium salt was dissolved in water and added to the alkaline washings of the ether. The combined alkaline solution was acidified and the resultant crude dye crystallised from toluene, yielding orange-brown plates, with a purple sheen, of 4,4′-*dihydroxy*-2,2′-*dimethoxyazobenzene* (0·25 g.), m. p. 203—204° (Found: C, 61·2; H, 5·3; N, 9·8. $C_{14}H_{14}N_2O_4$ requires C, 61·3; H, 5·1; N, 10·2%). The dye gives a blue-black colour in concentrated sulphuric acid which slowly turns orange-red.

2,4,2′,4′-*Tetrahydroxyazobenzene*.—(1) Resorcinol (2·2 g.) was treated with sodium methoxide [from sodium (0·25 g.) and methanol (20 c.c.)] as described above. The resultant solid was suspended in ether (50 c.c.), treated with toluene-*p*-sulphonazide (2·0 g.), and refluxed for ½ hr. The purple precipitate was washed with ether, dried, and then dissolved in water from which the free dye (0·84 g.) was precipitated by acidification. A portion was precipitated from ether by addition of light petroleum (b. p. 40—60°); the brown powder decomposed above 260° without melting. It was dried *in vacuo* (P_2O_5) at 150° for 3 hr. (Found: C, 57·9; H, 4·9. $C_{12}H_{10}N_2O_4$ requires C, 58·5; H, 4·1%).

(2) A solution of resorcinol (2·2 g.) in 2N-aqueous sodium hydroxide (50 c.c.) and toluene-*p*-sulphonazide (2·0 g.) were heated in a steam-bath for 10 min. After cooling the unchanged azide was removed with chloroform. The aqueous layer was acidified, a brown precipitate (1·3 g.) forming which was very difficult to purify. It gave an initial black colour with sulphuric acid which slowly changed to red.

Phenyl Toluene-p-*sulphonate*.—A solution of phenol (1·0 g.) in ether was treated with sodium (0·25 g.). When no further hydrogen was evolved a solution of toluene-*p*-sulphonazide (2·0 g.) in ether was added. The mixture was refluxed; sodium azide was filtered off and the ether evaporated to yield yellow crystals. On digestion with water, the colour passed into solution leaving the crystals colourless. The yellow solution did not couple with alkaline resorcinol. The crystals were recrystallised from alcohol, yielding needles, m. p. 94—95° alone or in admixture with phenyl toluene-*p*-sulphonate.

o-*Tolyl Toluene*-p-*sulphonate*.—*o*-Cresol was treated in an analogous manner. As before, the resultant solution would not couple with resorcinol and the main organic product was *o*-tolyl toluene-*p*-sulphonate, m. p. 49·5°.

Naphthalene 1,2-*Diazo-oxide*.—β-Naphthol (2·9 g.) and sodium (0·5 g.) were heated in refluxing ether (50 c.c.) for 2 hr. The resultant mixture was decanted into a solution of toluene-*p*-sulphonazide (8 g.) in dry ether (20 c.c.). When a precipitate of the sodium salt of 2,2′-dihydroxy-1,1′-azonaphthalene had just begun to form (*ca.* 2 min.), the ether solution was extracted with 6N-hydrochloric acid (2 × 100 c.c.), the acid solution filtered, and azide precipitated by the evaporation of the dissolved ether. The solution, now yellow, was diluted to 400 c.c. and then neutralised with sodium carbonate; a yellow precipitate formed. The filtrate was extracted with ether, the extract dried (Na_2SO_4), and evaporated, and the yellow-brown oil extracted with light petroleum (b. p. 40—60°) to give a solution from which yellow needles were obtained. These were combined with the precipitate and recrystallised from more petroleum. The pure diazo-oxide (0·30 g.) had m. p. 94·5—95° (Bamberger[7] reports m. p. 94—94·5°), a strong peak (2110 cm.$^{-1}$; diazo) in the infrared spectrum, and coupled readily with alkaline resorcinol (Found: C, 70·9; H, 4·1; N, 16·6. Calc. for $C_{10}H_6N_2O$: C, 70·6; H, 3·5; N, 16·5%).

Naphthalene 2,1-*Diazo-oxide*.—This was prepared from α-naphthol (2·9 g.), as described for the 1,2-diazo-oxide. The filtration and subsequent neutralisation of the acid solution were carried out in the dark room. The ether extract of the neutral solution yielded only a dark tar, but the precipitate filtered off first was recrystallised from petrol to give dull yellow needles (0·10 g.), m. p. 75°, $\nu_{max.}$ 2090 cm.$^{-1}$ (Found: C, 70·3; H, 4·4; N, 16·5. Calc. for $C_{10}H_6N_2O$: C, 70·6; H, 3·5; N, 16·5%). (The m. p. agrees with that reported by Bamberger[8] for the 2,1-diazo-oxide.) Since it was expected that the main product would be the 1,4-diazo-oxide the 2,1-diazo-oxide was synthesised from 2-naphthalenediazonium chloride by oxidation with potassium ferricyanide according to Bamberger's method.[8] The product was identical with that described above (mixed m. p. and identical infrared spectra). The 2,1-diazo-oxide couples slowly with sodium 1-naphthoxide in ether; the dye so obtained, though similar, is

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[7] Bamberger, *Ber.*, 1922, **55**, 3383.

[8] Bamberger, *Ber.*, 1894, **27**, 679.

not identical with that obtained *via* the synthesis of 4,4′-dihydroxy-1,1′-azonaphthalene. described above.

The authors thank the Department of Scientific and Industrial Research for the award of a maintenance grant (to B. W.).

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[*Received, March 1st*, 1960.]