

Electrophilic Displacement of Arylazo-cations from Azophenols

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Displacement of diazonium cations from *o*-arylazophenols has been observed with several electrophiles. Product studies suggest that the phenylazo-group is a better leaving group than Br^+ , Cl^+ , NO_2^+ , or $p\text{-NO}_2\text{C}_6\text{H}_4\cdot\text{N}_2^+$.

DIAZONIUM cations are met with only infrequently as leaving groups in electrophilic aromatic substitution. However, the arylazo-group seems not to be an intrinsically poor leaving group, for the detailed studies of Zollinger¹ and Ridd² and their co-workers on the mechanism of azo-couplings clearly show the need for a base to be present to remove the proton from the intermediate σ complex, otherwise ejection of the diazonium ion competes successfully with proton loss, and the σ complex reverts to starting materials. Likewise, the acid catalysed rearrangement of 4-arylazo-1-hydroxynaphthalene-3-sulphonic acids involves protolytic displacement of the arylazo-group as the first step.³ Less thoroughly studied reactions in which arylazo-groups are lost include substitution of a diazonium group by a more electrophilic diazonium ion⁴ and by nitrosonium ion.⁵ Recently Cadogan has reported that diazonium ions are formed by the action of organic nitrites on 1-phenylazo-2-naphthol, but this does not appear to involve a direct displacement mechanism.⁶ In this paper are reported observations which suggest that the arylazo-group may function as a leaving group more readily than has hitherto been recognised.

In connection with a photochemical problem, knowledge of the bromination products of 2-hydroxyazobenzene (1) was required. In neutral solutions 5-bromo-2-hydroxyazobenzene (2) and two different dibromides form, depending upon conditions.⁷ Since these products are very hard to separate, attention was turned to basic media in the hope of obtaining a cleaner product. Bromination in acetonitrile-aqueous sodium hydroxide gave four products and some starting material; two of these were (2) and one of the dibromides found previously. The remaining compounds identified were 2,4-bisphenylazophenol (3) and a new compound which was recognised as a monobromo-derivative of (3) by the similarity of its u.v. spectrum and from its mass spectrum, the fragmentation pattern of which located the bromine atom in the hydroxy-substituted ring, and suggested (4) as the structure of this compound.

The benzenediazonium ion seems an obvious choice

¹ H. Zollinger, *Helv. Chim. Acta*, 1955, **38**, 1597, 1617; R. Ernst, O. A. Stamm, and H. Zollinger, *ibid.*, 1958, **41**, 2274.

² A. Grimison and J. H. Ridd, *J. Chem. Soc.*, 1959, 3019; J. H. Binks and J. H. Ridd, *ibid.*, 1957, 2398.

³ O. A. Stamm and H. Zollinger, *Helv. Chim. Acta*, 1957, **40**, 1955.

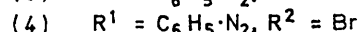
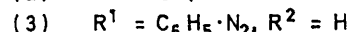
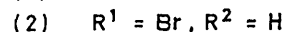
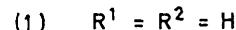
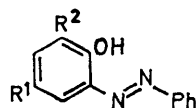
⁴ S. A. Filippuichev and M. A. Chekalin, *Anilinokras. Prom.*, 1935, **5**, 76 (*Chem. Abs.*, 1935, **29**, 5087).

⁵ R. Huisgen, in 'Azo and Diazo Chemistry,' H. Zollinger, Interscience, London, 1961, p. 241.

⁶ J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Chem. Comm.*, 1973, 572.

⁷ N. J. Bunce, *Bull. Chem. Soc. Japan*, in the press.

for the immediate precursor of (3) since (3) can be prepared by coupling (1) with diazotised aniline.⁸ The presence of diazonium ions in solution implies that



electrophilic bromine had attacked (1) at the carbon carrying the phenylazo-substituent (*ipso*⁹ attack), displacing this group under the powerful activation of the *ortho*-phenoxide. This suggestion is consistent with the tendency of phenols and phenoxides to undergo predominantly *ortho*-halogenation;¹⁰ however, displacement of arylazo-groups by halogen has apparently not been observed previously, although the reverse reaction, expulsion of halogen during diazonium coupling on azophenols, has been reported occasionally.¹¹

When 1-phenylazo-2-naphthol (5a) was treated with bromine in CH_3CN -aq. NaOH an exothermic reaction ensued and the dye was immediately decolourised, but no tractable products were formed. When acidic reaction mixtures were quenched with iodide ion, the azo-compound (5a) was at once regenerated suggesting that the σ complex (6) might have been present as an intermediate. Attempts to date to isolate such an intermediate have been unsuccessful, although other 1,1-disubstituted-2-oxo-1,2-dihydronaphthalenes are known.^{12,13} However, the existence of this intermediate may be inferred from the beneficial effect on the yield of 1-arylazo-2-naphthol when sodium thiosulphate is added to reaction mixtures of diazonium salts with 1-bromo-2-naphthol.¹¹

The arylazo-group was lost completely from (5a) when the azo-compound was treated with bromine in acetic acid in the presence of sodium acetate, evidence being obtained for the 1,1-dibromo-compound (7). Likewise, nitration of (5a) in acetic acid gave 1,6-dinitro-2-naphthol (75%), and reaction with *p*-nitrobenzenediazonium chloride in dioxan-aq. NaOH gave (6b) (47%), together with 5% of unchanged (6a).

⁸ E. Bamberger, *Ber.*, 1902, **35**, 1606.

⁹ C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389.

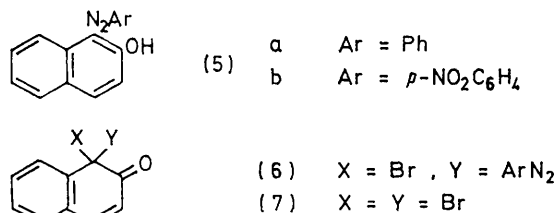
¹⁰ D. A. R. Happer and J. Vaughan, 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Wiley-Interscience, London, 1970, ch. 8.

¹¹ K. H. Saunders, 'The Aromatic Diazocompounds,' Arnold, London, 1949, p. 221.

¹² (a) T. Zinke, *Ber.*, 1888, **21**, 3378, 3540; (b) K. Fries and E. Hempelmann, *ibid.*, 1908, **41**, 2614; K. Fries, *Annalen*, 1912, **389**, 315; K. Fries and H. Engel, *ibid.*, 1924, **439**, 232; K. Fries and G. Oehmke, *ibid.*, 1928, **462**, 1.

¹³ C. L. Perrin, *J. Org. Chem.*, 1971, **36**, 420.

Displacement of the *p*-nitrophenylazo-group from (5b) is less easily accomplished. Two reasons might be advanced for this; first, the more electrophilic diazonium ion should be intrinsically a poorer leaving group; and



secondly, initial attack at the *ipso*-position in (5b) should be less favoured since the activating or deactivating influence of a substituent is in the same direction at the *ipso*-position as at other sites in the molecule.⁹ Thus, (5b) was recovered quantitatively from an attempted nitration in acetic acid, and from treatment with benzenediazonium chloride in dioxan-aq. NaOH. Decolourisation of (5b) was effected using a large excess of bromine in dioxan-aq. NaOH, but the colour was always quickly restored on standing.

As well as studying the displacement of arylazo-groups from these azonaphthols, the attack of diazonium ions on other 1-substituted-2-naphthols was investigated, as shown in the Table.

Reaction of 1-substituted-2-naphthols with diazonium salts

Substituent	Diazonium salt	Product	Yield (%)
Br	C ₆ H ₅ ·N ₂ ⁺	(5a)	5
Br	<i>p</i> -NO ₂ C ₆ H ₄ ·N ₂ ⁺	(5b)	51
Cl	C ₆ H ₅ ·N ₂ ⁺	(5a)	<1
Cl	<i>p</i> -NO ₂ C ₆ H ₄ ·N ₂ ⁺	(5b)	5
<i>p</i> -NO ₂ C ₆ H ₄ ·N ₂	C ₆ H ₅ ·N ₂ ⁺	(5a)	47
C ₆ H ₅ ·N ₂	<i>p</i> -NO ₂ C ₆ H ₄ ·N ₂ ⁺	(5b)	22
NO ₂	<i>p</i> -NO ₂ C ₆ H ₄ ·N ₂ ⁺	(5b)	22

One would like to interpret these results in terms of Perrin's relative leaving abilities,¹³ but without very detailed knowledge of the mechanisms of all these reactions, the relative leaving order cannot be obtained confidently from product studies. There is the additional complication¹³ that some potential leaving groups (*e.g.* H⁺, Cl⁺) require the intervention of a nucleophile to remove them (S_N2-like behaviour), whereas others such as NO₂⁺ may leave without any assistance (S_N1); consequently the leaving order may be influenced by the nature and concentrations of any nucleophiles in the reaction mixture. Tentatively, one may conclude that C₆H₅·N₂⁺ is a better leaving group than any of Br⁺, Cl⁺, NO₂⁺, and *p*-NO₂C₆H₄·N₂⁺, but that Br⁺ leaves more readily than *p*-NO₂C₆H₄·N₂⁺.

Finally, it may be noted that the ease of displacement of arylazo-groups by halogen is relevant to the stabilities of azo-dyes to chlorine bleaches. In this connection, commercially successful azonaphthols of the Colour Index having satisfactory chlorine resistance have the naphthol ring substituted with electron-withdrawing

groups. Presumably this deactivates the molecule towards attack of Cl⁺ at the arylazo-bearing carbon, thus protecting against loss of the arylazo-group.

EXPERIMENTAL

Solvents were reagent grade materials, used without further purification. Column chromatography employed alumina or silica gel adsorbents of 80–200 mesh; analytical t.l.c. used J. T. Baker type 9F alumina or E. Merck PF₂₅₄ silica gel. The latter adsorbent was used also for preparative t.l.c. (p.l.c.), which was run on 20 × 100 cm plates. The bands were extracted, usually with chloroform, using a Soxhlet extractor. Products were identified by comparison of m.p., t.l.c., and u.v. spectra with those of authentic samples. Spectroscopic data were recorded on Beckman IR5A (i.r.), Unicam SP 800 (u.v.–visible), and Varian-MAT CH7 (mass), the latter operating at 70 eV ionising voltage.

2-Hydroxyazobenzene, m.p. 80–81° (lit.,¹⁴ 81°), was prepared by photorearrangement of azoxybenzene in benzene solution. 1-Arylazo-2-naphthols were prepared by the action of the appropriate diazonium chloride on alkaline 2-naphthol; 1-phenylazo-2-naphthol (5a) had m.p. 130–131° (lit.,¹⁵ 133°); 1-*p*-nitrophenylazo-2-naphthol (5b) had m.p. 250–251° (lit.,¹⁶ 249°). 1-Bromo-2-naphthol, m.p. 76–78° (lit.,¹⁷ 82°), and 1-chloro-2-naphthol, m.p. 68–69° (lit.,^{12a} 70°), were synthesised from 2-naphthol and the halogen using acetic acid as solvent; 1-chloro-2-naphthol required four recrystallisations from ligroin following chromatography over alumina for purification.

Reaction of (1) with Bromine–Sodium Hydroxide.—To a solution of (1) (265 mg) in acetonitrile (10 ml) was added 0.5M-NaOH (5 ml) and 1.03M-bromine in acetonitrile (1.3 ml). The mixture was stirred for 20 min, poured into water (100 ml) and sodium thiosulphate (1.0 g) was added. Extraction into chloroform and evaporation gave a residue (0.43 g) which was resolved by p.l.c. using 10% benzene in ligroin as the eluant. Five bands were obtained; the two most mobile, which were incompletely resolved, were mono- and di-bromides (53 mg) as obtained in neutral solution.⁷ Band 3 (100 mg) was starting material. Band 4 (41 mg) was dark brown, but crystallised from ethanol as an amorphous dark green powder, m.p. 158–160°, identified as 2-bromo-4,6-bisphenylazophenol (4), λ_{max.} (EtOH) 405 (log ε 4.07) and 337 nm (4.61); λ_{max.} (EtOH–0.1M-KOH) 410 nm (log ε 4.39), M⁺ 380/382 (one Br) (Found: M⁺, 380.0271. C₁₈H₁₃BrN₄O requires M, 380.0273). Band 5 (85 mg) was identified as 2,4-bisphenylazophenol (3), dark brown needles from ethanol, m.p. 129–130.5° (lit.,⁸ 131°), λ_{max.} (EtOH) 399 (log ε 3.98) and 331 nm (4.64), λ_{max.} (EtOH–0.1M-KOH) 405 nm (log ε 4.37), M⁺ 302.

Reaction of (5a) with Bromine.—(i) To a solution of (5a) (1.0 g) in acetonitrile (25 ml) was added sodium hydroxide (1.0 g) and water (5 ml) and the mixture cooled to 5°. Bromine (3 ml) was added; the solution became hot, and a tar was deposited. Treatment with aqueous potassium iodide, sodium thiosulphate, and extraction into chloroform gave a brown solution, shown by t.l.c. to be lacking in (5a) but containing no significant quantities of any products. When the reaction was repeated with dropwise bromine addition, keeping the temperature <7°, similar results were obtained. When acetic acid was the solvent, addition

¹⁴ E. Bamberger, *Ber.*, 1900, **33**, 1950.

¹⁵ G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 1954, 2243.

¹⁶ R. Meldola, *J. Chem. Soc.*, 1885, **47**, 657.

¹⁷ A. J. Smith, *J. Chem. Soc.*, 1879, **35**, 789.

of potassium iodide caused the red colour of the dye to be regenerated, and (5a) could be recovered almost quantitatively.

(ii) To an ice-cooled solution of (5a) (0.20 g) and sodium acetate trihydrate (1.0 g) in acetic acid (15 ml) was added 1.03M-Br₂ in acetonitrile (4 ml). After 10 min the mixture was poured into water and extracted into chloroform. The organic phase was washed with sodium thiosulphate to give a yellow solution, which was evaporated at low temperature to form a residue (0.26 g). The residue was at once resolved by p.l.c. (eluant benzene), and the bands were scraped off and extracted with cold acetone (avoiding the use of a Soxhlet extractor). One major band was isolated with some decomposition as a yellowish oil; the mass spectrum *m/e* 300/302/304 fits C₁₀H₆Br₂O. Similar results were obtained using 1-*o*-tolylazo-2-naphthol instead of (5a).

Nitration of (5a).—To a stirred solution of (5a) (1.0 g) in acetic acid (25 ml) was added 70% nitric acid (1.2 ml) in portions over 2 h. The mixture was poured into water affording a fine yellow powder, m.p. 170—185°. Passage through a column of silica gel eluting with chloroform afforded 1,6-dinitro-2-naphthol (0.71 g), m.p. 189—192° (decomp.) [lit.,¹⁸ 195° (decomp.)], *M*⁺ 234. An identical compound was obtained by nitrating 2-naphthol under similar conditions.

Diazotisation of 1-Substituted-2-naphthols.—The following procedures are typical; others are reported in the Table.

(i) *p*-Nitrobenzenediazonium chloride with 1-nitro-2-naphthol. To a mixture of 1-nitro-2-naphthol (0.95 g) in water (50 ml) and sodium hydroxide (2 g) was added a solution of

p-nitroaniline (0.70 g) in 5M-HCl (5 ml) previously diazotised with sodium nitrite (0.35 g). The mixture was stirred at 5° for 30 min and then kept at room temperature overnight. Acidification and extraction into chloroform, evaporation, and chromatography of the residue over alumina, eluting with benzene, gave (5b) (76 mg), m.p. 240—244°, without recrystallisation, having u.v. and t.l.c. behaviour the same as those of authentic (5b).

(ii) *Benzenediazonium chloride with 1-bromo-2-naphthol*. Aniline (0.47 g) was diazotised as above and poured into a mixture of 1-bromo-2-naphthol (1.1 g), sodium hydroxide (1.0 g), and water (10 ml). After 2 min, the mixture was extracted with chloroform without acidification to give a red solution, which was found by t.l.c. to contain much tarry material. Evaporation, and passage of the concentrate through a short alumina column, eluting with chloroform, gave a red solution which was evaporated and the residue resolved further by p.l.c. (eluant benzene-ligroin, 1:1). The major, red band was extracted to give (5a) (69 mg), with properties identical with those of authentic (5a).

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¹⁸ O. Wallach and H. Wickelhaus, *Ber.*, 1870, **3**, 846.