Conversion of 1-Phenylazo-2-naphthol into the Benzenediazonium Ion: Another Route to Phenyl Radicals

By J. I. G. CADOGAN,* CHARLES D. MURRAY, and JOHN T. SHARP
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary 1-Phenylazo-2-naphthol and related compounds react with *p*-chlorobenzoyl nitrite in benzene to give the benzenediazonium cation, which may be trapped as such or allowed to decompose *in situ* to give phenyl radicals.

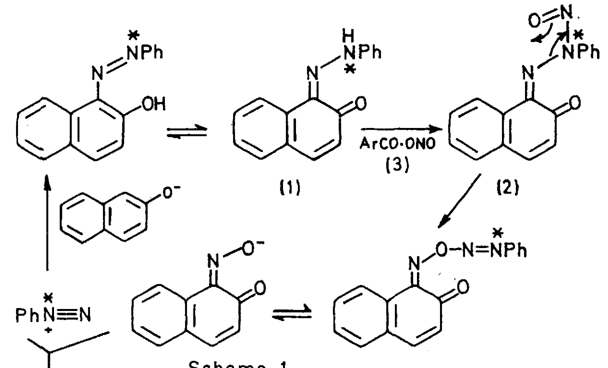
THE coupling of the benzenediazonium cation with alkaline β-naphthol is one of the best known reactions in organic chemistry. We now describe a process whereby the resulting 1-phenylazo-2-naphthol is reconverted into the benzenediazonium compound which may be trapped as such or allowed to decompose *in situ* to provide another source of phenyl radicals.

Since 1-phenylazo-2-naphthol exists partially in the hydrazone form (**1**), nitrosation should proceed *via* the nitrosohydrazone (**2**) then by rearrangement through the diazo ether to the diazonium cation (Scheme 1), by analogy with nitrosation and decomposition of acetanilide.[1,2] This expectation appeared to be fulfilled when reaction of *p*-chlorobenzoyl nitrite (**3**) (3 mol) (CBN), as nitrosating agent,[3] with 1-phenylazo-2-naphthol (1 mol) in benzene at room temperature led to rapid decomposition of the azo-compound. Subsequent addition of aqueous alkaline β-naphthol to the reaction mixture after decolourisation had occurred, led to the instant regeneration of 1-phenylazo-2-naphthol. That Scheme **1** was not wholly satisfactory followed, however, from the results of experiments using ^{15}N-labelled 1-phenylazo-2-naphthol (**1**; $N^* = {}^{15}N$). Reaction of this with CBN, followed by addition of sodium β-naphthoxide, after decomposition of the original ^{15}N-azo-compound was complete, gave 1-phenylazo-2-naphthol (32%), 70% of which had undergone nitrogen exchange with loss of the ^{15}N label. Since Scheme 1 calls for complete retention of this label an alternative route to the regenerated benzenediazonium ion was required. In the absence of exchange with atmospheric nitrogen, ruled out by control experiments, the only source of nitrogen is the nitrosating agent itself. Since it is known that phenyl radicals react with nitrosating agents to give the diazonium cation, as in Scheme 2,[4] it follows that our results can be accommodated by formation of the diazonium cation, as in Scheme 1, some of which survives to be trapped by sodium β-naphthoxide to give ^{15}N-labelled azo-compound, but the remainder decomposes with loss of ^{15}N label to give phenyl radicals which subsequently react *via* Scheme 2 with the nitrosating agent to give the unlabelled diazonium cation. In accord with this, reaction of 1-phenylazo-2-naphthol with CBN in benzene, without subsequent addition of sodium β-naphthoxide, gave biphenyl (30%). That this was formed *via* phenyl radicals followed from the formation of a mixture of isomeric t-butylbiphenyls of the correct, *i.e.* radical derived, isomeric composition (2-, 20%; 3-, 57%; 4-, 23%)[5] when the reaction was carried out in t-butylbenzene rather than benzene. Under the conditions employed, the β-naphthol moiety was converted into an unresolved complex tarry mixture, but further confirmation of the proposed reaction path is provided by the following:

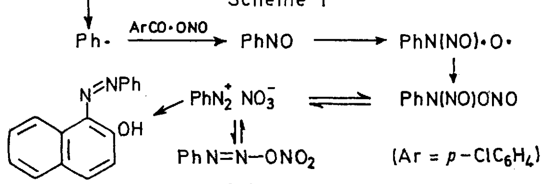
(i) reaction of phenyl radicals from phenylazotriphenylmethane with CBN in benzene gave the benzenediazonium cation (27%) as shown by subsequent reaction with aqueous sodium β-naphthoxide.

$$Ph_3CN{=}NPh \longrightarrow Ph\cdot \xrightarrow{CBN} PhN_2^+$$

(ii) Reaction of CBN with nitrosobenzene and *p*-methylnitrosobenzene gave the corresponding diazonium cations. (iii) No reaction was observed between CBN and azobenzene in benzene. (iv) Reactions using pentyl nitrite instead of CBN, or 1-phenylazo-4-naphthol, 2-phenylazo-1-naphthol, and 2-phenylazo-4-methylphenol instead of 1-phenylazo-2-naphthol, proceeded as expected from the combined Schemes 1 and 2. (v) No reaction occurred between CBN and 1-phenylazo-4-methoxynaphthalene, which cannot exist in the hydrazone form. (vi) Reaction of 1-phenylazo-2-naphthol with CBN followed by treatment with sodium 7-methoxy-2-naphthoxide gave 1-phenylazo-7-methoxy-2-naphthol. (vii) Reaction of 1-phenylazo-4-naphthol with CBN followed by treatment with sodium β-naphthoxide gave 1-phenylazo-2-naphthol.



Scheme 1



Scheme 2

These results underline the need to avoid the use of excess of diazotising agent in the preparation of diazonium salts to be used subsequently in azo-coupling.

(*Received*, 11*th June* 1973; *Com.* 826.)

---

[1] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1934, 1797; R. Huisgen and G. Horeld, *Annalen*, 1951, **562**, 181; A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, *J. Chem. Soc.* (*B*), 1968, 1308.

[2] J. I. G. Cadogan, *Chem. Soc. Special Publ.*, 1970, **24**, 71; *Accounts Chem. Res.*, 1971, **4**, 186.

[3] B. D. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563,

[4] E. Bamberger, *Ber.* 1897, **30**, 50; J. M. Tedder and G. Theaker, *Tetrahedron*, 1959, **5**, 288.

[5] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 3352.