# Synthesis and Photolysis of Some 1-Naphthyl Azoxy-compounds

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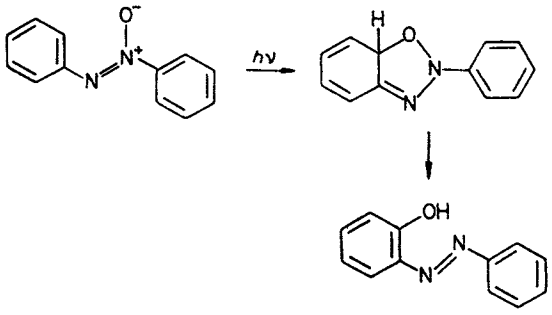
Azoxy-compounds of the naphthalene series fail to undergo migration of the oxygen atom into the *peri*-position. This implies that the azo nitrogen function is intimately involved in the transfer process.

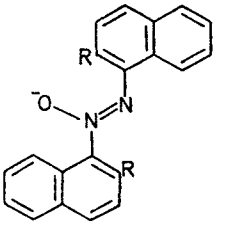
THE photorearrangement of azoxybenzene to 2-hydroxyazobenzene is an intramolecular reaction resulting in the migration of the azoxy oxygen atom to an *ortho*-position in the distant aromatic ring.[1] The transfer is believed [2,3] to be an aromatic substitution [equation (i)] in which the oxygen atom attacks the *ortho*-carbon atom directly rather than first abstracting the *ortho*-hydrogen atom.



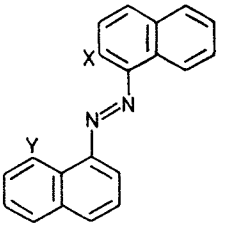
(i)

In continuation of our studies of the mechanism of this reaction, we now report the synthesis and photolysis of a number of 1,1′-azoxynaphthalenes.

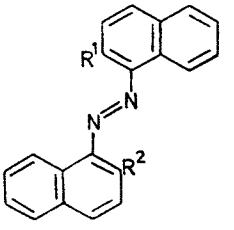
The *peri*-position of a 1,1′-azoxynaphthalene bears a relationship geometrically equivalent to that of the 2′-position into which oxygen migration would normally occur. Unless activation by the nitrogen function adjacent to the site of attack by oxygen is important to the success of the reaction, we would expect that irradiation of 1,1′-azoxynaphthalene (1) would afford 8-hydroxy-1,1′-azonaphthalene (2) in addition to 2-hydroxy-1,1′-azonaphthalene (3), the usual product, especially since the *peri*-position is an α site whereas the normal photorearrangement affords a β-naphthol derivative. Cumming and Steel [4] had previously reported the photorearrangement (1) ⟶ (3); repetition of their work gave a minor product in addition to (3) which was isomeric with the starting material. The new compound was not a geometric isomer of (1), for it was unaffected by prolonged refluxing in benzene; nor could authentic (3) be transformed into (2) either thermally or photochemically, with or without the assistance of a sensitiser (benzophenone). An attempt to prepare authentic (2) for comparison by coupling 1-nitrosonaphthalene‡ with 8-amino-1-naphthol [6] was unsuccessful (*cf.* other reports [7] of the failure of this method for synthesising azonaphthalenes), so the structure of the minor product is unknown. However,



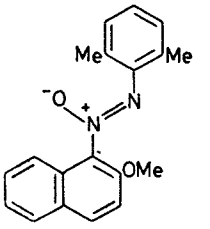
(1) R = H
(4) R = Me
(5) R = OMe
(10) R = F



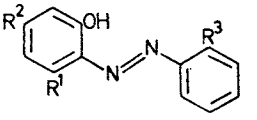
(2) X = H, Y = OH
(3) X = OH, Y = H



(6) $R^1 = R^2 = OMe$
(7) $R^1 = OH, R^2 = OMe$
(8) $R^1 = OMe, R^2 = O[CH_2]_4 \cdot OMe$
(11) $R^1 = R^2 = Me$



(9)



(12) $R^1 = OMe, R^2 = H, R^3 = OMe$
(13) $R^1 = H, R^2 = OMe, R^3 = OMe$
(14) $R^1 = R^3 = Ph, R^2 = H$

the observation that the minor product is suppressed in the presence of 2-naphthol suggests that it is not (2), but rather a product of diazonium ion fragmentation.[8]

Attention was then turned to azoxynaphthalenes in which the site of normal photorearrangement is blocked,

‡ Prepared by the action of nitrosyl chloride on di-1-naphthylmercury.[5]

[1] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231; E. Buncel, in 'Mechanisms of Molecular Migrations,' vol. 1, ed. B. S. Thyagarajan, Interscience, New York, 1969, pp. 104—110.

[2] D. J. W. Goon, N. G. Murray, J.-P. Schoch, and N. J. Bunce, *Canad. J. Chem.*, 1973, **51**, 3827.

[3] G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 1954, 2243.

[4] W. M. Cumming and J. K. Steel, *J. Chem. Soc.*, 1923, **123**, 2464.

[5] F. F. Blicke and F. D. Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 3479.

[6] Beilstein's Handbuch, **13**, 672 (main work).

[7] H. E. Fierz-David, L. Blangey, and E. Marian, *Helv. Chim. Acta*, 1951, **34**, 846.

[8] N. J. Bunce, *Bull. Chem. Soc. Japan*, 1974, **47**, 725.

so that any migration of oxygen would be diverted into the 8-position. The dimethyl compound (4) was inaccessible through direct reduction of the nitro-compound, by either thallium in ethanol[9] or lithium aluminium hydride, although the apparently equally hindered 2,6-dinitrobenzene can be reduced by these methods.[2] Instead, the amine was converted into the diazonium salt, which was coupled by the method previously used for the corresponding dinitro- and dichloro-azonaphthalenes.[10] Oxidation of the resulting azo-compound yielded (4). No rearrangement was observed on irradiation of this azoxy-compound, but a slow photoreduction occurred, even in solution in benzene.

2,2′-Dihydroxy-1,1′-azonaphthalene was the starting material for the dimethoxy-compound (5). This naphthol was extremely resistant to methylation; several methods were unsuccessful,* but partial methylation was achieved with dimethyl sulphate–sodium hydride in dimethylformamide, giving a mixture of ethers (6) and (7). When tetrahydrofuran was used as solvent, methylation proceeded to completion, but attack on the solvent competed with methylation of the substrate and as a result the ring-opened tetrahydrofuran substitution product (8) was obtained in addition to (6). Trimethyloxonium tetrafluoroborate[12] in the presence of sodium was the most effective methylating agent found, and the product (6) was converted into (5) by careful oxidation. This azoxy-compound also failed to photorearrange; *cis–trans*-isomerisation was its main photoreaction.

The unsymmetrical azoxy-compound (9) was also obtained by oxidising the azo-compound, itself prepared by methylating the coupling product of 2,6-dimethylbenzenediazonium chloride with 2-naphthol. In this case, methylation was a little easier ($Me_2SO_4$–NaH–$Me_2N$·CHO); oxidation gave a single isomer whose structure was inferred to be that shown by analogy with the work of Berwick and Rondeau.[13] The azoxy-compound was extremely resistant to photolysis however, and was unchanged after prolonged irradiation.

From the foregoing results, it was concluded that oxygen migration into the *peri*-position of 1,1′-azoxynaphthalenes is not a favoured reaction, and hence that activation by the nitrogen function *ortho* to the point of attack by oxygen is necessary for the success of the photorearrangement. A possible problem is steric hindrance in the 2,2′-disubstituted azoxynaphthalenes; we had hoped to study the unencumbered difluoride (10), but were unable to do so owing to the inaccessibility of the desired precursor, 2-fluoro-1-nitronaphthalene, which could be prepared only extremely inefficiently by a Schiemann procedure; indeed, this method has previously been reported[14] as failing entirely to afford the fluoride. Failure of the azoxy-compounds to photorearrange is not the result of specific inhibition of the reaction by the blocking substituents chosen; photorearrangement of 2,2′-azoxytoluene is well known, and although anomalous products are formed[2,15] in addition to the expected photorearrangement product, these have now been explained[8] as arising by way of diazonium ion intermediates. We also find that 2,2′-azoxyanisole behaves similarly to the azoxytoluene. Thus, direct irradiation affords a mixture of two hydroxy-azo-compounds, one of which is suppressed in the presence of β-naphthol. We note that oxygen migration does not take place into geometrically available sites (other than the distant *ortho*-position) in *o*-azoxybiphenyl; although azo-compounds besides the expected photorearrangement product were formed, these were suppressed in the presence of β-naphthol, showing that they, too, were formed through diazonium ion fragmentation.

## EXPERIMENTAL

Procedures for photolysis and methods of separation and identification have been described in detail previously.[2] In this work irradiations were carried out without deoxygenation of the solutions. Elemental analytical data for new compounds are in the Table. Spectroscopic data for compounds marked with an obelus (†) are available as Supplementary Publication No. SUP 21621 (5 pp.).‡

*1,1′-Azoxynaphthalene.*—Originally, the method of Cumming and Steel[4] was used. The crude azoxy-compound was purified by preparative t.l.c.; 1-nitronaphthalene (8.5 g) gave 1,1′-azonaphthalene (0.15 g), m.p. 191—192° (lit.,[16] 191°), and 1,1′-azoxynaphthalene (1.28 g), m.p. 129—129.5° (lit.,[4] 127°), as well as unchanged 1-nitronaphthalene (0.4 g). Subsequent preparations employed reduction with thallium in ethanol;[9] here also, over-reduction to the azo-compound was a problem, and it was advantageous to oxidise the crude azoxynaphthalene preparation with hydrogen peroxide–acetic acid before purification.

*Irradiation of 1,1′-Azoxynaphthalene* (1).—A solution of compound (1) (0.98 g) in benzene (300 ml) was irradiated for 1 h, then evaporated, and the residue was separated by preparative t.l.c. (benzene–hexane,§ 2 : 3). The most mobile band was 1,1′-azonaphthalene (3.4 mg). A second band afforded deep red crystals (29 mg), m.p. 202—203°,† stable under reflux in benzene for 24 h; its yields were variable: this was the highest achieved. A third band gave starting material (1) (420 mg), and a fourth afforded 2-hydroxy-1,1′-azonaphthalene (3)(70 mg), which crystallised from chloroform as dark red needles with a green lustre, m.p. 229—230°, identified by comparison with an authentic sample[17] prepared by coupling diazotised 1-naphthylamine

* Reagents used included dimethyl sulphate in aqueous or alcoholic alkaline solution, methyl toluene-*p*-sulphonate,[11] and methyl fluorosulphate (Aldrich).

‡ For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

§ Hexane indicates the hexane fraction of petroleum, b.p. 66—73°

[9] A. McKillop, R. A. Raphael, and E. C. Taylor, *J. Org. Chem.*, 1970, **35**, 1670.

[10] H. H. Hodgson, C. Leigh, and G. Turner *J. Chem. Soc.*, 1942, 744.

[11] V. Rodianov, *Bull. Soc. chim. France*, 1926, **39**, 305; 1929, **45**, 109.

[12] H. Meerwein, *Org. Synth.*, Coll. Vol. V, 1973, pp. 1080, 1096.

[13] M. A. Berwick and R. E. Rondeau, *J. Org. Chem.*, 1972, **37**, 2409.

[14] A. Roe, *Org. Reactions*, 1949, **5**, 193 (see p. 199).

[15] G. E. Lewis and J. A. Reiss, *Austral. J. Chem.*, 1966, **19**, 1887.

[16] L. Wacker, *Annalen*, 1901, **317**, 384.

[17] R. Meldola and E. S. Hanes, *J. Chem. Soc.*, 1894, **65**, 834.

with 2-naphthol.† No change was observed when a solution of (3) (245 mg) was irradiated in benzene (300 ml) for 7.5 h, either alone or in the presence of benzophenone (0.5 g)

*2,2′-Dimethyl-1,1′-azoxynaphthalene* (4).—2-Methyl-1-nitronaphthalene (25 g) was reduced with tin(II) chloride dihydrate (91 g), concentrated hydrochloric acid (100 ml), and glacial acetic acid (180 ml) in a modification of a published method.[18] The mixture was heated to reflux for 10.5 h, cooled, and filtered. The free amines were liberated with sodium hydroxide, and extracted into ether; evaporation yielded a greenish liquid (14 g). Subsequent experiments showed that the expected 1-amino-2-methylnaphthalene was contaminated with 1-amino-4-chloro-2-methylnaphthalene, which could be removed only by preparative t.l.c. [m.p. 63.5—64° (lit.,[19] 65°), $M^+$ ($^{35}$Cl) 191]. However, in the actual procedure, the impure material was used.

To a stirred, cooled suspension of 1-amino-2-methylnaphthalene (4.7 g) in water (75 ml) was added concentrated sulphuric acid (12 ml), followed successively by sodium nitrite (2.5 g) in water (20 ml), sodium acetate (50 g) in water (100 ml), and sodium sulphite (7.5 g) in water (50 ml). Stirring was continued for 1 h, after which the mixture was extracted with chloroform; the extract was washed ($NaHCO_3$), dried, and evaporated. Chromatography of the residue over silica gel (elution with benzene) gave material (1.45 g) which was further separated by preparative t.l.c. (hexane) into *4-chloro-2,2′-dimethyl-1,1′-azonaphthalene* (0.23 g), red-brown needles (from ethanol),† m.p. 101—102°; *2,2′-dimethyl-1,1′-azonaphthalene* (11) (0.43 g), brown needles (from ethanol),† m.p. 84—85°; and a brown solid (2 mg), m.p. 206—208°. From its mass spectrum, *m/e* 450 ($M^+$?, 69%), 435 (39), 297 (16), 282 (17), 281 (50), 280 (20), 279 (14), 267 (19), 266 (56), 265 (67), 141 (100), and 105 (73), it is likely that this compound is a 2-methylnaphthyl-substituted 2,2′-dimethyl-1,1′-azonaphthalene.

From two preparations, 2,2′-dimethyl-1,1′-azonaphthalene (0.9 g) was oxidised with 30% hydrogen peroxide (3 ml) in glacial acetic acid (20 ml) at 60—70 °C for 4.5 h. The cooled mixture was diluted with water and extracted into chloroform. The usual work-up gave a yellow solid (0.53 g); two crystallisations from ethanol gave *2,2′-dimethyl-1,1′-azoxynaphthalene* (4), m.p. 115—116°.†

Analytical data

| Compd. | Formula | Required (%) C | H | N | Found (%) C | H | N |
|---|---|---|---|---|---|---|---|
| (2) (?) | $C_{20}H_{14}N_2O$ | 80.55 | 4.75 | 9.4 | 79.85 | 4.55 | 8.95 |
| (4) | $C_{22}H_{18}N_2O$ | 80.95 | 5.55 | 8.6 | 81.1 | 5.4 | 8.45 |
| (5) | $C_{22}H_{18}N_2O_3$ | 73.75 | 5.05 | 7.8 | 73.4 | 4.95 | 7.6 |
| (6) | $C_{22}H_{18}N_2O_2$ | 77.15 | 5.3 | 8.2 | 76.95 | 5.25 | 8.15 |
| (7) | $C_{21}H_{16}N_2O_2$ | 76.8 | 4.9 | 8.55 | 76.55 | 5.15 | 8.4 |
| (8) | $C_{26}H_{26}N_2O_3$ | 75.35 | 6.3 | 6.75 | 74.8 | 6.25 | 6.6 |
| (9) | $C_{19}H_{18}N_2O_2$ | 74.45 | 5.9 | 9.15 | 74.0 | 5.85 | 9.1 |
| (A) * | $C_{22}H_{17}ClN_2$ | 76.6 | 4.95 | 8.15 | 76.7 | 4.75 | 8.05 |
| (11) | $C_{22}H_{18}N_2$ | 85.15 | 5.85 | 9.05 | 85.2 | 5.6 | 9.05 |
| (B) † | $C_{26}H_{26}N_2O_4$ | 72.55 | 6.1 | 6.5 | 72.85 | 5.9 | 6.25 |
| (C) ‡ | $C_{10}H_6FNO_3$ | 62.85 | 3.15 | | 62.9 | 3.3 | |
| (12) | $C_{14}H_{14}N_2O_3$ | 65.1 | 5.45 | 10.85 | 65.0 | 5.5 | 11.3 |
| (13) | $C_{14}H_{14}N_2O_3$ | 65.1 | 5.45 | 10.85 | 65.45 | 5.7 | 10.9 |
| (14) | $C_{24}H_{18}N_2O$ | 82.25 | 5.2 | 8.0 | 82.15 | 4.9 | 7.85 |
| (D) § | $C_{22}H_{16}N_2O$ | 81.45 | 4.95 | 8.65 | 81.6 | 5.2 | 8.5 |

* 4-Chloro-2,2′-dimethyl-1,1′-azonaphthalene. † 2-Methoxy-2′-(4-methoxybutoxy)-1,1′-*NON*-azoxynaphthalene. ‡ 2-Fluoro-1-nitronaphthalene. § 1-(Biphenyl-2-ylazo)-2-naphthol.

*Irradiation of the Azoxynaphthalene* (4).—A solution of compound (4) (0.42 g) in benzene (300 ml) was irradiated for 4.3 h. The solvent was removed and the residue separated by preparative t.l.c. (benzene–hexane, 2 : 3) affording numerous products mostly in trace quantities only: (i) colourless (26 mg), δ ($CCl_4$) 2.50 (s, $CH_3$) and 7.1—7.9 (m, ArH) (ratio 1 : 4.1), unidentified; (ii) red (22 mg), brown needles from ethanol, m.p. 83—84°, identified by comparison of mass and n.m.r. spectra as 2,2′-dimethyl-1,1′-azonaphthalene; (iii) colourless (8 mg), δ ($CCl_4$) 1.97 (d), 2.18 (s), 2.57 (s), 2.72 (s), and 7.2—8.1 (m) (ratio 1 : 2 : 2 : 2 : 12), unidentified; (iv) yellow (39 mg) unchanged (4), orange crystals from ethanol, m.p. 115.5—116.5°, identical (mass and n.m.r. spectra) with an authentic sample; (v) colourless (23 mg), crystals from petroleum, m.p. 64—66°, *m/e* 326 (17%), 311 (33), 267 (11), 169 (15), 157 (17), 156 (22), 155 (42), 154 (58), 143(14), 142 (20), 141 (83), 140 (30), 139 (19), 129 (17), 128 (31), 127 (28), 116 (19), and 115 (100), possibly *cis*-2,2′-dimethyl-1,1′-azoxynaphthalene.

*2,2′-Dimethoxy-1,1′-azonaphthalene* (6).—(i) *Dimethyl sulphate method.* To a stirred mixture of 2,2′-dihydroxy-1,1′-azonaphthalene [prepared[20] as red crystals with green gleam, m.p. 248—249° (from chloroform) (lit.,[20] 246°)] (8.45 mmol) and dry dimethylformamide (DMF) (40 ml) was added sodium hydride (19 mmol; 57% dispersion in oil), and after 10 min, a solution of dimethyl sulphate (32 mmol) in DMF was added over 1.5 h. Four hours later more dimethyl sulphate (1 ml) was added, and after 2 h more the mixture was poured into water and cooled; the solids were collected and dried at 70 °C. The crude material was separated by preparative t.l.c. (chloroform). The more mobile brown band was *2,2′-dimethoxy-1,1′-azonaphthalene* (6) (0.52 g, 18%), shiny brown plates (from ethanol), m.p. 171—172°.† The second band (purple), was *2-hydroxy-2′-methoxy-1,1′-azonaphthalene*† (7) (0.75 g, 27%), red-brown crystals (from benzene–hexane), m.p. 187—188°, which could be converted into the dimethoxy-derivative (but never completely) by repeating the methylation procedure.

When a similar procedure was carried out with dry tetrahydrofuran (THF) as solvent the dimethoxy-compound (6) was accompanied by a by-product, isolated as brown flakes from ethanol, m.p. 128—129°, and identified as *2-methoxy-2′-(4-methoxybutoxy)-1,1′-azonaphthalene* (8).†

(ii) *Trimethyloxonium tetrafluoroborate method.* To a suspension of the dihydroxyazonaphthalene (0.5 g) in dry tetrahydrofuran (100 ml) was added an excess of sodium metal. After heating to reflux, the mixture was cooled, and trimethyloxonium tetrafluoroborate[12] (0.5 g) was added. The mixture was stirred for 30 min then decanted from the residual sodium, and passed through a short column of alumina, with chloroform for elution. Sometimes the reaction proceeded to complete dimethylation; at other times a mixture of mono- and di-methyl derivatives was obtained. In the latter case, the methylation procedure was repeated. The yield of recrystallised 2,2′-dimethoxy-1,1′-azonaphthalene, m.p. 169—170°, was 39%.

*2,2′-Dimethoxy-1,1′-azoxynaphthalene* (5).—Oxidation of 2,2′-dimethoxy-1,1′-azonaphthalene was effected with peracetic acid solution, prepared by the method of Okata and Urasaki[21] and 0.85M in peracetic acid by iodimetric titration. The azo-compound (0.30 g) was dissolved in chloroform (25 ml) and the peracetic acid solution (1.1 m

[18] H. E. Fierz-David and E. Mannhart, *Helv. Chim. Acta*, 1937, **20**, 1024.

[19] R. Lesser, *Annalen*, 1914, **402**, 1.

[20] J. M. Tedder and B. Webster, *J. Chem. Soc.* 1960, 4417.

[21] Y. Okata and I. Urasaki, *J. Chem. Soc.* (*C*), 1970, 1689.

was added. The mixture was stirred at room temperature for 26 h, washed ($NaHCO_3$), dried ($MgSO_4$), and evaporated. The residue was separated by preparative t.l.c. (chloroform); one major green band was obtained with a darker green fore-band and a lighter green after-band. The fore-band gave red crystals (from chloroform–ether) (5 mg), m.p. 196—198° (decomp.). The main band afforded yellow crystals (from chloroform–ether) (132 mg), m.p. 198—199° (decomp.), identified as *2,2′-dimethoxy-1,1′-azoxynaphthalene*† (5). The after-band yielded orange crystals (from chloroform–ether) (12 mg), m.p. 199—200° (decomp.). When the oxidation was carried out with using chloroform (50 ml), 30% hydrogen peroxide (0.3 ml), and acetic anhydride (1.5 g), the yield of (5) was much lower and some demethylation to 2-hydroxy-2′-methoxy-1,1′-azonaphthalene occurred. In one experiment, a portion of the crude azo-compound (0.5 g) from the THF procedure was oxidised directly; the azoxy-compound (6) (0.24 g) was then accompanied by *2-methoxy-2′-(4-methoxybutoxy)-1,1′-NON-azoxynaphthalene*† (0.04 g), light tan flakes (from ethanol), m.p. 149—150°.

*Irradiation of the Azoxynaphthalene* (5).—A solution of compound (5) (0.49 g) in benzene (300 ml) was irradiated for 18 h then evaporated, and the residue was separated by preparative t.l.c. (chloroform) to give (i) material (177 mg) which appeared to contain both red and yellow crystals, m.p 191—194° [m.p. 197—199° (decomp.) after recrystallisation from chloroform–ether], and was starting material, *m/e* 358 (27%), 171 (40), 170 (100), 156 (35), 143 (70), 142 (54), 129 (23), 128 (72), 115 (27), 114 (35), and 101 (23); and (ii) a red solid (53 mg), m.p. 175—176° [after recrystallisation, orange needles, m.p. 194—196° (decomp.)]. The mass spectrum of the recrystallised material (ii) appeared to be the same as that of material (i). Material (ii) is probably *cis*-2,2′-dimethoxy-1,1′-azoxynaphthalene, which reverts to the *trans*-isomer during work-up. Material from an intermediate band (12 mg) also had m.p. 199—202° (decomp.) after recrystallisation. No other substances were obtained in more than trace amounts.

*1-(2,6-Dimethylphenyl-NNO-azoxyl)-2-methoxynaphthalene* (9).—1-(2,6-Dimethylphenylazo)-2-naphthol, prepared by coupling diazotised 2,6-dimethylaniline with 2-naphthol, had m.p. 143—144° [red needles from ethanol (lit.,[22] 146—147°)]. The azo-compound (5.5 g) was dissolved in dry DMF (75 ml) and sodium hydride (1.6 g; 57% dispersion in oil) was added to the stirred solution. After 15 min, dimethyl sulphate was added, followed 2 h later by more sodium hydride (0.8 g) and dimethyl sulphate (1.9 g). After 3.5 h more, the mixture was poured into water, and extracted with chloroform, affording, after conventional work-up, a viscous red liquid, which was purified by chromatography on silica gel; yield 4.0 g. This material was further purified by vacuum distillation, giving a viscous red liquid (2.64 g) which had crystallised after several months. Recrystallisation from hexane at −60 °C afforded 1-(2,6-dimethylphenylazo)-2-methoxynaphthalene, m.p. 44—46°, δ ($CCl_4$) 2.4 (6 H, s, $CH_3$), 3.7 (3 H, s, $OCH_3$), and 6.8—8.2 (9 H, m, ArH). Oxidation by dissolving the azo-compound (2.95 g) in acetic acid (75 ml) and heating for 9 h to 60 °C with 30% hydrogen peroxide (6 ml; added over the first 2 h), followed by conventional work-up, gave an oil which, after chromatography over silica gel and removal of solvent, crystallised upon trituration with petroleum. Crystallisation from ethanol afforded the *azoxy-compound*† (1.11 g) as orange needles, m.p. 119—120°.

*Irradiation of the Azoxynaphthalene* (9).—The azoxy-compound (0.75 g) in benzene (300 ml) was irradiated for 7 h. The solvent was removed and the residue was separated by t.l.c. (benzene–hexane, 2 : 3) giving one main band (0.63 g), m.p. 116.5—118.5°, raised to 120—121° after recrystallisation from ethanol. The n.m.r. spectrum was identical with that of the starting material. No other mobile bands were obtained.

*2-Fluoro-1-nitronaphthalene.*—To a slurry of 2-amino-1-nitronaphthalene (5 g) in 45% tetrafluoroboric acid * (20 ml) at 0 °C was added aqueous sodium nitrite (2 g). The mixture was then stirred for 15 min and filtered, and the solid was washed with ethanol, then with ether, and dried under vacuum. The resultant diazonium tetrafluoroborate (3.5 g) was heated in a 250 ml flask equipped with distillation condenser. Decomposition began when the surrounding oil-bath reached 130 °C, leaving a black tarry material. Both the residue and the apparatus were rinsed with warm benzene and the resulting solution was chromatographed over alumina (30 g), affording *2-fluoro-1-nitronaphthalene* (0.18 g), pale yellow needles (from methanol–water), m.p. 61—62°, $M^+$ 191.

Other methods were investigated for preparing this compound. Decomposition of the diazonium fluoride [23] *in situ* was unsuccessful. Nitration of 2-fluoronaphthalene gave a complex mixture (g.l.c.) in which the desired isomer was not a major component.

*2,2′-Azoxyanisole.*—*o*-Nitroanisole was reduced with methanol–sodium hydroxide,[24] affording the azoxy-compound (69%), m.p. 79.5—80° (lit.,[25] 81°).

*Irradiation of 2,2′-Azoxyanisole.*—(i) The azoxy-compound (0.25 g) in benzene (190 ml) was irradiated for 30 min. The solvent was removed and the residue was separated by preparative t.l.c. [eluant benzene–hexane (2 : 3) then benzene] giving two major bands. The first gave deep orange crystals (24 mg) (from methanol), m.p. 172—173° (in another experiment m.p. 175—176°), of *3-hydroxy-2,2′-azoanisole* (12);† it was also a product of an irradiation conducted in the presence of 2-naphthol (see below). The second afforded red needles (54 mg) (from methanol) of *3′-hydroxy-2,4′-azoanisole* (13),† m.p. 131—132°. An authentic sample was prepared as the minor product (1%) of the coupling reaction of *o*-anisidine with *m*-methoxyphenol. The desired azo-compound was the most mobile band chromatographically on alumina and on silica and had m.p. 130—131°. The *ortho*-location of the hydroxy-function was demonstrated by its resistance to deprotonation in ethanolic $10^{-2}$M-potassium hydroxide (no change in u.v. spectrum).‡

(ii) A solution of *o*-azoxyanisole (0.5 g) and 2-naphthol (1.0 g) in benzene (325 ml) was irradiated for 18 h. Extraction of the excess of 2-naphthol with dilute sodium hydroxide and evaporation afforded a residue that was separated by preparative t.l.c. The most mobile band (10 mg) gave the

*As observed previously, the use of hydrochloric acid for this reaction gives exclusively 1-chloro-2-fluoronaphthalene: see ref. 14.

‡ Observations indicating the structure 3′-hydroxy-2,4′-azoanisole for this compound rather than the alternative 4-hydroxy-2,2′-azoanisole are the low-field OH resonance in the n.m.r. spectrum [26] and the resistance to deprotonation in ethanolic $10^{-2}$M-potassium hydroxide.[15]

[22] W. Przybylski, unpublished observations; we thank Dr. Przybylski for this information.

[23] Ref. 14, p. 214.

[24] A. Lachman, *J. Amer. Chem. Soc.*, 1902, **24**, 1178.

[25] L. Gattermann and A. Ritsche, *Ber.*, 1890, **23**, 1738.

[26] L. W. Reeves, *Canad. J. Chem.*, 1960, **38**, 748.

hydroxyazoanisole (12), m.p. 175—177°. A second red band afforded 1-*o*-methoxyphenylazo-2-naphthol (129 mg), red needles (from ethanol), m.p. 182—183° (lit.,[27] 178°), $M^+$ 278. In addition, unchanged azoxyanisole (0.34 g) was recovered.

*2,2'-Azoxybiphenyl.*—2-Nitrobiphenyl was reduced to the azo-compound in 54% yield by the lithium aluminium hydride method.[2] The azo-compound (3.0 g) was dissolved in benzene (100 ml) and acetic acid (100 ml) and 30% hydrogen peroxide (10 ml) was added to the stirred solution, which was maintained near 65 °C. Further hydrogen peroxide (10 and 5 ml) was added after 5 and 14 h, the last addition causing the layers to separate. After 11 h more, the mixture was cooled and the benzene layer removed and worked up conventionally affording 2,2'-azoxybiphenyl as light yellow crystals (1.57 g, 50%) (from benzene–petroleum), m.p. 156—157° (lit.,[28] 156°; lit.,[29] 158°) (Found: C, 82.1; H, 5.1; N, 7.75. Calc. for $C_{24}H_{18}N_2O$: C, 82.25; H, 5.2; N, 8.0%).

Subsequent preparations employed the thallium–ethanol method,[9] affording the azoxy-compound in 60% yield.

*Irradiation of 2,2'-Azoxybiphenyl.*—(*a*) A solution of the azoxy-compound (1.00 g) in benzene (300 ml) was irradiated for 2.5 h. The solvent was removed and the residue was separated by preparative t.l.c. (benzene–hexane, 2 : 3), giving five bands: (i) red (47 mg), δ ($CDCl_3$) 6.8—7.9 (m, ArH) and 11.63 (s, OH), unchanged after heating to reflux in benzene for 22 h, a hydroxylated azobiphenyl not further identified; (ii) (193 mg), red needles (from ethanol), m.p. 187—188°, unchanged after heating for 17 h in benzene, identified as *3-hydroxy-2,2'-azobiphenyl* (14),† since it was also a product of the irradiation in the presence of 2-naphthol (below); (iii) (14 mg), red crystals (from ethanol), m.p. 224—225° (decomp.), δ ($CDCl_3$) 6.7—7.5 (m, ArH) and 12.2 (s, OH), $M^+$ 350, an hydroxylated azobiphenyl, not further identified; (iv) (180 mg), starting material; (v) (162 mg), n.m.r. spectrum showing only aromatic C–H, but after 16 h at reflux in benzene identical with that of band (iv), probably *cis*-2,2'-azoxybiphenyl.

(*b*) A solution of 2,2'-azoxybiphenyl (0.70 g) and 2-naphthol (1.0 g) in chloroform (20 ml) was irradiated with an external source for 17 h. The solution was extracted with dilute sodium hydroxide to remove most of the 2-naphthol then separated by preparative t.l.c. (benzene) giving four bands; (i) red needles (from ethanol) (124 mg), identical (mixed m.p.) with the 3-hydroxy-2,2'-azobiphenyl described above; (ii) starting material (460 mg); (iii) red crystals (from ethanol), m.p. 128—130° (20 mg); $M^+$ 324 [1-(biphenyl-2-ylazo)-2-naphthol]* and 350 (isomer of starting material) (too little material to purify further); (iv) (117 mg), yellow crystals, m.p. 156—157.5° (from ethanol), presumably originally *cis*-azoxy-compound, converted into *trans* during recrystallisation.

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* An authentic sample † [bright red *needles* (from ethanol–chloroform), m.p. 161—162°] was prepared by coupling diazotised 2-aminobiphenyl with alkaline 2-naphthol.

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[28] G. W. Gray and D. Lewis, *J. Chem. Soc.*, 1964, 3501.
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# Reaction of Benzylidenetriphenylphosphorane with Carbon Disulphide

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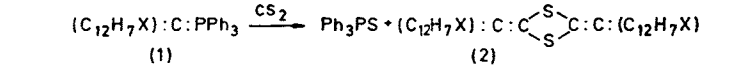
Benzylidenetriphenylphosphorane (4) reacts with carbon disulphide to give 2,4-dibenzylidene-1,3-dithietan (10), 2-phenyl-2-triphenylphosphoniodithioacetate (5), 2-benzylidene-4-phenyl-1,3-dithiole (11), and 2-phenyl-1-(phenyldithioacetyl)-2-triphenylphosphonioethenethiolate (16). The isolation and yield of each compound depend strictly on the experimental conditions and, in particular, on the work-up procedure.

SCHÖNBERG *et al.*[1] report that some fluorenylidenetriphenylphosphoranes (1) react with carbon disulphide



in refluxing chloroform to give 2,4-difluorenylidene-1,3-dithietans (2). Since compounds (1) have no hydrogen atoms attached to the ylide carbon atom, their overall reaction with carbon disulphide is necessarily restricted to dimerization of the intermediate thioketen system to give 1,3-dithietan derivatives.[1-5] However in the case of compounds such as (4) we considered that the initial adduct (5) might react in a different way, producing alkynethiolates [*e.g.* (7) and/or (8)] from which 1,3-

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[2] K. Dickoré and R. Wegler, *Angew. Chem. Internat. Edn.*, 1966, **5**, 970.
[3] A. Schönberg, L. Vargha, and H. Kaltschmit, *Ber.*, 1931, **64**, 2582.
[4] H. Ulrich, in 'Cycloaddition Reactions of Heterocumulenes,' ed. A. T. Blomquist, Academic Press, New York, 1967, p. 95.
[5] H. Behringer and E. Meinetsberger, *Tetrahedron Letters*, 1973, 1915.