Aromatic Azo-Compounds. Part VI. The Action of Light on Azoxy-Compounds.*

By G. M. Badger and R. G. Buttery.

[Reprint Order No. 5126.]

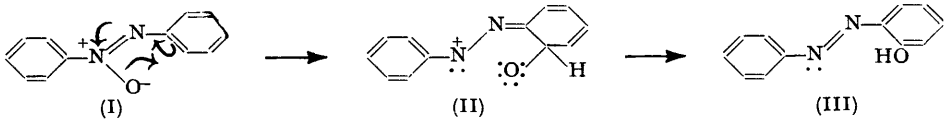
A number of azoxy-derivatives have been isomerised to *o*-hydroxyazo-derivatives by exposure to sunlight, the oxygen atom migrating from nitrogen to the further nucleus. An intramolecular mechanism is therefore proposed. The supposed red " isomers " of the azoxynaphthalenes are mixtures.

Cumming and Steel (*J.*, 1923, **123**, 2464) reported that exposure of yellow 1 : 1'-azoxynaphthalene to sunlight or ultra-violet light rapidly converted it into a red form. A similar change was claimed for 2 : 2'-azoxynaphthalene (Cumming and Ferrier, *J.*, 1924, **125**, 1108). In each case the two forms had identical or almost identical melting points, and it was suggested that they were structural isomers. On the other hand, many azoxy-compounds (including 1 : 1'-azoxynaphthalene) are known to be converted into *o*-hydroxyazo-compounds by *prolonged* exposure to light (Cumming and Ferrier, *J.*, 1925, **127**, 2374; Cumming and Howie, *J.*, 1931, 3181). The interpretation put forward by Cumming *et al.* is not in accord with the modern view that azoxy-compounds contain a co-ordinate covalent bond [R·N(→O):N·R'], so these changes have been reinvestigated.

By using chromatography we have shown that the red " isomer " of 1 : 1'-azoxynaphthalene is a mixture of unchanged material with 2-hydroxy-1 : 1'-azonaphthalene, $C_{10}H_7$·N:N·$C_{10}H_6$·OH, in agreement with Cumming and Howie's conclusion (*loc. cit.*) that this naphthol is formed by the prolonged exposure of 1 : 1'-azoxynaphthalene to light. Similarly, the red " isomer " of 2 : 2'-azonaphthalene is a mixture of unchanged material and of 1-hydroxy-2 : 2'-azonaphthalene.

This rearrangement of azoxy-derivatives by light is formally similar to the Wallach transformation by sulphuric acid (see Gore and Hughes, *Austral. J. Sci. Res.*, 1950, **3**, *A*, 136); but the acid-catalysed rearrangement of azoxybenzenes gives derivatives of 4-hydroxyazobenzene with smaller quantities of 2-hydroxyazobenzenes and other products, whereas the light-catalysed isomerisation seems to lead exclusively, or almost exclusively, to 2-hydroxy-derivatives.

To establish whether the oxygen atom migrates from the nitrogen atom to the adjacent or the non-adjacent aromatic ring, some unsymmetrical azo-compounds have been investigated. α-2-Phenylazoxynaphthalene, Ph·N(→O):N·$C_{10}H_7$, gave 1-hydroxy-2-phenylazonaphthalene on exposure to light; the β-isomer, Ph·N:N(→O)·$C_{10}H_7$, was partly converted into 2-*o*-hydroxyphenylazonaphthalene. Similarly, β-1-phenylazoxynaphthalene gave 2-hydroxy-1-phenylazonaphthalene. Again, α-4-bromoazoxybenzene, Ph·N(→O):N·C_6H_4Br, gave 4-bromo-2-hydroxyazobenzene, and the β-isomer gave 4-bromo-2'-hydroxyazobenzene. In all these cases, therefore, the oxygen migrates from the nitrogen atom to which it is attached to the nucleus which is attached to the other nitrogen atom. As the −N= valency angle is 120°, the *ortho*-position of the nucleus affected is closer in space to the oxygen atom than is the *ortho*-position of the other nucleus (cf. I).



(I) (II) (III)

This, together with the fact that *o*-hydroxy-derivatives appear to be formed exclusively, indicates that an intramolecular mechanism is probably involved and the scheme (I) ⟶ (III) is tentatively suggested.

That α-2-phenylazoxynaphthalene gives the 1-hydroxy-derivative exclusively, is in agreement with this mechanism, for the quinonoid transition state (as II), leading to

* Part V, *J.*, 1954, 1888.

substitution in the 1-position, would be much more stable than that leading to substitution in the 3-position (cf. naphtha-1 : 2- and -2 : 3-quinone).

In several cases the solvent had a marked effect on the rate of the rearrangement: migration was extremely slow in light petroleum, slow in benzene, and relatively rapid in ethanol. The yields also varied with the time of exposure, but were generally about 5—15% for 1 month's irradiation.

The azoxy-derivatives were prepared by peracetic acid oxidation of the azo-compounds. 2-Phenylazonaphthalene gave a mixture of the isomers, which were separated by fractional crystallisation from light petroleum (cf. Badger and Lewis, *J.*, 1953, 2151). 4-Bromoazobenzene also gave a mixture; fractional crystallisation from light petroleum gave the two isomers, the structures of which have been established by Angeli and Valori (*Atti R. Accad. Lincei*, 1912, **21**, I, 155). 1-Hydroxy-2 : 2'-azonaphthalene was prepared, in poor yield, from 1 : 2-naphthaquinone and 2-naphthylhydrazine. For the preparation of 2-*o*-hydroxyphenylazonaphthalene, *o*-nitroanisole was condensed with 2-naphthylamine in the presence of sodium hydroxide (cf. Martynoff, *Compt. rend.*, 1946, **223**, 747), and the product demethylated; 4-bromo-2'-hydroxyazobenzene was prepared similarly (cf. Martynoff, *loc. cit.*).

Experimental

Irradiations.—(a) 1 : 1'-*Azoxynaphthalene.* A benzene solution of 1 : 1'-azoxynaphthalene (m. p. 127°) was exposed to sunlight for 1 month. The resulting red solution was chromatographed on alumina whereby it was separated into unchanged material and 2-hydroxy-1 : 1'-azonaphthalene. After recrystallisation from alcohol the latter had m. p. 229° alone or admixed with an authentic specimen prepared according to Meldola and Hanes (*J.*, 1894, **65**, 834). The specimens had identical spectra with maxima at 5100 (log ε 4·31) and 4440 Å (log ε 4·10), and points of inflexion at 3200 (log ε 3·91) and 2720 Å (log ε 4·16).

The supposed red "isomer" of 1 : 1'-azoxynaphthalene was also prepared according to Cumming and Steel (*loc. cit.*) by allowing its solution in chloroform to evaporate in sunlight. The red solid obtained had m. p. 127°, not depressed by admixture with yellow 1 : 1'-azoxynaphthalene. Chromatography on alumina gave unchanged azoxynaphthalene and 2-hydroxy-1 : 1'-azonaphthalene.

(b) 2 : 2'-*Azoxynaphthalene.* A chloroform solution of 2 : 2'-azoxynaphthalene (m. p. 166°) was irradiated by sunlight for 1 month. After removal of the chloroform the product was chromatographed in benzene on alumina. Unchanged 2 : 2'-azoxynaphthalene was isolated, together with 1-*hydroxy*-2 : 2'-*azonaphthalene*, red-brown needles, m. p. 168° (from ethanol) (Found: C, 80·6; H, 4·7; N, 9·5. $C_{20}H_{14}ON_2$ requires C, 80·5; H, 4·7; N, 9·4%). The m. p. was not depressed by admixture with a specimen prepared as described below, and the specimens had identical spectra with maxima at 5080 (log ε 4·32), 3520 (log ε 4·14), and 2980 Å (log ε 4·36).

The supposed red "isomer" of 2 : 2'-azoxynaphthalene was also prepared as described by Cumming and Ferrier (*loc. cit.*) by exposing a saturated ethanolic solution to sunlight. The red crystals obtained had m. p. 164°, and when mixed with the original material had m. p. 165°. Chromatography of a benzene solution of the red "isomer" gave unchanged 2 : 2'-azoxynaphthalene and 1-hydroxy-2 - 2'-azonaphthalene.

(c) β-1-*Phenylazoxynaphthalene.* A benzene solution was exposed to sunlight for 1 month and then chromatographed on alumina. Elution of the red band and recrystallisation of the product from ethanol gave 2-hydroxy-1-phenylazonaphthalene as red needles, m. p. 133—134° alone or admixed with an authentic specimen prepared according to Liebermann (*Ber.*, 1883, **16**, 2858). The specimens had identical spectra with maxima at 4780 (log ε 4·17), 3120 (log ε 3·86), and 2300 Å (log ε 4·56), and points of inflexion at 2600 (log ε 4·02) and 4200 Å (log ε 4·01).

(d) α-2-*Phenylazoxynaphthalene.* This was irradiated in benzene solution for 1 month and then chromatographed. Elution of the red band and recrystallisation from ethanol gave 1-hydroxy-2-phenylazonaphthalene as red needles, m. p. 137° alone or mixed with a specimen prepared according to Zincke and Bindewald (*Ber.*, 1884, **17**, 3026). The specimens had identical spectra with maxima at 4900 (log ε 4·12), 3560 (log ε 3·92), and 2940 Å (log ε 4·12).

(e) β-2-*Phenylazoxynaphthalene.* Irradiation and chromatography, as for the isomer, gave 2-*o*-hydroxyphenylazonaphthalene as orange needles, m. p. 125° (from ethanol) alone or

mixed with a specimen prepared as described below. The specimens had identical spectra with maxima at 3940 (log ε 4·21), 3330 (log ε 4·36), and 2940 Å (log ε 4·12), and a point of inflexion at 2840 Å (log ε 4·06).

(f) α-4-*Bromoazoxybenzene*. An ethanolic solution was exposed to sunlight for 1 month. After removal of the ethanol the product was dissolved in equal quantities of benzene and light petroleum (b. p. 40—100°), and the solution chromatographed. 4-*Bromo*-2-*hydroxyazobenzene* separated from ethanol as red needles, m. p. 136—137° (Found: C, 51·95; H, 3·4; N, 10·1. $C_{12}H_9ON_2Br$ requires C, 52·0; H, 3·3; N, 10·1%). It was identified by comparison of its methyl ether with an authentic specimen prepared as below.

(g) β-4-*Bromoazoxybenzene*. The isomerisation and purification were carried out as for the α-compound. 4-Bromo-2′-hydroxyazobenzene separated from ethanol as orange-yellow needles, m. p. 133° alone or mixed with an authentic specimen prepared as described below. The specimens also had identical spectra with maxima at 3800 (log ε 4·06), 3320 (log ε 4·32), and 2440 Å (log ε 4·00).

Preparations.—1-*Hydroxy*-2 : 2′-*azonaphthalene*. A solution of 2-naphthylhydrazine hydrochloride (2 g.) in glacial acetic acid (100 c.c.) was added to one of naphtha-1 : 2-quinone (1·6 g.) in glacial acetic acid (100 c.c.), and the mixture kept at room temperature for 2 days. Water was added and the precipitated solid was collected, dried, and extracted with benzene. Chromatography on alumina gave a bright red band and a considerable quantity of strongly adsorbed tarry material. Elution of the red band gave 1-hydroxy-2 : 2′-azonaphthalene (0·2 g.) identical with the specimen described above.

2-o-*Hydroxyphenylazonaphthalene*. *o*-Nitroanisole (50 g.) and 2-naphthylamine (100 g.) were heated to 170—180°, and powdered sodium hydroxide (36 g.) added during 30 min. The reaction was strongly exothermic and cooling at times was necessary. After a further 30 minutes' stirring the mixture was cooled and the product washed with 6N-hydrochloric acid, dried, and then extracted with equal quantities of benzene and light petroleum (b. p. 40—100°). The resulting solution was chromatographed on alumina. The most weakly adsorbed band was eluted, the solvent evaporated, and the product recrystallised from ethanol. 2-o-*Methoxyphenylazonaphthalene* was obtained as orange needles (10 g.), m. p. 92·5° (Found: C, 77·9; H, 5·4; N, 10·9. $C_{17}H_{14}ON_2$ requires C, 77·9; H, 5·4; N, 10·7%). Demethylation was effected by an equal weight of aluminium chloride in boiling benzene, for 7 min. After decomposition with water and purification by chromatography and recrystallisation, 2-o-*hydroxyphenylazonaphthalene* was obtained as orange needles, m. p. 125° (Found: C, 77·5; H, 4·9; N, 11·25. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·9; N, 11·3%).

4-*Bromo*-2-*methoxyazobenzene*. 4-Amino-2-methoxyazobenzene (10 g.; Earl and Robson, *J. Proc. Austral. Chem. Inst.*, 1939, **6**, 268) was stirred into hydrobromic acid (*d* 1·46; 25 c.c.) and water (200 c.c.). After cooling to 5°, sodium nitrite (3·5 g.) in a little water was added gradually with stirring. After a further 15 minutes' stirring the solution was added slowly at 60° to one of cuprous bromide [prepared by refluxing copper sulphate (6 g.), copper turnings (10 g.), potassium bromide (18 g.), concentrated sulphuric acid (5 g.), and water (40 c.c.)]. The brown solid which was precipitated was purified by chromatography and recrystallisation from ethanol. 4-*Bromo*-2-*methoxyazobenzene* (3 g.) was obtained as orange needles, m. p. 76·5° (Found: C, 53·9; H, 3·9; N, 9·8. $C_{13}H_{11}ON_2Br$ requires C, 53·6; H, 3·8; N, 9·6%). The m. p. was not depressed by admixture with a specimen prepared by methylation of the above 4-bromo-2-hydroxyazobenzene with methyl sulphate. The specimens had identical spectra with maxima at 4360 (log ε 3·18), 3560 (log ε 4·11), and 3200 Å (log ε 4·07).

4-*Bromo*-2′-*hydroxyazobenzene*. *o*-Nitroanisole (30 g.) and *p*-bromoaniline (60 g.) were heated to 170—180° and powdered sodium hydroxide (22 g.) added with stirring during 30 min. Stirring was continued for a further 30 min. at the same temperature, with cooling when necessary. The cold solid was washed with 6N-hydrochloric acid, dried, dissolved in a mixture of equal parts of benzene and light petroleum (b. p. 40—100°), and chromatographed. The least adsorbed band was eluted and the solvent evaporated. 4-*Bromo*-2′-*methoxyazobenzene* (30 g.) separated from ethanol as orange needles, m. p. 83° (Found: C, 53·8; H, 3·8; N, 9·6%). It was demethylated as above to 4-*bromo*-2′-*hydroxyazobenzene*, orange-yellow needles, m. p. 133° (Found: C, 52·25; H, 3·4; N, 9·8. $C_{12}H_9ON_2Br$ requires C, 52·0; H, 3·3; N, 10·1%), identical with the specimen described above.

Microanalyses were carried out at the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, February 15th*, 1954.]