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

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A number of azoxy-derivatives have been isomerised to o-hydroxyazoderivatives 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 azoxycompounds (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(\rightarrow 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(\rightarrow O):N·C₁₀H₇, gave 1-hydroxy-2phenylazonaphthalene on exposure to light; the β -isomer, Ph·N:N(\rightarrow O)·C₁₀H₇, was partly converted into 2-o-hydroxyphenylazonaphthalene. Similarly, β -1-phenylazoxynaphthalene gave 2-hydroxy-1-phenylazonaphthalene. Again, α -4-bromoazoxybenzene, Ph·N(\rightarrow O):N·C₆H₄Br, 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).



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) \longrightarrow (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-Bromoazozybenzene. 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. C₁₂H₉ON₂Br 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.

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