CCCCXLI.—*Reactions of Some Azoxy- and Azo-compounds with Benzyl Alcohol, Benzaldehyde, and Quinoline.*

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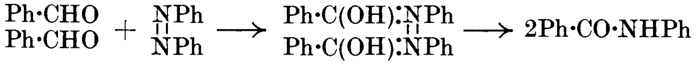
CUMMING and FERRIER (J., 1925, **127**, 2374) have shown that azoxy-compounds under the influence of light are converted into the corresponding *o*-hydroxyazo-compounds, *via as.*-azoxy-compounds (Cumming and Steel, J., 1923, **123**, 2464). It seems reasonable, therefore, that this labile oxygen atom should be capable of oxidising certain organic compounds, with probable formation of azo-compounds. Suter and Dains (*J. Amer. Chem. Soc.*, 1928, **50**, 2733) have found that the replacement of methyl and ethyl alcoholates by benzyl alcoholate in the reduction of nitro- to azoxy-compounds resulted in greatly improved yields, theoretical in some cases. While neither benzyl alcohol nor benzaldehyde reacted with nitro-compounds, we found that the former reduced azoxy- to azo-benzene, and the latter gave rise to a remarkable reaction in which 10% of the azoxy-compound was converted into benzanilide. Azobenzene was almost quantitatively converted into the latter by benzaldehyde.

In seeking a possible explanation of this reaction we have proved that benzoin is not a factor in the reduction, since no trace of benzoin, benzil, or an anil of either was isolated. Nevertheless, we found that benzoin readily reduced azobenzene to aniline when both were fused together or refluxed in benzyl alcohol solution. Benzaldehyde, however, might combine with azobenzene, forming an unstable intermediate additive product yielding benzanilide :



$$\begin{array}{l}\text{Ph·CHO}\\\text{Ph·CHO}\end{array}+\begin{array}{l}\text{NPh}\\\|\\\text{NPh}\end{array}\longrightarrow\begin{array}{l}\text{Ph·C(OH):NPh}\\\qquad\qquad\quad\|\\\text{Ph·C(OH):NPh}\end{array}\longrightarrow 2\text{Ph·CO·NHPh}$$

Similarly, benzyl alcohol reduced *p*-azoxytoluene to *p*-azotoluene, while benzaldehyde partially converted it into azotoluene. With benzaldehyde and *p*-azotoluene, the only compound isolated was benzo-*p*-toluidide.

From *s*.-1 : 1′-azoxynaphthalene, no reduction product was obtained with either benzyl alcohol or benzaldehyde, but the yellow symmetrical form was quantitatively converted into the red unsymmetrical form (compare Cumming and Steel, *loc. cit.*). 1 : 1′- and 2 : 2′-Azonaphthalenes did not react with benzaldehyde.

The addition of a base which would inhibit the formation of perbenzoic acid, and so prevent reoxidation of any azonaphthalene—quinoline was used, as the b. p. of pyridine prevented its use in the reaction—resulted in the formation of 2-*hydroxy*-1 : 1′-*azonaphthalene*, m. p. 230°, as well as *as*.-1 : 1′-azoxynaphthalene. The constitution of the hydroxyazonaphthalene was established by its identity with 2-hydroxy-1 : 1′-azonaphthalene obtained by coupling 1-naphthylamine to 2-naphthol (Meldola and Hanes, J., 1894, **65**, 837). Cumming and Steel (J., 1925, **127**, 2374) record the formation of a hydroxyazo-compound, m. p. 224°, by exposure of 1 : 1′-azoxynaphthalene to light. Recrystallisation of their specimen gave m. p. 230°. A mixed m. p. with that obtained above gave no depression. As expected, light converted *as*.-1 : 1′-azoxynaphthalene into 2-hydroxy-1 : 1′-azonaphthalene, continued exposure effecting no further change. The hydroxyazonaphthalene obtained by the action of light on 1 : 1′-azoxynaphthalene is therefore 2-hydroxy-1 : 1′-azonaphthalene, and not the 4-hydroxyazo-compound as suggested by Baudisch and Fürst (*Ber.*, 1912, **45**, 3426). The above experiments repeated in the dark gave the same results and hence the conversion into *as*.-azoxynaphthalene and into the hydroxyazo-compound was not due to light.

The addition of quinoline to the reaction mixtures of benzaldehyde and azoxy- and azo-benzenes completely inhibited the reaction. This is noteworthy in view of the work of Fry and Bowman (*J. Amer. Chem. Soc.*, 1930, **52**, 1531), who found that the addition of quinoline caused reduction of azoxy- to azo-benzene by sodium methoxide, a reduction which did not take place in absence of the organic base.

An interesting basic condensation product of quinoline and benzaldehyde has been isolated, which is being further investigated.

EXPERIMENTAL.

Benzyl Alcohol and Azoxybenzene.—5 G. of azoxybenzene were vigorously refluxed with 100 c.c. of freshly distilled benzyl alcohol for 8 hours, in presence of carbon dioxide to prevent oxidation. The pale yellow solution slowly turned bright red and was then steam-distilled until no more red oily drops passed over. The oil was repeatedly extracted with hot water until the residue solidified on cooling. This, recrystallised from light petroleum, gave 0·5 g. of azobenzene, m. p. 68°. Similar treatment of the residue after steam distillation gave unchanged azoxybenzene.

Benzyl Alcohol and p-*Azoxytoluene.*—0·4 G. of *p*-azoxytoluene and 7 c.c. of benzyl alcohol were refluxed and treated as above. The residue after steam distillation was extracted with light petroleum, which was removed after heating with decolorising carbon. The residue, recrystallised several times from glacial acetic acid, gave about 0·1 g. of *p*-azotoluene, m. p. 141—142°. A mixed m. p. with authentic *p*-azotoluene showed no depression.

Benzaldehyde and Azoxybenzene.—10 G. of azoxybenzene and 100 c.c. of benzaldehyde, previously purified by being shaken with sodium carbonate solution, dried over solid sodium hydroxide and calcium chloride, and distilled in a current of carbon dioxide, were refluxed for 12 hours in presence of carbon dioxide. The reddish residue from the steam distillation, recrystallised from carbon tetrachloride, gave 1 g. of benzanilide in colourless plates, m. p. 162°. The filtrate from the recrystallisation gave, on evaporation to dryness and recrystallisation from alcohol, azoxybenzene, m. p. 36°. The benzanilide was identified by (1) mixed m. p. with authentic benzanilide showing no depression; (2) hydrolysis with 50% sulphuric acid giving benzoic acid, m. p. 122°; (3) bromination, giving *p*-bromobenzanilide, m. p. 202°.

Benzaldehyde and p-*Azoxytoluene.*—2 G. of *p*-azoxytoluene were refluxed as above with 20 c.c. of purified benzaldehyde for 10 hours. The residue after steam distillation, recrystallised several times from glacial acetic acid with addition of decolorising carbon, gave a small quantity of *p*-azotoluene, m. p. 140—141°.

Benzaldehyde and Azobenzene.—5 G. of azobenzene and 100 c.c. of benzaldehyde were refluxed as above for 8 hours. The dark brown residue from the steam distillation, recrystallised from carbon tetrachloride, again gave benzanilide. The yield of the crude benzanilide was almost quantitative, and no other product was isolated.

Benzaldehyde and p-*Azotoluene.*—1 G. of *p*-azotoluene and 10 c.c. of benzaldehyde were refluxed as before for 8 hours. After steam distillation, the residue was extracted with benzene, and the extract refluxed with decolorising carbon to remove the large amount of decomposition matter present. The crystals obtained on concentration of the benzene solution, recrystallised several times from alcohol, gave benzo-*p*-toluidide, m. p. 155—156° (alone or mixed with authentic benzo-*p*-toluidide).

Benzaldehyde and Quinoline.—53 G. of quinoline and 100 c.c. of purified benzaldehyde were refluxed for 6 hours. Much water was given off at first. The residue after steam distillation was cooled in a freezing mixture, pressed on porous tile until dry, and recrystallised from acetone, carbon tetrachloride, or light petroleum, colourless needles, m. p. 99—100°, being obtained. Solutions of this base turned bright pink on exposure to air. Dry hydrogen chloride passed through a solution of the base in chloroform gave the anhydrous hydrochloride in lemon-yellow needles, m. p. 221—221·5°. It may be crystallised from dry acetone. Treatment of the base with dilute hydrochloric acid gave a hydrated form; from concentrated hydrochloric acid it crystallised in lemon needles, m. p. 106—107°. It is sparingly soluble in most common organic solvents, but extremely soluble in alcohol; it is dissociated in water; recrystallised from acetone, it loses water, giving the anhydrous hydrochloride. On being heated, it loses water at about 110° and melts, then solidifies to a lemon-yellow mass without decomposition, and finally melts at about 220° to a dark orange-coloured liquid.

Benzyl Alcohol and 1 : 1′-*Azoxynaphthalene.*—A solution of 5 g. of yellow *s*.-azoxynaphthalene in 70 c.c. of benzyl alcohol was employed and the following results were noted: (*a*) when the solution was maintained for several hours at 100°, no colour change took place; (*b*) at 140° the colour slowly deepened to an intense red (6 hours); (*c*) at 170° the colour change was complete in 4 hours. The red solution, on concentration under reduced pressure, yielded a deep red solid which, slowly crystallised from alcohol, formed bright scarlet crystals, m. p. 127°, having the properties of *as*.-1 : 1′-azoxynaphthalene. Concentration of the red solution under ordinary pressure or steam distillation caused tarring.

Benzaldehyde and 1 : 1′-*Azoxynaphthalene.*—1·5 G. of yellow *s*.-azoxynaphthalene were refluxed with 40 c.c. of benzaldehyde for 1½ hours as before, the colour rapidly turning deep red. Treatment as above again gave *as*.-azoxynaphthalene.

Benzaldehyde, Quinoline, and 1 : 1′-*Azoxynaphthalene.*—2 G. of yellow *s*.-azoxynaphthalene, 60 c.c. of benzaldehyde, and 30 c.c. of quinoline were heated for 12 hours at 170° as above. The concentration product, washed with ether and recrystallised twice from benzene, gave greenish-brown prismatic needles, m. p. 230°, of 2-*hydroxy*-1 : 1′-*azonaphthalene* (yield, 33%) (Found: N, 9·3. $C_{20}H_{14}ON_2$ requires N, 9·4%). The filtrate from the hydroxyazonaphthalene, extracted with sodium hydroxide and hydrochloric acid, yielded a gummy mass which could not be crystallised but appeared to contain *as.*-azoxynaphthalene. The hydroxyazonaphthalene is insoluble in dilute sodium hydroxide solution, but slightly soluble in alcohol; it gives with concentrated sulphuric acid a blue colour, turning red on dilution. On addition of concentrated hydrochloric acid, an alcoholic solution, which is of an intense red colour, passes through a reddish-violet stage and finally becomes colourless. The original red colour is restored on neutralisation by sodium hydroxide.

Quinoline and 1 : 1′-*Azoxynaphthalene.*—2 G. of yellow *s.*-azoxynaphthalene heated (12 hours) as above with 20 c.c. of benzaldehyde at 170°, and subsequent treatment as before, yielded both *as.*-azoxynaphthalene and 2-hydroxy-1 : 1′-azonaphthalene. The yield of the latter was greater when benzaldehyde was present.

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