III.—*Azo-derivatives of 4:6-Dimethylcoumarin.*

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IN a recent communication by one of the authors, it has been shown that the benzeneazocoumarin described by Borsche (*Ber.*, 1904, **37**, 346, 4116), when dissolved in aqueous alkali with formation of the coumarinate, is precipitated from solution either by excess of hydrochloric acid or by carbon dioxide in the form of the azocoumarin, and not as an azocoumarinic acid (Mitchell, *Trans.*, 1905, **87**, 1229). Such behaviour is more in accord with the hydroxyazo- than with the quinonehydrazone-structure of this and analogous compounds, and is not surprising, seeing that parahydroxyazo-compounds of the benzene series behave in practically all respects as if they possessed a hydroxyazo-structure, and are almost universally regarded as having this configuration.

In the case of orthohydroxyazo-compounds, the facts are by no means as clear, for whilst alkylation both in the ortho- and para-series leads to oxygen ethers, some difference of view has been expressed as to the constitution of the substances formed by acylating orthohydroxyazo-compounds. The formation of acetanilide by the reduction of benzene-azo-*p*-tolyl acetate and of Meldola and East's benzeneazo- β -naphthyl acetate observed by Goldschmidt and Brubacher (*Ber.*, 1891, **24**, 2300) certainly appears to favour a quinonehydrazone constitution for these substances, whilst the reduction of *p*-tolueneazo- β -naphthyl acetate studied by Meldola and Hawkins (*Trans.*, 1893, **63**, 926) led to a result which also points to a hydrazone formula, aceto-*p*-toluidide being obtained as a chief product.

Other objections to a hydroxyazo-formulation of these compounds may be seen in the insolubility of many *o*-hydroxyazo-compounds in aqueous alkalis (compare Meldola, *Phil. Mag.*, 1888, [v], 26, 403; Meldola and Forster, *Trans.*, 1891, 59, 710; and Meldola and Hawkins, *Trans.*, 1893, 63, 923, concerning the possibility of the oxygen atom becoming a member of a closed chain) and in the fact that ortho-hydroxyazo-compounds do not appreciably associate in non-hydroxylic solvents (Auwers and Orton, *Zeit. physikal. Chem.*, 1896, 21, 337).

Too much weight must not be placed on the above arguments; that reduction of an acyl derivative of an azophenol should give rise to fission products in which the acyl group is attached to nitrogen is not altogether unexpected, as not merely might intramolecular change take place during the process of reduction, but also intermolecular change between the products of complete fission, the reaction

being of very general occurrence.

Auwers and Orton's conclusions as to parahydroxyazo-compounds possessing a structure corresponding to their name, whilst the ortho-compounds are of quinonehydrazone type, are not justified by their own results. They find that ortho-substituted phenols generally show less association in non-hydroxylic solvents than the corresponding meta- or para-compounds, so that the complete inhibition of association by the somewhat negative and large arylazo-group when in an ortho-position with respect to a phenolic hydroxyl is not unlikely.

Moreover, it must be remembered that benzeneazo-*p*-cresol, when treated with bromine in acetic acid suspension, sodium acetate being present, gives benzeneazobromo-*p*-cresol in nearly quantitative yield, a fact strongly in favour of the hydroxyazo-formulation of the compound (Hewitt and Phillips, *Trans.*, 1901, 79, 160).

EXPERIMENTAL.

Some months ago an attempt was made to nitrate benzeneazo-*p*-cresol with warm dilute nitric acid in the hope of confirming Hewitt and Phillips' bromination results. So far the results have been disappointing, and we have now turned our attention to the behaviour of azocoumarins containing the azo-group in the ortho-position with respect to the oxygen atom of the lactonic ring. To obtain substances of this type, it was necessary to use a coumarin in which the para-position to the oxygen atom was already substituted. We hence chose the 4:6-dimethylcoumarin described by von Pechmann and Cohen (*Ber.*, 1884, 17, 2188), as it is readily prepared by the condensation of *p*-cresol with ethyl acetoacetate.

Benzeneazo-4:6-dimethylcoumarin,

Dimethylcoumarin (1.7 grams) was boiled with fairly concentrated potassium hydroxide until completely dissolved, when water and ice were added in considerable quantities. To this solution of potassium dimethylcoumarinate a phenyldiazonium chloride solution, prepared from 0.93 gram of aniline, 0.72 gram of sodium nitrite, 3 c.c. of fuming hydrochloric acid, and sufficient ice, was added. By acidification of the intensely red solution of the alkaline salt of benzeneazodimethylcoumarinic acid, a yellow precipitate is deposited consisting not of the acid, but of the corresponding lactone. By twice crystallising from alcohol, the substance is obtained in lustrous, orange-red needles which melt at 199—200°.

0.1169 gave 0.3162 CO₂ and 0.0583 H₂O. C = 73.7; H = 5.5.

C₁₇H₁₄O₂N₂ requires C = 73.4; H = 5.0 per cent.

Benzeneazodimethylcoumarin dissolves in alcohol, toluene, chloroform, and pyridine; it is insoluble in light petroleum. Like the nitro-derivatives about to be described, it resembles the acyl derivatives rather than the azophenols themselves.

Although insoluble in cold alkaline solutions, prolonged boiling brings about solution with formation of an azocoumarinate and development of an intense coloration.

o-Nitrobenzeneazo-4:6-dimethylcoumarin, NO₂·C₆H₄·N:N·C₁₁H₉O₂.

This substance was prepared in the usual manner. The colour of the solution of its alkaline azocoumarinate is reddish-violet. The free azocoumarin separates from chloroform as scarlet needles which melt at 250° with decomposition. The substance is also soluble in pyridine, but dissolves sparingly in alcohol.

0.1082 gave 0.2507 CO₂ and 0.0404 H₂O. C = 63.2; H = 4.1.

0.1465 „, 16.4 c.c. nitrogen at 13° and 748 mm. N = 13.0.

C₁₇H₁₃O₄N₃ requires C = 63.2; H = 4.0; N = 13.0 per cent.

m-Nitrobenzeneazo-4:6-dimethylcoumarin, prepared in the usual manner, separates from chloroform in large, transparent, reddish-

brown tablets. These soon become opaque owing to the volatilisation of one molecule of chloroform of crystallisation.

3.3354 lost 0.8919 at 120°. Loss = 26.75 per cent.

$C_{17}H_{13}O_4N_3 \cdot CHCl_3$ requires $CHCl_3$ = 27.05 per cent.

The dried substance melted at 212° and gave the following figures on analysis :

0.1612 gave 18.2 c.c. nitrogen at 12° and 760 mm. N = 13.4.

0.2482 „ 28.1 c.c. „ 12° „ 733 mm. N = 13.0.

$C_{17}H_{13}O_4N_3$ requires N = 13.0 per cent.

m-Nitrobenzeneazo-4:6-dimethylcoumarin is also soluble in acetic acid, somewhat sparingly so in alcohol. The solutions of the alkaline coumarinates are red in colour.

p-Nitrobenzeneazo-4:6-dimethylcoumarin was obtained by coupling potassium dimethylcoumarinate with *p*-nitrophenyldiazonium chloride ; its alkaline solution is intensely violet, the colour being far bluer in shade than is the case with the two isomerides. After the precipitated azocoumarin had been twice recrystallised from dilute acetic acid and once from chloroform, it was obtained as small, brown crystals melting at 229°.

0.1018 gave 11.4 c.c. nitrogen at 15° and 755 mm. N = 13.0.

$C_{17}H_{13}O_4N_3$ requires N = 13.0 per cent.

p-Nitrobenzeneazodimethylcoumarin also dissolves in pyridine ; it is sparingly soluble in benzene and insoluble in light petroleum.

The immediate production of lactones on acidification indicates the presence of ready-formed hydroxyl groups, and attention may again be drawn to the fact that the passage of carbon dioxide into a solution of benzeneazocoumarin in alkali leads to the precipitation of benzeneazocoumarin (Mitchell, Trans., 1905, 87, 1230). If we assume the equation

to be correct, we must express the first stage of the action of carbonic acid on the dipotassium salt of benzeneazocoumarinic acid by the equation

The last formula indicates the sodium salt of a fairly strong carboxylic acid from which the weak carbonic acid would only liberate very small quantities of the corresponding free acid. The formation of benzeneazocoumarin would then have to be represented by the following equations :

Since the product on the right-hand side of equation (a) can only be present in very small quantity, the equilibrium expressed in equation (b) must be established with enormous rapidity in order to explain anything more than the very slow formation of a lactone. Such an extremely rapid establishment of equilibrium, even if not definitely disproved, is at least improbable.

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