XVII.—*The Bromination of o-Oxyazo-compounds and its bearing on their Constitution.*

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THE constitution of the *o*-oxyazo-compounds has for some years been a matter of considerable discussion. These, as well as the *p*-derivatives, were at the time of their discovery looked upon as hydroxylic compounds, this view being first of all disputed by Liebermann (*Ber.*, 1883, 16, 2929). Zincke and Bindewald's discovery that phenylhydrazine reacts with α -naphthaquinone with production of benzeneazo- α -naphthol (*Ber.*, 1884, 17, 3026), whilst with β -naphthaquinone a substance strongly resembling, although not identical with, benzeneazo- β -naphthol is obtained (*loc. cit.* 3029), led the two latter chemists to look upon *p*-oxyazo-compounds as true azophenols, but upon the *o*-oxyazo-compounds, however, as hydrazones. The possibility then arose that all the substances hitherto regarded as hydroxyl derivatives of azo-compounds might perhaps be hydrazones of quinones.

Many attempts have been made to settle this question. Reduction of alkyl and acyl derivatives has led to somewhat conflicting statements, although, speaking generally, the alkyl derivatives may be regarded as of the true azo-type, that is, they are oxygen ethers both in the ortho- and the para-series (Compare Meldola and Morgan, *Trans.*, 1889, 55, 608, 609; Witt and Schmidt, *Ber.*, 1892, 25, 1013; Jacobson, *Annalen*, 1895, 287, 97, &c.).

Experiments with acyl derivatives have not given such definite results, for whilst in certain cases the scission of these derivatives seems to have been complete and primary amines obtained, from which the conclusion might be drawn that acylation had not taken place with respect to the nitrogen atom, in others acylated amines and aminophenols have been isolated as sole products of the reduction; for example, the acetyl derivative of benzeneazo-*p*-cresol yields only acetanilide and amino-*p*-cresol (Goldschmidt and Brubacher, *Ber.*, 1891, 24, 2301; compare Meldola, *Phil. Mag.*, 1888, 26, 403; Meldola and Morgan, *Trans.*, 1889, 55, 114; Meldola and Forster, *Trans.*, 1891, 59, 710; Meldola, Hawkins, and Burls, *Trans.*, 1893, 63, 923; Meldola and Hanes, *Trans.*, 1894, 65, 834). Goldschmidt was indeed inclined to regard the oxyazo-compounds as in all cases quinonehydrazones acylating with respect to a nitrogen atom. The incorrectness of this view was proved by McPherson, who found that *as*-benzoylphenylhydrazine condenses with benzoquinone to form an isomeride of the benzoyl derivative of benzeneazophenol (*Ber.*, 1895, 28, 2414; *Amer. Chem. J.*, 1899, 22, 364). Since McPherson's

compound must be acylated with regard to nitrogen, the substance obtained by the benzylation of benzeneazophenol must have the constitution

The balance of evidence would seem to be in favour of the acyl as well as the alkyl derivatives being oxygen ethers. Quite recently, however, Möhlau has shown that benzeneazotetramethyldiaminobenzhydryl- α -naphthol,

reacts towards acetic anhydride as if it were a quinonehydrazone of the constitution

its acetyl derivative giving a practically quantitative yield of acetanilide on reduction (*Ber.*, 1900, 33, 2858). From this fact and the further observation that other *p*-oxyazo-compounds react readily with tetramethyldiaminobenzhydryl, Möhlau draws the conclusion that the *p*-derivatives must be represented as quinonehydrazones.

In so many instances do compounds undergo change in constitution on alkylation or acylation, that any conclusions drawn from the structure of derivatives must of necessity be doubtful; oxyazo-compounds so easily unite with acids to form additive products of the quinonehydrazone type that the production of a nitrogen ether from an oxyazo-compound might easily take place according to the scheme:

On the contrary, the acylation of a quinonehydrazone with regard to oxygen would not be surprising,

in fact, it would closely correspond to the conversion of a quinonehydrazone salt into the azophenol through the intermediate stage of the "pseudohydrate" (to use Hantzsch's nomenclature), which in the case of *p*-ethoxybenzeneazophenol, for instance, can be represented in the following manner (compare Auwers, *Ber.*, 1900, 33, 1302):

It might be expected that physical measurements would give the

most trustworthy results in a case of this sort, and Auwers and Orton's method (*Zeit. physikal. Chem.*, 1896, 21, 355) of determining the molecular weight in non-hydroxylic solvents seemed to give a definite solution to the problem of the constitution of the oxyazo-compounds. Broadly speaking, hydroxylic compounds exhibit association in solutions in benzene and naphthalene, hydrazones, on the contrary, do not; and corresponding to this difference of behaviour, the *p*-oxyazo-compounds give abnormal, whilst the *o*-oxyazo-compounds give normal, values when their molecular weights are determined. The conclusion that the ortho-compounds are quinonehydrazones and the para-compounds true azophenols agrees well with the insolubility of the former and the ready solubility of the latter in cold dilute alkalis.

To obtain chemical evidence in favour of this view, both Auwers and Hewitt (Auwers, *Ber.*, 1900, 33, 1302; Hewitt, *Trans.*, 1900, 77, 99; Hewitt and Aston, *ibid.*, 712, 810; Hewitt and Fox, this vol., 49; Hewitt and Lindfield, *ibid.*, 155) have instituted experiments on the behaviour of oxyazo-compounds with bromine and dilute nitric acid, the conditions chosen being such as to preclude salt formation. In the case of the *p*-oxyazo-compounds, the results obtained were such as were to be expected for true hydroxyl derivatives, and it may be pointed out that in such substitution experiments the group to be detected is not directly attacked but only used to influence the course of substitution; a hydroxyl derivative of azobenzene should be substituted in the phenol nucleus, a quinonephenylhydrazone, on the other hand, in the benzene nucleus of the phenylhydrazine residue.

The results obtained for the *p*-oxyazo-compounds have been fully in accordance with Auwers' view that these substances are true hydroxylic compounds in the free state, and it seemed to be an interesting problem to continue the study of the substitution of oxyazo-compounds in the ortho-series. Using benzeneazo-*p*-cresol as material, it was confidently expected that either the *p*- or the *o*-bromobenzeneazo-*p*-cresol would be obtained on brominating in glacial acetic acid solution in the presence of sodium acetate. On carrying out an experiment it was found that a monobromo-derivative was indeed produced, which, however, on comparison, immediately proved not to be *p*-bromobenzeneazo-*p*-cresol; on synthesising the corresponding *o*-bromobenzeneazo-*p*-cresol, a substance was obtained which differed from the direct bromination product of the azocresol in no very marked degree with regard to melting point. As the purity of any *o*-bromobenzeneazo-compound must depend on the purity of the *o*-bromoaniline diazotised, considerable care must be exercised in the purification of this base. A pure sample of *o*-bromoaniline having been obtained by a process which will be subsequently described, it was diazotised and coupled with alkaline *p*-cresol. A beautiful azo-com-

pound was obtained which in appearance showed a close resemblance to the product of the bromination of benzeneazo-*p*-cresol, but whereas the latter melts at 123°, *o*-bromobenzeneazo-*p*-cresol melts constantly at 116°, and a mixture of the two substances indefinitely at about 90°. Finally, benzeneazobromo-*p*-cresol of the constitution

was prepared by the coupling of diazotised aniline with *o*-bromo-*p*-cresol and found to be identical with the product we had obtained by the action of bromine on the oxyazo-compound.

Hence benzeneazo-*p*-cresol brominates as if it were a true hydroxylic compound, a result which is at variance with the physical results of Auwers and scarcely agrees with the insolubility of the *o*-oxyazo-compounds in alkalis.

Of such behaviour only three explanations seem possible:

1. That the *o*-oxyazo-compounds are true hydroxylic derivatives.
2. That the *o*-oxyazo-compounds behave in solution in hydrocarbon solvents as quinonehydrazones, but in acetic acid solution on the contrary are hydroxyl derivatives of azo-compounds.
3. That in solution the two forms are in equilibrium, but the oxyazo-form is so much more reactive than the quinonehydrazone that only the derivatives of the first form are obtained in appreciable yield.

EXPERIMENTAL.

Bromination of Benzeneazo-p-cresol.

5·3 grams of benzeneazo-*p*-cresol and 5 grams of fused sodium acetate are dissolved in 150 c.c. of glacial acetic acid, and 4 grams of bromine dissolved in 5 c.c. of glacial acetic acid are added gradually from a dropping funnel, the temperature being kept below 12°. The brominated compound separates out, being less soluble than the benzeneazocresol. On warming, the substance passed into solution and separated on cooling in long red needles; these were collected, washed, and dried; the corrected melting point is 123°. If the substance is fractionally crystallised, the separations have the same melting point, showing that only one substance results in any appreciable quantity on the bromination of this *o*-oxyazo-compound.

Synthesis from diazotised Aniline and o-Bromo-p-cresol.—12·5 grams of *o*-bromo-*p*-cresol were dissolved in 8 grams of sodium hydroxide and about 100 c.c. of water. 6·2 grams of aniline were dissolved in 14 c.c. of strong hydrochloric acid and about 100 c.c. of water. The latter solution was treated with 4·8 grams of sodium nitrite dissolved in a little water, the solution of the diazonium salt then being added to that of the bromocresol. Coupling took place with considerably greater

readiness than has been noticed in the case of *o*-dibromophenol and *o*-nitrophenol. After being allowed to stand for 2 hours, the precipitated oxyazo-compound was collected, washed, and extracted with alcohol. The alcoholic solution was allowed to slowly evaporate to dryness; a tarry mass, in which groups of crystals were distributed, was thus obtained. On washing this with cold glacial acetic acid, the tar was dissolved, the crystals being to a certain extent undissolved. The crystals were collected and recrystallised from ether; the substance was then found to melt at 121° . By dissolving it in ether with an equal quantity of the substance obtained by the bromination of benzeneazo-*p*-cresol, and allowing the solution to gradually crystallise, brilliant red needles melting sharply at 123° were obtained. Hence there is no doubt that the two substances are identical, and that in the bromination of benzeneazo-*p*-cresol bromine takes up the ortho-position to the hydroxyl group.

Benzeneazo-*o*-bromo-*p*-cresol is very sparingly soluble in dilute alkalis; it is very soluble in ether, benzene, or hot glacial acetic acid, and fairly so in alcohol, acetone, or light petroleum.

0.2078 gave 0.1362 AgBr. Br = 27.9.

$C_{13}H_{11}ON_2Br$ requires Br = 27.5 per cent.

The *acetyl* derivative, obtained by boiling this compound with three times its weight of acetic anhydride for 2 hours, forms brilliant orange-red needles after recrystallisation from alcohol.

0.1572 gave 11.9 c.c. moist nitrogen at 23° and 750 mm. N = 8.6.

$C_{15}H_{13}O_2N_2Br$ requires N = 8.4 per cent.

The substance is very soluble in acetone or benzene, and is taken up fairly readily by alcohol, acetic acid, or light petroleum. It melts at 83° .

The *benzoyl* derivative was prepared by boiling with an excess of benzoyl chloride. After destruction of the excess of the acid chloride with cold spirit, the substance was collected and recrystallised from boiling spirit, from which it separates in small, yellowish-orange needles.

0.1133 gave 6.8 c.c. moist nitrogen at 20° and 766 mm. N = 6.9.

$C_{20}H_{15}O_2N_2Br$ requires N = 7.1 per cent.

This compound, which melts at 110° , is very soluble in acetone or benzene, fairly so in acetic acid or ether, but only sparingly so in alcohol or light petroleum.

o-Bromobenzeneazo-*p*-cresol.

As has been explained in the introductory part of the paper, it was at one time thought that this substance was identical with that obtained by the bromination of benzeneazo-*p*-cresol. The first preparation was made with an ordinary specimen of *o*-bromoaniline, and separated as minute, orange crystals melting at 113°. Since the substance yielded unsatisfactory acetyl and benzoyl derivatives, it was concluded that the *o*-bromoaniline used was contaminated with the para-isomeride, and that the *o*-bromooxyazo-compound was likewise mixed with a small quantity of *p*-bromobenzeneazo-*p*-cresol. This supposition proved to be correct, although even when *o*-bromobenzeneazo-*p*-cresol is obtained in a state of purity it does not melt higher than 116°.

As *o*-bromonitrobenzene is never obtained pure commercially, and as *o*-bromoaniline is usually somewhat impure, the following process, which furnishes a pure base, has been devised. Commercial *o*-nitro-bromobenzene is reduced in the usual way with tin and hydrochloric acid, and the base driven over with steam after the solution has been rendered alkaline. The crude *o*-bromoaniline is collected, and slightly more than a molecular proportion of acetic anhydride added; the mixture becomes warm, and on dilution with water the acetobromo-anilide is precipitated. This is recrystallised from alcohol until it shows a constant melting point (99°); it is then hydrolysed by boiling with aqueous caustic potash, and distilled over in a current of steam. On distillation, the base passes over with a constant boiling point.

If this pure base is dissolved in acid, diazotised, and then coupled with alkaline *p*-cresol, an oxyazo-compound is obtained which crystallises from hot acetic acid in the form of brilliant, dark-red needles melting sharply at 116°. A mixture of this substance with about an equal weight of benzeneazo-*o*-bromo-*p*-cresol melted at about 90°.

0.1606 gave 14 c.c. moist nitrogen at 20° and 762 mm. $N = 9.9$.

$C_{13}H_{11}ON_2Br$ requires $N = 9.6$ per cent.

o-Bromobenzeneazo-*p*-cresol dissolves moderately in ether, benzene, acetone, or acetic acid, but is sparingly soluble in alcohol or light petroleum.

The *acetyl* derivative.—When the pure *o*-bromobenzeneazo-*p*-cresol is boiled with acetic anhydride, a well defined compound is obtained, which crystallises in flat, orange-brown needles and melts sharply at 85°.

0.2959 gave 22.8 c.c. moist nitrogen at 20° and 762 mm. $N = 8.8$.

$C_{15}H_{13}O_2N_2Br$ requires $N = 8.4$ per cent.

This substance is very soluble in acetone, benzene, or ether, but less so in acetic acid, light petroleum, or alcohol.

The *benzoyl* derivative also crystallises well in small orange plates when prepared from the pure oxyazo-compound; its solubilities resemble those of the acetyl derivative. The substance melts at 106.5° .

0.1166 gave 6.6 c.c. moist nitrogen at 12° and 768 mm. $N = 6.75$.

$C_{20}H_{15}O_2N_2Br$ requires $N = 7.1$ per cent.

m-Bromobenzeneazo-p-cresol.

m-Bromobenzeneazo-p-cresol was prepared in the usual manner. It forms small, orange-brown needles which melt at 112° and dissolve readily in acetone or benzene, moderately in acetic acid, ether or light petroleum, and only sparingly in cold alcohol.

0.1482 gave 0.2948 CO_2 and 0.0506 H_2O . $C = 54.25$; $H = 3.8$.

0.1949 „ 0.1248 $AgBr$. $Br = 27.3$.

$C_{13}H_{11}ON_2Br$ requires $C = 53.6$; $H = 3.8$; $Br = 27.5$ per cent.

These compounds usually give very high values for carbon on analysis, no doubt owing to the presence both of halogen and nitrogen.

The *acetyl* derivative forms small, dark reddish-brown crystals melting at $61-62^{\circ}$ which are easily soluble in benzene or ether, and moderately so in other solvents.

0.2085 gave 15.8 c.c. moist nitrogen at 20° and 762 mm. $N = 8.7$.

$C_{15}H_{13}O_2N_2Br$ requires $N = 8.4$ per cent.

The *benzoyl* derivative melts at 94° and forms very small, yellow crystals. It dissolves easily in acetone or benzene, moderately in acetic acid or ether, but only sparingly in alcohol or light petroleum.

0.1220 gave 0.2755 CO_2 and 0.0406 H_2O . $C = 61.5$; $H = 4.0$.

$C_{20}H_{15}O_2N_2Br$ requires $C = 60.6$; $H = 4.0$ per cent.

p-Bromobenzeneazo-p-cresol.

This substance forms small, orange leaflets melting at 147° . It dissolves fairly in most solvents, but only sparingly in light petroleum.

0.1894 gave 16.4 c.c. moist nitrogen at 20° and 766 mm. $N = 9.9$.

$C_{13}H_{11}ON_2Br$ requires $N = 9.6$ per cent.

The *acetyl* derivative forms small, bright orange crystals melting at 123° . It is very soluble in acetone or benzene, and is taken up fairly readily by most other solvents with the exception of light petroleum.

0.2052 gave 15.2 c.c. moist nitrogen at 20° and 762 mm. $N = 8.4$.

$C_{15}H_{13}O_2N_2Br$ requires $N = 8.4$ per cent.

The *benzoyl* derivative melts at 112° and separates from solution in very small crystals.

0.1585 gave 10.0 c.c. moist nitrogen at 23° and 753 mm. $N = 7.2$.

$C_{20}H_{15}O_2N_2Br$ requires $N = 7.1$ per cent.

Its solubilities, although less than, resemble those of the acetyl derivative.

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