

CXVI.—*Action of Bromine on the Three Tolueneazophenols.*

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THE action of substituting agents on oxyazo-compounds has been studied somewhat extensively by one of the authors of this communication and his co-workers. It has been generally found that towards dilute nitric acid and bromine (in presence of sodium acetate) these substances behave as true hydroxyl derivatives of azo-substances and not as the tautomeric quinonehydrazones. Whilst, however, the behaviour towards warm dilute nitric acid has been examined, not only in the case of benzeneazophenol itself (Trans., 1900, 77, 229), but also for three tolueneazophenols (Trans., 1901, 79, 155) and benzeneazosalicylic acid (Trans., 1901, 79, 49), no other *p*-hydroxyazo-compound has been studied with regard to its action on bromine.* It seemed, therefore, of some interest to examine other *p*-hydroxyazo-compounds, and for this purpose, the three tolueneazophenols were chosen, since their nitration had already been studied with the result that *m*-tolueneazophenol had been found to nitrate far less smoothly than its two isomerides, and, moreover, when *m*-tolueneazo-*o*-nitrophenol had been obtained, no means were devised of obtaining its acetyl and benzoyl derivatives, although ethyl might easily be introduced in place of hydrogen. We found, however, that *m*-tolueneazodibromophenol not only furnished an ethyl ether but also was acetylated and benzoylated quite normally.

o-Tolueneazodibromophenol.

Ten grams of *o*-tolueneazophenol and 20 grams of fused sodium acetate were made into a paste with glacial acetic acid. The mixture was cooled to 10° and 16 grams of bromine, diluted with 40 grams of glacial acetic acid, were slowly added. The dibromo-derivative separated in a crystalline condition, and after a further recrystallisation from boiling glacial acetic acid, it formed yellow needles melting at 121° (corr.).

0.1530 gave 0.2351 CO₂ and 0.0391 H₂O. C = 41.90; H = 2.84.

C₁₃H₁₀ON₂Br₂ requires C = 42.16; H = 2.72 per cent.

The substance is very soluble in acetone; fairly so in aniline, benzene, nitrobenzene, ethyl acetate, or ethyl ether; sparingly so in carbon disulphide and chloroform, and nearly insoluble in light petroleum.

* Benzeneazo-*p*-cresol (Hewitt and Phillips, Trans., 1901, 79, 160) belongs of course to the ortho-series.

The two bromine atoms enter the phenol nucleus, since on reduction with tin and hydrochloric acid, *o*-toluidine is obtained. The presence of the latter was rendered certain by making the reduction product alkaline, blowing steam through the liquid, and shaking the distillate with sodium hydroxide and benzoyl chloride. The benzoyl derivative which separated melted at 139° (uncorr.) after recrystallisation from benzene.

Ethyl Ether.—A solution of 0.2 gram of sodium in 10 c.c. of absolute alcohol was heated with 3 grams of the dibromoazophenol and 1.2 grams of ethyl bromide for 4 hours at 140°. The product was isolated in the usual manner and recrystallised from spirit; it melted at 95°.

0.0719 gave 0.0681 AgBr. Br = 40.30.

$C_{15}H_{14}ON_2Br_2$ requires Br = 40.15 per cent.

The substance, which forms orange plates, is very soluble in benzene, carbon disulphide, ether, or ethyl acetate; fairly so in chloroform or light petroleum, and sparingly so in cold alcohol or acetic acid.

Acetyl Derivative.—Prepared by heating with an equal weight of fused sodium acetate and five times the weight of acetic anhydride. Acetylation is complete after one hour at 100°. When recrystallised from glacial acetic acid, the substance forms orange needles melting at 153°.

0.0992 gave 0.0896 AgBr. Br = 38.43.

$C_{15}H_{12}O_2N_2Br_2$ requires Br = 38.79 per cent.

It is very soluble in carbon disulphide or chloroform, fairly so in aniline, nitrobenzene, acetone, ethyl acetate, or ether, sparingly so in benzene, and nearly insoluble in light petroleum, cold alcohol, or cold acetic acid.

Benzoyl Derivative.—Obtained by boiling with three times its weight of benzoyl chloride for 2½ hours in a reflux apparatus. By pouring into excess of cold spirit, the substance is obtained crystalline, and when once recrystallised from boiling spirit, in which it is very sparingly soluble, small, orange prisms, melting at 168.5°, are obtained. It is fairly soluble in benzene, aniline, nitrobenzene, carbon disulphide, or chloroform.

0.1754 gave 0.1399 AgBr. Br = 33.94.

$C_{20}H_{14}O_2N_2Br_2$ requires Br = 33.73 per cent.

m-Tolueneazodibromophenol.

In the preparation of this substance, considerable care is necessary. If *m*-tolueneazophenol is merely ground up with fused sodium acetate and acetic acid and then brominated, the mixture becomes warm, considerable destruction of the azo-compound takes place, and bromine

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derivatives of phenol are formed in considerable quantity. The desired dibromo-derivative may, however, be obtained in nearly quantitative yield, by dissolving 5 grams of *m*-tolueneazophenol in 150 c.c. of glacial acetic acid to which 10 grams of fused sodium acetate have been added. The solution is then carefully cooled to 0° and 8 grams of bromine diluted with 25 grams of glacial acetic acid added drop by drop, the mixture being vigorously stirred, since the bromination product crystallises out nearly completely during the process. Collected and recrystallised from glacial acetic acid, the product is obtained in yellow needles melting at 129°.

0.1417 gave 0.1442 AgBr. Br = 43.00.

$C_{13}H_{10}ON_2Br_2$ requires Br = 43.19 per cent.

The solubilities resemble those of the ortho-compound, but are somewhat greater. The constitution of the substance was determined by reduction; the product, after being rendered alkaline, was distilled with steam, and the *m*-toluidine in the distillate detected by benzoylation. The benzoyl derivative was free from halogen and melted at 119° (121—122° corr.).

The *ethyl ether*, prepared in the usual manner and recrystallised from spirit, forms yellow leaflets melting at 88°. The solubilities of the substance resemble those of the ortho-isomeride.

The *acetyl* derivative, when recrystallised from glacial acetic acid, forms orange needles of considerable brilliancy and melts at 118°.

0.1650 gave 10.3 c.c. moist nitrogen at 23° and 760 mm. N = 7.04.

$C_{15}H_{12}O_2N_2Br_2$ requires N = 6.81 per cent.

It is very soluble in ethyl acetate, benzene, carbon disulphide, or chloroform; fairly so in ether, and nearly insoluble in cold acetic acid.

The *benzoyl* derivative separates from hot spirit, in which it is very sparingly soluble, as very small, pale yellow needles melting at 141°.

0.1865 gave 10.1 c.c. moist nitrogen at 22° and 752 mm. N = 6.17.

$C_{20}H_{14}O_2N_2Br_2$ requires N = 5.90 per cent.

The solubilities of the substance generally resemble those of the isomeric ortho-compound.

p-Tolueneazodibromophenol.

This substance was prepared in exactly the same manner as the corresponding derivative of *o*-tolueneazophenol. When recrystallised from glacial acetic acid, it forms dark yellow, shining needles melting at 137°.

0.1744 gave 11.7 c.c. moist nitrogen at 16° and 748 mm. $N = 7.67$.
 $C_{13}H_{10}O_2N_2Br_2$ requires $N = 7.58$ per cent.

The solubility of the substance in the usual organic solvents is somewhat greater than that of the corresponding *o*-tolueneazodibromophenol. Complete reduction of the compound gave *p*-toluidine as one of the products. After the reduction mixture had been rendered alkaline, steam carried over a volatile base which had a melting point of 45°, and gave the usual tests for *p*-toluidine.

The *ethyl ether* separates from spirit in shining, brownish-yellow needles melting at 95°.

0.0984 gave 0.0927 AgBr. $Br = 40.09$.
 $C_{15}H_{14}ON_2Br_2$ requires $N = 40.15$.

The substance dissolves readily or fairly easily in most organic solvents, but like its isomerides is sparingly soluble in cold alcohol or acetic acid.

The *acetyl* derivative crystallises from acetic acid in orange needles melting at 148°.

0.1020 gave 0.0942 AgBr. $Br = 39.31$.
 $C_{15}H_{12}O_2N_2Br_2$ requires $Br = 38.79$.

The solubilities of the substance resemble those of the ortho-compound.

The *benzoyl* derivative separates from boiling spirit, in which it dissolves only sparingly, as orange-yellow prisms melting at 114°.

0.0996 gave 0.0790 AgBr. $Br = 33.75$.
 $C_{20}H_{14}O_2N_2Br_2$ requires $Br = 33.73$.

Again, the solubilities were found to agree closely with those of the isomeric ortho-compound.

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