
LXXXVII.—2:4-*Dibromo-5-nitro-* and 2:4-*Dibromo-3:5-dinitro-toluenes and their Behaviour on Reduction.*

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ON nitration with fuming nitric acid (*d.* 1.52), 2:4-dibromotoluene yields initially, as stated by Nevile and Winther (Trans., 1880, 37, 440), a mononitro-derivative melting at 81°; this is not 2:4-dibromo-6-nitrotoluene, as suggested in Beilstein's *Handbuch* (3^{te} Auflage, II, 97), but

2 : 4-dibromo-3-nitrotoluene, the nitro-group having entered the nucleus in the ortho-position relatively to the *p*-bromine atom and not to the methyl radicle. The structure of the nitro-compound follows from its yielding 4 : 6-dibromo-*m*-toluidine (m. p. 74·5°, Nevile and Winther, *loc. cit.*) on reduction with tin and hydrochloric acid.

Unless the nitration of 2 : 4-dibromotoluene be carefully regulated, a dinitro-compound is formed, which crystallises from ethyl acetate in magnificent, light yellow prisms, melts at 127·5°, and has the structure of a 2 : 4-dibromo-3 : 6-dinitrotoluene. This substance is remarkable, inasmuch as on reduction with tin and hydrochloric acid it loses the whole of its bromine and yields *s*-tolylenediamine. The removal of the bromine atoms under these conditions is due to the simultaneous influence of the two nitro-groups contiguous to the bromine ; a single nitro-group is without such an effect, as the reduction of 2 : 4-dibromo-5-nitrotoluene occurs in a normal manner, the same being true of the reduction of 3-, 4-, and 5-*o*-nitrotoluenes, 4-, 5-, and 6-*m*-nitrotoluenes, 2-bromo-*p*-nitrotoluene, and of all the other dibromonitrotoluenes.

The nature of the *s*-tolylenediamine obtained was inferred from the fact that it was liquid, whereas all the other diamines which could possibly be derived from a dinitro-derivative of 2 : 4-dibromotoluene are known to be crystalline solids ; it was shown not to be 2 : 3-tolylenediamine by failing to yield a crystalline derivative with phenanthraquinone and by yielding a *diacetyl* derivative, and not an amidine, with acetic anhydride. This *diacetyl* derivative melts at 236—237°, and is therefore not identical with diacetyl-2 : 5-tolylenediamine, which melts at 220° (Nietzki, *Ber.*, 1879, 12, 2237).

EXPERIMENTAL.

The 2 : 4-dibromotoluene used was prepared from *o*-nitro-*p*-toluidine, obtained either by nitrating *p*-toluidine or by reducing 2 : 4-dinitrotoluene with ammonium sulphide ; in displacing the amino-group by bromine, Sandmeyer's method was adopted instead of Griess's (compare Beilstein and Kuhlberg, *Annalen*, 1871, 158, 340). To ensure a good yield, a mixture of the diazo-nitrate with hydrobromic acid is added to cuprous bromide suspended in water at 40°, care being taken that the mixture is not subsequently heated above 60°. The *p*-bromo-*o*-nitrotoluene is extracted from the cuprous bromide by alcohol, from which it crystallises in well-formed, yellow prisms. On reducing the nitro-compound with tin and hydrochloric acid and distilling with steam, a nearly theoretical yield of *p*-bromo-*o*-toluidine is obtained. On diazotising this in hydrobromic acid solution, decomposing the diazo-compound by means of cuprous bromide, and distilling in steam, a 65 per cent. yield of 2 : 4-dibromotoluene is obtained.

2:4-Dibromo-5-nitrotoluene.

In order to obtain the mononitro-compound, 5 grams of 2:4-dibromotoluene, freed from all phenolic impurities by washing with a dilute solution of sodium hydroxide and carefully dried over calcium chloride, are added to 15 grams of nitric acid (*d.* 1.52) and the mixture gently warmed on a water-bath; a vigorous action usually begins, which should be moderated by rapidly cooling the mixture. After the action has subsided, the mixture is again heated on the water-bath and constantly shaken during 40 minutes, after which the separated oil should solidify on cooling with water. On pouring into water and crystallising the solid product once from alcohol, it melts at 79–80°, but by repeated crystallisation the melting point is raised to 81–82° (Neville and Winther give 80–81°). If, during the nitration, the heating is continued too long, a product somewhat more difficult to purify is obtained; when first crystallised from alcohol, it forms long, slender needles, which, although apparently pure, melt at 70–71°; the correct melting point is reached only after eight or ten recrystallisations.

2:4-Dibromo-5-toluidine.

Fifteen grams of 2:4-dibromo-5-nitrotoluene are heated on the water-bath with 12 grams of tin and 120 grams of concentrated hydrochloric acid; after reduction is complete, 60 grams of sodium hydroxide are added and the product distilled with steam. The yield is nearly a theoretical one; the crude product melts at about 55°, crystallising from alcohol in long, slender needles radiating from a centre, which, although apparently homogeneous, melt at about 56°; such a product contains an impurity rich in bromine,* as the following analyses of different samples show:

0.0711 gave 0.1180 AgBr. Found Br = 70.61.

0.0766 „ 0.1231 AgBr. „ Br = 68.66.

$C_7H_7NBr_2$ requires Br = 60.37 per cent.

A single crystallisation from light petroleum, however, raises the melting point to 74°, and a constant value, 74.5–75°, is reached after one more crystallisation; the base separates in small, dull greyish,

* The base was prepared from slightly impure dibromonitrotoluene (m. p. 75–80°); from the petroleum mother liquors of the purified base, two well-defined substances were isolated, one crystallising from alcohol in short needles melting at 94°, the other in large, slender needles melting at 104–105°. Although both substances contained the same amount of bromine (74.61 and 74.71 per cent. respectively), they were not identical, as shown by the fact that a mixture of the two melted at 70–80°. They were not further investigated.

radiating prisms and is obviously identical with Nevile and Winther's 2 : 4-dibromo-5-toluidine, obtained by brominating *p*-bromo-*m*-acetotoluidide :

0.0576 gave 0.0821 AgBr. Br = 60.66.

$C_7H_7NBr_2$ requires Br = 60.37 per cent.

2 : 4-*Dibromo-5-acetotoluidide*, $C_6H_2MeBr_2 \cdot NHAc$, prepared by boiling the base for a few minutes with acetic anhydride, crystallises from alcohol in small, white prisms or needles, melts at 167° , and has not hitherto been described :

0.1063 gave 0.1316 AgBr. Br = 52.65.

$C_9H_9ONBr_2$ requires Br = 52.12 per cent.

2 : 4-*Dibromo-3 : 5-dinitrotoluene*.

This is formed in considerable quantity if, in preparing 2 : 4-dibromotoluene, the nitration mixture is heated too long ; it can easily be prepared in excellent yield by heating the dibromotoluene with a mixture of fuming nitric acid and concentrated sulphuric acid, initially for 2—3 hours on the water-bath, and finally for 5—10 minutes gently on the sand-bath. The product is poured into water, dried, and crystallised from ethyl acetate ; it forms magnificent, slightly yellow prisms, often half-an-inch in length, and melts at 127.5° . From alcohol, it crystallises in tufts of lustreless prisms :

0.2167 gave 0.1990 CO_2 and 0.0245 H_2O . C = 25.04 ; H = 1.25.

0.2000 „ 15.0 c.c. moist nitrogen at 11° and 761.7 mm. N = 8.96.

0.1090 „ 0.1214 AgBr. Br = 47.40.

$C_7H_4O_4N_2Br_2$ requires C = 24.70 ; H = 1.18 ; N = 8.23 ; Br = 47.06 percent.

Reduction of 2 : 4-Dibromo-3 : 5-dinitrotoluene.

Five grams of the finely powdered pure dinitro-compound were heated with 6.5 grams of tin and 30 grams of concentrated hydrochloric acid for about 5 hours on the water-bath. The tin was precipitated from the hot diluted solution by means of hydrogen sulphide and the clear solution evaporated, first in an open dish over the water-bath, finally, when the solution became slightly brownish in colour, in a vacuum desiccator over concentrated sulphuric acid and potash. Small, white rosettes of needles separated, which were very soluble in water, decomposed between 255° and 260° , and had the composition of a *s-tolyl-enediamine dihydrochloride* :

0.0544 gave, by Carius' method, 0.0789 AgCl. Cl = 35.86.

0.0626 „ „ direct precipitation, 0.0910 AgCl. Cl (as HCl) = 35.93.

$C_6H_2Me(NH_2)_2 \cdot 2HCl$ requires Cl = 36.38 per cent.

The base was prepared from the dihydrochloride by adding sodium hydroxide to its aqueous solution and extracting with ether; on evaporating the ether completely in a vacuum, a syrupy liquid was obtained, which was very soluble in water and did not solidify in a freezing mixture; owing to lack of material, the boiling point was not observed. The substance was converted into a *diacetyl* derivative by gently warming with acetic anhydride; this crystallised from alcohol in small, pike-shaped, hemimorphic prisms melting at $235\text{--}236^\circ$, which became strongly electrical when removed from the solution and allowed to dry on filter paper. Under these circumstances, several of the crystals, especially when stroked with a spatula, leaped into the air to the height of 2 or 3 inches. Diacetyl-*s*-tolylenediamine has not hitherto been described:

0.1600 gave 0.3761 CO_2 and 0.0970 H_2O . $\text{C} = 64.10$; $\text{H} = 6.74$.

$\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 64.01$; $\text{H} = 6.86$ per cent.

A little of the free base was combined with diazobenzene chloride, when it readily yielded a brown, chrysoidine dye-stuff.

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