437. *Products of Nitration of Some Derivatives of Dimethylaniline, Auramine, and Crystal-violet.*

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Nitration of auramine yields 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-bismethylnitroaminobenzophenone previously obtained by Van Romburgh (*Rec. Trav. chim.*, 1887, **6**, 368) by nitration of Michler's ketone.

Nitration of crystal-violet yields 3 : 5 : 3′ : 5′ : 3″ : 5″-*hexanitro*-4 : 4′ : 4″-*trismethylnitroaminotriphenylcarbinol ;* this, under the action of dilute alkalis or acetic anhydride, loses a molecule of nitric acid and yields a corresponding quinoneimine which, with addition of nitric acid, regenerates the original carbinol.

IF auramine is nitrated by adding a solution of its hydrochloride in sulphuric acid to an excess of concentrated nitric acid, a crystalline product is precipitated, which is identical with 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-bismethylnitroaminobenzophenone, prepared by Van Romburgh (*loc. cit.*) by nitration of Michler's ketone. Hence, it is evident that in the course of the nitration the imino-group of auramine is hydrolysed to the carbonyl group.

The same result was obtained when nitration was carried out in presence of acetic anhydride or phosphoric oxide instead of sulphuric acid. Also acetylation of the imino-group with acetic anhydride before nitration does not prevent this group from being transformed into a carbonyl group. Further, we attempted unsuccessfully to form a nitroimino-group by the action of dehydrating agents, such as acetic anhydride alone or with sulphuric acid, zinc chloride, or phosphoric oxide on auramine nitrate.

The nitration of crystal-violet was carried out by dissolving the sulphate of the base in concentrated sulphuric acid and adding the solution to concentrated nitric acid. A strongly exothermic reaction accompanied by gas-evolution occurs, and crystalline 3 : 5 : 3′ : 5′ : 3″ : 5″-*hexanitro*-4 : 4′ : 4″-*trismethylnitroaminotriphenylcarbinol* (I) is precipitated. This substance is acidic and gives a sodium salt on reaction with sodium methoxide.

The colourless product (I) or its sodium salt, boiled with dilute sodium hydroxide, furnishes the yellow quinonoid *compound* (II) and a substance soluble in alkalis, probably 3 : 5 : 3′ : 5′ : 3″ : 5″-hexanitroaurin (III). The proportion of the products (II) and (III) varies according to the concentration of the alkali with which (I) is boiled : the lower this concentration the higher the proportion of (II).

The formation of (II) is accompanied by that of sodium nitrate. This, however, was obscured by the simultaneous formation of (III) and of sodium nitrate and nitrite and methylamine.

The imide (II) can be prepared from (I) by boiling it with acetic anhydride. This is accompanied by strong evolution of nitrogen and carbon dioxide, probably owing to the reaction between nitric acid and acetic anhydride at high temperature.

Both products (I) and (II) were oxidised by chromic anhydride in presence of acetic anhydride and furnished 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-bismethylnitroaminobenzophenone (above).

$$\text{(I.)}\quad \mathrm{OH{\cdot}C[C_6H_2(NO_2)_2{\cdot}NMe{\cdot}NO_2]_3}$$

$$\text{(II.)}\quad \mathrm{NMe{:}C_6H_2(NO_2)_2{:}C[C_6H_2(NO_2)_2{\cdot}NMe{\cdot}NO_2]_2} \qquad \text{(III.)}\quad \mathrm{OH{\cdot}C[C_6H_2(NO_2)_2{\cdot}OH]_3}$$

The product (II) is soluble in methyl-alcoholic sodium methoxide and can be precipitated unchanged by acidifying the solution with dilute acid.

EXPERIMENTAL.

Nitration of Auramine.—Auramine hydrochloride monohydrate (20 g.) was dissolved in concentrated sulphuric acid (100 g.) and the solution was added dropwise during *ca.* 1 hour with stirring to anhydrous nitric acid (100 g.) at 60—70°. The reaction proceeds with evolution of gas and precipitation of 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-bismethylnitroaminobenzophenone (27 g., 85%). Crystallised thrice from nitrobenzene and benzene or from concentrated nitric acid, it had m. p. 200°, unchanged when mixed with the product prepared according to Van Romburgh from Michler's ketone (Found : C, 35·3; N, 21·5. Calc. for $C_{15}H_{10}O_{13}N_8$: C, 35·3; N, 21·9%).

3 : 5 : 3′ : 5′ : 3″ : 5″-*Hexanitro*-4 : 4′ : 4″-*trismethylnitroaminotriphenylcarbinol* (I).—Crystal-violet hydrochloride (13 g., 100% purity) was dissolved in concentrated sulphuric acid (100 g.), and the solution added dropwise during 2 hours with stirring to anhydrous nitric acid (150 g.) at 60—70°. The crystalline *product* (I) was precipitated, and was filtered off, washed, dried (22—24 g., 88—96%), and recrystallised from nitric acid (*d* 1·50); decomp. 228° (capillary tube) [Found : C, 34·3; H, 2·7; N, 22·7; NO_2 (nitrometer), 18·3. $C_{22}H_{16}O_{19}N_{12}$ requires C, 35·1; H, 2·1; N, 22·3; NO_2 (nitroamine), 18·4%].

Sodium salt. The substance (I) was suspended in methyl alcohol and a 5% solution of sodium methoxide in methyl alcohol was added dropwise with stirring until complete solution of (I) took place. A small excess of (I) was then added to avoid any excess of methoxide, and the solution was filtered and evaporated under reduced pressure. A brown sodium salt remained. It was not analysed as it could not be purified from any solvent. On reaction with hydrochloric acid, it regenerated (I).

Action of Alkalis on (I).—The substance (I) (37 g.) was boiled with a 2% solution of potassium hydroxide by injecting steam for 30 minutes. The vapours were trapped in dilute hydrochloric acid. The liquid turned brown, methylamine distilled over, and the yellow suspension of 2 : 6-*dinitro*-4-*bis*-(3′ : 5′-*dinitro*-4′-*methylnitroaminophenyl*)*methylene*-N-*methylsemiquinone* (II) was filtered off (16 g.). Crystallised from acetic acid, it had m. p. 210° (decomp.) [Found : C, 39·5; H, 2·7; N, 21·5; NO_2 (nitrometer), 13·0. $C_{22}H_{15}O_{16}N_{11}$ requires C, 38·3; H, 2·2; N, 22·3; NO_2 (nitroamine), 13·3%].

Examination of the By-products of the Formation of (II).—The filtrate from (II) was acidified with hydrochloric acid and a precipitate, possibly 3 : 5 : 3′ : 5′ : 3″ : 5″-hexanitroaurin (III) (10 g.) was filtered off. It could not be satisfactorily purified and was not analysed. When heated (8 g.) with nitric acid (*d* 1·50) at 100° for 20 hours it yielded picric acid (1·5 g.). The filtrate from (III) contained nitrous and nitric acid.

Action of Acetic Anhydride on the Product (I).—The substance (I) (50 g.) was boiled under reflux with acetic anhydride (250 c.c.) for 6 hours. Evolution of nitrogen and carbon dioxide (3·3 l.) occurred. The product (II) (35 g.), which crystallised after addition of water (50 c.c.), was identical with that prepared as described above.

Oxidation of (I) *or* (II).—The substance (I) or (II) (20 g.) was boiled for 10 mins. with acetic anhydride (100 c.c.) and then a solution of chromic anhydride (10 g.) in acetic anhydride (50 c.c.) was added dropwise, and the whole boiled for 30 minutes. The resulting solution was poured into water, and the precipitate filtered off, and identified as 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-bismethylnitroaminobenzophenone.

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