

CCXCIII.—*Polynitroarylnitroamines. Part I. 2:4:6-Trinitrophenylnitroamine.*

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DURING a study of the nitration of *o*- and *p*-nitroanilines, Witt and Witte (*Ber.*, 1908, 41, 3090) obtained, in addition to a 60—70% yield of picramide and some picric acid, a yellow explosive product which yielded a stable sodium salt. Analysis of the latter indicated that the new product was 2:4:6-trinitrophenylnitroamine, but it was not further characterised.

We have found that 2:4:6-trinitrophenylnitroamine can be obtained in good yield by the nitration of sulphanilic acid under suitable conditions. It is a yellow crystalline solid which deflagrates between 80° and 110°. It dissolves in aqueous alkalis, giving deep purple-red solutions (compare Franchimont, *Rec. trav. chim.*, 1910, 29, 298), from which well-defined salts can be isolated.

Proof of the constitution of this material is afforded (a) by its conversion into 2:4:6-trinitrophenylmethylnitroamine when treated with methyl sulphate and aqueous alkali, (b) by its decomposition in the Lunge nitrometer with quantitative liberation of nitric oxide, (c) by its formation from picramide by nitration, and (d) by the formation of picramide, in practically quantitative yield, when it is dissolved, together with an equimolecular amount of 2:4-dinitroaniline, in cold concentrated sulphuric acid.

Riegel, Post, and Reid (*J. Amer. Chem. Soc.*, 1929, 51, 508) state that treatment of sulphanilic acid in sulphuric acid solution with 1.1 mols. of nitric acid affords 2-nitro-4-aminobenzenesulphonic acid, but give no proof of this constitution of the product. The above results indicate that, if a mononitro-derivative is formed under these conditions, it will be the 3-nitro-4-aminobenzenesulphonic acid.

Macciotta (*Gazzetta*, 1930, 60, 408) claims to have isolated "picramide nitrate" by adding fuming sulphuric acid (30% free SO₃) to

a solution of *p*-nitroaniline in nitric acid (*d* 1.52). His product is described as a yellow crystalline compound, which deflagrates when heated. It is also stated that picramide remains unchanged when treated similarly.

We have repeated Macciotta's nitration of *p*-nitroaniline, and find that his product is identical with that obtained as above from sulphanilic acid, *i.e.*, it is 2 : 4 : 6-trinitrophenylnitroamine.

Nitration of 2 : 6-dinitrosulphanilic acid (Holleman and Haeftler, *Rec. trav. chim.*, 1921, **40**, 93) also affords 2 : 4 : 6-trinitrophenylnitroamine.

EXPERIMENTAL.

Nitration of Sulphanilic Acid.—A solution of anhydrous sulphanilic acid (104 g.) in warm sulphuric acid (*d* 1.84; 400 c.c.) is cooled to 15° and stirred mechanically, and nitric acid free from nitrous acid (*d* 1.5; 240 c.c.) is added slowly during about 2 hours, the temperature being kept below 20° by means of an external ice-bath. The stirring is continued for 24 hours, but renewal of the ice is unnecessary after 6 hours. The mixture is then kept for a further 48 hours at the ordinary temperature. The 2 : 4 : 6-trinitrophenylnitroamine separates in finely divided, crystalline condition, and is readily collected on a sintered glass funnel. The crude product is placed in ice-water, again filtered off, drained, and dried at a low temperature (yield, 120 g., or 75% of the theoretical). It is best recrystallised from a mixture of chloroform and acetone (6 c.c. and 1 c.c. respectively per g. of product) [Found : N (Lunge), 5.04. Calc. for $C_6H_2(NO_2)_3 \cdot NH \cdot NO_2$: N, 5.12%. Calc. for $C_6H_2(NO_2)_3 \cdot NH_2, HNO_3$: N, 4.83%]. Dilution of the waste acid yields only about 10 g. of gummy material. The nitration is slow, and the prolonged stirring and cooling are essential to prevent inflammation of the charge.

Methylation of 2 : 4 : 6-Trinitrophenylnitroamine.—The nitroamine (9 g.) is dissolved in aqueous 1.5% sodium hydroxide (100 c.c.). Methyl sulphate (5 c.c.) is added gradually, and the mixture stirred until the solution, originally deep red, has become yellow. The precipitated solid is filtered off, washed with water, and dried (yield, 3 g.); m. p. 115—120°. It is purified by reprecipitation from solution in nitric acid (*d* 1.5) with water. Thus obtained, the product has m. p. 125—128°, not depressed by admixture with 2 : 4 : 6-trinitrophenylmethylnitroamine.

Nitration of Picramide.—Picramide (2 g.) is dissolved in warm concentrated sulphuric acid (10 c.c.), and nitric acid (*d* 1.5; 2.8 c.c.) added gradually at below 20° to the stirred solution. After 2 hours, the precipitated nitroamine is collected, washed with water, and dried (yield, 2 g.).

Picramide from 2:4:6-Trinitrophenylnitroamine and 2:4-Dinitroaniline.—The nitroamine (3.0 g.) and 2:4-dinitroaniline (2.0 g.) are dissolved successively in concentrated sulphuric acid (25 c.c.) and the solution is kept for 24 hours at the ordinary temperature and then poured on ice, picramide (4.5 g.) being obtained; m. p. 172—180°, mixed m. p. 177—185°.

Nitration of 2:6-Dinitrosulphanilic Acid.—Potassium 2:6-dinitrosulphanilate (30 g.) is dissolved in concentrated sulphuric acid (70 c.c.), and nitric acid (*d* 1.5; 30 c.c.) is added gradually with stirring and cooling. After 24 hours, when the mixture is poured on ice, 2:4:6-trinitrophenylnitroamine is obtained (yield, 15 g., or 55% of the theoretical).

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