CXXVIII.—*The Synthesis of some Nitro-derivatives of Toluene.*

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IN the course of an investigation it was found necessary to prepare a considerable quantity of pure 3:4-dinitrotoluene. This compound is formed with the 2:3- and 2:5-isomerides by the nitration of *m*-nitrotoluene, and can be readily separated from the mixture by freezing (Beilstein and Kuhlberg, *Annalen*, 1870, **155**, 25; Haeussermann and Grell, *Ber.*, 1894, **27**, 2209; Holleman and Sirks, *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 280). This method is satisfactory, although the yields are not large. Haeussermann and Grell (*loc. cit.*) mention the preparation from 3-nitro-*p*-toluidine by the Sandmeyer reaction, but do not give details. As a trial of Haeussermann and Grell's method did not give good results, and as *m*-nitrotoluene was unobtainable at the time and its preparation on a laboratory scale was very tedious, other methods of preparation of 3:4-dinitrotoluene were considered. The present paper deals with one of these methods. The starting material was *o*-toluidine, and the reactions involved may be summarised as follows:

The nitration of *o*-toluidine to 4-nitro-*o*-toluidine has been described by Noelting and Collin (*Ber.*, 1884, **17**, 265), but by a modification of their process, the separation of the isomeric nitrotoluidines formed has been greatly simplified. The yields obtained to the stage of the dinitrotoluidines were satisfactory, but the

removal of the amino-group from these compounds did not prove as easy as experience with similar compounds had led the authors to expect, and the yield of 3:4-dinitrotoluene was disappointing. On the other hand, the oxidation of the amino-group in the dinitrotoluidines to the nitro-group by means of Caro's acid proceeds very smoothly and provides a convenient method of synthesis of 2:3:4- and 2:4:5-trinitrotoluenes, which hitherto have been obtained only by the nitration of *m*-nitrotoluene and separation of the two isomerides by fractional crystallisation (Hepp, *Annalen*, 1882, **215**, 366) or by nitration of the rare 2:3- and 2:5-dinitrotoluenes (Will, *Ber.*, 1914, **47**, 704).

EXPERIMENTAL.

4-Nitroaceto-*o*-toluidide.—One hundred grams of *o*-toluidine were dissolved in 1087 c.c. of sulphuric acid (D 1·8), care being taken to avoid rise of temperature. The mixture was cooled below 0° in a freezing mixture, and a mixture of 163 c.c. of sulphuric acid (D 1·8) and 50·8 c.c. of nitric acid (D 1·42) cooled to 0° slowly run in so that the temperature did not rise above 0°. When all the acid had been added, the mixture was allowed to remain for one hour. At this stage Noelting and Collin (*loc. cit.*) neutralised all the acid with sodium hydroxide. A more economical method which avoids a great increase in the bulk of the liquid and the formation of tarry products consists in adding to the nitration mixture one-half its bulk of water with thorough cooling and stirring. On keeping, the sulphate of 4-nitro-*o*-toluidine separated, and was removed by filtration and washed with alcohol. The yield of sulphate was about 60 per cent. of the theoretical. The 6-nitro-*o*-toluidine formed during the nitration (Green and Lawson, T., 1891, **59**, 1014, say 20 per cent.) remained in the filtrate. The sulphate was ground in a mortar with a slight excess of 10 per cent. sodium hydroxide, and the free base collected, washed thoroughly with water, dried, and acetylated with acetic anhydride.

Nitration of 4-Nitroaceto-*o*-toluidide.—A solution of 20 grams of 4-nitroaceto-*o*-toluidide in 60 c.c. of concentrated sulphuric acid was added slowly with stirring to 60 c.c. of nitric acid (D 1·5) cooled in ice. When all the solution had been added, the mixture was allowed to remain in ice for thirty minutes, and then poured into 4 litres of ice-water. The solid separating was collected at once and thoroughly washed by grinding three or four times in a mortar with water and filtering. A 70 to 80 per cent. yield of the mixed dinitroaceto-*o*-toluidides was obtained.

Separation of the Dinitro-*o*-toluidines.—Fifty grams of the mix-

ture of dinitroaceto-*o*-toluidides were hydrolysed by heating for four or five hours on the water-bath with a mixture of 200 c.c. of concentrated sulphuric acid and 400 c.c. of water. On cooling the mixture, filtering, and washing the precipitate, first with 50 per cent. sulphuric acid and then with water, a 45 per cent. yield of a substance melting at 122° was obtained. On diluting the filtrate, a 25 per cent. yield of a material melting at $150\text{--}170^{\circ}$ was precipitated. The compound melting at 122° was recrystallised several times from alcohol until the product was of constant melting point, and oriented by conversion into 2:3:4-trinitrotoluene (see below). 3:4-Dinitro-*o*-toluidine crystallises in lustrous, yellowish-brown needles melting at $131\text{--}131.5^{\circ}$ (Found: $N=21.5$. $C_7H_7O_4N_3$ requires $N=21.3$ per cent.).

The substance melting at $150\text{--}170^{\circ}$ was recrystallised twice from alcohol and oriented by conversion into 2:4:5-trinitrotoluene (see below). 4:5-Dinitro-*o*-toluidine crystallises in yellow needles melting at $191\text{--}191.5^{\circ}$ (Found: $N=21.6$. $C_7H_7O_4N_3$ requires $N=21.3$ per cent.).

Preparation of 3:4-Dinitrotoluene.—For this purpose it is not necessary to separate the mixture of dinitro-*o*-toluidines, as both give 3:4-dinitrotoluene on removal of the amino-group. Nine grams of the mixture were dried and dissolved in a mixture of 180 c.c. of freshly distilled absolute alcohol and 45 c.c. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide). The solution was heated on the water-bath, and 27 grams of finely powdered dry sodium nitrite were added in small portions with vigorous shaking. When all the nitrite had been added, the mixture was heated for five minutes, cooled, and diluted with water. The oily solid which separated was crystallised first from hot nitric acid (D 1.4) to destroy tarry matter, and then from alcohol with the addition of animal charcoal, when pure 3:4-dinitrotoluene was obtained. The yield was not good, 2 grams only being obtained from 9 grams of the mixture of dinitrotoluidines.

Preparation of 2:4:5-Trinitrotoluene.—To Caro's acid, prepared from 10 grams of ammonium persulphate and 7 c.c. of concentrated sulphuric acid poured on 20 grams of crushed ice, a solution of 2 grams of 4:5-dinitro-*o*-toluidine (m. p. 191°) in 10 c.c. of 80 per cent. sulphuric acid was added. A clear solution was obtained which, on keeping overnight, deposited dinitronitroso-toluene; it was then diluted with water, and the precipitated nitroso-compound added to ten times its weight of nitric acid (D 1.5) and warmed until red fumes were no longer evolved. On cooling and diluting the solution, a crystalline precipitate of 2:4:5-trinitrotoluene was obtained which, after one recrystallisa-

tion from alcohol, was pure. The yield was about 80 per cent. of the theoretical.

Preparation of 2:3:4-Trinitrotoluene.—A solution of 3:4-dinitro-*o*-toluidine in 80 per cent. sulphuric acid was added to Caro's acid as above; in this case, however, the amine was precipitated by the dilution of the sulphuric acid, so the mixture was transferred to a stoppered bottle and left for four days, with frequent shaking. At the end of that time the precipitate was collected and treated with nitric acid, as in the previous case, when 2:3:4-trinitrotoluene was obtained in good yield.

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