

on recrystallization from water, melted at 189.4° (corr.). This compound is soluble also in alcohol or benzene.

Found: N, 10.9. Calculated for  $C_{13}H_{16}O_4N_2$ : N, 10.6.

The crystals have not been further examined, as only a small amount was obtained, but we believe them to be the *ethyl 2,4-diacetaminobenzoate*,  $(CH_3CONH)_2C_6H_3COOC_2H_5$ . If this assumption is correct, the dark-colored product (m. p. 102°) which first separated was probably the impure ethyl 2,4-diaminobenzoate. The free diaminobenzoic acid (m. p. about 140°) and its diacetyl derivative (m. p. 261°) have been described by Ullmann and Uzbachian.<sup>1</sup> The free acid is unstable.

#### NOTE.

*The Action of Nitric Acid on Triphenylmethane.*<sup>2</sup>—E. and O. Fischer<sup>3</sup> have shown that trinitrotriphenylmethane can readily be prepared by the action of strong nitric acid (sp. gr. 1.5) upon triphenylmethane, calling attention to the fact, however, that the best yield is obtained by slowly adding the finely ground substance to an excess of strong acid at a low temperature. In an attempt to repeat this work, E. S. Smith<sup>4</sup> obtained a white crystalline product closely resembling triphenylcarbinol. This substance had a melting point of 161° (uncorr.), did not contain nitrogen, and on combustion gave figures for carbon and hydrogen similar to those calculated for triphenylcarbinol (m. p. 159° corr.). In this test dilute acid (sp. gr. 1.34) was poured upon the triphenylmethane, some fuming nitric acid added, and the mixture finally heated on a water bath.

As Smith, however, was unable to duplicate his results, a number of experiments were undertaken by the writer to determine the conditions leading to the formation of the carbinol, and those giving the trinitrotriphenylmethane as a product.

For these tests a sample of triphenylmethane was recrystallized from alcohol until it was pure white and melted sharply at 92° (corr.). The acids used were:

I. Baker's brown fuming nitric acid, sp. gr. ....	1.58
II. Baker's yellow fuming " " " " .....	1.505
III. <sup>5</sup> A red fuming nitric acid, " " .....	1.48

The experiments are divided into two series. In the first, following the work of the Fischers, five grams of finely ground triphenylmethane were added in small portions to amounts of acids I, II, or III varying between 25 cc. and 60 cc., the temperature being kept at 0° by carrying on the reaction in a freezing mixture. When the triphenylmethane

<sup>1</sup> *Ber.*, 36, 1802 (1903).

<sup>2</sup> Read before the New York Section, April 9, 1909.

<sup>3</sup> *Ann.*, 194, 254.

<sup>4</sup> *Am. Chem. J.*, 19, 702.

<sup>5</sup> This was an old sample which had been standing in the laboratory and was rather dark from nitrogen peroxide.

had entirely dissolved, the solution was allowed to drip into a beaker filled with ice which was constantly stirred to break up the resulting precipitate into small granules. Recrystallizing this precipitate from glacial acetic acid gave more or less pure trinitrotriphenylmethane, the pure white crystals melting at  $206^{\circ}$  (corr.), as found by Fischer. The mother liquors on concentration invariably deposited a heavy reddish oil which could not be separated in a state pure enough to warrant its further investigation.

In the second series of tests, the acid was added to the triphenylmethane, and the reaction allowed to proceed at room temperature. The use of the yellow acid (sp. gr. 1.505), and of the brown acid (sp. gr. 1.58), in quantities varying from 7 cc. to 15 cc., resulted in a violent reaction, the solution heating to boiling and giving off large amounts of nitric fumes. By dripping this solution upon ice, as already described, a granular substance was usually obtained, but the solution of this in glacial acetic acid always yielded an oily product similar to that deposited by the mother liquors in the first series of tests.

The action of 10 cc. of red fuming acid (sp. gr. 1.48) upon five grams of triphenylmethane, always gave a mild reaction, the temperature rising but a few degrees, and a final heating to  $80^{\circ}$  on a sand-bath being necessary to effect entire solution of the hydrocarbon. The product obtained was a white crystalline solid, melting sharply at  $159^{\circ}$  (corr.), the melting point of triphenylcarbinol. Careful examination showed that this salt did not contain nitrogen and actually was triphenylcarbinol.

To determine whether this reaction was only peculiar to this sample of (1.48 sp. gr.) acid used, two acids of 1.48 sp. gr. were prepared: the first by mixing calculated quantities of the brown acid (sp. gr. 1.58) with colorless concentrated nitric acid (sp. gr. 1.42); the second from the yellow acid (sp. gr. 1.505) and the same concentrated nitric acid. Tests with these mixtures in each case resulted in the formation of triphenylcarbinol, the first, however, giving a much greater yield, which seems to show that the presence of nitric fumes in the original acid has considerable influence upon the reaction.

These tests show that, under varying conditions, trinitrotriphenylmethane, triphenylcarbinol, and an unknown red oil can be obtained by the action of nitric acid upon triphenylmethane. When the hydrocarbon is added to an excess of strong fuming acid at  $0^{\circ}$ , the trinitrotriphenylmethane results; when small amounts of red fuming acid of about 1.48 sp. gr. are added to triphenylmethane, and the reaction takes place at moderate temperature, the product is triphenylcarbinol and no trinitrotriphenylmethane is formed; but when stronger acids are used under the latter conditions and the temperature allowed to rise to the boiling-point, the red oil results.

The best yield of triphenylcarbinol obtained was about 45 per cent. of the theoretical.

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