XXXIV.—*The Constitution of the Products of Nitration of Aceto-m-toluidide.*

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IN the course of some experiments which had for their object the preparation of the trichlorotoluenes from the chlorine derivatives of nitroaceto-*m*-toluidide, it was found that a degree of uncertainty

existed as to the constitution of the nitroacetotoluidide obtained by Beilstein and Kühlberg (*Annalen*, 1871, 158, 348). On reinvestigating the subject, definite evidence was obtained as to the constitution of the substance, and it was also found that a previously overlooked isomeric nitro-compound was formed during the nitration.

Beilstein and Kühlberg describe the nitroaceto-*m*-toluidide as a substance crystallising in red prisms melting at 101—102°. On hydrolysis they obtained a base melting at 133—134°, and showed that on removing the amino-group from this substance, they obtained a liquid nitrotoluene which on subsequent reduction and acetylation gave aceto-*o*-toluidide.

These experiments whilst proving that the nitro-group is in the ortho-position relative to the methyl group, are obviously insufficient to decide between the two possible ortho- and para-positions respectively to the amino-group.

Limpricht (*Ber.*, 1885, 18, 403) ascribes the 2-nitroacetylaminotoluene formula to Beilstein and Kühlberg's compound and reserves the 6-nitro-3-acetylaminotoluene formula for a substance obtained by the partial reduction of a dinitro-compound of unknown constitution, obtained as a by-product in the nitration of toluene. It is not clear that Limpricht had any experimental evidence in support of the constitutions he assigned to the two substances.

Fileti and Crosa (*Gazzetta*, 1888, 18, 298) obtained a base apparently identical with the nitrotoluidine of Beilstein and Kühlberg by heating bromonitrotoluic acid with alcoholic ammonia at 180°. The bromonitrotoluic acid was obtained by the oxidation of bromonitrocymene ($\text{Me} : \text{NO}_2 : \text{Br} : \text{Pr}^{\beta} = 1 : 6 : 3 : 4$), from which it follows that the nitrotoluidine should be represented as containing its substituent radicles in the following positions: $\text{Me} : \text{NH}_2 : \text{NO}_2 = 1 : 3 : 6$. They also showed that on further reducing the base, they obtained a substance melting at 64°, which accords with 2:5-tolylenediamine. 2:3-Tolylenediamine, however, melts at almost the same temperature. The results of the experiments that follow show that the nitration of aceto-*m*-toluidide results in the formation of two nitro-derivatives. The main product consists of 6-nitro-3-acetylaminotoluene and is identical with the product described by Beilstein and Kühlberg. The nitro-group was proved to occupy position 6, by converting the substance successively into 3-chloro-6-nitrotoluene and 3-chloro-4:6-dinitrotoluene and also by showing that the tolylenediamine obtained by hydrolysis and reduction gave the green colouring matter described by Nietzki (*Ber.*, 1877, 10, 1158) on treatment with *o*-toluidine and ferric chloride. Limpricht's formula is therefore shown to be incorrect.

A smaller quantity of an isomeric nitro-compound was separated by fractional crystallisation from alcohol, and was proved to be 4-nitro-

3-acetylaminotoluene. On hydrolysis, it gave a base which was identical with the product obtained by Staedel and Kolb (*Annalen*, 1890, 259, 224) by heating 4-nitro-*m*-tolyl ethyl ether with ammonia.

The simultaneous formation of *o*- and *p*-derivatives in this case is interesting since the nitration of aceto-*o*-toluidide is thereby shown to be essentially similar to that of its *m*-isomeride. Aceto-*o*-toluidide was originally supposed to give simply the *p*-derivative (Beilstein and Kühlberg, *Annalen*, 1871, 158, 345) but Lellman and Würthner (*Annalen*, 1885, 228, 240) showed that the *o*-compound was also present in quite large quantities.

EXPERIMENTAL.

Twenty grams of aceto-*m*-toluidide were added in small portions at a time to 75 grams of freshly distilled fuming nitric acid and 25 grams of glacial acetic acid. The mixture was maintained at about 15°, and about two hours after the whole of the acetotoluidide had been added, the clear reddish solution was poured into water, the precipitated nitroacetotoluidides being crystallised from alcohol. The crystals first deposited were fine, massive, red prisms, which collected in a compact layer at the bottom of the vessel. On further standing, long, yellowish needles were deposited. The two kinds of crystals were separated mechanically as far as possible, and then repeatedly crystallised from alcohol. The prisms, which form the main product of the reaction, melted at 103–104° (Beilstein and Kühlberg give 101–102°). The yellow needles, which amounted to about 15 per cent. of the whole product, melted at 86–87°, and gave on hydrolysis 4-nitro-3-aminotoluene melting at 110–110.5°.

6-Nitro-3-acetotoluidide is readily hydrolysed with boiling hydrochloric acid, the nitrotoluidine hydrochloride crystallising out from the acid solution. On boiling the hydrochloride with water the free base is obtained, and crystallises from hot water or dilute alcohol in long, yellow needles melting at 133–134°.

The conversion of the nitrotoluidine into 3-chloro-4 : 6-dinitrotoluene was carried out as follows : pure nitrotoluidine was converted into the hydrochloride by boiling with a large excess of concentrated hydrochloric acid ; the solution was then cooled in a freezing mixture, and diazotised with solid sodium nitrite. Diazotisation was somewhat slow and required an excess of nitrite, but was eventually complete. On pouring the solution into cold cuprous chloride solution, a rapid evolution of nitrogen occurred, and an almost theoretical yield of liquid chloronitrotoluene was obtained on subsequent distillation in steam. The chloronitrotoluene was next nitrated with fuming nitric acid and con-

centrated sulphuric acid. After the reaction had been completed by warming on the water-bath, the dinitro-compound was precipitated with water and crystallised from alcohol. The substance crystallised in fine, shining leaflets melting at $90-91^{\circ}$, and was identical with 3-chloro-4 : 6-dinitrotoluene (Reverdin and Crépieux, *Ber.*, 1900, 33, 2505). The constitution of the original substance must obviously be 6-nitro-3-aminotoluene, if it can be converted into *o*-toluidine on the one hand, and into 3-chloro-4 : 6-dinitrotoluene on the other.

6-Nitro-3-acetylaminotoluene readily yields chlorine derivatives when dissolved in acetic and hydrochloric acids and treated with sodium chlorate. So far only preliminary experiments have been made in this direction, but the di- and tri-chloro-derivatives have been obtained as follows.

Nine grams of the nitro-compound were dissolved in 75 c.c. of glacial acetic acid and 37 c.c. of concentrated hydrochloric acid. The solution was then carefully cooled and 4 grams of sodium chlorate dissolved in the minimum amount of water, gradually added in small portions. After some time, water was added and the precipitate crystallised from alcohol. The product was not uniform in appearance and melted indefinitely between $110-115^{\circ}$. On analysis, it was found to contain 21.5 per cent. of chlorine corresponding with a mixture of about equal quantities of the mono- and di-chloro-derivatives. The substance was then redissolved in the same acid mixture as before, and a further addition of 2 grams of sodium chlorate made. The substance was subsequently precipitated and repeatedly crystallised from alcohol. Dichloro-6-nitro-3-acetylaminotoluene was obtained in colourless crystals melting at $181-183^{\circ}$.

0.0772 gave 0.0854 AgCl. Cl = 27.2.

$C_9H_8O_3N_2Cl_2$ requires Cl = 27.0 per cent.

A small quantity of substance was separated which was more insoluble in alcohol than the dichloro-derivative and was apparently 2 : 4 : 5-trichloro-6-nitro-3-acetylaminotoluene. It did not melt below 200° .

The hydrolysis of the isomeric nitro-acetotoluidide was effected with boiling hydrochloric acid, and the base was precipitated from the acid solution by the addition of caustic soda. It crystallised from alcohol in fine, prismatic needles melting at $110-110.5^{\circ}$ in agreement with 4-nitro-3-aminotoluene.

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