CXXVIII.—*Some Dinitroethylbenzenes.*

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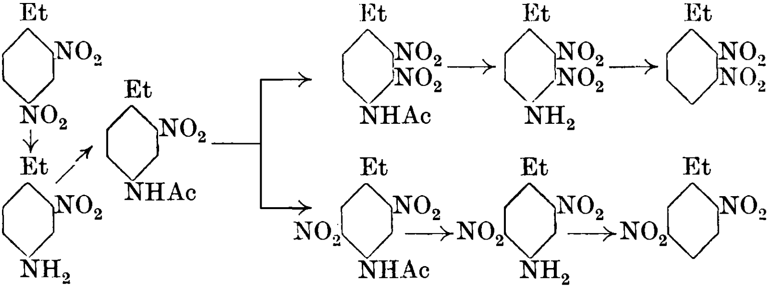
THE present work is preliminary to an investigation of the nitration of *p*-ethyltoluene and similar compounds which is being undertaken with the view of ascertaining the relative ortho-directing influence of the various alkyl groups. The most convenient way of orienting the substituents in the nitroethyltoluenes seems to consist in the oxidation of one alkyl group and the elimination of carbon dioxide from the resulting acid, leaving either nitrotoluenes or nitroethylbenzenes.

The early work on the latter compounds is not entirely satisfactory, but the investigations of Cline and Reid (*J. Amer. Chem. Soc.*, 1927, **49**, 3150), to whose paper reference may be made for an account of previous work, have removed much of the uncertainty regarding the properties of *o*- and *p*-nitroethylbenzene. Of the dinitro-compounds, only the 2 : 4-isomeride has been described and we have now prepared the 2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-dinitroethylbenzenes, the compounds which were likely to be of importance in connexion with the other investigation. 2 : 6- and 3 : 5-*Dinitroethylbenzenes* were prepared by the removal of the amino-group from 2 : 6-dinitro-4-aminoethylbenzene, prepared by the reduction of 2 : 4 : 6-trinitroethylbenzene, and from 3 : 5-dinitro-4-aminoethylbenzene, prepared by the nitration of *p*-acetamidoethylbenzene. The 2 : 3- and 2 : 5-*dinitroethylbenzenes* were prepared by the following series of reactions :



In the nitration of 2-nitro-4-acetamidoethylbenzene the 2 : 3-dinitro-compound is the chief product of the reaction in all cases, but a greater proportion of the 2 : 5-dinitro-compound is formed if a mixture of sulphuric and nitric acids is used instead of fuming nitric acid alone (compare Brady, Day, and Rolt, J., 1922, **121**, 527). The same behaviour has been observed in the case of 2-nitro-4-acetamidotoluene (compare Scott and Robinson, J., 1922, **121**, 844; Page and Heasman, J., 1923, **123**, 3235).

EXPERIMENTAL.

2 : 6-*Dinitroethylbenzene*.—Ammonium sulphide (29 c.c. of a 15% solution) was added slowly with frequent shaking to a solution of 2 : 4 : 6-trinitroethylbenzene (5 g.) (compare Schultz and Sander, *Ber.*, 1909, **42**, 2634) in boiling alcohol (30 c.c.), and the mixture

was then boiled for 30 minutes and filtered hot. On cooling, the filtrate deposited crystals (m. p. 160—165°). The solid residue was repeatedly extracted with boiling 2*N*-hydrochloric acid until the extract no longer gave a precipitate on the addition of ammonia. The extracts were neutralised with ammonia and the precipitate (m. p. 170°) obtained was crystallised, together with the above-mentioned crystals, from alcohol, giving 2 : 6-dinitro-4-aminoethylbenzene in golden-yellow needles, m. p. 175° (Found: N, 19·9. Calc.: N, 19·9%). Schultz and Sander (*loc. cit.*) give m. p. 110° for this compound.

A solution of 2 : 6-dinitro-4-aminoethylbenzene (2 g.) in a mixture of absolute alcohol (40 c.c.) and fuming sulphuric acid (10 c.c. containing 20% SO_3) was warmed on the water-bath, and dry sodium nitrite (6 g.) added in small quantities. After heating for 15 minutes, the pasty mass was diluted with water and distilled in steam. The volatile 2 : 6-*dinitroethylbenzene*, isolated by means of ether, crystallised from alcohol in colourless plates, m. p. 57·5° (Found: N, 14·7. $C_8H_8O_4N_2$ requires N, 14·3%). The compound was oxidised with boiling fuming nitric acid to 2 : 6-dinitrobenzoic acid, which was converted into the methyl ester; both acid and ester were compared with specimens prepared from 2 : 6-dinitrotoluene.

2-*Nitro*-4-*acetamidoethylbenzene*.—Ethylbenzene (21 g.) was added slowly to a mixture of nitric acid (28 c.c., *d* 1·42) and sulphuric acid (60 c.c., *d* 1·8), kept at 50—60°. The whole was heated on the water-bath for 30 minutes and cooled, and the liquid 2 : 4-dinitroethylbenzene was separated, washed with water, dissolved in boiling alcohol (10 g. in 30 c.c.), and treated with successive small portions of ammonium sulphide (70 c.c. of a 15% solution). After boiling for 30 minutes, the solution was filtered and cooled, the dark oil obtained was converted by concentrated hydrochloric acid into 2-nitro-4-aminoethylbenzene hydrochloride, and this was washed with ether to remove oily impurities and reconverted into the base by grinding with 2*N*-sodium hydroxide. The base (10 g.) was boiled for a few minutes with acetic anhydride (20 c.c.), and the cooled solution poured into water; the 2-nitro-4-acetamidoethylbenzene obtained, after crystallisation from benzene and light petroleum, melted at 111° (Found: N, 13·6. Calc.: N, 13·5%). Schultz and Sander (*loc. cit.*) give m. p. 100—101°, and Cline and Reid (*loc. cit.*), 110°.

Nitration of 2-*Nitro*-4-*acetamidoethylbenzene*.—The acetamido-compound (10 g.) was added slowly with stirring to a mixture of nitric acid (20 c.c., *d* 1·42) and sulphuric acid (20 c.c., *d* 1·8), kept below 30°. After 30 minutes, the solution was poured into a large excess of water, and the precipitate was collected as rapidly as possible, washed free from acid with much ice-cold water, dried at room temperature, and dissolved in boiling glacial acetic acid (40 c.c.). The solid which separated on cooling, after one further crystallisation from glacial acetic acid, gave 2 : 3-*dinitro*-4-*acetamidoethylbenzene* in long, white needles, m. p. 143° (Found : N, 16·6. $C_{10}H_{11}O_5N_3$ requires N, 16·6%). The mother-liquor from the above was diluted with much water, the precipitate hydrolysed by heating on the water-bath for an hour with 45% sulphuric acid (30 c.c.), and the solution cooled and partly neutralised with 2*N*-sodium hydroxide. The precipitated mixture of amines (m. p. 87—92°) was crystallised from the minimum quantity of boiling alcohol. The crystals which separated (m. p. 120°), on further crystallisation from alcohol, gave 2 : 5-*dinitro*-4-*aminoethylbenzene* as red prisms, m. p. 125° (Found : N, 19·9. $C_8H_9O_4N_3$ requires N, 19·9%). A mixture of about equal quantities of this compound and 2 : 3-dinitro-4-aminoethylbenzene (m. p. 121·6°) melted at 87—93°.

2 : 3-*Dinitroethylbenzene*.—2 : 3-Dinitro-4-acetamidoethylbenzene was hydrolysed by heating on the water-bath with 45% sulphuric acid; 2 : 3-*dinitro*-4-*aminoethylbenzene* separated on cooling and after two crystallisations from dilute alcohol it was obtained in golden-yellow needles, m. p. 121·6° (Found : N, 20·1. $C_8H_9O_4N_3$ requires N, 19·9%). A solution of this compound (3 g.) in a mixture of absolute alcohol (50 c.c.) and fuming sulphuric acid (15 c.c. containing 20% SO_3) was warmed on the water-bath, and dry sodium nitrite added in small portions with stirring. On distillation with steam 2 : 3-*dinitroethylbenzene* passed over; it crystallised from dilute alcohol in white needles, m. p. 58·5° (Found : N, 14·4. $C_8H_8O_4N_2$ requires N, 14·3%). The compound (0·4 g.) was boiled under reflux with potassium dichromate (2 g.), sulphuric acid (10 c.c.), and water (10 c.c.), and from the cooled, diluted solution ether extracted 2 : 3-dinitrobenzoic acid, which was compared with a specimen prepared from 2 : 3-dinitrotoluene. The methyl ester was prepared by boiling the acid (0·5 g., obtained from either of the above sources) under reflux for 2 hours with methyl iodide and dry silver oxide (1 g.). The excess of methyl iodide was distilled off, and the ester extracted with hot methyl alcohol. On cooling, *methyl* 2 : 3-*dinitrobenzoate* separated in white plates, m. p. 134° in both cases (Found : N, 12·6. $C_8H_6O_6N_2$ requires N, 12·4%).

2 : 5-*Dinitroethylbenzene*, obtained, in the same way as the 2 : 3-compound, from 2 : 5-dinitro-4-aminoethylbenzene, separated from dilute alcohol or light petroleum in yellowish-white crystals, m. p. 59·5° (Found : N, 14·5. $C_8H_8O_4N_2$ requires N, 14·3%).

This compound was oxidised to 2 : 5-dinitrobenzoic acid, which was compared, and also its methyl ester, with specimens prepared from 2 ; 5-dinitrotoluene.

3 : 5-*Dinitroethylbenzene*.—For the preparation of 3 : 5-dinitro-4-aminoethylbenzene the method of Paucksch was followed (*Ber.*, 1884, **17**, 769). Ethylbenzene was mononitrated, and the product reduced with tin and hydrochloric acid. Distillation in steam of the acid mixture removed a considerable quantity of unchanged nitro-compound, which was probably mainly *o*-nitroethylbenzene, since this compound is reduced with difficulty (Cline and Reid, *loc. cit.*). The crude amine (11 g. from 32 g. of ethylbenzene) obtained by distillation in steam of the solution after being made alkaline, was accordingly comparatively rich in *p*-aminoethylbenzene. Paucksch separated the two amines by crystallisation of their acetyl derivatives from water, but we were unable to achieve this satisfactorily. The mixture of amines (50 g.) was acetylated with acetic anhydride and a few drops of concentrated sulphuric acid, and the mixture poured into water. The oily solid produced, isolated by means of chloroform, became pasty after some days and was then pressed on a porous tile. The solid residue (20 g.) was added in small quantities to fuming nitric acid (200 c.c.) at − 6° to − 10°. The solution, after being kept in the freezing mixture for 35 minutes, was poured into ice-water and the precipitate obtained was washed with water and crystallised from alcohol, giving 7 g. of 3 : 5-dinitro-4-acetamidoethylbenzene, m. p. 182—183° (Found: N, 16·7. Calc.: N, 16·6%). Hydrolysis of this compound with 50% sulphuric acid gave 3 : 5-dinitro-4-aminoethylbenzene, m. p. 135° (Found: N, 20·1. Calc.: N, 19·9%). Paucksch (*loc. cit.*) gives m. p.'s 182° and 135° for the acetyl and amino-compounds, respectively.

The amino-group in 3 : 5-dinitro-4-aminoethylbenzene (2·8 g.) was removed by diazotisation and treatment with boiling alcohol. By distillation in steam and crystallisation from light petroleum 3 : 5-*dinitroethylbenzene* (1·5 g.) was obtained as large, yellow plates, m. p. 41° (Found: N, 14·4. $C_8H_8O_4N_2$ requires N, 14·3%).

3 : 5-Dinitroethylbenzene (0·9 g.) was boiled under reflux for 3 hours with potassium dichromate (3·5 g.) and 50% sulphuric acid (30 c.c.). From the diluted solution, ether extracted 3 : 5-dinitrobenzoic acid, which, after crystallising from very dilute alcohol, was compared with an authentic specimen; the methyl esters also were compared.

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