XXXVII.—*Some Trinitroethylbenzenes.*

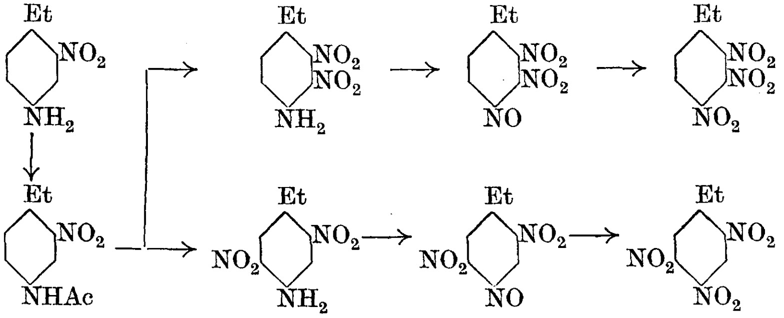
By James Nelson Edmund Day.

An account is here given of the preparation of 3 : 4 : 5-, 2 : 3 : 4-, and 2 : 4 : 5-*trinitroethylbenzenes*, together with some of their reactions. One of the difficulties in the study of derivatives of ethylbenzene has been a suitable initial material of undoubted purity; this has been overcome by using *p*-aminoethylbenzene, prepared from pure *p*-aminoacetophenone by the reduction method of Clemmensen (*Ber.*, 1913, **46**, 1837; 1914, **47**, 51, 681).

On acetylation of *p*-aminoethylbenzene the acetyl derivative described by Paucksch (*Ber.*, 1884, **17**, 769) was obtained, and this on nitration gave 3 : 5-dinitro-4-acetamidoethylbenzene (m. p. 182—183°) identical with that previously described (Paucksch, *loc. cit.*; Brady, Day, and Allam, J., 1928, 982). These experiments were carried out to make certain that the compound described by Paucksch was the *p*- and not the *o*-amino-compound, as it was obtained by separation of the *o*- and *p*-acetamidoethylbenzenes by crystallisation, a process which it had been found difficult to repeat satisfactorily.

3 : 5-Dinitro-4-aminoethylbenzene, on diazotisation and treatment with sodium nitrite and copper sulphate, gave 3 : 4 : 5-trinitroethylbenzene.

p-Aminoethylbenzene, on nitration in presence of excess of sulphuric acid, gave 2-nitro-4-aminoethylbenzene identical with the compound prepared by reduction of crude 2 : 4-dinitroethylbenzene (compare Cline and Read, *J. Amer. Chem. Soc.*, 1927, **49**, 3150, who have shown that some 4-nitro-2-aminoethylbenzene is also produced in this reaction; compare also Brady, Day, and Allam, *loc. cit.*). Nitration of 2-nitro-4-acetamidoethylbenzene gave a mixture of 2 : 3-dinitro- and 2 : 5-dinitro-4-aminoethylbenzenes which on oxidation with Caro's acid gave respectively 2 : 3-*dinitro*-4-*nitrosoethylbenzene* and 2 : 5-*dinitro*-4-*nitrosoethylbenzene*. Oxidation of the latter compounds with nitric acid gave the required 2 : 3 : 4- and 2 : 4 : 5-trinitroethylbenzenes.



2 : 3 : 4-Trinitroethylbenzene has also been prepared by the direct nitration of 2 : 3-dinitroethylbenzene.

These trinitroethylbenzenes are very similar to the corresponding trinitrotoluenes, but their melting points are lower. They form well-defined *methylamine* and *hydrazine* derivatives by replacement of the mobile nitro-group. Their alcoholic solutions give colorations with dilute sodium hydroxide solution. 2 : 3 : 4-Trinitroethylbenzene gives a bright green-yellow colour, changing to brown and brownish-red; the corresponding trinitrotoluene gives a green and then a brown colour. 2 : 4 : 5-Trinitroethylbenzene gives a bright green, changing to dark green and red; the corresponding trinitrotoluene gives blue, green, and then brown colours. 3 : 4 : 5-Trinitroethylbenzene and the corresponding trinitrotoluene both give a bright pink colour, changing to brown.

EXPERIMENTAL.

p-*Aminoethylbenzene*.—A mixture of granulated zinc (100 g., left in contact with mercuric chloride, 20 g., in water, 400 c.c., for 12 hours and then washed with water), concentrated hydrochloric acid (200 c.c.), and water (200 c.c.) was gently heated while *p*-aminoacetophenone (25 g.), dissolved in concentrated hydrochloric acid (200 c.c.), was added slowly through an upright condenser, followed by concentrated hydrochloric acid (100 c.c.). After being heated for 5 hours, the mixture was cooled and, a slight excess of a concentrated solution of sodium hydroxide having been added, submitted to steam distillation. The *p*-aminoethylbenzene was extracted from the distillate with ether (average yield, 19·5%; varying the time of boiling or the amount of hydrochloric acid did not greatly affect the yield).

On acetylation with acetic anhydride, the amine gave *p*-acetamidoethylbenzene, identified by its m. p. and mixed m. p. with a specimen prepared from ethylbenzene.

On nitration with ten times its weight of nitric acid (*d* 1·5), the acetyl compound gave 3 : 5-dinitro-4-acetamidoethylbenzene, m. p. 182—183° after crystallisation from alcohol. Addition of this substance did not lower the melting point of the 3 : 5-dinitroacetamidoethylbenzene previously prepared (Brady, Day, and Allam, *loc. cit.*). This experiment supplied the direct evidence required, that the amino-group in the dinitroacetamidoethylbenzene, m. p. 183°, previously isolated from the nitrated mixture of *o*- and *p*-acetamidoethylbenzenes, was in the 4-position.

3 : 4 : 5-*Trinitroethylbenzene*.—Sulphur dioxide was passed into nitric acid (*d* 1·5) (5·7 g.) at 0° until the gain in weight was 0·6 g. The solution was cooled to − 12°, 3 : 5-dinitro-4-aminoethylbenzene (1·4 g.) dissolved in it, the solution poured on ice (20 g.), and the whole added to a mixture of copper sulphate (5·7 g.) and sodium nitrite (1·6 g.) in water (25 c.c.) containing ice (50 g.). After 12

hours, the precipitate was collected, washed, and heated with nitric acid (*d* 1·42) on the water-bath for 30 minutes, the mixture cooled and diluted, and the product crystallised from nitric acid (*d* 1·42). A final crystallisation from alcohol containing a little acetic acid gave 3 : 4 : 5-*trinitroethylbenzene* in white needles, m. p. 92·5° (Found : C, 39·8; H, 2·9; N, 17·3. $C_8H_7O_6N_3$ requires C, 39·8; H, 2·9; N, 17·4%).

3 : 4 : 5-Trinitroethylbenzene (0·2 g.) in alcohol (6 c.c.) was warmed with 33% methylamine solution (0·3 g.) in alcohol (2 c.c.) on the water-bath for 5 minutes, and the solution diluted with an equal volume of water and cooled. Crystallisation of the precipitate from dilute alcohol gave 3 : 5-*dinitro*-4-*methylaminoethylbenzene* in orange needles, m. p. 73° (Found : C, 47·9; H, 5·0. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9%).

Similarly, from 3 : 4 : 5-trinitroethylbenzene (0·2 g.) in alcohol (6 c.c.) and 50% hydrazine hydrate solution (0·2 g.) in alcohol (4 c.c.), 3 : 5-*dinitro*-4-*hydrazinoethylbenzene* was obtained; it formed copper-red plates, m. p. 85°, on crystallisation from alcohol (Found : C, 42·5; H, 4·5. $C_8H_{10}O_4N_4$ requires C, 42·5; H, 4·5%).

2-*Nitro*-4-*aminoethylbenzene*.—Sulphuric acid (*d* 1·84) (55 c.c.) was cooled to 0°, and *p*-aminoethylbenzene (5 g.) added slowly. The solution was cooled to − 8°, and stirred while a mixture of nitric acid (*d* 1·5) (3·3 g.) and sulphuric acid (*d* 1·84) (8 c.c.) was added drop by drop. After being kept at 0° for 30 minutes, the mixture was poured on ice. The precipitated sulphate was decomposed with 2*N*-sodium hydroxide, and the amine extracted with ether. Crystallised from light petroleum, the product melted at the same temperature (45°) as the compound described by Cline and Read (*loc. cit.*).

2 : 3-*Dinitro*-4-*nitrosoethylbenzene*.—2 : 3-Dinitro-4-aminoethylbenzene (1·58 g.) (Brady, Day, and Allam, *loc. cit.*) was dissolved in sulphuric acid (*d* 1·84) (5 c.c.) at 0°. Sulphuric acid (*d* 1·84) (5 c.c.) was cooled in a freezing mixture, finely powdered ammonium persulphate (5·13 g.) added in small quantities at a time, and the solution kept at 0° for an hour and then poured on ice (12 g.) in a stoppered bottle. The sulphuric acid solution of the amine was added, and the mixture shaken occasionally during the following 5 days. The precipitate, after being washed with water and crystallised from alcohol, gave 2 : 3-*dinitro*-4-*nitrosoethylbenzene* in fine yellow crystals, which melted at 80—81° to a dark green liquid (Found : N, 18·5. $C_8H_7O_5N_3$ requires N, 18·7%). The dark green hot alcoholic solution of this compound became yellow on cooling.

2 : 3 : 4-*Trinitroethylbenzene*.—2 : 3-Dinitro-4-nitrosoethylbenzene was heated on the water-bath for 30 minutes with an excess of

nitric acid (*d* 1·42), the solution diluted, and the precipitate crystallised from benzene–light petroleum, 2 : 3 : 4-*trinitroethylbenzene* being obtained in pale yellow plates, m. p. 80° (Found: C, 39·7; H, 2·9; N, 17·2. $C_8H_7O_6N_3$ requires C, 39·8; H, 2·9; N, 17·4%). This compound was also obtained by adding 2 : 3-dinitroethylbenzene (1 g.) slowly to a mixture of nitric acid (*d* 1·5) (1 g.) and sulphuric acid (*d* 1·84) (12 c.c.) and heating the whole at 100° for 2 hours; it separated on cooling and was crystallised as before.

Treated with methylamine as was 3 : 4 : 5-trinitroethylbenzene, it gave 2 : 4-*dinitro*-3-*methylaminoethylbenzene*, which crystallised from dilute alcohol in yellow plates, m. p. 92—93° (Found: C, 48·2; H, 4·8. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9%).

Treated with hydrazine hydrate as described above, it gave 2 : 4-*dinitro*-3-*hydrazinoethylbenzene*, which separated from alcohol in bright orange-red needles, m. p. 149° (Found: C, 42·5; H, 4·5. $C_8H_{10}O_4N_4$ requires C, 42·5; H, 4·5%).

2 : 5-*Dinitro*-4-*nitrosoethylbenzene.*—2 : 5-Dinitro-4-aminoethylbenzene (Brady, Day, and Allam, *loc. cit.*) was oxidised with persulphuric acid in the same way as 2 : 3-dinitro-4-aminoethylbenzene. The precipitate was collected after 4 days and crystallised from alcohol, 2 : 5-*dinitro*-4-*nitrosoethylbenzene* being obtained in small, deep yellow prisms, m. p. 111—112° (Found: N, 18·4. $C_8H_7O_5N_3$ requires N, 18·7%). The hot alcoholic solution was dark yellowish-green and the pure substance melted to a dark green liquid.

2 : 4 : 5-*Trinitroethylbenzene.*—2 : 5-Dinitro-4-nitrosoethylbenzene, on oxidation with nitric acid (*d* 1·42), gave 2 : 4 : 5-*trinitroethylbenzene*, which separated from benzene–light petroleum in light yellow crystals, m. p. 40° (Found: C, 40·0; H, 3·0; N, 17·6. $C_8H_7O_6N_3$ requires C, 39·8; H, 2·9; N, 17·4%).

With methylamine, it gave 2 : 4-*dinitro*-5-*methylaminoethylbenzene*, which crystallised from alcohol in yellow needles, m. p. 149° (Found: C, 48·2; H, 5·0. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9%). With hydrazine, it gave 2 : 4-*dinitro*-5-*hydrazinoethylbenzene*, which crystallised from alcohol in yellow-brown needles, m. p. 141° (Found: C, 42·7; H, 4·6. $C_8H_{10}O_4N_4$ requires C, 42·5; H, 4·5%).

The author wishes to thank Dr. O. L. Brady for his interest in this work.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, December* 23*rd*, 1929.]