31. *The Nitration of Alkyl Benzenes. Part I. The Nitration of* p-*Ethyltoluene.*

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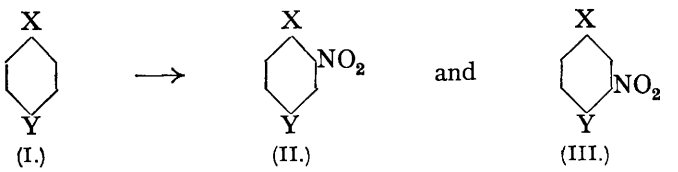
Some years ago (Brady, Day, and Allam, J., 1928, 978) it was announced that an investigation was being made on the influence of alkyl groups in the benzene ring upon the entry of another substituent, particularly the nitro-group. The method of attack suggested was the nitration of *p*-ethyltoluene and similar compounds and we had in mind the determination of the relative amounts of (II) and (III) formed in the mononitration of (I), where X and Y are different alkyl groups.



No pairs of compounds of the type (II) and (III) have been described in the literature and consequently we had to undertake much preliminary synthetic work, not only on, for example, *p*-ethyltoluene, but also on the nitro-derivatives of ethyl- and the higher alkyl-benzenes, these compounds being required for purposes of orientation. The work on ethylbenzene is now sufficiently complete (Cline and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 3150; Brady, Day, and Allam, *loc. cit.*; Day, J., 1930, 252) and some progress has been made with the study of *n*-propylbenzene (Brady and Cunningham, following paper).

Unexpected difficulties arose in the work (*e.g.*, although the nitration of toluene and the xylenes proceeds smoothly, this is very far from being the case where alkyl groups with longer chains are present) and have delayed its completion, but the investigation along similar lines of the nitration of *p-iso*propyltoluene * by Le Fèvre (*Nature*, 1933, 655; J., 1933, 980) makes it desirable to publish our preliminary synthetic work in its present state and to indicate the ideas with which it was started.

Ingold with Hanhart (J., 1927, 997) and Vass (J., 1928, 3125) advanced evidence that the electron-donating power of alkyl groups increases with the length of the carbon chain and that branched chains are more effective than isomeric normal chains. Support is afforded to this view by the decreasing dissociation constants of the fatty acids with increasing length of chain. If the donating power of the group were the sole or dominating factor governing substitution in the benzene ring, ethylbenzene should be more readily nitrated than toluene, *n*-propyl than ethyl, *iso*propyl than *n*-propyl, and so on. It seemed that the relative quantities of (II) and (III) formed in the mononitration of (I) would give a quantitative measure of the relative influences of the groups X and Y on the entry of the nitro-group and that the difficulties of the accurate measurement of nitration velocities would be avoided.

Qualitative experience tended to show that ethyl- and propyl-benzene are not so readily nitrated as toluene and the fact that 4-*iso*propyltoluene is claimed to give only 2-nitro-4-*iso*propyltoluene on nitration (Andrews, *J. Ind. Eng. Chem.*, 1918, **10**, 453) indicated that some other factors must be considered.

We were led to think that the methyl group might be abnormal in its activating effect by observations of previous workers; *e.g.*, Wislicenus (*Annalen*, 1882, **212**, 239) found that the relation between the velocities of reaction of alkyl iodides and ethyl sodioaceto-

* 3-Nitro-4-*iso*propyltoluene has not been described and for the last six months one of us and Patwardan have been attempting its synthesis in quantity.

acetate was Me = 198, Et = 21, *n*-Pr = 5, and Menschutkin (*Z. physikal. Chem.*, 1890, **5**, 589), investigating the velocity of combination of alkyl iodides with triethylamine, found that the relative velocity coefficients were Me = 1140, Et = 10·1, *n*-Pr = 1·9, *n*-butyl = 1·38, *n*-heptyl = 1·08, and *n*-octyl = 1·0. It is remarkable that while the reactivities of ethyl, propyl, etc., derivatives are of the same order, that of the methyl compound stands apart. A possible explanation of these facts may be found in the idea put forward by Bennett and Mosses (J., 1930, 2366). If the methyl group be regarded as a small dipole exerting an electron repulsion towards the remainder of the molecule and along the line of its attachment to it, the force along this same line in the opposite direction outside the group must be of the opposite sign, namely, an electron attraction. By this means these authors explained the abnormally high dissociation constants of acids, *e.g.*, *o*-toluic acid, where, from stereochemical considerations, the methyl group is close to the carboxyl group. In applying this to the alkyl benzenes, much will depend upon the angular direction through which this external electron attraction can be exercised; with toluene, provided this angular direction is not greater than 240° (assuming the angle between the valency directions in benzene to be 120°), the external electron attraction will not affect the ortho-positions, but with ethylbenzene and *iso*propylbenzene the deflection of the methyl group may well bring the ortho-positions within its influence. In *n*-propylbenzene the external field of the CH_2 group would have the same effect, reinforced whenever free rotation brings the methyl group near to the ortho-position.

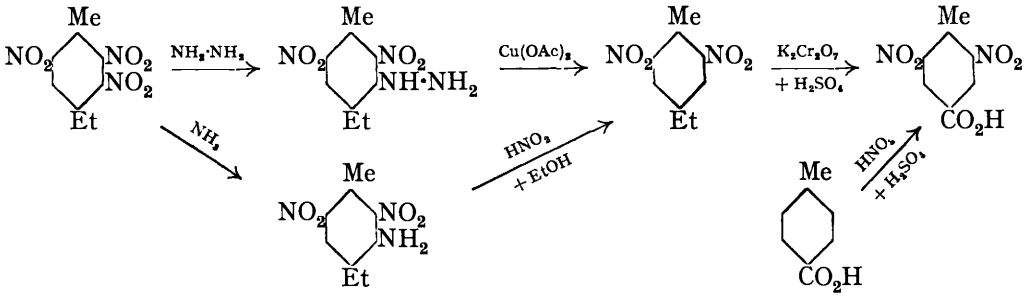
Support is lent to this idea by the fact that *o*-ethylbenzoic acid has a higher dissociation constant ($1{\cdot}7 \times 10^{-4}$) than *o*-toluic acid ($1{\cdot}17 \times 10^{-4}$) instead of the reverse (Pfaff, *Dissert.*, Heidelberg, 1877); purely steric influences could not affect this constant.

There are a number of other experimental facts which are not readily explicable on current theories. For example, in the mononitration of toluene the *m*-nitro-compound is formed to the extent of 4·2—4·5% (Gibson, Duckham, and Fairbairn, J., 1922, **121**, 275): in the further nitration of *m*-nitrotoluene the nitro-group should have less deactivating effect on the 5-position than on the 2-, 4-, or 6-position ortho or para to it; yet substitution occurs in the 2-, 4-, and 6-positions exclusively and no indication of the formation of 3 : 5-dinitrotoluene has been obtained, whereas if the nitro-group had been absent one would have expected 2% substitution in this position. It was with the intention of obtaining further information on points such as the above that the present investigations were started.

On mononitration with a mixture of nitric and sulphuric acids under conditions which ensure complete mononitration of ethylbenzene, *p*-ethyltoluene is only partly nitrated, some 14% being recovered unchanged; at the same time oxidation occurs with the production of *p*-methylacetophenone and *p*-toluic acid. Fractional distillation under reduced pressure brought about a partial separation of the products; *p*-ethyltoluene was recovered from the lowest-boiling fraction, and in all the lower fractions *p*-methylacetophenone was detected through its dinitrophenylhydrazone. The highest-boiling fraction (b. p. 247—249°/760 mm.) consisted essentially of 2-nitro-*p*-ethyltoluene; on oxidation it gave 2-nitro-*p*-toluic acid and on reduction and acetylation 2-acetamido-*p*-ethyltoluene, identified by comparison with a specimen prepared from 3-nitro-4-methylacetophenone. The intermediate fractions appeared to be mixtures and many attempts to isolate 3-nitro-*p*-ethyltoluene were unsuccessful, although there were undoubted indications that it was present. When less drastic conditions, but still sufficient for the complete mononitration of toluene, were employed, a larger amount of *p*-ethyltoluene was recovered unchanged and, although *p*-toluic acid was not found, more *p*-methylacetophenone was produced together with what was probably *p*-tolylacetaldehyde. Owing, probably, to the presence of these compounds prolonged fractionation did not effectively separate the isomerides, so other methods of preparing them were investigated, but from the results of lengthy fractionation experiments there seems no doubt that 2-nitro-*p*-ethyltoluene is the main product of the nitration.

On dinitration *p*-ethyltoluene gave an oil which very slowly deposited about 25% of 2 : 3-dinitro-*p*-ethyltoluene, identified by oxidation to 2 : 3-dinitro-*p*-toluic acid.

On trinitration *p*-ethyltoluene gave an oil which partly solidified; the solid was shown to be 2 : 3 : 6-trinitro-*p*-ethyltoluene by the following series of reactions:



As 2 : 6-dinitro-*p*-ethyltoluene is a solid which can be purified by crystallisation, it provides a source of pure 2-nitro-*p*-ethyltoluene, and the first stage in the preparation has been completed, namely, the reduction to 2-nitro-6-amino-*p*-ethyltoluene.

The loss involved in proceeding first to the trinitro-compound and then removing two nitro-groups led us to attempt a different method of approach *via* 4-methylacetophenone. The commercial product was carefully purified and nitrated to give 3-nitro-4-methylacetophenone (Errera, *Gazzetta*, 1891, **21**, i, 92), which was crystallised and oriented. This provided a compound of known constitution and purity. It was reduced to the amine, which was further reduced by Clemmensen's method to 2-amino-*p*-ethyltoluene; the yield in the latter reduction was very poor (5%) and a direct Clemmensen reduction of 3-nitro-4-methylacetophenone gave no improvement (4·5%). However, this work enabled us to orient with certainty some of the compounds prepared by the direct nitration method. The 2-acetamido-*p*-ethyltoluene obtained in this way was identical with that obtained by the reduction of the 2-nitro-*p*-ethyltoluene formed in the direct nitration. This was of some importance, since experience has shown that differences in the rate of oxidation or reduction of isomerides, together with marked differences in solubility of the products, may lead one to suppose that a mixture of two compounds is a single entity. For example, when mixtures of *o*- and *p*-nitroethylbenzene are reduced, the *p*-compound is attacked much more readily than the *o*- and almost pure *p*-aminoethylbenzene is obtained from the mixture (Cline and Reid, *loc. cit.*).

On oxidation of the lower-boiling fractions obtained from the nitration of *p*-ethyltoluene, only 2-nitro-*p*-toluic acid was isolated, yet on reduction an amine was obtained which gave a benzoyl derivative different from 2-benzamido-*p*-ethyltoluene; further, this same amine gave an acetyl derivative which after crystallisation to constant melting point was still a mixture.

As a result of these preliminary studies we can now see our way to making pure 2- and 3-nitroethyltoluene, the physical constants of which are required for the analysis of the nitration product of *p*-ethyltoluene. Qualitatively our results indicate that more 2- than 3-nitro-*p*-ethyltoluene is formed in the mononitration and that more 2 : 3 : 6- than 2 : 3 : 5-trinitro-*p*-ethyltoluene is formed on trinitration; that is, substitution takes place more readily in the position ortho to the methyl than to the ethyl group.

Experimental.

p-*Ethyltoluene*.—At first a purchased specimen was used, but having found that one batch consisted essentially of *m*-ethyltoluene we decided to prepare the starting material. Commercial 4-methylacetophenone was fractionated under reduced pressure and then at ordinary pressure with an eight-bulb Young column, electrically heated for two-thirds of its length. The fraction used boiled within ½° at 221·5—222°/767 mm., the oxime melted at 88—89° (Widman and Bladin, *Ber.*, 1886, **19**, 587, give m. p. 88°), and the semicarbazone at 207° (Henderson and Cameron, J., 1909, **95**, 973, give m. p. 205°). 4-*Methylacetophenone*-2 : 4-*dinitrophenylhydrazone*, prepared by the addition of the ketone to an alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate (Brady, J., 1931, 757), crystallised from xylene in clusters of red needles, m. p. 256°

(decomp.) (Found : C, 57·9; H, 4·7; N, 17·6. $C_{15}H_{14}O_4N_4$ requires C, 57·3; H, 4·5; N, 17·8%).

Granulated zinc (400 g.) was covered with 5% mercuric chloride solution (1600 c.c.) for 24 hours, the solution then poured off, the amalgamated zinc washed with water and covered with water (300 c.c.), the whole heated to boiling under reflux, and 4-methylacetophenone (100 g.) added in ten portions during 3 hours. After each addition of the ketone 200 c.c. of dilute hydrochloric acid (2000 c.c. of conc. acid and 500 c.c. of water) were added drop by drop. The whole was boiled for a further 3 hours while a further 500 c.c. of acid were added. Unless the concentration of hydrochloric acid is kept high throughout the reduction, polymerised styrenes are produced in quantity. The mixture was diluted with water (500 c.c.) and distilled until 500 c.c. had been collected. The top layer of *p*-ethyltoluene was separated, the aqueous distillate extracted with ether, the extract added to the *p*-ethyltoluene, and the whole dried with potassium carbonate and fractionally distilled with a column; 72 g. of *p*-ethyltoluene were obtained, b. p. 160—161°/748 mm. A test with 2 : 4-dinitrophenylhydrazine sulphate in alcohol indicated the absence of 4-methylacetophenone.

Mononitration. To *p*-ethyltoluene (100 g.), mechanically stirred at 40°, a mixture of nitric acid (50 g., *d* 1·42), nitric acid (24 g., *d* 1·5), and sulphuric acid (95 g., *d* 1·84) was added drop by drop during 90 minutes. The mixture was kept at 50° for 60 minutes, the temperature raised slowly to 95° during a further 60 minutes and held for a further 50 minutes. The mixture was cooled and the top layer was separated, washed with water, taken up in ether, dried with calcium chloride, and distilled under reduced pressure through an eight-bulb Young column (the lower six bulbs being electrically heated). The last fraction to distil solidified on cooling and was found to be *p*-toluic acid by comparison with an authentic specimen (Found : C, 70·3; H, 5·9. Calc. : C, 70·6; H, 5·9%). The first fraction (17 g., b. p. up to 115°/14 mm.) gave on redistillation 14 g. of *p*-ethyltoluene. The remaining fractions, which all contained *p*-toluic acid were combined, diluted with ether, kept over solid potassium carbonate, and refractionated, six fractions being obtained. The rate of distillation was too slow to enable satisfactory temperature readings to be obtained, but the fractions were collected as follows : (1) up to 118°/11 mm., 5 g.; (2) up to 120°/12 mm., 8 g.; (3) up to 120°/11 mm., 6 g.; (4) up to 121°/11 mm., 4 g.; (5) up to 119°/10 mm., 4 g.; (6) without column, 244—250°/755 mm., 8 g. On redistillation, fraction (1) gave 3 g., b. p. 226—228°/760 mm., fraction (2) came over almost entirely at 245—246°/756 mm., and fraction (6) at 247—249°/760 mm. Fractions (1) and (2) on treatment in alcohol with 2 : 4-dinitrophenylhydrazine sulphate gave a red precipitate of 4-methylacetophenonedinitrophenylhydrazone, identified by comparison with a specimen prepared from the ketone. Fractions (3) to (6) gave no such precipitate in 18 hours. The small difference in boiling point between fractions 2 and 6 rendered it unlikely that an effective separation had been achieved.

Examination of fraction (6). This seems to be essentially 2-*nitro*-p-*ethyltoluene*, b. p. 248°/760 mm. (Found : C, 65·4; H, 6·5; N, 8·7. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·7; N, 8·5%). The compound (1 g.) was boiled with nitric acid (40 c.c., *d* 1·4, and 20 c.c. of water) until no oily drops remained; 2-nitro-*p*-toluic acid (0·6 g.) separated on cooling and was identified by comparison with a specimen prepared from *p*-toluic acid (Fittig and Ramsay, *Annalen*, 1873, **168**, 251). The methyl ester was also prepared (Found : C, 55·3; H, 4·6. Calc. : C, 55·4; H, 4·6%) and compared with that prepared from the synthetic 2-nitro-*p*-toluic acid (Noad, *Annalen*, 1847, **63**, 303). The 2-nitro-*p*-ethyltoluene (4 g.) was reduced with tin and hydrochloric acid, 1·65 g. of 2-amino-*p*-ethyltoluene being obtained, b. p. 220—230°/773 mm. With acetic anhydride this gave an acetyl derivative which, after crystallising twice from 40% acetic acid, had m. p. 136°, alone or mixed with 2-acetamido-*p*-ethyltoluene prepared from 3-nitro-4-methylacetophenone (see below). Nitration of the acetyl derivative with ten times its weight of nitric acid (*d* 1·5) at −10° gave 3 : 5-dinitro-2-acetamido-*p*-ethyltoluene, m. p. 176°, identical with that prepared from the 2-acetamido-*p*-ethyltoluene obtained from 3-nitro-4-methylacetophenone.

Examination of fractions (4) *and* (5). These were mixed and reduced with tin and hydrochloric acid. The amine obtained (5 g., b. p. 220—228°) was fractionated and collected at 224—226°/757 mm. (Found : C, 80·0; H, 9·8. Calc. : C, 79·9; H, 9·7%). Benzoylation by the Schotten–Baumann method gave a crude product, m. p. 110—115°, which, crystallised three times from 80% alcohol, gave what was probably 3-*benzamido*-p-*ethyltoluene* in white needles, m. p. 131° (Found : C, 80·2; H, 7·2. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%). We have not yet oriented this compound, but 2-benzamido-*p*-ethyltoluene melts at 119° (see below). Acetylation of the amine with acetic anhydride gave a product, m. p. 114—115°, which on

crystallisation from light petroleum yielded what appeared to be a homogeneous substance consisting of colourless needles, m. p. 118° (Found: C, 74·3; H, 8·6. $C_{11}H_{15}ON$ requires C, 74·5; H, 8·5%). Further crystallisation did not alter the melting point, but the substance probably consists of mixed crystals of 2- and 3-acetamido-*p*-ethyltoluene. 2-Acetamido-*p*-ethyltoluene of undoubted orientation and purity, prepared from 3-nitro-4-methylacetophenone, has m. p. 137° (see below). The above compound (m. p. 114—115°) on dinitration gives a dinitroacetamido-*p*-ethyltoluene of approximately the same m. p. as that of the dinitro-compound obtained from 2-acetamido-*p*-ethyltoluene, but some depression of m. p. occurs in admixture. On hydrolysis, both dinitroacetamido-*p*-ethyltoluenes give dinitroamino-*p*-ethyltoluenes, m. p. 183° (separately or mixed). The separation of the two isomerides by crystallisation is brought about apparently only in the last stage.

Fraction (1) contained a considerable quantity of 4-methylacetophenone and on oxidation gave a mixture of acids which could not be separated.

Part of fraction (2) on oxidation gave 2-nitro-*p*-toluic acid; the rest was reduced and the amine acetylated, but no pure acetyl derivative could be isolated.

Fraction (3) was further nitrated in the hope of obtaining 2 : 3 : 5-trinitro-*p*-ethyltoluene, but only the 2 : 3 : 6-compound could be isolated.

In a second nitration, to *p*-ethyltoluene (45 g.), stirred and heated at 25—30°, was added a mixture of nitric acid (34 g., *d* 1·42), sulphuric acid (61 g., *d* 1·84), and water (5 g.) drop by drop during 90 minutes, and the mixture was kept for a further 90 minutes at 30°. Six experiments were carried out and in each one 10—15 g. of unchanged *p*-ethyltoluene were recovered after a preliminary fractionation and used in the subsequent experiment. The products were worked up and fractionated as before. Sixteen fractions were collected, most of which contained 4-methylacetophenone as indicated by dinitrophenylhydrazine; possibly owing to the presence of this compound, no satisfactory separation was achieved. The boiling points of the various fractions at 10 mm. did not vary by more than 3°. When each of the first three fractions was dissolved in alcohol and fractionally precipitated with dinitrophenylhydrazine sulphate in alcohol, first yellow and then a mixture of red and yellow and finally red crystals were precipitated. The red material was 4-methylacetophenonedinitrophenylhydrazone, m. p. 256°. The yellow substance on recrystallisation from xylene gave yellow plates, m. p. 206° (Found: C, 57·5; H, 4·4; N, 17·8. $C_{15}H_{14}O_4N_4$ requires C, 57·3; H, 4·5; N, 17·8%). When these were mixed with 3-methylacetophenonedinitrophenylhydrazone (m. p. 206—207°), the m. p. was *ca.* 175°. The yellow colour suggests that this compound is *4-methylphenylacetaldehyde-dinitrophenylhydrazone*, since the dinitrophenylhydrazones of benzaldehyde, *p*-tolualdehyde, cuminaldehyde, and of acetophenone and *p*-methylacetophenone are red, but those of phenylacetaldehyde and of phenylpropaldehyde are yellow.

The last three fractions redistilled under ordinary pressure almost completely at 248—250°, the distillate being essentially 2-nitro-*p*-ethyltoluene. Attempts were made to remove the ketone from the middle fractions by treatment with hydroxylamine and sodium hydroxide, but without complete success. After this treatment, however, further fractionation gave a considerable quantity of a product, b. p. 248—250°, which was free from ketone and apparently similar to that obtained above.

Dinitration. *p*-Ethyltoluene (6 g.) was added drop by drop to nitric acid (40 c.c., *d* 1·5) at 20°. The mixture was kept for an hour at room temperature and poured on ice. The oil obtained solidified in a desiccator after a year. The solid (1·75 g.), after crystallisation from 70% alcohol, proved to be 2 : 3-dinitro-*p*-ethyltoluene, m. p. 51·5° (Found: C, 51·7; H, 4·8; N, 13·2. Calc.: C, 51·4; H, 4·8; N, 13·3%). This (0·4 g.) was boiled for 2 hours with potassium dichromate (2 g.), water (10 c.c.), and sulphuric acid (6 c.c.), and the cooled solution extracted with ether. The ethereal solution was extracted with sodium carbonate solution, and the latter acidified with concentrated hydrochloric acid; ether then extracted 2 : 3-dinitro-*p*-toluic acid, m. p. 249° after crystallisation from 20% alcohol (Found: C, 42·4; H, 2·7. Calc.: C, 42·5; H, 2·7%) (Rozanski, *Ber.*, 1889, **22**, 2680). Jannasch and Dieckmann (*Ber.*, 1874, **7**, 1514) described a dinitro-*p*-ethyltoluene, m. p. 52°, but did not orient it.

Trinitration. The trinitration was carried out in three stages. *p*-Ethyltoluene (24 g.) was added drop by drop to a mixture of nitric acid (36 c.c., *d* 1·4) and sulphuric acid (80 c.c. of 80% conc.) at 40°, and the mixture kept at 40—50° for a further 30 minutes, then cooled and separated. The oil was added slowly to a mixture of nitric acid (36 c.c., *d* 1·4) and sulphuric acid (80 c.c., *d* 1·8) at 60°, and the mixture kept at 60° for a further 45 minutes. After cooling, the oil was separated, added slowly to a mixture of nitric acid (28 c.c., *d* 1·5) and sulphuric acid (88 c.c., *d* 1·8) at 70°, and finally heated at 80° for 60 minutes. (At this stage the temperature

must not exceed 80°, otherwise violent oxidation occurs.) The nitro-compound was separated, washed with water, and dissolved in ether, and the solution washed with *N*-sodium carbonate until the washing was free from yellow colour, then with water, dried with calcium chloride, and evaporated. The average yield of crude trinitro-product was equal to the weight of *p*-ethyltoluene taken: loss occurred by oxidation and by the solubility of the nitro-compounds in the spent acids. Somewhat better yields were obtained by using the spent acid from the final nitration, after addition of nitric acid, for the mononitration. The residue partly solidified after some days and was pressed on a porous tile. The solid (40—50% of the total trinitration product), on crystallising from alcohol, gave 2 : 3 : 6-trinitro-*p*-ethyltoluene, m. p. 93° (Found: C, 42·5; H, 3·6; N, 16·7. Calc.: C, 42·4; H, 3·6; N, 16·5%). The waste acid, after several days, deposited a small precipitate which proved to be the same compound. Glinzer and Fittig (*Annalen*, 1865, **136**, 313) described a trinitro-*p*-ethyltoluene, m. p. 92°, but did not orient it. The conversion of the above solid into 2 : 6-dinitro-*p*-ethyltoluene and 2 : 6-dinitro-*p*-toluic acid (see below) establishes that the nitro-groups are in the positions indicated.

The oil (7 g.) absorbed in the tile was recovered by extraction with ether, dissolved in alcohol (100 c.c.), and warmed for 15 minutes with hydrazine hydrate (2 c.c. of 50% solution). On cooling, yellow crystals (1·1 g.) separated which were found to be the hydrazine derived from the above 2 : 3 : 6-trinitro-*p*-ethyltoluene: no hydrazine corresponding to the missing 2 : 3 : 5-trinitro-compound was obtained. The oil extracted from the tile was deficient in nitrogen (Found: N, 15·6. The tri- and the di-nitro-compound require N, 16·5 and 13·3% respectively) and may have contained dinitro-*p*-ethyltoluenes; no ketones or aldehydes were present.

2 : 6-*Dinitro*-p-*ethyltoluene*.—When 2 : 3 : 6-trinitro-*p*-ethyltoluene (1·3 g.) in alcohol (30 c.c.) was heated for 10 minutes with hydrazine hydrate (1 c.c. of 50% solution), a yellow precipitate separated. Crystallised from alcohol, this gave 2 : 6-*dinitro*-3-*hydrazino*-p-*ethyltoluene* in yellow needles, m. p. 171° (decomp.) (Found: C, 45·1; H, 5·2; N, 23·4. $C_9H_{12}O_4N_4$ requires C, 45·0; H, 5·0; N, 23·3%).

2 : 3 : 6-Trinitro-*p*-ethyltoluene (2 g.) in alcohol (50 c.c.) was warmed with aqueous ammonia (10 c.c., *d* 0·88), two more equal quantities of ammonia being added at intervals of an hour. After cooling, the precipitate was collected and crystallised from alcohol, 2 : 6-*dinitro*-3-*amino*-p-*ethyltoluene* being obtained in yellow needles, m. p. 143° (Found: C, 48·1; H, 5·0; N, 19·0. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9; N, 18·7%).

2 : 6-Dinitro-3-hydrazino-*p*-ethyltoluene (0·8 g.) in glacial acetic acid was heated at 100° for 30 minutes with cupric acetate (4 g.), an equal volume of water added, and the whole submitted to steam distillation. The solid which separated from the distillate, on crystallisation from alcohol, gave 2 : 6-*dinitro*-p-*ethyltoluene* in long white needles, m. p. 60° (Found: N, 13·4. $C_9H_{10}O_4N_2$ requires N, 13·3%).

2 : 6-Dinitro-3-amino-*p*-ethyltoluene (0·3 g.) in absolute alcohol (6 c.c.) containing 20% oleum (1·5 c.c.) was heated, and dry sodium nitrite (1 g.) added. After dilution, distillation in steam, and extraction of the distillate with ether, a product was isolated which on crystallisation gave the same 2 : 6-dinitro-*p*-ethyltoluene as that obtained above.

2 : 6-Dinitro-*p*-ethyltoluene (0·45 g.) was boiled for 1½ hours with potassium dichromate (1·7 g.), sulphuric acid (5 c.c., *d* 1·8), and water (10 c.c.), and the mixture was cooled, diluted, and extracted with ether. The ethereal solution was extracted with dilute aqueous sodium carbonate, and the extract acidified with hydrochloric acid. The precipitate (m. p. 158—159°), crystallised from water, gave 2 : 6-dinitro-*p*-toluic acid, m. p. 159°, which was compared with an authentic specimen prepared by the nitration of *p*-toluic acid (Brückner, *Ber.*, 1875, **8**, 1678). Each specimen of the acid (0·5 g.), boiled with silver oxide (0·5 g.) and excess of methyl iodide under reflux for 2 hours, gave the same *methyl* 2 : 6-*dinitro*-p-*toluate*, which crystallised from methyl alcohol in long white needles, m. p. 87—88° (Found: C, 44·7; H, 3·5; N, 11·7. $C_9H_8O_6N_2$ requires C, 45·0; H, 3·4; N, 11·7%).

Other Derivatives from 2 : 3 : 6-*Trinitro*-p-*ethyltoluene*.—2 : 3 : 6-Trinitro-*p*-ethyltoluene (1·5 g.), alcohol (30 c.c.), and methylamine (1·5 g. of 33% solution), boiled for 30 minutes, gave 2 : 6-*dinitro*-3-*methylamino*-p-*ethyltoluene*, which separated from alcohol in yellow plates, m. p. 168° (Found: C, 50·4; H, 5·5; N, 17·7. $C_{10}H_{13}O_4N_3$ requires C, 50·2; H, 5·5; N, 17·6%).

When 2 : 3 : 6-trinitro-*p*-ethyltoluene (2·5 g.) in alcohol (30 c.c.) was boiled for 1½ hours with hydrazine hydrate (4 g. of 50% solution), and the product cooled and acidified with dilute hydrochloric acid, 6-*nitro*-1-*hydroxy*-7-*methyl*-4-*ethyl*-1 : 2 : 3-*benztriazole* was obtained, which separated from 60% alcohol, containing a drop of hydrochloric acid, as a white crystalline powder, m. p. 224° (decomp.) (Found: C, 48·7; H, 4·6; N, 25·2. $C_9H_{10}O_3N_4$ requires C, 48·6; H, 4·6; N, 25·2%).

2-*Nitro*-6-*amino*-p-*ethyltoluene*.—2 : 6-Dinitro-*p*-ethyltoluene (2 g.) in alcohol (20 c.c.) was warmed, and ammonium sulphide (10 c.c. of 15% solution) added in small quantities at a time. The mixture was boiled for an hour and filtered hot. On cooling, yellow crystals separated, which were collected, extracted with boiling 2*N*-hydrochloric acid, and reprecipitated with ammonia. Crystallised from alcohol, these gave 2-*nitro*-6-*amino*-p-*ethyltoluene* in yellow needles, m. p. 96° (Found : C, 60·1; H, 6·7; N, 15·7. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7; N, 15·6%). 2-*Nitro*-6-*acetamido*-p-*ethyltoluene*, prepared by the action of acetic anhydride, crystallised from alcohol in white needles, m. p. 166° (Found : C, 59·5; H, 6·4; N, 12·9. $C_{11}H_{14}O_3N_2$ requires C, 59·4; H, 6·3; N, 12·6%).

3-*Nitro*-4-*methylacetophenone*.—This was prepared by adding 4-methylacetophenone (60 g., purified as described above) drop by drop to nitric acid (400 c.c., *d* 1·5) at 5—10°, diluting the mixture, collecting the product and crystallising it from alcohol; m. p. 61° (Errera, *Gazzetta*, 1891, **21**, i, 92). The *oxime* crystallised from alcohol in prisms, m. p. 133° (Found : C, 55·8; H, 5·2. $C_9H_{10}O_3N_2$ requires C, 55·7; H, 5·2%); the *semicarbazone* from glacial acetic acid as a microcrystalline yellow powder, m. p. 262° (decomp.) (Found : C, 51·3; H, 5·1. $C_{10}H_{12}O_3N_4$ requires C, 50·8; H, 5·1%); and the 2 : 4-*dinitrophenylhydrazone* from xylene in orange-yellow plates, m. p. 232° (Found : C, 50·3; H, 3·6. $C_{15}H_{13}O_6N_5$ requires C, 50·1; H, 3·6%).

3-Nitro-4-methylacetophenone (1 g.) was boiled with nitric acid (15 c.c., *d* 1·4) and water (15 c.c.) for 2½ hours. On cooling, 2-nitro-*p*-toluic acid crystallised; it was identified by comparison with another specimen and by conversion into the methyl ester.

3-*Amino*-4-*methylacetophenone*.—The above compound (36 g.) in alcohol (100 c.c.) was boiled with hydrochloric acid (5 c.c.) and iron filings (34 g.) under reflux for 4 hours. After filtration and evaporation the residual 3-*amino*-4-*methylacetophenone* crystallised from light petroleum in thin white plates, m. p. 80° (Found : C, 72·3; H, 7·5. $C_9H_{11}ON$ requires C, 72·4; H, 7·4%). The same substance was obtained when the nitroacetophenone (2 g.) in alcohol (50 c.c.) was boiled for 2 hours with sodium hydrosulphite (7 g.).

3-*Amino*-4-*methylacetophenone*-2 : 4-*dinitrophenylhydrazone*, prepared in alcohol with 2 : 4-dinitrophenylhydrazine sulphate, contained sulphate, which was removed by treatment with dilute aqueous ammonia; it separated from xylene as a red crystalline powder, m. p. 265° (decomp.) (Found : C, 55·4; H, 4·6; N, 21·2. $C_{15}H_{15}O_4N_5$ requires C, 54·7; H, 4·6; N, 21·3%).

3-*Acetamido*-4-*methylacetophenone*, prepared with acetic anhydride, crystallised from alcohol in long colourless plates, m. p. 142° (Found : C, 69·0; H, 6·9. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8%). 3-*Acetamido*-4-*methylacetophenonesemicarbazone* crystallised from alcohol (4 vols.) –acetic acid (1 vol.) in white needles, m. p. 252° (decomp.) (Found : C, 58·0; H, 6·5. $C_{12}H_{16}O_2N_4$ requires C, 58·0; H, 6·5%), and the 2 : 4-*dinitrophenylhydrazone* from xylene in orange-red crystals, m. p. 280° (decomp.) (Found : C, 55·3; H, 4·7. $C_{17}H_{17}O_5N_5$ requires C, 55·0; H, 4·6%).

2-*Amino*-p-*ethyltoluene*.—A mixture of zinc (200 g., amalgamated as described before and covered with concentrated hydrochloric acid, 200 c.c., and water, 200 c.c.) with 3-nitro-4-methylacetophenone (25 g.) was heated, cautiously until the first reduction of the nitro-group had occurred, under reflux for 6 hours, a further 600 c.c. of hydrochloric acid being added during this time. After cooling, sodium hydroxide (400 g.) in water (600 c.c.) was added, and the mixture distilled in steam. From the distillate, ether extracted 3 g. of 2-amino-*p*-ethyltoluene, b. p. 220—228°/768 mm. Acetylation with acetic anhydride gave the *acetyl* derivative, which was identical with that obtained by nitration of *p*-ethyltoluene and subsequent reduction and acetylation (p. 117), and crystallised from alcohol in white needles, m. p. 137° (Found : C, 74·5; H, 8·4; N, 7·8. $C_{11}H_{15}ON$ requires C, 74·5; H, 8·5; N, 7·9%). Reduction of 3-amino-4-methylacetophenone (25 g.) in an exactly similar manner gave only 1·3 g. of 2-amino-*p*-ethyltoluene, b. p. 224—228°. 2-*Benzamido*-p-*ethyltoluene* crystallised from 80% alcohol in white needles, m. p. 119° (Found : C, 80·2; H, 7·0; N, 6·0. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2; N, 5·9%).

3 : 5-*Dinitro*-2-*acetamido*-p-*ethyltoluene*.—2-Acetamido-*p*-ethyltoluene (1 g.) was added slowly to nitric acid (10 c.c., *d* 1·5) between −5° and −10°. The mixture was kept for 15 minutes and poured on ice, and the precipitate at once well washed with water. Crystallisation first from 50% alcohol and then from acetic anhydride gave 3 : 5-*dinitro*-2-*acetamido*-p-*ethyltoluene* in colourless needles, m. p. 176° (Found : C, 49·8; H, 5·0; N, 15·3. $C_{11}H_{13}O_5N_3$ requires C, 49·4; H, 4·9; N, 15·7%). When this compound (1 g.) was boiled for 3 hours with alcoholic sulphuric acid (acid, 5 c.c., *d* 1·84; water, 5 c.c.; alcohol, 10 c.c.) and cooled, crystals separated

which gave **3 : 5-*dinitro*-2-*amino*-p-*ethyltoluene*** in yellow needles (from alcohol), m. p. 183° (Found : C, 48·0; H, 4·9; N, 18·7. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9; N, 18·7%).

2 : 4-*Dinitrophenylhydrazones of* 2- *and* 3-*Methylacetophenone*.—*o*-Toluic acid (6 g.) in boiling water (600 c.c.) was neutralised with calcium carbonate, and the filtered solution evaporated to dryness. The calcium salt was mixed with calcium acetate (both dried at 120°) and distilled in nitrogen, and the distillate fractionated. The 2-methylacetophenone, collected between 212° and 218°, gave with alcoholic 2 : 4-dinitrophenylhydrazine sulphate, **2-*methylacetophenone*-2 : 4-*dinitrophenylhydrazone***, yellow crystals (from xylene), m. p. 159° (Found : C, 57·8; H, 4·4; N, 17·7. $C_{15}H_{14}O_4N_4$ requires C, 57·3; H, 4·5; N, 17·8%). Similarly, from *m*-toluic acid, **3-*methylacetophenone*-2 : 4-*dinitrophenylhydrazone*** was obtained in orange-red needles (from xylene), m. p. 207° (Found : C, 57·5; H, 4·5; N, 17·6. $C_{15}H_{14}O_4N_4$ requires C, 57·3; H, 4·5; N, 17·8%).

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