

CCCXCIX.—*Pentanitroaniline.*

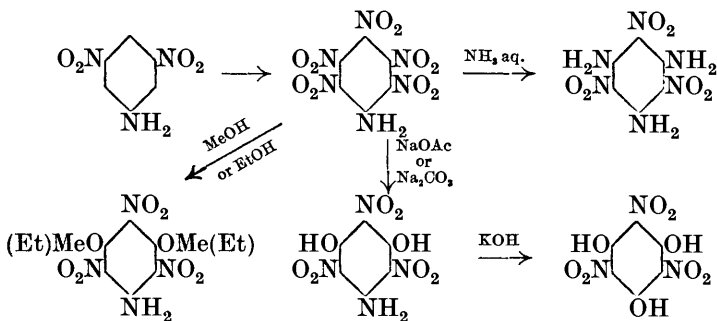
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PRELIMINARY experiments had indicated (Flürscheim and Simon, P., 1910, 26, 81) that when 3 : 5-dinitroaniline is nitrated in mixed acid, "a nitroamine is first formed, which is subsequently converted into a compound which may be pentanitroaniline." At that time, this "compound" had only been obtained in a very impure condition and in very poor yield, so that its nature could not be definitely ascertained. The investigation of this reaction has now again been taken up.

3 : 5-Dinitroaniline and *m*-nitroaniline behave quite differently towards mixed acid. In both cases, nitroamides are primarily formed, but whereas with *m*-nitroaniline these remain in solution (provided that the acid is sufficiently concentrated), so that the first and only product which separates is pure 2 : 3 : 4 : 6-tetranitroaniline, 3 : 5-dinitroaniline gives rise to sparingly soluble nitroamides. Their rearrangement to the corresponding nuclear nitro-derivatives is retarded by their low solubility, and before it can be completed, they decompose—unless special precautions are taken—with violent flashes. When, however, such decomposition is prevented, the colour gradually changes from orange-red to deep yellow, corresponding to a transition of the nitroamides into nearly pure pentanitroaniline. The latter can be obtained quite pure by recrystallisation from benzene; one molecule of benzene is retained at first, but can be easily removed.

In most respects, the chemical and physical properties of pentanitroaniline are similar to those of tetranitroaniline. For instance, both compounds are golden-yellow; both melt with decomposition near 200° (the latter at 216—217°, the former at 192°; heating at the rate of 5° per minute). Both, when dropped into a red-hot crucible, a few centigrams at a time, flash without detonation and with the formation of mere traces of carbon. In both, the nitro-groups in the meta-positions (one in tetranitroaniline, two in pentanitroaniline) are readily replaced, and the amino-group less readily, by the same reagents, corresponding derivatives being formed in either case. In this way, just as numerous penta-substituted derivatives of benzene had become easily accessible by means of tetranitroaniline, many completely substituted benzene derivatives have become available *via* pentanitroaniline. So far,

reactions have been carried out represented by the following formulæ :



These transformations prove that all five nitro-groups are in the nucleus—as was to be expected, since pentanitroaniline has not the properties of a nitroamide.

In two directions only has pentanitroaniline been found to differ essentially from tetranitroaniline: its greater solubility in organic solvents, and its behaviour on acetylation. The table of approximate solubilities given below for 2:4:6-trinitroaniline, tetranitroaniline and pentanitroaniline reveals marked differences and, it seems, no connexion between the number of nitro-groups and the solubility in a given solvent. On acetylation by means of acetic anhydride with a little concentrated sulphuric acid, tetranitroaniline yields its acetyl derivative, but from pentanitroaniline an acetyl derivative is produced in which at least one nitro-group has been replaced. Preliminary tests appear to indicate that this compound does not belong to the series obtained by the removal of *m*-nitro-groups, so that the possibility that acidic reagents may replace a *p*-nitro-group must be examined; it should be remembered that in pentanitroaniline even the *p*-nitro-group has two other nitro-groups adjacent to it.

The work is being continued.

#### EXPERIMENTAL.

*Pentanitroaniline.*—1 Part of 3:5-dinitroaniline, prepared by Flürscheim's modification of Bader's method (*J. pr. Chem.*, 1905, **71**, 537), is dissolved in 20 parts (by volume) of oleum (5%SO<sub>3</sub>), and 1.5 parts (by volume) of nitric acid (*d* 1.52) are added below 20°. The solution is then heated at 70—75° for 3 hours *without shaking or stirring*. In this way the nitroamides remain suspended in a finely divided state, whereas shaking or stirring causes them to cake together, whereupon they usually decompose with a vivid flash.

The spent acid is removed by suction, and the product (nearly pure pentanitroaniline, decomp. 189°) recrystallised from benzene. Up to 3 g. of 3 : 5-dinitroaniline have, so far, been nitrated at a time,\* giving an average yield of 1.5 g. of pure pentanitroaniline (containing 1 mol. of benzene) per 3 g. of 3 : 5-dinitroaniline used. Pentanitroaniline crystallises with 1 mol. of benzene in golden-yellow prisms. Dr. I. Knaggs, of the Davy Faraday Laboratory, who very kindly examined these microscopically, informs us that they are either monoclinic or triclinic, a decision between these alternatives not being feasible without detailed measurements. The ground material, when brought to constant weight by 18 hours' exposure in a vacuum at room temperature, lost 19.6% in weight ( $C_6H_2O_{10}N_6 \cdot C_6H_6$  requires  $C_6H_6$ , 19.7%). The crystals remain unaffected in shape and colour by the loss of benzene, but become opaque. Benzene-free *pentanitroaniline* melts at 192° with rapid decomposition, after darkening to a deep orange at 160—170° (rate of heating 5° per minute) (Found : C, 22.7; H, 0.65; N, 26.45, 26.4.  $C_6H_2O_{10}N_6$  requires C, 22.6; H, 0.6; N, 26.4%). Approximate comparative solubilities are given in the following table :

	2 : 4 : 6-Trinitro- aniline.	Tetranitro- aniline.	Pentanitro- aniline.
Benzene.	0.025 g. in 0.5—1.0 c.c. at 74.5°. Cryst.	0.02 g. in 5—6 c.c. at 74.5°. Cryst.	0.023 g. in less than 0.5 c.c. at 74.5°. Cryst.
Acetic acid.	0.019 g. in 0.25—0.5 c.c. at 75°. Cryst.	0.025 g. in 0.95— 1.2 c.c. at 75°. Cryst.	0.019 g. in less than 0.2 c.c. at 20°. No cryst.
Acetone.	0.030 g. in 0.25—0.4 c.c. at 50°. Cryst.	0.021 g. in 0.25— 0.4 c.c. at 50°. No cryst.	0.024 g. in less than 0.1 c.c. at 20°. No cryst.
H <sub>2</sub> SO <sub>4</sub> (100%).	0.021 g. in less than 0.3 c.c. at 20°. No cryst.	0.020 g. in 4.5— 5.0 c.c. at 75°. Cryst.	0.023 g. in 11.5— 13.5 c.c. at 75°. No cryst.

"Cryst." or "no cryst." indicates whether or no the nitro-compound crystallises on cooling in running water. The lower values, for c.c. used, indicate a deficiency, the higher values an excess, of solvent required for complete solution.

From 3 : 5-dinitroacetanilide a lower yield of pentanitroaniline was obtained than from dinitroaniline itself : 4.5 g. of the acetyl derivative, nitrated in 80 c.c. of sulphuric acid monohydrate with 6.0 c.c. of nitric acid (*d* 1.52) for 6 hours at 65—70°, gave only 0.6 g.

\* An improved method of nitrating 3 : 5-dinitroaniline which we have since found (in which 1 part of this amine in 40 parts by vol. of 100% sulphuric acid and 2.5 parts by vol. of nitric acid, *d* 1.52, is heated to 75° during ½ hour and kept at 75° for 1 hour) avoids the separation of nitroamides altogether, and thereby makes it possible to nitrate any desired amount at a time and gives the improved yield of 0.62 part of pentanitroaniline, immediately pure as it separates from the acid.

of pentanitroaniline; and 12.3 g., nitrated with the same proportions of oleum (5%  $\text{SO}_3$ ) and nitric acid as were used for the amine, gave in 5 hours at 65–70° only 1.5 g. of pentanitroaniline.

2 : 4 : 6-*Trinitro-5-aminoresorcinol*.—To a solution of 0.50 g. of benzene-free pentanitroaniline in 5 c.c. of acetone, an excess of aqueous sodium acetate was added gradually with good shaking. The solution, which turned red with some effervescence, was frequently shaken during  $\frac{1}{2}$  hour, the acetone driven off, and an excess of concentrated hydrochloric acid added to the residue. The yellow precipitate obtained (m. p. 220°, decomp.) crystallised from benzene-alcohol in small deep yellow crystals, m. p. 236–237° (decomp.) (heating, 5° per minute). This compound was obtained in brownish-yellow, fine needles of the same m. p. and mixed m. p. when 1 g. of pentanitroaniline was heated on a water-bath with 10 c.c. of saturated sodium carbonate solution, with subsequent dilution with water, until the separated sodium salt had redissolved, and precipitation with hydrochloric acid. Yield, 0.609 g. of crude material (decomp. 230°), which was recrystallised from water (Found : N, 21.8.  $\text{C}_6\text{H}_4\text{O}_8\text{N}_4$  requires N, 21.5%).

2 : 4 : 6-*Trinitrophenylroglucinol*.—1 G. of benzene-free pentanitroaniline in 10 c.c. of a saturated sodium carbonate solution and 10 c.c. of water was heated until it dissolved, 10 c.c. of 10% aqueous potassium hydroxide were then added, and heating was continued on a water-bath until the evolution of ammonia had ceased. Water was added, to redissolve the separated potassium salt, followed by an excess of hydrochloric acid. After evaporation in a vacuum over sulphuric acid, the compound was extracted with ether (yield, 0.562 g.). Trinitrophenylroglucinol is very soluble in hot water and appreciably soluble in cold water, but it can easily be recrystallised from water by adding a very little hydrochloric acid, whereby the solubility is much reduced. It was thus obtained in characteristic, long, spear-like crystals with an ochre colour, m. p. 167° (in agreement with Jackson and Warren, *Amer. Chem. J.*, 1893, **15**, 615) after prior heating to remove water of crystallisation (Found : N, 16.1. Calc. : N, 16.1%).

2 : 4 : 6-*Trinitro-5-aminoresorcinol Dimethyl Ether*.—Benzene-free pentanitroaniline (2.8 g.) was refluxed for 6 hours with 28 c.c. of dry methyl alcohol and then cooled. A little bicarbonate solution was added to transform traces of free hydroxy-compounds into their salts, and the ether was then precipitated by an excess of water (yield, 1.76 g.; m. p. 125°). After recrystallisation from ethyl acetate-ligroin it had m. p. 127–127.5°, and after further recrystallisation from benzene lemon-yellow needles, m. p. 127.5°, were obtained (Found : C, 33.1; H, 2.8; N, 19.7.  $\text{C}_8\text{H}_8\text{O}_8\text{N}_4$  requires

C, 33.3; H, 2.8; N, 19.4%). A small quantity of a mixture of bicarbonate-soluble hydroxy-compounds was isolated. These must be produced by the action of traces of water during the replacement of the nitro-groups, since the ether, once formed, is not attacked even by boiling aqueous methyl alcohol; from 0.5 g. of the ether, after 2 hours' boiling with 95% methyl alcohol, 0.496 g. was recovered unchanged.

2 : 4 : 6-*Trinitro-5-aminoresorcinol Diethyl Ether*.—This was prepared in a similar manner from 2 g. of benzene-free pentanitroaniline and 20 c.c. of dry ethyl alcohol (yield, 1.176 g.; m. p. 123°). After solution in alcohol, and retreatment with bicarbonate and water as above, the ether had m. p. 125–126°, which became constant at 127.25–127.75° after successive recrystallisations from alcohol and petrol. The product crystallised in yellow blades (Found : C, 38.0; H, 3.9; N, 17.95, 18.1.  $C_{10}H_{12}O_8N_4$  requires C, 38.0; H, 3.8; N, 17.7%). The dimethyl and diethyl ethers have the same melting point; a mixture of the two, however, melts at a lower temperature.

2 : 4 : 6-*Trinitro-1 : 3 : 5-triaminobenzene*.\*—1.000 G. of benzene-free pentanitroaniline was gradually added to 18 c.c. of 10% aqueous ammonia. The material instantly became red, then light brown on shaking. After boiling, an orange-yellow powder (0.670 g.) was obtained corresponding to the description of trinitro-1 : 3 : 5-triaminobenzene given by Jackson and Wing (*Amer. Chem. J.*, 1888, **10**, 282), being insoluble in nearly all solvents, but recrystallisable from aniline, and showing no signs of melting up to 300° (Found : N, 32.6.  $C_6H_6O_6N_6$  requires N, 32.6%). The symmetrical constitution of this compound, involving the adjacency of two nitro-groups to each amino-group, is confirmed by the fact that 0.030 g., dissolved in 1.84 g. of concentrated sulphuric acid, is precipitated by 0.15 g. of water.

*Acetylation of Pentanitroaniline*.—Pentanitroaniline (0.42 g.) did not react with 5 c.c. of acetic anhydride and two drops of concentrated sulphuric acid on heating on a water-bath for 15 minutes, the cooled solution being subsequently poured on ice. When, however, 0.5 g. of benzene-free pentanitroaniline was boiled with 5 c.c. of acetic anhydride and two drops of concentrated sulphuric acid, either for 5 minutes, or better for only a few seconds, followed by immediate water-cooling, the excess of acetic anhydride then being

\* Addendum.—We have since succeeded in reducing this compound to hexa-aminobenzene, a crystalline compound, readily soluble in water, which melts and decomposes at about 255° (rate of heating, 30° per min.), slowly darkens in the air, gives a hexa-acetyl derivative (not melted at 300°) and a triperate, and is characterised by the precipitation of a tetrahydrochloride when 0.2 g. of the base in 3 c.c. of water is added to 10 c.c. of concentrated hydrochloric acid.

mostly removed in a vacuum and the residue mixed with snow, a solid was obtained which crystallised from benzene or from petrol (b. p. 100—120°) in almost colourless, short, sword-shaped crystals of constant m. p. 147—147·5°. Yield (in the case of only brief boiling), 0·25 g. (Found : N, 18·9. A tetranitrodiacetamidophenol,  $C_{10}H_7O_{11}N_5$ , requires N, 18·8%). The nitrogen content of this compound makes it certain that at least one nitro-group has been replaced, but preliminary tests with the small amount available on its behaviour toward sodium acetate and ammonia render it probable that the replaced nitro-group did *not* occupy one of the meta-positions.

*Acetylation of Tetranitroaniline.*—When tetranitroaniline was treated similarly, *viz.*, 0·8 g. boiled for 5 minutes with 8 c.c. of acetic anhydride and three drops of concentrated sulphuric acid, most of the acetic anhydride removed in a vacuum, and snow added, 0·76 g. of crude tetranitroacetanilide, m. p. 163—164° (decomp.) (heating at the rate of 5° per minute), was obtained. This compound, which has been mentioned (P., *loc. cit.*) but not described, forms, on recrystallisation from benzene-glacial acetic acid, slightly yellow, small needles, decomp. 169° (constant) (Found : N, 22·4.  $C_8H_5O_9N_5$  requires N, 22·2%). Acetylation in this case, therefore, is not attended by the removal of a nitro-group.

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