

CCCLV.—*Nitration of Fluorene. 2 : 5-Dinitrofluorene.*

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IN 1876, the hydrocarbon fluorene was nitrated in glacial acetic acid with fuming nitric acid to yield a dinitrofluorene which has been examined since by several investigators who record melting points for this product ranging from 199° to 260° (*Ann. Chim. Phys.*, 1876, **7**, 498; Fittig and Schmitz, *Annalen*, 1878, **193**, 140; Barth and Goldschmidt, *Ber.*, 1878, **11**, 849; Meyer, *ibid.*, 1912, **45**, 1632).

This variation in fusibility suggests that the product is a mixture and we have accordingly attempted to separate its components. On crystallisation from glacial acetic acid, the crude material was apparently homogeneous and decomposed vigorously at 198°, but fractional crystallisation from this solvent led to a separation of two dinitrofluorenes of which the less soluble decomposed energetically at 269° and yielded on oxidation 2 : 7-dinitrofluorenone, a substance of known constitution obtained by Schmidt and Bauer from the corresponding dinitrophenanthraquinone (*Ber.*, 1905, **38**, 3746). This identity characterised the less fusible dinitro-compound as 2 : 7-dinitrofluorene.

The more soluble isomeride, which was present in the crude nitration product to a smaller extent, melted at 207° and on oxidation furnished a dinitrofluorenone of unknown constitution melting at 241°. Since the 2 : 4-, 2 : 7-, and 4 : 5-dinitrofluorenone have been obtained, these orientations of nitro-groups in the new dinitrofluorene are excluded. Moreover, the new product is not identical with the 1 : 8- or 2 : 9-dinitrofluorene already recorded.

When fluorene is nitrated under mild conditions, 2-nitrofluorene is obtained, that is, the phenylene group directs the nitro-group into the other aromatic nucleus in the para-position with respect to the mutual linking of the two benzene rings.

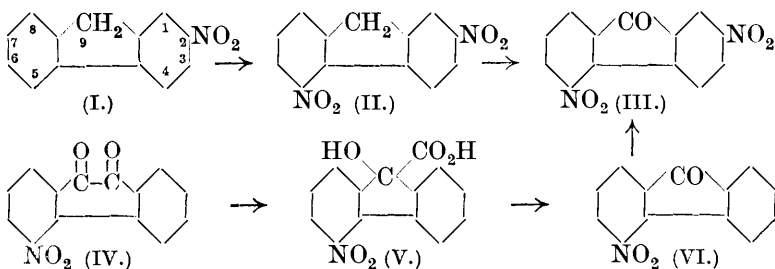
In the dinitration of fluorene, the production of 2-nitrofluorene may be regarded as the first stage. The second nitro-group enters the other ring and, as the phenylene radical rather than the methylene group is the directing influence, the entrant group will go into the ortho- and para-positions. Experiments show that the entry is mainly (85%) into the para-position, giving rise to 2 : 7-dinitrofluorene, but the by-product, the new dinitrofluorene, may result from an entry of the second nitro-group into the 5- or ortho-position, in which case the new isomeride would be 2 : 5-dinitrofluorene.

Carefully purified 2-nitrofluorene was nitrated further in glacial acetic acid, the main product being 2 : 7-dinitrofluorene; there was a smaller proportion of the new dinitrofluorene and some unchanged 2-nitrofluorene. This experiment indicates that one nitro-group in the new dinitrofluorene is in position 2.

To determine the orientation of the second nitro-group, the following synthesis has been carried through: Phenanthraquinone was nitrated and 4-nitrophenanthraquinone (IV) was carefully separated from the isomeric 2-nitrophenanthraquinone and converted into 4-nitrodiphenyleneglycollic acid (V) by the benzil-benzilic acid reaction. The carboxy-acid was decomposed by boiling with water into 4-nitrofluorenone (VI, positions 4 and 5 being identical in the molecule). When 4-nitrofluorenone (VI)

was nitrated, it yielded the new dinitrofluorenone (m. p. 241°), which is thus shown to be 2 : 5-dinitrofluorenone (III). And since this ketone is also obtained by oxidising the new dinitrofluorene, this derivative must be 2 : 5-dinitrofluorene (II).

The demonstration of this constitution is summarised in the following diagram :



#### EXPERIMENTAL.

Ten g. of fluorene were added gradually to 50 c.c. of fuming nitric acid, diluted with 50 c.c. of glacial acetic acid and maintained at the laboratory temperature. The solid product was filtered through glass wool, washed with cold water, and boiled with glacial acetic acid to dissolve the more soluble portion. The solution, filtered from undissolved dinitro-compound, was allowed to crystallise and this fractionation repeated until the more soluble 2 : 5-dinitrofluorene (II) was obtained in long, straw-coloured needles, m. p. 207°. A further quantity of this isomeride was obtained by pouring into water the original nitration liquors, the precipitated solid being crystallised repeatedly from glacial acetic acid (Found : C, 60·8; H, 3·1; N, 11·0. C<sub>13</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub> requires C, 60·9; H, 3·1; N, 10·9%).

The less soluble portion of the above preparation was also crystallised repeatedly from glacial acetic acid; yellow needles of 2 : 7-dinitrofluorene were then obtained which became slightly discoloured at 238° and decomposed vigorously at 269°.

For the purpose of identifying one of its nitro-groups, 2 : 5-dinitrofluorene was also obtained from 2-nitrofluorene (*Ber.*, 1884, 17, 107), the latter nitro-compound being prepared by adding four times the calculated quantity of nitric acid (*d* 1·4) to a cold saturated solution of fluorene in glacial acetic acid. The hydrocarbon separated gradually, but was redissolved by warming on the water-bath. After 12 hours, the nitration mixture gave a practically quantitative yield of 2-nitrofluorene, which was purified by crystallisation from alcohol. 2-Nitrofluorene was added slowly to a mixture of equal volumes of glacial acetic and fuming nitric acids; a yellow solid

then separated consisting of almost pure 2 : 7-dinitrofluorene. The filtrate poured into water gave a precipitate from which 2-nitrofluorene was extracted with hot alcohol. The residue crystallised from glacial acetic acid consisted of 2 : 5-dinitrofluorene (m. p. 207°) identical with the product of direct nitration.

*2 : 5-Dinitrofluorenone.*—2 : 5-Dinitrofluorene dissolved in glacial acetic acid was heated under reflux with chromium trioxide for an hour. The crude ketone separated on cooling and was crystallised from glacial acetic acid, in which it was much less soluble than 2 : 5-dinitrofluorene. It separated in light yellow needles, m. p. 241° (Found : N, 10.55.  $C_{13}H_6O_5N_2$  requires N, 10.6%).

*2 : 7-Dinitrofluorenone* was obtained from 2 : 7-dinitrofluorene as in the preceding oxidation, and crystallised from the same solvent in bright yellow needles, m. p. 290°, identical with the dinitroketone obtained from 2 : 7-dinitrophenanthraquinone (Schmidt and Bauer, *Ber.*, 1905, **38**, 3744). This dinitrofluorenone was also identified by conversion into its oxime (m. p. 285—286°; *loc cit.*).

*2 : 7-Diaminofluorene.*—The dinitro-compound was reduced to the diamine either by tin and hydrochloric acid or by sodium hyposulphite ("hydros").

In the former case, tin, hydrochloric acid, and some platinum foil were added to a suspension of the dinitro-compound in alcohol, and the mixture was heated under reflux until the yellow solid had disappeared. On cooling, a colourless, crystalline stannichloride separated; this, on treatment with sodium hydroxide, liberated the diamine, which was extracted with ether. If a large excess of alcohol was used, the stannichloride remained dissolved; the solution, rendered alkaline with sodium hydroxide, was extracted with benzene to remove the diamine. From ether or benzene, the diamine crystallised in colourless plates, m. p. 165°.

In the "hydros" reduction, 50 g. of sodium hyposulphite were added gradually to 5.4 g. of 2 : 7-dinitrofluorene suspended in 250 c.c. of alcohol diluted with an equal volume of water, the mixture being heated under reflux until the liquor, which reddened at first, became colourless. The alcohol was removed by distillation, and the residue boiled with 100 c.c. of concentrated hydrochloric acid and 100 c.c. of water. The solution was filtered, and the residual solid again boiled repeatedly with dilute acid. The filtrates were combined, cooled with ice, and rendered ammoniacal. The black precipitate was collected and extracted with benzene, and the base was obtained from this solvent in colourless plates which dissolved readily in alcohol or chloroform and developed an olive-green coloration with ferric chloride.

*Acetylation of 2 : 7-Diaminofluorene.*—2 : 7-Diaminofluorene was

dissolved in hot acetic anhydride; the solution, on cooling in ice, yielded *diacetyl-2 : 7-diaminofluorene* as a colourless, crystalline solid which dissolved sparingly in benzene or carbon tetrachloride and separated from the former solvent in colourless, glistening plates, m. p.  $281^{\circ}$  (Found : N, 10.2.  $C_{17}H_{16}O_2N_2$  requires N, 10.0%).

On being poured into water, the acetic anhydride filtrate yielded other acetyl derivatives, which were separated by fractional crystallisation from benzene. The less soluble *triacetyl-2 : 7-diaminofluorene* separated in colourless needles, m. p.  $234^{\circ}$  (Found : N, 8.5.  $C_{19}H_{18}O_3N_2$  requires N, 8.7%). The more soluble *tetraacetyl-2 : 7-diaminofluorene* crystallised from petroleum (b. p.  $80-120^{\circ}$ ) in colourless, iridescent needles, m. p.  $179-181^{\circ}$  (Found : N, 7.7.  $C_{21}H_{20}O_4N_2$  requires N, 7.7%).

The lowering of melting point with the increase of acetyl groups is comparable with the changes of fusibility recorded for the acetyl derivatives of benzidine.

On boiling 2 : 7-diaminofluorene with glacial acetic acid, the main product was diacetyl-2 : 7-diaminofluorene. By heating the diamine with excess of 90% formic acid, a formyl derivative was obtained which separated in glistening, lath-like crystals, m. p.  $272^{\circ}$ .

*2 : 5-Diaminofluorene.*—The reduction of 2 : 5-dinitrofluorene was made with hyposulphite and with tin and hydrochloric acid, the former process giving the purer product.

To 2 g. of the dinitro-compound in 600 c.c. of alcohol and 100 c.c. of hot water were slowly added 20 g. of sodium hyposulphite, the mixture being boiled until the red colour had disappeared. The solution was then treated as in the case of 2 : 7-diaminofluorene. The benzene extract yielded pinkish-white needles, m. p.  $175^{\circ}$ , which dissolved in alcohol and developed an olive-green coloration with ferric chloride (Found : N, 13.9.  $C_{13}H_{12}N_2$  requires N, 14.3%).

The reduction with tin and hydrochloric acid was effected as in the case of the isomeric diamine. The new diamine obtained by ether extraction was accompanied by a tarry impurity which also had basic properties.

*Diacetyl-2 : 5-diaminofluorene*, obtained by heating the diamine with glacial acetic acid, crystallised from methyl alcohol in colourless, transparent, six-sided prisms, m. p.  $289^{\circ}$  (Found : N, 10.5.  $C_{17}H_{16}O_2N_2$  requires N, 10.0%).

*Production of 2 : 5-Dinitrofluorenone from Phenanthraquinone.*—Phenanthraquinone nitrated by Schmidt and Austin's method (*Ber.*, 1903, 36, 3731) yielded 2- and 4-nitrophenanthraquinones, which were separated by fractional crystallisation from glacial acetic acid,

in which the 2-nitro-compound was only sparingly soluble. The more soluble 4-nitrophenanthraquinone (IV) was crystallised from alcohol and converted into 4-nitrodiphenyleneglycollic acid (V) by warming 3.5 g. with 350 c.c. of 10% potassium hydroxide solution for 20 minutes at 65° (Schmidt and Bauer, *Ber.*, 1905, **38**, 3741). The purified 4-nitrodiphenyleneglycollic acid (23 g.) was boiled with 350 c.c. of water, and the solution concentrated to 150 c.c. A mixture of two compounds separated (Schmidt and Bauer, *loc. cit.*); 4-nitrofluorenone (VI) was isolated from this by means of its much greater solubility in glacial acetic acid, and purified by crystallisation from alcohol.

To 4-nitrofluorenone, dissolved in glacial acetic acid, an equal volume of fuming nitric acid was added and the mixture was brought to the boiling point and maintained at 100° for 20 minutes. The nitration mixture was poured into water, and the yellow product crystallised from glacial acetic acid; long, yellow needles of 2 : 5-dinitrofluorenone (III), m. p. 241°, were thus obtained. This preparation did not depress the melting point of the ketone obtained on oxidising 2 : 5-dinitrofluorene.

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