381. Substitution in Polycyclic Systems. Part I. The Nitration of Fluorene and 9-Bromofluorene.

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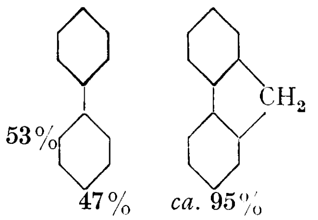
It is generally agreed that mononitration of fluorene gives 2-nitrofluorene in almost quantitative yield. Morgan and Thomason (J., 1926, 2691) isolated 2 : 5-dinitrofluorene, m. p. 207°, and 2 : 7-dinitrofluorene, decomposing at 269°, in preponderating amount. Courtot (*Ann. Chim.*, 1930, **14**, 5) gives m. p. 334° for 2 : 7-dinitrofluorene.

We have repeated the nitration. The 2 : 5-dinitrofluorene melted sharply at 207°. The 2 : 7-dinitrofluorene became discoloured at 275° and decomposed vigorously at 295—300° (depending on the rate of heating). On oxidation with chromic acid the latter isomeride gave pure 2 : 7-dinitrofluorenone, m. p. 292°. The yields (22% of 2 : 5- and 60% of 2 : 7-dinitrofluorene) agree with those recorded by Courtot (23% and 60%). Similar results were obtained when 2-nitrofluorene was nitrated.

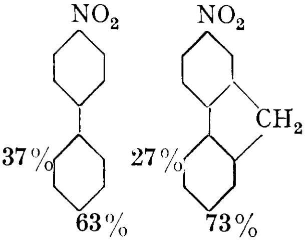
Mild treatment of 9-bromofluorene with nitric acid in acetic anhydride gave 9-bromo-2-nitrofluorene, m. p. 145°, identical with the bromination product of 2-nitrofluorene (Korczynski, Karlowska, and Kierzek, *Bull. Soc. chim.*, 1927, **41**, 70) and yielding 2-nitrofluorenone on oxidation. No isomeride could be isolated. More vigorous treatment with nitric acid in acetic anhydride gave a mixture of dinitro-derivatives, separable by fractional crystallisation from acetone. The less soluble, m. p. 255° (decomp.), gave 2 : 7-dinitrofluorenone on oxidation and was therefore 9-*bromo*-2 : 7-*dinitrofluorene.* The more soluble, m. p. 199°, was similarly identified as 9-*bromo*-2 : 5-*dinitrofluorene.* The same products were obtained by the nitration of 9-bromo-2-nitrofluorene in acetic anhydride.

Nitration in acetic acid was complicated by oxidation and nuclear bromination and led to the isolation of a ketone, $C_{13}H_6O_3NBr$, m. p. 230°. If it is identical with the ketone of the same m. p. obtained by Schmidt and Bauer (*Ber.*, 1905, **38**, 3755) from 7-bromo-2-nitrophenanthraquinone, it must be 7-bromo-2-nitrofluorenone.

On comparing the nitration of fluorene and diphenyl (Gull and Turner, J., 1929, 491), a large difference in the first stage of nitration is seen, fluorene giving much more *p*-compound. We may explain this by supposing that the quasi-aromatic *cyclo*pentadiene ring tends to hold its double bonds, with the result that an orienting polarisation generated by one benzene ring almost always enters the other benzene ring *via* the ortho-carbon atom which is not available for substitution. When a nitro-group is already present, the two types become much more alike with respect to further nitration. This is intelligible on the above assumption, because the conjugation of the nitro-group with the *cyclo*pentadiene double bonds must tend to break up the quasi-aromatic system responsible for the inhibition of *o*-substitution. In diphenyl the first nitro-group increases the para-/ortho-ratio on account of the " direct " (or " field ") effect. In fluorene the ratio is decreased, and we assume that the influence of the disintegration of the quasi-aromatic unit outweighs that of the external field.



First stage of nitration.



Second stage.

EXPERIMENTAL.

Dinitration of Fluorene.—The nitration and the separation of the isomerides were carried out as described by Courtot (*loc. cit.*). The results are recorded above. The 2 : 7-dinitrofluorene remained unchanged in properties after a series of partial extractions with boiling glacial acetic acid and two recrystallisations each from nitrobenzene, nitromethane, acetone, and ethyl acetate.

Identical results were obtained when the nitration was effected by adding fuming nitric acid drop by drop to a solution of fluorene in glacial acetic acid.

Mononitration of 9-*Bromofluorene.*—Nitric acid (1·5 c.c., *d* 1·5) in acetic anhydride (10 c.c.) was added drop by drop to a mechanically stirred suspension of 9-bromofluorene (5 g.) in acetic anhydride (25 c.c.) at 0° After 1 hour, the product was collected, washed with light petroleum, and crystallised from alcohol, forming small colourless needles, m. p. 145° (Found : C, 53·8; H, 2·8; N, 5·1; Br, 27·3. Calc. for $C_{13}H_8O_2NBr$: C, 53·8; H, 2·8; N, 4·8; Br, 27·6%). The yield was 50%.

Oxidation of 9-*Bromo*-2-*nitrofluorene.*—The bromide (1 g.) in glacial acetic acid (10 c.c.) was refluxed with sodium dichromate (5 g.) for 30 minutes. The ketone separated on cooling; recrystallised from acetic acid, it had m. p. and mixed m. p. with 2-nitrofluorenone (obtained from 2-nitrofluorene by a similar oxidation) 221° (Found : C, 69·3; H, 3·1. Calc. : C, 69·3; H, 3·1%).

Dinitration of 9-*Bromofluorene.*—(a) *In acetic anhydride.* Nitric acid (30 c.c., *d* 1·5) in acetic anhydride (50 c.c.) was added slowly to a well-stirred, ice-cooled suspension of 9-bromofluorene (10 g.) in acetic anhydride (30 c.c.). After 2 hours, the mixture was left at room temperature for 15 hours. The solid product was collected and washed with light petroleum. The filtrate was poured into ice-water and the solid obtained from it after prolonged agitation was washed with a little ethyl acetate to remove a coloured impurity. The combined solids were partly dissolved in boiling acetone (100 c.c.) and the insoluble portion, which consisted of almost pure 9-*bromo*-2 : 7-*dinitrofluorene*, was crystallised from the same solvent, separating in long, almost colourless needles, m. p. 255—260° (decomp. into a red liquid) (Found : C, 46·6; H, 2·2; N, 8·3; Br, 23·5. $C_{13}H_7O_4N_2Br$ requires C, 46·6; H, 2·1; N, 8·4; Br, 23·9%). The acetone solution on cooling deposited a further quantity of the same compound (total yield, 60%). The cold solution was filtered and evaporated to dryness and the 9-*bromo*-2 : 5-*dinitrofluorene* obtained was crystallised from ethyl acetate; m. p. 199° (yield, 20%) (Found: C, 46·8; H, 2·2; N, 8·9; Br, 24·7%).

(b) *In glacial acetic acid.* To 9-bromofluorene (5 g.), suspended in glacial acetic acid (25 c.c.) and mechanically stirred at 0°, a mixture of nitric acid (20 c.c., *d* 1·5) and glacial acetic acid (20 c.c.) was added drop by drop during 30 minutes. The temperature was kept at 0° for a further 60 minutes, then raised slowly to 20° and maintained for 5 hours. The product was mixed with ice, and the solid collected, washed with water, and partly dissolved in acetone (20 c.c.). The undissolved portion was crystallised twice from acetone; m. p. and mixed m. p. with 9-bromo-2 : 7-dinitrofluorene 255° (decomp.). The soluble portion was crystallised twice from aqueous acetic acid and once from ethyl acetate; m. p. 230° (Found: C, 51·5; H, 2·2; Br, 26·8. $C_{13}H_6O_3NBr$ requires C, 51·3; H, 2·0; Br, 26·3%).

Oxidation of 9-*Bromo*-2 : 7-*dinitrofluorene*.—The bromide (1 g.) in glacial acetic acid (15 c.c.) was refluxed with sodium dichromate (5 g.) for 2 hours. The solid product was washed with acetic acid and crystallised from the same solvent; m. p. and mixed m. p. with 2 : 7-dinitrofluorenone (obtained from 2 : 7-dinitrofluorene) 292°.

Oxidation of 9-*Bromo*-2 : 5-*dinitrofluorene*.—Oxidation was effected as in the previous example and the product was crystallised from glacial acetic acid; m. p. 241°. It was identical with the ketone obtained from the similar oxidation of 2 : 5-dinitrofluorene (Found: C, 57·9; H, 2·4; N, 10·8. Calc.: C, 57·8; H, 2·2; N, 10·4%).

Nitration of 9-*Bromo*-2-*nitrofluorene*.—The substance (5 g.) in acetic anhydride (20 c.c.) was nitrated with fuming nitric acid (15 c.c.) in acetic anhydride (25 c.c.), and the product treated as described for the direct dinitration of 9-bromofluorene in the same medium; 9-bromo-2 : 5-dinitrofluorene, m. p. 199°, and 9-bromo-2 : 7-dinitrofluorene, decomposing at 255°, were again obtained.

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