

292. *Electrophilic Substitution. Part II.* The Nitration of Naphthalene and Perylene.*

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Naphthalene and perylene have been nitrated with nitric acid in acetic anhydride. The proportions of α - and β -nitronaphthalene have been obtained spectrophotometrically. It has been established that mononitration of perylene yields very largely one isomer, which is believed to be 3-nitroperylene. Aminoperylene has been prepared by reduction of the nitrocompound.

FIERZ-DAVID and SPONAGEL¹ nitrated naphthalene in sulphuric acid and in a mixture of acetic acid and acetic anhydride. By comparing the melting points of the mixtures of mononitronaphthalenes formed with those of synthetic mixtures of the α - and the β -isomer they calculated the ratio of the isomers as $\alpha/\beta = 17.2$. This value compares well with the value, 17.87, quoted by Fedorow and Spryskow² on the basis of spectrophotometric studies. Bavin³ nitrated naphthalene in acetic anhydride, and, using the analytical method of Fierz-David and Sponagel, he deduced that $\alpha/\beta = 15.1$. The method is, however, not accurate; further, the earlier workers, except Bavin, did not use exclusively mononitrating media. The ultraviolet spectra of α - and β -nitronaphthalene differ

* Part I, *J.*, 1956, 164.

¹ Fierz-David and Sponagel, *Helv. Chim. Acta*, 1943, **26**, 98.

² Fedorow and Spryskow, *Chem. Zentr.*, 1935, I, 1423; II, 90; *Z. analyt. Chem.*, 1935, **101**, 188.

³ Bavin, Thesis, London, 1955; *Anilinokrassotschaja Promyschlennost*, 1934, **4**, 103, 627.

appreciably, and it should be possible to determine spectrophotometrically the percentage of the β -isomer in a mixture of the two isomers to within $\pm\frac{1}{2}\%$.

We have nitrated naphthalene with nitric acid in acetic anhydride at 0° , 20° , and 45° , using an excess of the hydrocarbon. Chromatography on alumina was used to free the mixed mononitronaphthalenes from excess of naphthalene and from the small amount of quinones formed ($<2\%$ of the naphthalene which reacted). The ratio $\alpha : \beta$ was determined by comparing the ultraviolet spectra of the mixtures with the spectra of the pure isomers.

Pure α -nitronaphthalene was obtained by recrystallisation and chromatography of commercial α -nitronaphthalene. β -Nitronaphthalene was synthesised from β -naphthylamine *via* the diazonium fluoroborate and was purified in the same way as the α -isomer. Spectra were measured in ethanol solutions, of total nitronaphthalene concentration 20 mg./l. ($1.155 \times 10^{-4}M$), over the range 240—380 $m\mu$, with a Unicam S.P. 500 spectrophotometer. Under these conditions the spectra of synthetic mixtures were reproducible and were additive functions of the percentages of α - and β -isomers. With more dilute solutions ($2 \times 10^{-5}M$) in ethanol, and with solutions in *cyclohexane*, these spectra were not readily reproducible and did not always obey Beer's law. Specimen results are quoted in Table 1.

TABLE 1. *Molar extinction coefficients ($\times 10^{-3}$) measured in $1.155 \times 10^{-4}M$ -solutions in ethanol.*

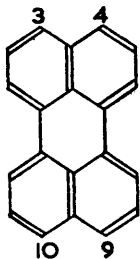
λ ($m\mu$)	α	β	$\alpha + \beta$ at 0°	$\alpha + \beta$ at 20°	$\alpha + \beta$ at 45°
330	4.1	2.3	4.0	4.0	4.0
300	2.4	8.2	2.9	2.9	3.1
260	5.9	23.2	7.6	7.5	7.9
250	8.2	19.6	9.3	9.2	9.5

Our measurements have led us to conclude that, for the nitrations at 0° and 20° , $\alpha/\beta = 10$; for the nitration at 45° the ratio is somewhat lower (see Table 2).

TABLE 2.

Temperature	0°	20°	45°
β -Isomer (%)	9—10	8.5—9.5	11—12
Ratio, $\alpha : \beta$	10 : 1	10 : 1	8 : 1

Examples of the monosubstitution of perylene are rare,⁴ but the hydrocarbon readily undergoes polysubstitution. Di- and tetra-nitration have already been described;⁵ in tetranitroperylene⁶ the nitro-groups occupy positions 3, 4, 9, and 10. Mononitration must therefore occur in the 3-position.



(I)

Perylene has now been mononitrated in acetic anhydride solution, with an excess of hydrocarbon present. The product was chromatographed on alumina to free the nitro-compounds from residual hydrocarbon and a small quantity of quinone by-product. At least 94% of the nitro-compounds formed was shown to consist of a single isomer of m. p. 210—211°, and no other isomer could be isolated.

3-Nitroperylene was rapidly reduced to the corresponding amine with hydrazine hydrate in ethanol in the presence of palladised charcoal, the yield being good. We believe this to be the first recorded instance of the use of palladised charcoal to catalyse the reduction of aromatic nitro-compounds by hydrazine hydrate.

EXPERIMENTAL

Pure α -nitronaphthalene was obtained as yellow needles, m. p. 57.3—58.3°, by recrystallising commercial α -nitronaphthalene twice from alcohol and chromatographing this product on alumina from benzene-light petroleum.

⁴ Zinke, Troger, and Ziegler, *Ber.*, 1940, **73**, 1042.

⁵ Zinke and Unterkreuter, *Monatsh.*, 1919, **40**, 405; Zinke, Funke, and Lorber, *Ber.*, 1927, **60**, 580.

⁶ Zinke, Hirsch, and Brozek, *Monatsh.*, 1929, **51**, 205.

Naphthalene-2-diazonium fluoroborate, prepared from β -naphthylamine,⁷ was converted into β -nitronaphthalene by the method of Hodgson and Marsden;⁸ the crude nitro-compound was purified in the same way as α -nitronaphthalene, giving pale yellow needles, m. p. 77.5—78.2°.

Nitration of Naphthalene.—Nitric acid (0.8 ml.; *d* 1.5) in ice-cold acetic anhydride (5 ml.) was slowly added to a stirred solution of naphthalene (B.D.H. microanalytical standard; 4.00 g.) in acetic anhydride (200 ml.) at 0°; the solution was kept at 0° for 2 days. In other experiments nitration was at 20° and 45°.

The acetic anhydride was hydrolysed in excess of water and the product was extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue was chromatographed in light petroleum four times on 20×4 cm. columns of alumina (Peter Spence, type "H"). In each case as much naphthalene as possible was removed by elution with light petroleum, and the nitronaphthalene band was then eluted with ether. Some quinone (<10 mg.) was left on the columns.

Temperature	0°	20°	45°
$\text{C}_{10}\text{H}_7\text{NO}_2$ (g.)	2.12	2.84	3.04
Yield, % with respect to HNO_3	68	92	99

Perylene.—Perylenetetracarboxylic acid dianhydride, prepared from dinaphthalimide,⁹ was decarboxylated by heating to 400—500° with soda-lime; the hydrocarbon was sublimed and recrystallised from α -methylnaphthalene—light petroleum (b. p. 100—120°), giving golden-yellow plates (50%), m. p. 271—272°.

Nitration of Perylene.—Nitric acid (0.2 ml.; *d* 1.5) in ice-cold acetic anhydride (20 ml.) was slowly added to a stirred solution of perylene (1.04 g.) in acetic anhydride (1.5 l.) at 15°. After 24 hr. the anhydride was hydrolysed in excess of water, and the product was extracted with chloroform (1 l.). The extract was washed with sodium hydrogen carbonate solution and the chloroform was distilled off; the residue was chromatographed in benzene on a 20×4 cm. column of alumina (Peter Spence, type "H"). The yellow perylene band was eluted with light petroleum—benzene (1 : 1), and the nitroperylene was then removed with benzene—alcohol (4 : 1). The nitroperylene was rechromatographed; the column was eluted with benzene—light petroleum, then with benzene, and finally with benzene—alcohol (10 : 1). Several fractions were taken and recrystallised; the mother-liquors were combined and rechromatographed, and fractions were again taken. Only one isomer was found, the brick-red, crystalline 3-nitroperylene, m. p. 210—211° (Found: C, 80.2; H, 3.9; N, 4.6. $\text{C}_{20}\text{H}_{11}\text{O}_2\text{N}$ requires C, 80.8; H, 3.7; N 4.7%). Light absorption max. in EtOH at 295, 347, 459 $\text{m}\mu$ ($\log_{10} \epsilon$ 3.60, 3.57, 4.66). Of 494 mg. of nitroperylene isolated, 467 mg. (94%) were identified by m. p. with this isomer.

Reduction of 3-Nitroperylene.—Hydrazine hydrate (1 ml.) and 5% palladium—charcoal (20—50 mg.) were added to nitroperylene (50 mg.) in boiling alcohol (50 ml.). After 10 min. the solution had become bright yellow; it was filtered and the alcohol distilled off. The residue crystallised from benzene as yellow-brown plates of 3-aminoperylene, m. p. 220—230° (decomp.) (30 mg.) (Found: C, 89.3; H, 5.1; N, 5.3. $\text{C}_{20}\text{H}_{13}\text{N}$ requires C, 89.8; H, 4.9; N, 5.3%). Light absorption max. in EtOH at 261, 325, 462 $\text{m}\mu$ ($\log_{10} \epsilon$ 4.44, 3.66, 4.30).

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⁷ *Org. Reactions*, 5, 193.

⁸ Hodgson and Marsden, *J.*, 1944, 22.

⁹ G.P. 394,794/1921.