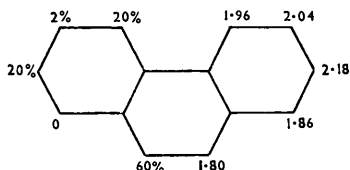


688. *Electrophilic Substitution. Part III.* The Nitration of Phenanthrene.*

By M. J. S. DEWAR and E. W. T. WARFORD.

Nitration of phenanthrene in acetic anhydride has been studied under conditions where mononitrophenanthrenes are almost the sole products; the proportions of isomers in this mixture have been determined by isotope analysis. The results are very much at variance with those reported by Schmidt and Heinle,¹ but agree quite well with the relative reactivities predicted^{2a} on the basis of molecular-orbital theory.

In the first papers of this series,^{2a} Bavin and Dewar drew attention to a serious discrepancy between the predicted reactivities of the various positions in phenanthrene (I) and the



(I)

proportions of isomers which Schmidt and Heinle¹ had reported for its nitration in hot acetic acid. The reactivity numbers † and proportions of isomers are shown in (I). Bavin and Dewar^{2a} were able to show that Schmidt and Heinle's work was unreliable, but their attempts to analyse the mixture of mononitrophenanthrenes by chromatography failed. We have now determined the proportions of isomers quantitatively.

Nitration of phenanthrene containing [9-¹⁴C]phenanthrene gave almost exclusively a mixture of radioactive mononitrophenanthrenes, which were analysed by isotope dilution analysis, using inactive specimens of the five mononitrophenanthrenes prepared according to Bavin and Dewar.^{2b} The nitrations were carried out at three different temperatures, with a large excess of phenanthrene to avoid formation of by-products.¹ Our results are shown in the annexed Table. The propor-

Temp. nitration	Proportions of isomers (%)				
	1-	2-	3-	4-	9-
0°	27.1	4.0	25.4	—	34.2
25	26.2	6.8	21.8	5.6	36.1
35	24.7	5.3	22.9	—	33.4

tions of isomers are quite different from those reported by Schmidt and Heinle;¹ in particular the 9- and the 1-position differ little in reactivity, as one would predict from

* Part II, *J.*, 1956, 1441.

† The reactivity number of position 3 was wrongly given as 2.07 in Part I.

¹ Schmidt and Heinle, *Ber.*, 1911, **44**, 1448.

² Bavin and Dewar, (a) *J.*, 1956, 167; (b) 1955, 4477.

the reactivity numbers (see I). Schmidt and Heinle stated that, despite a careful search, they could find no trace of 1-nitrophenanthrene in their nitration product.

The ratio (*ca.* 7) of reactivities at the most reactive (9-) and the least reactive (2-) position is also satisfactory; the difference (0.36) between the reactivity numbers of these positions is almost the same as that (0.31) between the α - and the β -position of naphthalene where the corresponding isomer³ ratio is about 9.

The 4-position shows a lower reactivity than predicted, but this can reasonably be ascribed to steric hindrance; even in phenanthrene itself there is appreciable hindrance between the 4- and the 5-hydrogen atom. The relatively high reactivity of the 3-position is unexpected and more difficult to explain; part of it could be ascribed to steric hindrance in the α -naphthalenic 1- and 9-position in phenanthrene, as opposed to the lack of hindrance in the β -naphthalenic 3-position.

The proportions of isomers do not seem to vary much with temperature. Unfortunately the proportion of 4-nitrophenanthrene could not be determined directly at 0° and 35° for lack of synthetic material; the synthesis of this isomer is very troublesome.

EXPERIMENTAL

[9-¹⁴C]Phenanthrene.—The radioactive phenanthrene was prepared from fluorene and Ba¹⁴CO₃ by Collins's method.⁴ 9-Fluorenylmethanol was cyclised very conveniently with hot polyphosphoric acid. The radioactive phenanthrene was diluted with pure phenanthrene to an activity of *ca.* 20,000 counts min⁻¹, mg.⁻¹.

Mononitrophenanthrenes.—These were prepared according to Bavin and Dewar.^{2b}

Nitration of [9-¹⁴C]Phenanthrene.—(a) *At 0°.* [9-¹⁴C]Phenanthrene (10.353 g.; 18,150 counts min⁻¹ mg.⁻¹) was dissolved in redistilled acetic anhydride (500 ml.) at 0°. A solution of nitric acid (0.5 ml.; *d* 1.5) in acetic anhydride (20 ml.), cooled to 0°, was added during 10 min. with stirring. Stirring was continued at 0° for 8 hr., and the solution was then hydrolysed with water (3 l.) containing sulphuric acid (4 ml.). The pale yellow crystalline residue was isolated with chloroform and chromatographed from light petroleum (b. p. 40–60°). The mononitrophenanthrene fraction was eluted with ether, and the chromatographic purification then repeated twice. The first runs from the columns gave unchanged phenanthrene (9.913 g.). The mixed mononitrophenanthrenes (0.152 g.) were used for isotope dilution analysis. The only other product was a trace of coloured material which adhered strongly to alumina.

(b) *At 25°.* Nitric acid (0.25 ml.; *d* 1.5) in acetic anhydride (5 ml.) was added during 4 min. to a well-stirred solution of phenanthrene (9.552 g.; 18,150 counts min⁻¹ mg.⁻¹) in acetic anhydride (300 ml.) at 25°, and the mixed mononitrophenanthrenes (0.374 g.) isolated as above.

(c) *At 35°.* The nitration was carried out as at 25°, with similar volumes of nitric acid and acetic anhydride, and 9.809 g. of phenanthrene; the mixed mononitrophenanthrenes weighed 0.622 g. In this case appreciably more of the coloured by-product was formed than at the lower temperature.

Estimation of Radio-carbon.—The specific activities of samples of [9-¹⁴C]phenanthrene and the isomers obtained by nitration were found by converting the organic compound into carbon dioxide by the Van Slyke wet combustion method.⁵ The active carbon dioxide was introduced into a Geiger-Müller gas-counting tube containing argon and ethanol, and the filling was counted in the Geiger region.⁶

A modified Van Slyke mixture (potassium iodate omitted) generally gave consistent values of carbon dioxide (based on theoretical yield) of <96% for 2–5 mg. samples which had been boiled gently for 4 min. at <1 mm. It was noticed, however, that 9-nitrophenanthrene required a longer combustion period and also gave a greater percentage spread when counted. It is possible that the carbon attached to the nitro-group is not split off with ease, and, should it be radioactive (as in the 9-isomer), a considerable error will result.

The Geiger-Müller gas-counting tubes (50 ml.; 20th Century Electronics Ltd.) had satisfactory characteristics at low pressures of carbon dioxide when filled with argon (3.0 cm.) and ethanol (1.5 cm.). At 1 cm. of carbon dioxide (used in these experiments) a plateau of 200–280 v with a slope of 5% per 100 v was obtained. Maximum consistency was achieved by making a rough determination of the plateau for each sample and counting at 100 v above the starting

³ Dewar and Mole, *J.*, 1956, 1441.

⁴ Collins, *J. Amer. Chem. Soc.*, 1948, **70**, 2418.

⁵ Van Slyke and Folch, *J. Biol. Chem.*, 1940, **136**, 509.

⁶ Broda and Feldstein, *Nature*, 1951, **168**, 4275.

voltage (approx. 1150 v). The apparatus and counting tubes were kept in an atmosphere of inactive carbon dioxide when idle, to avoid memory effects.

Isotope Dilution Analysis.—The mixture of mononitrophenanthrenes from a nitration was dissolved in acetone. Portions of the solution were used for analysis for individual isomers. The weighed residue left on evaporation was diluted with a weighed quantity (about four times its weight) of a synthetic inactive isomer, and a pure specimen of the isomer recovered from the mixture by repeated recrystallisation from ethanol. Recrystallisation was continued until the radioactivity of the sample was constant; about ten recrystallisations were normally sufficient. The complete analysis of the 25° nitration product (see Table) shows this procedure to have been sufficient; radioactive contamination would lead to a high estimate for the concentration of a given isomer, but the sum of the individual percentages is less than 100%. Fuller details of the combustion of samples and of the method of isotope dilution analysis are given elsewhere.⁷

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.

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⁷ Warford, M.Sc. Thesis, London, 1954; Ph.D. Thesis, London, 1956.
