690. *Electrophilic Substitution. Part V.* Competitive Nitrations.*

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Competitive nitrations have been carried out in order to determine the reactivities of several unsubsituted polycyclic aromatic hydrocarbons relative to one another.

A theory which correlates the structure of aromatic hydrocarbons with their reactivity towards substitution must predict, first, the isomeric distribution of substitution products and, secondly, the reactivities of the hydrocarbons relative to one another. This paper, which forms part of a systematic study of the mononitration of polycyclic hydrocarbons by nitric acid in acetic anhydride, deals with the second of these problems. Competitive nitrations of naphthalene and phenanthrene with each other and with benzene, pyrene, triphenylene, and chrysene, and of naphthalene with perylene, benzo[*a*]pyrene, anthanthrene, and coronene, are described. Phenanthrene has also been nitrated in competition with diphenyl.

The competitive method of comparing reaction rates does not require an accurate knowledge of the reaction kinetics, provided we assume that both hydrocarbons are nitrated by the same nitrating agent or agents, and that the rates of nitration are of the first order with respect to the hydrocarbon concentrations. Then, for the reaction of the nitrating agent, X, with hydrocarbons HC_1 and HC_2 at time t, we have

$$\left.\begin{aligned} d[HC_1]_t/dt &= -k_1[X]_t^n[HC_1]_t \\ d[HC_2]_t/dt &= -k_2[X]_t^n[HC_2]_t \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the order of reaction with respect to X. Hence

$$d[HC_1]_t/d[HC_2]_t = k_1[HC_1]_t/k_2[HC_2]_t \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If another nitrating agent, X′, is also active and the ratio k_1'/k_2' of the corresponding rate constants is equal to k_1/k_2, equation (2) still holds.

The justification for the assumptions of the previous paragraph lies in the reproducibility of results. Given the ratios k_1/k_2 and k_1/k_3, we can predict k_2/k_3 correctly to an accuracy of $\pm 50\%$, which is satisfactory as a test of theory in view of the wide experimental range of reactivity ($10^5 : 1$).

Integrating equation (2) from $t = 0$ to $t = T$, the time when the reaction is stopped, we have:

$$k_1/k_2 = (\log_{10}[HC_1]_0 - \log_{10}[HC_1]_T)/(\log_{10}[HC_2]_0 - \log_{10}[HC_2]_T) \quad . \quad . \quad (3)$$

If the only products formed from the hydrocarbons are their nitro-derivatives, equation (3) can be written in the form

$$\frac{k_1}{k_2} = \frac{\log_{10}[HC_1]_0 - \log_{10}([HC_1]_0 - [N_1])}{\log_{10}[HC_2]_0 - \log_{10}([HC_2]_0 - [N_2])} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $[N_1]$ and $[N_2]$ are the concentrations of the nitro-derivatives of HC_1 and HC_2 respectively. The equation can be written thus reasonably, since under the conditions employed very little quinone is formed as by-product ($<2\%$ in the case of naphthalene,[1] for instance) and since approximately 95% of the material can be recovered as unchanged hydrocarbon and nitro-compounds; no doubt much of the small loss is due to imperfect mechanical handling.

* Part IV, preceding paper.

[1] Dewar and Mole, *J.*, 1956, 1441.

Since the volume in which all reactants and products are contained is constant throughout, equation (4) can be written in the equivalent form

$$\frac{k_1}{k_2} = \frac{\log_{10}(HC_1)_0 - \log_{10}\{(HC_1)_0 - (N_1)\}}{\log_{10}(HC_2)_0 - \log_{10}\{(HC_2)_0 - (N_2)\}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $(HC_1)_0$, etc., represent the molar amounts of substances used or formed in the experiment. The concentration of nitric acid does not enter into this expression and therefore does not need to be known. It is of course necessary to ensure that appreciable amounts of each hydrocarbon remain unchanged; this was the case in each of the experiments described below.

The problem then resolves itself into one of estimating the amounts of the nitro-compounds of each hydrocarbon in the products of the competitive nitrations. In some cases (experiments *a*—*e*) it was possible to separate the nitro-compounds from each other and from the parent hydrocarbons by chromatography and by making use of the low solubilities of the higher hydrocarbons and their nitro-compounds. In the benzene–phenanthrene experiment (*f*) the nitrobenzene was isolated as a mixture with unchanged phenanthrene and was estimated by microdetermination of nitrogen in the mixture. In experiments (*g*—*m*) the nitro-derivatives could not be separated from each other

Hydrocarbon (HC)	$k_{(HC)}/k_{(X)}$ relative to naphthalene	$k_{(HC)}/k_{(X)}$ relative to phenanthrene	Hydrocarbon (HC)	$k_{(HC)}/k_{(X)}$ relative to naphthalene
Benzene *	0·0025	0·0026	Perylene	150
Diphenyl	—	0·042	Benzo[*a*]pyrene	64
Pyrene	29	29	Anthanthrene	290
Triphenylene	4·4	2·3	Coronene	6·9 †
Chrysene	4·1	2·6		

* The volatility of nitrobenzene made it difficult to obtain accurate results for competitive nitrations with benzene.

† At room temperature.

conveniently, but the mixture of nitro-compounds could be separated from the parent hydrocarbons. The compositions of the mixtures and hence the quantities of nitro-compounds formed were determined by analysis or from the radioactivity of the mixtures, by using [9-^{14}C]phenanthrene in the competitive nitrations.[2] In the naphthalene–coronene experiment (*n*) the nitronaphthalenes could be isolated but it was not possible to separate the nitrocoronene from coronene completely. The nitrocoronene was determined as a mixture with coronene by analysis.

It was found that the ratio k(phenanthrene)/k(naphthalene) = 1·3 : 1. The results of the other experiments are summarised in the Table. Their significance will be discussed in a later paper.

In passing we draw attention to an improvement in the Mannich synthesis of triphenylene. This consists in distilling the condensation product and pouring the distillate into acetone, thereby separating dodecahydrotriphenylene from acetone-soluble impurities.

Experimental

Some microanalyses were carried out by Imperial College microanalytical laboratory. Where an analysis has been used to give quantitative results, the figures quoted are the mean of two or more self-consistent determinations.

Peter Spence type " H " alumina was used for chromatography; chromatographic solvents were distilled. Unless otherwise stated, columns were approximately 20 × 4 cm. Where fuller details are not given nitro-compounds were freed from the parent hydrocarbons and quinone by-products by chromatography on alumina from light petroleum (b. p. 40—60°) or benzene–light petroleum until the front of the nitro-compound bands was washed three-quarters of the way down the column. The nitro-compounds were then eluted with ether, which eluted

[2] Dewar and Warford, *J.*, 1956, 3570.

quinones only very slowly. This procedure usually had to be repeated five or six times to remove the last trace of hydrocarbon. The development of the columns could be followed by virtue of the colour of the nitro-compounds and the fluorescence of the hydrocarbons and nitro-compounds under ultraviolet light.

Materials.—Unless otherwise stated, these were from British Drug Houses Limited. Diphenyl (m. p. 69·5—70·5°), pyrene, benzo[*a*]pyrene (from Messrs. Lights; m. p. 176—177°), coronene (kindly given by Imperial Chemical Industries Limited), naphthalene (microanalytical standard), fuming nitric acid (*d* 1·5), and acetic anhydride were not purified before use. Benzene (for molecular-weight determination) was shaken with sulphuric acid to remove thiophen. Phenanthrene was freed from anthracene by treatment with maleic anhydride.[3] Commercial chrysene was purified by chromatography and recrystallisation from benzene–light petroleum. Perylene [1] and anthanthrene [4] were prepared and purified as described earlier.

*Triphenylene.—cyclo*Hexanone (400 ml.) was condensed by Mannich's method.[5] The product was poured into water and extracted with benzene; the extract was distilled. The syrupy fraction, b. p. 160/0·3 mm., was collected, poured into acetone (100 ml.), and stirred, giving dodecahydrotriphenylene (37 g., 10·5%), m. p. 180—210°. Dehydrogenation [6] by 5% palladised charcoal at 400°, followed by chromatography, gave triphenylene (65%), m. p. 190—194°. The m. p. was raised to 195·5—196·5° by decomposition of the recrystallised picrate on an alumina column.

Estimation of [9-^{14}C]*Nitrophenanthrene.*—These estimations were carried out, as described in Part III,[2] by wet combustion to carbon dioxide, which was then counted in a gas-filled Geiger tube containing argon–alcohol. Mononitro-compounds of naphthalene, diphenyl, triphenylene, chrysene, and pyrene were analysed satisfactorily in this manner.

Competitive Nitrations.—(a) *Naphthalene–pyrene.* Fuming nitric acid (0·13 ml.) in ice-cold acetic anhydride (20 ml.) was added to a solution of pyrene (0·636 g.) and naphthalene (8·741 g.) in acetic anhydride (300 ml.) at 0°. The solution was stirred for 2 hr. at 0° and then left overnight at 2°. The acetic anhydride was hydrolysed in water (2 l.) containing sulphuric acid (2 ml.); the mixture was extracted with chloroform (500 ml.), and the extract was washed with water, potassium hydrogen carbonate solution, and water. The chloroform was distilled off, the residue was dissolved in benzene, and the parent hydrocarbons were then removed by chromatography four times from light petroleum containing 5% of benzene. The mixture of nitro-compounds was then taken up in benzene and eluted from a column (12 × 3 cm.), first with light petroleum (2 l.) to remove the last traces of hydrocarbon, then with light petroleum (7 l.) containing 15% of benzene, which eluted nitronaphthalenes (55·9 mg.) (Found: N, 7·9. Calc. for $C_{10}H_7O_2N$: N, 8·1%), and finally with ether (1·5 l.), which removed nitropyrene (99·2 mg.) (Found: N, 5·7. Calc. for $C_{16}H_9O_2N$: N, 5·6%). These weights of products in conjunction with equation (3) lead to the value k(HC)/k(naphthalene) = 29 (see Table). Bavin [7] reports a value 30 : 1.

(b) *Naphthalene–chrysene.* Fuming nitric acid (2 ml.) in ice-cold acetic anhydride (20 ml.) was added to a solution of chrysene (0·546 g.) and naphthalene (1·781 g.) in acetic anhydride (2 l.) at 0°. The nitration was continued as in the previous experiment. After removal of the chloroform, the residue was chromatographed three times from 1 : 1 benzene–light petroleum in order to remove naphthalene and part of the chrysene. The residue from the third column was chromatographed; the column was eluted first with 1 : 1 benzene–light petroleum to remove hydrocarbon and then with ether to remove first the pale yellow band of nitronaphthalenes (contaminated by much chrysene) and then the deeper yellow nitrochrysene band. The residue from the nitrochrysene eluate was chromatographed twice from 1 : 1 benzene–light petroleum (to remove traces of chrysene), yielding nitrochrysenes as a partially crystalline, yellow solid (0·287 g.) (Found: C, 79·1; H, 4·3; N, 5·0. Calc. for $C_{18}H_{11}O_2N$: C, 79·1; H, 4·1; N, 5·0%). The residue from the pale yellow eluate was extracted with ether (2 × 50 ml.). Chrysene was filtered off and the residue from the extract was chromatographed twice from light petroleum containing 10% of benzene, giving nitronaphthalenes as pale yellow crystals (0·363 g.) (Found: N, 8·6%).

(c) *Naphthalene–benzo*[a]*pyrene.* Fuming nitric acid (0·4 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of naphthalene (13·222 g.) and benzo[*a*]pyrene (0·407 g.) in

[3] Bavin and Dewar, *J.*, 1956, 164.
[4] Dewar, Mole, Urch, and Warford, preceding paper.
[5] Mannich, *Ber.*, 1907, **40**, 163.
[6] Diels and Karstens, *Ber.*, 1927, **60**, 2323; Bavin and Dewar, *J.*, 1955, 4479.
[7] Bavin, Ph.D. Thesis, London, 1955.

acetic anhydride (700 ml.) at 0°; the nitration was continued and chromatography was effected as in experiment (*b*). Nitronaphthalene was obtained crystalline (0·170 g.) (Found: N, 7·9%). Two bands of nitrobenzopyrene [4] were separated by chromatography: (i) 6-Nitrobenzo[*a*]pyrene (Ring Index numbering) (0·177 g.) (Found: N, 4·5. Calc. for $C_{20}H_{11}O_2N$: N, 4·7%), m. p. 252—254°; and (ii) an orange solid (0·041 g.) (Found: N, 4·6%), m. p. 175—210°.

(d) *Naphthalene–anthanthrene.* Fuming nitric acid (0·3 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of naphthalene (17·600 g.) and anthanthrene (0·136 g.) in acetic anhydride (1·5 l.) at 0°. The experiment was continued in a way very similar to that described for experiment (b). Nitronaphthalene was isolated crystalline (35 mg.) (Found: N, 7·9%). Two nitroanthanthrene bands were separated by chromatography: (i) brown needles (39 mg.) (Found: N, 4·2. Calc. for $C_{22}H_{11}O_2N$: N, 4·4%); and (ii) a red solid (34 mg.) (Found: N, 4·3%).

(e) *Naphthalene–perylene.* Fuming nitric acid (1 ml.) in ice-cold acetic anhydride was added to a solution of perylene (0·972 g.) and naphthalene (18·052 g.) in acetic anhydride (1·5 l.) at 0°. The experiment was continued as described in experiment (b), giving nitronaphthalenes as pale yellow crystals (0·188 g.) (Found: N, 8·0%) and nitroperylene [1] as red crystals (0·750 mg.), m. p. 208—210° (Found: N, 4·9. Calc. for $C_{20}H_{11}O_2N$: N, 4·7%).

(f) *Benzene–phenanthrene.* Fuming nitric acid (2·5 ml.) in ice-cold acetic anhydride (20 ml.) was added to a solution of benzene (169 g.) and phenanthrene (0·876 g.) in acetic anhydride (600 ml.) at 0°. The solution was stirred at 0° for 2 hr. and then stored at 2° overnight. The acetic anhydride was hydrolysed in water (2 l.) containing sulphuric acid (2 ml.), and the mixture was extracted with light petroleum (b. p. 40—60°; 500 ml.). The extract was washed with potassium hydrogen carbonate solution and dried (Na_2SO_4). All except 50 ml. of the solvent was distilled through a Dixon gauze ring column, and the residue was chromatographed. The column was eluted first with light petroleum (400 ml.) to remove benzene, next with 1 : 1 light petroleum–ether (350 ml.) to remove nitrobenzene, phenanthrene, and, probably, a little benzene, and finally with ether (500 ml.) to remove nitrophenanthrenes (0·192 g.) (Found: N, 6·2. Calc. for $C_{12}H_9O_2N$: N, 6·2%). As much of the solvent as possible was distilled from the second eluate; microanalysis of the residue (0·971 g.) (Found: N, 1·7, 1·8, 1·9%) indicated a nitrobenzene content of 0·151 g.

(g) *Phenanthrene–*[9-^{14}C]*diphenyl.* Fuming nitric acid (0·4 ml.) in ice-cold acetic anhydride (30 ml.) was added to a solution of [9-^{14}C]phenanthrene (0·955 g.; 17,240 counts min.$^{-1}$ mg.$^{-1}$) and diphenyl (6·293 g.) in acetic anhydride (300 ml.) at 0°. The acetic anhydride was hydrolysed in water (3 l.) containing sulphuric acid (5 ml.); the mixture was extracted with chloroform (500 ml.), and the extract was washed with potassium hydrogen carbonate solution and dried (Na_2SO_4). The chloroform was distilled and the residue was chromatographed six times from light petroleum, yielding a pale yellow paste of mixed nitro-compounds (0·331 g., 11,150 counts min.$^{-1}$ mg.$^{-1}$, indicating a nitro[9-^{14}C]phenanthrene content of 0·253 g.; the sample of the mixture for combustion was weighed as an oil in order to ensure homogeneity).

(h) [9-^{14}C]*Phenanthrene–pyrene.* Fuming nitric acid (0·2 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of [9-^{14}C]phenanthrene (4·784 g.; 5709 counts min.$^{-1}$ mg.$^{-1}$) and pyrene (0·398 g.) in acetic anhydride (250 ml.) at 0°. The experiment was continued as in experiment (g); after chromatography 5 times from 1 : 4 benzene–light petroleum, a mixture of nitropyrene and nitrophenanthrenes was obtained as a golden-yellow, partially crystalline solid (0·526 g.) (1802 counts min.$^{-1}$ mg.$^{-1}$, indicating a nitrophenanthrene content of 0·210 g.).

(i) [9-^{14}C]*Phenanthrene–chrysene.* Fuming nitric acid (1·5 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of chrysene (0·508 g.) and phenanthrene (1·777 g.; 5709 counts min.$^{-1}$ mg.$^{-1}$) in acetic anhydride (1·3 l.) at 0°. Treatment of the product as in experiment (h) yielded the mixture of nitro-compounds as a pale yellow solid (0·564 g.; 2322 counts min.$^{-1}$ mg.$^{-1}$, indicating a nitrophenanthrene content of 0·287 g.).

(j) [9-^{14}C]*Phenanthrene–triphenylene.* Fuming nitric acid (0·6 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of phenanthrene (2·751 g.; 7800 counts min.$^{-1}$ mg.$^{-1}$) and triphenylene (0·941 g.) in acetic anhydride (400 ml.) at 0°. The solid mixture of nitro-compounds (0·923 g.; 3710 counts min.$^{-1}$ mg.$^{-1}$, indicating a nitrophenanthrene content of 0·550 g.) was isolated as in experiment (g). (The sample for combustion was weighed as an oil to ensure homogeneity.)

(k) [9-^{14}C]*Phenanthrene–naphthalene.* Fuming nitric acid (0·3 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of naphthalene (0·980 g.) and phenanthrene (1·061 g.; 5709 counts min.$^{-1}$ mg.$^{-1}$) in acetic anhydride (200 ml.) at 0°. The experiment was continued as in experiment (g); chromatography five times from light petroleum containing 10% of

benzene yielded the mixed nitro-compounds as a pale yellow oil (0·670 g.; 2523 counts min.$^{-1}$ mg.$^{-1}$, indicating a nitrophenanthrene content of 0·372 g.).

A similar experiment with non-radioactive phenanthrene gave nitronaphthalene and nitrophenanthrene which was analysed for nitrogen. The value of k/k_1, 1·4, was in good agreement with that (1·3) quoted on p. 3577.

(l) *Naphthalene–benzene.* Fuming nitric acid (2·5 ml.) in ice-cold acetic anhydride (20 ml.) was added to a solution of benzene (130 g.) and naphthalene (0·956 g.) in acetic anhydride (300 ml.) at 0°. The nitration was continued and a solution of the product in light petroleum (b. p. 40—60°) was prepared as in experiment (f). All except 50 ml. of the solvent was distilled through a Dixon gauze column. The residue was chromatographed five times from light petroleum (1·3 l.) (b. p. 40—60°) on alumina (20 × 4 cm.) to remove naphthalene and benzene. The final ether eluate yielded a yellow oil (0·736 g.) (Found: C, 65·5; H, 4·3; N, 9·15%). Comparison of these figures with experimental analyses for nitronaphthalenes (Found: C, 69·7; H, 4·3; N, 8·3. Calc. for $C_{10}H_7O_2N$: C, 69·4; H, 4·1; N, 8·1%) and nitrobenzene (Found: C, 58·8; H, 4·3; N, 11·4. Calc. for $C_6H_5O_2N$: C, 58·5; H, 4·1; N, 11·4%) indicated that the mixture contained 33% of nitrobenzene. Experimental, rather than calculated, analyses were used in order that systematic errors in isolating the nitro-compounds and in analyses might be removed.

(m) *Naphthalene–triphenylene.* Fuming nitric acid (0·5 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of naphthalene (4·008 g.) and triphenylene (1·425 g.) in acetic anhydride (1·2 l.) at 0°. The experiment was continued as in experiment (g); chromatography five times from light petroleum containing 5% of benzene yielded the mixture of nitro-compounds as a yellow oil (1·034 g.) (Found: C, 75·0; H, 4·4; N, 6·7%). Comparison of these figures with experimental analyses for samples of nitronaphthalenes (Found: C, 69·7; H, 4·3; N, 8·3%) and nitrotriphenylenes (Found: C, 79·1; H, 4·3; N, 5·3. Calc. for $C_{18}H_{11}O_2N$: C, 79·1; H, 4·1; N, 5·1%), isolated by methods similar to the above, indicated that the mixture contained 45·8% of nitronaphthalenes.

(n) *Naphthalene–coronene.* Fuming nitric acid (3 ml.) in ice-cold acetic anhydride (10 ml.) was added to a solution of coronene (0·216 g.) and naphthalene (0·407 g.) in acetic anhydride (2 l.) at 23°. After 24 hr. the acetic anhydride was hydrolysed; the mixture was extracted with chloroform and the extract was washed with potassium hydrogen carbonate solution. The chloroform was distilled off and the light brown residue was extracted several times with ether (50 ml.). The ether was removed and the yellow residue was chromatographed four times from light petroleum, yielding crystalline nitronaphthalenes (80 mg.) (Found: N, 7·95%). The ether-insoluble material was chromatographed; no separation of bands was observed. The whole of the band was therefore eluted with benzene–ether, and the solvent removed, leaving a yellow residue (205 mg.) (Found: C, 86·55; H, 3·7; N, 3·4. Calc. for $C_{24}H_{12}$: C, 96·0; H, 4·0. Calc. for $C_{24}H_{11}O_2N$: C, 83·5; H, 3·5; N, 4·1%). Analysis indicated that the residue contained 20% of coronene and 80% of nitrocoronene.

The mixture (80 mg.) was recrystallised twice from benzene, giving golden-yellow needles of nitrocoronene (40 mg.), m. p. >360° (Found: C, 83·0; H, 3·5; N, 4·1%). Ultraviolet spectrum (in EtOH): $\lambda_{max.}$ (mμ) 390, 330, 300, 215 ($\log_{10}\varepsilon$ 3·30, 3·57, 3·82, 3·71.), $\lambda_{min.}$ 370, 323, 250 ($\log_{10}\varepsilon$ 3·27, 3·56, 3·34).

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