689. *Electrophilic Substitution. Part IV.* The Nitration of Diphenyl, Chrysene, Benzo*[a]*pyrene,*† *and Anthanthrene.*

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Diphenyl, chrysene, benzo[*a*]pyrene, and anthanthrene have been nitrated by nitric acid in acetic anhydride. The results are compared with the predictions of a molecular-orbital treatment.[1-2] The ratio of isomers formed by nitration of diphenyl has been determined spectrophotometrically. It has been established that chrysene and benzo[*a*]pyrene each yield more than one isomer on nitration. Anthanthrene has been substituted for the first time; two nitro-compounds are described, and their possible structures are discussed.

Bell, Kenyon, and Robinson[3] nitrated diphenyl (100 g.) with fuming nitric acid in acetic acid at 70—90°. They separated the 2- (35—39 g.) and 4-nitrodiphenyl (60—70 g.) by making use of the greater solubility of the former in cold ethanol. Jenkins, McCullough, and Booth[4] identified 57% of the crude product of nitration in sulphuric acid as 4-nitrodiphenyl and 34% as 2-nitrodiphenyl. We have nitrated diphenyl in cold acetic anhydride, using excess of the hydrocarbon. The mixture of nitrodiphenyls formed was isolated chromatographically. From a comparison of the ultraviolet spectrum of the mixture with the spectra of the pure isomers, obtained from the mixture by fractional crystallisation, we conclude that the ratio of 2- to 4-nitrodiphenyl = 3·3 : 1.

Nitration of chrysene yielded largely 6-nitrochrysene, the only isomer previously recorded.[5, 6, 7] We were, however, able to demonstrate that at least one other isomer is also formed.

Windaus and Rennhak[8] nitrated benzo[*a*]pyrene in benzene–acetic acid using a great excess of nitric acid, appreciable dinitration no doubt occurring. Fieser and Hershberg[9] and Creech[10] repeated the work using much less nitric acid. All these authors reported

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* Part III, preceding paper.

† Hydrocarbons are numbered as recommended in the "Ring Index." Benzo[*a*]pyrene has often been referred to as 3 : 4-benzopyrene.

[1] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.*

[2] Bavin and Dewar, *J.*, 1956, 164.

[3] Bell, Kenyon, and Robinson, *J.*, 1926, 1239.

[4] Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31.

[5] Schmidt, *J. prakt. Chem.*, 1874, **9**, 281.

[6] Bamberger and Bundorf, *Ber.*, 1890, **23**, 2433.

[7] Newman and Cathcart, *J. Org. Chem.*, 1940, **5**, 618.

[8] Windaus and Rennhak, *Z. physiol. Chem.*, 1937, **249**, 256.

[9] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1564.

[10] Creech, *ibid.*, 1941, **63**, 576.

the isolation of only one isomer, 6-nitrobenzo[*a*]pyrene. We have now shown that nitration in cold acetic anhydride yields in addition certainly one and probably two other isomers.

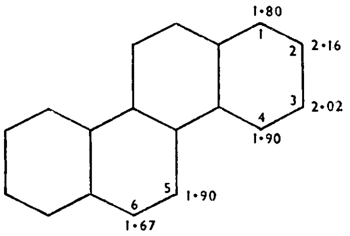
Nitration of anthanthrene in acetic anhydride yielded two mononitro-compounds of unknown structure. One was reduced to the corresponding amine by Dewar and Mole's method.[11]

Discussion.—The success of the molecular-orbital treatment (see Part VI, p. 3581) in accounting for the relative reactivities of hydrocarbons on nitration and for the distribution of the isomeric products prompts us to suggest structures for the new compounds described here, using the calculated reactivity numbers as a basis. The reactivity numbers [1, 2] of chrysene (I), benzo[*a*]pyrene (II), and anthanthrene (III) are as shown below.

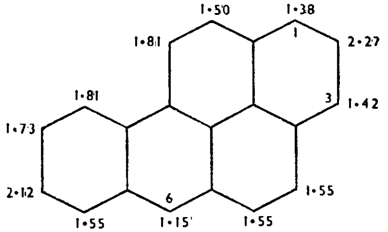
The 6-position is known to be the most reactive in chrysene; the 1-position should be the second most reactive. Since all other points of attack either have high reactivity numbers or, in the case of the 4- and the 5-position, are sterically hindered, we are able to suggest that the second nitrochrysene (m. p. 205—208°) described will prove to be 1-nitrochrysene.

The 6-position should be the most reactive in benzo[*a*]pyrene. Next in order of reactivity should come the 1- and the 3-position. Examination of Fig. 1 in Part VI of this series reveals that the 1- and the 3-isomer should each make up *ca.* 10% of the nitration product. It seems fairly certain, therefore, that the second isomer (m. p. 250—252°) isolated in our experiment was either 1- or 3-nitrobenzo[*a*]pyrene, and that it was initially contaminated by comparable quantities of the other isomer.

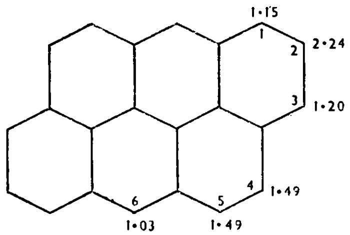
In anthanthrene the 1-, 3-, and 6-positions should be of comparable reactivity. We have isolated two mononitro-compounds. Some clue as to the structure of the compounds is provided by the colour changes which they show in concentrated sulphuric acid. By analogy with the behaviour of perylene derivatives in sulphuric acid, we might expect 6-nitro- and 6-amino-anthanthrene to be degraded, giving green solutions of anthanthrone. On the other hand we should expect 1- and 3-nitroanthanthrene, if degraded, to yield red solutions of the corresponding nitroanthanthrones (4-nitroanthanthrone [12] is known to give a red solution in sulphuric acid). The evidence suggests that the brown *x*-nitroanthanthrene is the 6-isomer. *y*-Nitroanthanthrene would then be the 1- or the 3-isomer. It is notable that the ease of chromatographic separation of *x*- and *y*-nitroanthanthrene



(I)



(II)



(III)

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[11] Dewar and Mole, *J.*, 1956, 2556.

[12] Corbellini and Atti, *Chimica e Industria*, 1936, **18**, 295.

is equalled only by the great facility with which 6-nitrobenzo[*a*]pyrene (a " *meso* "-isomer, comparable with 6-nitroanthanthrene) was separated from the supposed 1- and 3-nitrobenzo[*a*]pyrene.

EXPERIMENTAL

Some microanalyses were carried out by Imperial College microanalytical laboratory. Peter Spence type " H " alumina (100—200 mesh) was used for chromatography. Solvents for chromatography were distilled.

Materials.—Diphenyl (from British Drug Houses Ltd.; m. p. 69·5—70·5°), benzo[*a*]pyrene (from Messrs. Lights; m. p. 176—177°), nitric acid (*d* 1·5) (from British Drug Houses Ltd.), and acetic anhydride (from May and Baker Ltd.) were not purified before use. Chrysene was purified by chromatography and recrystallisation from benzene–light petroleum.

Anthanthrone, prepared from 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid[13] (kindly presented by Imperial Chemical Industries Limited, Dyestuffs Division), was reduced to anthanthrene by Clar's method.[14] The hydrocarbon was purified by chromatography from benzene.

Nitration of Diphenyl.—Fuming nitric acid (1·4 ml.) in ice-cold acetic anhydride (20 ml.) was added slowly to a solution of diphenyl (7·70 g.) in acetic anhydride (250 ml.) at 0°. After 24 hr. the anhydride was hydrolysed in water (2 l.) containing sulphuric acid (2 ml.). The mixture was extracted with chloroform. The extract was washed with potassium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue was chromatographed in light petroleum (b. p. 40—60°) on alumina (20 × 3 cm.). Elution with light petroleum was continued until the front of the yellow nitro-compound had been washed three-quarters of the way down the column. The yellow band was then eluted with ether; the residue from the ether eluate was chromatographed six times more in the above manner in order to get rid of all unchanged diphenyl and traces of quinones. The mixture of nitro-compounds so obtained was a yellow oil (3·07 g.) which slowly set to a pale yellow solid.

Part (2·2 g.) of the mixture of nitro-compounds was dissolved in ethanol (10 ml.) at 60° and cooled to room temperature. Very pale yellow needles (0·58 g.), m. p. 98—108°, crystallised; two recrystallisations from ethanol yielded needles of 4-nitrodiphenyl (Found: C, 72·3; H, 4·7; N, 6·95. Calc. for $C_{12}H_9O_2N$: C, 72·35; H, 4·55; N, 7·0%), m. p. 114—115°. The mother-liquors of the first recrystallisation yielded a pale yellow solid (1·59 g.), m. p. 30—35°; recrystallisation twice from ethanol yielded prisms of 2-nitrodiphenyl (Found: C, 72·3; H, 4·6%), m. p. 34—36°.

Analysis of the mixture of isomers formed by nitration. Spectra were measured in *cyclo*hexane. Beer's law was obeyed. Specimen results are quoted in the annexed Table. These results indicate that the mixture contains 23 ± 1% of the 4-isomer.

	$10^{-3}\varepsilon$ for x-nitrodiphenyl				$10^{-3}\varepsilon$ for x-nitrodiphenyl		
λ (mμ)	$x = 2$	$x = 4$	mixture	λ (mμ)	$x = 2$	$x = 4$	mixture
320	1·62	8·88	3·23	290	2·86	16·06	5·99
310	2·36	14·11	5·04	280	2·63	12·63	5·05
300	2·85	16·76	6·11	240	13·11	3·96	11·03

Nitration of Chrysene.—Fuming nitric acid (2 ml.) in ice-cold acetic anhydride (10 ml.) was added slowly to a solution of chrysene (1·2 g.) in acetic anhydride (2 l.) at 0°. The solution was stirred at 0° for 2 hr., then left at 2° overnight. The acetic anhydride was hydrolysed in water (2 l.) containing sulphuric acid (2 ml.). The mixture was extracted with chloroform, and the extract was washed with potassium hydrogen carbonate solution. The chloroform was distilled off; the residue was chromatographed in benzene on alumina (24 × 4 cm.) which was washed with 1 : 1 benzene–light petroleum (b. p. 40—60°) to remove chrysene. When the yellow nitrochrysene band had moved three-quarters of the way down the column, it was eluted with 1 : 1 benzene–ether. The residue from the latter eluate was chromatographed four times more in this manner, finally yielding nitrochrysenes as a partly crystalline, yellow solid (0·454 g.) (Found: C, 78·7; H, 4·3; N, 5·1. Calc. for $C_{18}H_{11}O_2N$: C, 79·1; H, 4·1; N, 5·1%), m. p. 165—185°. Part (0·224 g.) of the mixture of nitro-compounds was recrystallised twice from benzene, giving needles of 6-nitrochrysene (Found: C, 78·4; H, 4·1; N, 5·3%), m. p. 206·5—208·5° (64% recovery). Ultraviolet spectrum (in EtOH): $\lambda_{max.}$ 218, 259, 370 mμ ($\log_{10}\varepsilon$ 4·19, 4·45, 3·60); $\lambda_{min.}$ 234, 318 mμ ($\log_{10}\varepsilon$ 4·10, 3·36).

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[13] Kalb, *Ber.*, 1914, **47**, 1724.

[14] Clar, *Ber.*, 1939, **72**, 1645.

The mother-liquors from the recrystallisations were chromatographed on alumina (5 × 1 cm.) from 1 : 1 benzene–light petroleum. The first fractions yielded unchanged chrysene and later fractions yielded more 6-nitrochrysene. The tail of the yellow band was eluted with 1 : 1 benzene–ether, giving a solid, m. p. 170—190°, which, recrystallised twice from benzene, had m. p. 205—208°, depressed on admixture with 6-nitrochrysene. This material could not be 6 : 12-dinitrochrysene (lit.,[6] m. p. 380·5—382·5°). Altogether 73% of the mixture of nitrochrysenes was recovered as 6-nitrochrysene of sharp m. p.; this isomer must have comprised *ca.* 90% of the mixture.

Nitration of Benzo[a]*pyrene.*—Fuming nitric acid (0·6 ml.) in ice-cold acetic anhydride (15 ml.) was added to a solution of benzo[*a*]pyrene (0·90 g.) in acetic anhydride (750 ml.) at 0°. The nitration was continued and the nitro-compounds were freed from unchanged hydrocarbon and quinone by-products in a way very similar to that described in the previous experiment. In this case, however, two bands of nitro-compounds were very easily separated chromatographically. The more easily eluted band yielded golden-yellow plates of 6-nitrobenzo[*a*]pyrene (0·601 g.) (Found : C, 80·7; H, 4·0; N, 4·6. Calc. for $C_{20}H_{11}O_2N$: C, 80·7; H, 3·7; N, 4·7%), m. p. 252—253°. Ultraviolet spectrum (in EtOH) : $\lambda_{max.}$ 252, 265, 285, 300, 371, 390, 405 mμ ($\log_{10} \varepsilon$ 4·41, 4·43, 4·27, 4·37, 4·01, 4·00, 3·87), $\lambda_{min.}$ 232, 259, 280, 293, 327, 380, 400 mμ ($\log_{10}$ ε 4·08, 4·39, 4·17, 4·22, 3·48, 3·93, 3·82). The less easily eluted orange-brown band gave a non-crystalline solid (0·133 g.) (Found : C, 80·5; H, 4·0; N, 4·6%), m. p. 175—210°, which yielded a compound of sharp m. p. only with difficulty; simple recrystallisation from benzene was not very effective. The material was chromatographed from benzene and fractions were taken. The solid residues yielded by the earlier fractions were recrystallised four times from benzene, giving orange needles (Found : C, 80·7; H, 4·1; N, 4·9%), m. p. 250—252°. Ultraviolet spectrum (in EtOH) : $\lambda_{max.}$ 225, 266, 306, 432 mμ ($\log_{10} \varepsilon$ 4·26, 4·54, 4·13, 4·05), $\lambda_{min.}$ 216, 232, 284, 345 mμ ($\log_{10} \varepsilon$ 4·21, 4·14, 4·04, 3·55).

Nitration of Anthanthrene.—Fuming nitric acid in ice-cold acetic anhydride (10 ml.) was added slowly to a solution of anthanthrene (0·248 g.) in acetic anhydride (2 l.) at 0°. The nitration was continued and the nitro-compounds were isolated as in the nitration of chrysene. Two nitroanthanthrene bands were readily separated by chromatography. The more easily eluted brown band gave a crystalline residue (40 mg.), m. p. 253—259°, which was recrystallised twice from benzene, yielding light-brown needles, x-*nitroanthanthrene* (Found : C, 82·4; H, 3·8; N, 4·2. $C_{22}H_{11}O_2N$ requires C, 82·2; H, 3·45; N, 4·4%), m. p. 263—264°. Ultraviolet spectrum (in EtOH) : $\lambda_{max.}$ 231, 256, 329, 415, 439 mμ ($\log_{10} \varepsilon$ 4·51, 4·18, 4:34, 3·85, 3·94), $\lambda_{min.}$ 217, 251, 268, 345, 426 mμ ($\log_{10} \varepsilon$ 4·33, 4·15, 3·80, 3·37, 3·75). The compound gave a red solution in sulphuric acid which became green after 1 hr. at 60°.

The less easily eluted dark red band yielded a red solid (35 mg.) (Found : C, 81·6; H, 3·7; N, 4·3. $C_{22}H_{11}O_2N$ requires C, 82·2; H, 3·45; N, 4·4%), decomp. 210°, of poor crystalline development. The material was chromatographed from benzene and fractions were taken. The residues from the later fractions were recrystallised from benzene giving red needles, *y*-nitroanthanthrene, decomp. 255°. Examination of the other fractions failed to give positive evidence indicating whether or not any other isomer was present. Ultraviolet spectrum (in EtOH) : $\lambda_{max.}$ 232, 314, 405, 429, 478 mμ ($\log_{10} \varepsilon$ 4·55, 4·11, 3·65, 3·96, 4·02), $\lambda_{min.}$ 289, 390, 412, 440 mμ ($\log_{10} \varepsilon$ 3·80, 3·37, 3·59, 3·80). The compound gave a red solution in concentrated sulphuric acid, which did not change colour, even at *ca.* 200°.

Reduction of x-*Nitroanthanthrene.*[11]—Palladised charcoal (5%; 20 mg.) and hydrazine hydrate (2 drops) were added to a solution of *x*-nitroanthanthrene (10 mg.) in ethanol (60 ml.), and the solution was refluxed for 5 min. The solution was filtered. The ethanol and excess of hydrazine hydrate were distilled off and the residue was recrystallised from benzene, giving red needles (Found : N, 4·8. $C_{22}H_{13}N$ requires N, 4·8%), decomp. 210°. Ultraviolet spectrum (in EtOH) : $\lambda_{max.}$ 233, 245, 319, 470 mμ ($\log_{10} \varepsilon$ 4·66, 4·38, 4·37, 3·92), $\lambda_{min.}$ 239, 280, 365 mμ ($\log_{10} \varepsilon$ 4·34, 3·61, 3·01). The amine gave a red solution in concentrated sulphuric acid, which rapidly became green at 30°.

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[*Received, March* 16*th*, 1956.]