

468. *Phenanthrene Chemistry. Part IV.* Addition Reactions of Phenanthrene*

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The reaction of phenanthrene and some substituted phenanthrenes with reagents of the type O_2N-X ($X = NO, NO_2, NO_3, Cl, \text{ or } OH$) in non-polar solvents has been studied, and the structure of the products examined.

THE reaction of phenanthrene with certain oxides of nitrogen, in media of low polarity, has been studied previously. Schmidt¹ passed "nitrous fumes" into phenanthrene in benzene below 35°, and isolated two addition products; one of these, m. p. 154—155°, was formulated as di-(9,10-dihydro-10-nitro-9-phenanthryl) ether; the second, m. p. 199—200°, was formulated as 9,9',10,10'-tetrahydro-10,10'-dinitro-9,9'-biphenanthryl (I; $R = R' = NO_2$). Wieland and Rahn² obtained the same so-called ether by the action of dry nitric acid on phenanthrene in carbon tetrachloride at -10°; and Michael and Carlson³ using the same reagents in chloroform at -20°, obtained a product, which we have shown was almost certainly the same compound in an impure state. Subsequently Grey and Bavin⁴ showed that the so-called ether contained nitro and nitrate ester groups, and gave 9,9'-biphenanthryl on heating, and suggested that it should be formulated as 10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl-10-yl nitrate (I; $R = NO_2, R' = ONO_2$).† Our own chemical and physical studies support this structure and provide new evidence for it.

We find that the nitro-nitrate (I) can be prepared by the action of dinitrogen trioxide ($N_2O_3 \rightleftharpoons NO_2 + NO$), or dinitrogen tetroxide, or "anhydrous" nitric acid on phenanthrene in benzene at the ordinary temperature; or by the action of fuming nitric acid on phenanthrene in chloroform at -20°. It is most conveniently prepared by use of anhydrous nitric acid in benzene at 5—10° (10% yield).

From these reactions 1-, 3-, 4-, and 9-nitrophenanthrene and 3-nitrophenanthraquinone were also isolated.

* Part III, I. T. Millar and K. V. Wilson, *J.*, 1964, 2121. In this paper, the structural formula (XV) should be deleted and replaced by the molecular formula $C_{24}H_{16}O_6$.

† This Paper is entitled "Julius Schmidt's Addukt aus N_2O_5 und Phenanthren." In fact, Schmidt used nitrous fumes.

¹ J. Schmidt, *Ber.*, 1900, **33**, 3251.

² H. Wieland and F. Rahn, *Ber.*, 1921, **54**, 1770.

³ A. Michael and G. H. Carlson, *J. Amer. Chem. Soc.*, 1935, **57**, 1268.

⁴ G. W. Grey and P. M. G. Bavin, *Chem. Ber.*, 1963, **96**, 1277.

The nitro-nitrate (I) as obtained by us had m. p. 161—163° (decomp.) from acetone. The ultraviolet spectrum indicated a biphenyl rather than a phenanthrene chromophore.



The infrared spectrum showed the presence of nitrate ester and non-tertiary nitro-groups.

The compound was recovered after brief boiling under reflux in acetone or tetrahydrofuran. Decomposition is rapid in boiling benzene, giving 10-nitro-9,10-dihydro-9,9'-biphenanthryl, m. p. 118—120° (II; R = NO₂) in high yield. This compound and its precursor do not give a salt with alkali, which initially suggested that the nitro-group in each was tertiary. (Schmidt's "benzene adduct of the ether" m. p. 134—135°, obtained by recrystallisation from benzene, was probably a product of incomplete thermal decomposition).

The nitro-compounds (I; R = NO₂, R' = ONO₂) and (II; R = NO₂) decompose further at 180° in *p*-cymene, giving 9,9'-biphenanthryl in high yield; this two-stage synthesis from phenanthrene is more convenient than bromination followed by Krzewski-Turner condensation of 9-phenanthrylmagnesium bromide for the preparation of small amounts of 9,9'-biphenanthryl, although the yield in the first stage is lower.

With a variety of bases, the nitro-nitrate (I), gives 9-nitrophenanthrene and phenanthrene. The assigned structure for the nitro-compound (II; R = NO₂) is in accord with the ultraviolet spectrum (which indicates a phenanthrene chromophore) and the infrared spectrum (showing a non-tertiary nitro-group, and one isolated, and four adjacent, aromatic methines). Oxidation of the nitro-compound (II) with permanganate in acetone gave, in low yield, 10-nitro-9,9'-biphenanthryl. Hydrolysis of the nitro-nitrate (I) with dilute aqueous hydrochloric acid in acetone, or hydrogenolysis, gave in high yield 10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl-10-ol (I; R = NO₂, R' = OH). The nitro-group in both these compounds resisted catalytic reduction, but was reduced by lithium aluminium hydride. The hydroxyl-group in the alcohol (I; R = NO₂, R' = OH) was oxidised in Bordwell's test⁵ at a rate that showed that it was not tertiary. The major remaining requirement in the formulation of the nitro-nitrate is confirmation of the position of the substituents; Grey and Bavin assigned the substituents to the 10- and 10'-positions without discussion.

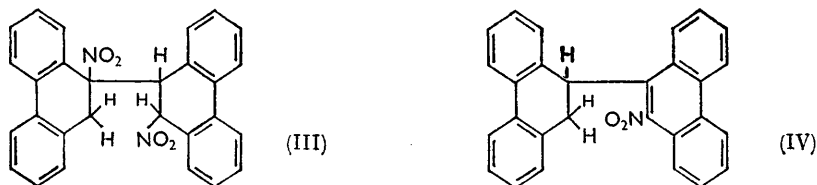
This hydroxyl group is strongly intramolecularly hydrogen-bonded to the nitro-group, as shown by the infrared spectrum, and possibly for this reason (and also for steric reasons), it is markedly resistant to bromination, oxidation, acylation, sulphonation and phosgenation. Vigorous oxidation of this secondary alcohol (I; R = NO₂, R' = OH) or of the nitro-nitrate (I; R = NO₂, R' = ONO₂) with chromic anhydride gave phenanthraquinone.

The secondary alcohol (I; R = NO₂, R' = OH) gave the amino-alcohol (I; R = NH₂, R' = OH) with lithium aluminium hydride in tetrahydrofuran; it resisted reduction by a variety of other reagents. Intramolecular hydrogen-bonding (hydroxyl to amino) is shown in this compound by its infrared spectrum.

The same reagent in diethyl ether reduced the nitro-compound (II; R = NO₂) to 10-amino-9,10-dihydro-9,9'-biphenanthryl (II; R = NH₂). This when heated at 210° in 1,2,4-trichlorobenzene gave 9,9'-biphenanthryl; it was unaffected by boiling concentrated hydrochloric acid, or by treatment in aqueous suspension with nitrous acid or in tetrahydrofuran.

⁵ F. G. Bordwell and K. M. Wellman, *J. Chem. Educ.*, 1962, **39**, 308.

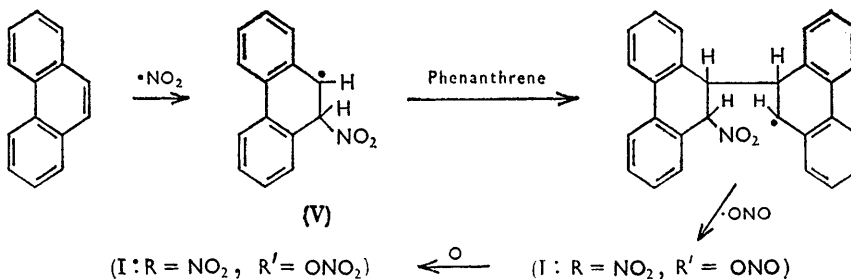
The reaction of "nitrous fumes" with phenanthrene in benzene gave, after separation of the nitro-nitrate (I), a solution which, in some experiments, deposited on standing



a small amount of a dinitro-compound, m. p. 199–200°, as reported by Schmidt,¹ but this has not been noted by later workers. Grey and Bavin⁴ concluded that this compound was derived from fluorene or anthracene present as impurities in the phenanthrene used by Schmidt.¹ Its u.v. spectrum shows the presence of a biphenyl chromophore, and the infrared spectrum shows bands assigned to four adjacent aromatic methines, and aliphatic secondary and tertiary nitro-groups. The dinitro-compound was soluble in aqueous sodium hydroxide; dilute acid regenerated the dinitro-compound from the salt, confirming the presence of at least one secondary nitro-group. When heated above its melting point, the dinitro-compound gave an alkali-insoluble mononitro-compound, whose i.r. absorption characteristics showed the presence of a tertiary nitro-group, and whose ultraviolet spectrum showed the presence of a phenanthrene chromophore.

The dinitro-compound is tentatively formulated as (III) and its thermal decomposition product as (IV). The formation of the nitro-compound (IV) from (III) requires the elimination of the tertiary nitro-group and tertiary hydrogen, followed by prototropic change.

It is noteworthy that the nitro-nitrate (I; R = NO₂, R' = ONO₂) is formed by the action of several reagents of the type O₂N-X (X = NO, NO₂, OH) on phenanthrene in a solvent of low polarity, whereas reagents of the type O₂N-Y (Y = NO₃ or Cl; see below), which are prone to heterolytic fission in the same solvents, fail to give the nitro-nitrate as also do typical nitration procedures in polar conditions. This suggests that the mechanism of formation of this compound is *via* attack by the radical ·NO₂. However, the reaction with dinitrogen tetroxide or nitric acid is not diverted in the presence of the radical-transfer agent, bromotrichloromethane; but this is not proof of a non-radical path. A possible route is therefore:



Phenanthrene is known to be attacked mainly at the 9-position by phenyl radicals;⁶ this selectivity should be even more marked with a reagent of lower reactivity and greater selectivity. Reaction of the radical (V) with 9-nitrophenanthrene could yield the dinitro-compound (III): alternatively, this may be formed by hydrogen transfer in the nitro-compound (V) followed by reaction with phenanthrene and ·NO₂.

Radical attack by ·NO₂ in these reactions is in accord with the view⁷ that reaction of

⁶ A. L. J. Beckwith and M. J. Thompson, *J.*, 1961, 73.

⁷ E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1960, p. 739; A. I. Titov, *Tetrahedron*, 1963, 19, 557.

dinitrogen tetroxide with olefins in non-hydroxylic solvents proceeds in this manner; moreover, recent studies on the reaction of dinitrogen tetroxide with anthracene in benzene, giving a mixture of stereoisomeric dinitro-compounds and nitro-nitrates (all monomeric products of addition at the 9,10-positions) have been interpreted also as being initiated by radical attack.⁸ The importance of moderate change in solvent polarity (*i.e.*, from benzene to chloroform) in determining the nature of the products from anthracene was emphasised.⁸ (Surprisingly, it has been reported that phenanthrene and anthracene with dinitrogen tetroxide in chloroform at 0° give only mononitro-substituted products.)⁹

Nitryl chloride resembles dinitrogen tetroxide in its reactions with olefins, giving dichloro-, dinitro-, and chloronitro-addition products;¹⁰⁻¹² this addition appears to be homolytic in solvents of low polarity.¹⁰ However, reactive aromatic compounds are nitro-substituted by this reagent in methylene chloride or benzene,¹² presumably through attack by the nitronium ion. Phenanthrene with nitryl chloride in benzene at 5–10° gave the nitro-nitrate in very small yield, and small yields also of 9,10-dichlorophenanthrene, 9-nitrophenanthrene and 3-nitrophenanthraquinone; the major products were 9-chloro-10-nitrophenanthrene and 9,10-dichloro-3-nitrophenanthrene. The 9-chloro-10-nitro-compound is best prepared by this means at –16° without a solvent.

Similarly, dinitrogen pentoxide with phenanthrene in cyclohexane at 0–5° gave nitrophenanthrenes and nitrophenanthraquinone, and the nitro-nitrate (I) was not isolated. This reagent would not be expected to generate $\cdot\text{NO}_2$ radicals in significant amount, even in a non-polar solvent.

The behaviour of certain of the above reagents with some 9-substituted phenanthrenes has been briefly investigated. It is noteworthy that 9,10-dichloro-, 9,10-diphenyl- or 9-chloro-10-phenyl-anthracene react similarly to anthracene to give the corresponding nitro-nitrates, with dinitrogen tetroxide in chloroform.⁸ However, we find that 9-methylphenanthrene in benzene with "nitrous fumes" or dinitrogen tetroxide and oxygen, or nitric acid, gives mainly 9-methyl-10-nitrophenanthrene.

The reaction of 9-bromophenanthrene in benzene with dinitrogen tetroxide to give 9-bromo-10-nitrophenanthrene has been studied previously:¹³ we find that 9-bromo-3-nitrophenanthrene and 3-nitro-9,10-phenanthraquinone are also formed. The 9-bromo-10-nitro-compound is also obtained by nitration with nitric acid or nitric and acetic acids; the yield is low and much 3-nitro-9,10-phenanthraquinone is then formed.¹⁴

Methyl 9-phenanthroate in benzene failed to react with dinitrogen tetroxide at 20°.

The reaction of 9,9'-biphenanthryl with dinitrogen tri- or tetra-oxide or with nitric acid or nitryl chloride in benzene has been described.¹⁵ The major product is 10-nitro-9,9'-biphenanthryl, which is formed in nearly quantitative yield in some conditions, although the yield is low with nitryl chloride. This contrasts with the unselective orientation and partial polynitration observed with the biphenanthryl in typical nitrating conditions; it is clearly possible that the reaction in benzene proceeds *via* addition of the reagent $\text{O}_2\text{N-X}$ ($\text{X} = \text{NO}, \text{NO}_2, \text{OH}, \text{or Cl}$) as a radical at the somewhat ethylenic 9,10-bond followed by elimination of HX .

The structures assigned above to biphenanthryl derivatives are in accord with the proton magnetic resonance spectra of the compounds. We are now carrying out further proton magnetic resonance studies on these and some related compounds, with a view in particular to establishing their stereochemistry.

⁸ C. Dufraisse, J. Rigaudy, and Kha Vang Thang, *Compt. rend.*, 1963, **356**, 548.

⁹ P. P. Shorygin, A. V. Topchlev, and V. A. Anan'ina, *J. Gen. Chem. (U.S.S.R.)*, 1938, **8**, 981.

¹⁰ H. Schechter, F. Conrad, A. L. Daulton, and R. B. Caplan, *J. Amer. Chem. Soc.*, 1952, **74**, 3052; *Chem. and Ind.*, 1955, 535.

¹¹ C. C. Prince and C. A. Sears, *J. Amer. Chem. Soc.*, 1953, **75**, 3275.

¹² M. J. Collis, F. P. Gintz, D. R. Goddard, E. A. Hebdon, and G. J. Minkoff, *J.*, 1958, 438; M. J. Collis and D. R. Goddard, *J.*, 1958, 1952.

¹³ J. Schmidt and A. Kämpf, *Ber.*, 1902, **35**, 3117; J. Schmidt and G. Ladner, *Ber.*, 1904, **37**, 3573.

¹⁴ R. S. W. Braithwaite and P. F. Holt, *J.*, 1959, 2304.

¹⁵ Part II, M. A. Ali, J. G. Carey, D. Cohen, A. J. Jones, I. T. Millar, and K. V. Wilson, *J.*, 1963, 387.

EXPERIMENTAL

All the compounds described, unless stated otherwise, are colourless. Melting points were determined on a Kofler hot stage apparatus. Ultraviolet and visible spectra were measured with a Unicam S.P. 700 spectrometer on solutions in tetrahydrofuran. Infrared spectra were measured with a Perkin-Elmer Infracord or 221 spectrophotometer, usually on Nujol mulls or potassium bromide discs respectively. Hydrogen-bonded compounds were examined in carbon tetrachloride solution.

9,9',10,10'-Tetrahydro-10'-nitro-9,9'-biphenanthryl-10-yl Nitrate (I; R = NO₂, R' = ONO₂).—(a) From phenanthrene and nitrous fumes or dinitrogen trioxide. "Nitrous fumes" (from nitric acid and arsenious oxide) were passed into a solution of phenanthrene (50 g.) in benzene (150 ml.) at ca. 30°. After absorption had ceased (1 hr.) the mixture was kept at 10–15° overnight. The nitro-nitrate was then filtered off and washed with hot benzene (3 × 30 ml.); (7.5 g., 11%), m. p. 156–158°. Crystallisation from anhydrous acetone gave material, m. p. 161–163° (decomp.) (lit.⁴ m. p. 155–157°) (Found: C, 72.3; H, 4.75; N, 6.05%; *M*, cryoscopic in ethylene dibromide, 462. Calc. for C₂₈H₂₀N₂O₅: C, 72.4; H, 4.35; N, 6.05%; *M*, 464). The infrared absorption spectrum showed bands at 1620, 1280, and 870 (–ONO₂ group), 1545 and 1360 (aliphatic –NO₂) and 765 and 740 cm.⁻¹ (four adjacent aromatic C–H groups). The ultraviolet absorption spectrum showed a biphenyl chromophore (λ_{max}. 2710 Å, log ε 4.48).

Chromatography of the mother liquor on alumina gave phenanthrene, 3- and 9-nitrophenanthrene, and 3-nitrophenanthraquinone.

A similar experiment with dinitrogen trioxide (from sodium nitrite and sulphuric acid) gave similar results, but the yield of the nitro-nitrate was lower.

(b) From phenanthrene and dinitrogen tetroxide or nitric acid. Dinitrogen tetroxide and oxygen (from heated lead nitrate) were passed into phenanthrene (50 g.) in benzene (150 ml.), kept below 30°, for 1 hr. Working-up as described above gave the nitro-nitrate (I) (10.3 g., 16%). Chromatography of the mother-liquors gave phenanthrene, 3-, 4-, and 9-nitrophenanthrene and 3-nitrophenanthraquinone.

Similar results were obtained when a mixture of liquid dinitrogen tetroxide and phenanthrene in benzene was kept for 12 hr. at 10°. The yield of the nitro-nitrate in these reactions was not affected by the addition of bromotrichloromethane (2 mol.) to the reaction mixture.

(c) In another experiment, anhydrous nitric acid (2 ml., 2 mol.) was added dropwise to a stirred solution of phenanthrene (8 g.) in benzene (40 ml.) at 5–10°. After 1 hr. the nitro-nitrate was filtered off and washed successively with hot benzene and ether (2.2 g., 21%). Chromatography of the mother-liquors gave phenanthrene and 1-, 3-, 4-, and 9-nitrophenanthrene and 3-nitrophenanthraquinone.

The yield of nitro-nitrate was unchanged in a similar experiment in which bromotrichloromethane (20 g., 2 mol.) was added.

In another experiment, fuming nitric acid (96%) (2.45 ml., 1.05 mol.) in chloroform (10 ml.) was added dropwise to phenanthrene (10 g.) in chloroform (80 ml.) at –20°. After 1 hr., the mixture was washed with water, dried, and evaporated; the residue gave the nitro-nitrate (2.7 g., 19%).

Thermal Decomposition of the Nitro-nitrate.—(a) The nitro nitrate was recovered after prolonged boiling in acetone or tetrahydrofuran.

(b) The nitro-nitrate (10 g.) in toluene or *p*-cymene (500 ml.) was boiled under reflux for 4 hr. Removal of the solvent and recrystallisation of the residue from ethanol gave 9,9'-biphenanthryl (7 g., 92%), m. p. and mixed m. p. 185–187°.

(c) The nitro-nitrate (1 g.) in benzene (200 ml.) was boiled under reflux for 3 hr. Removal of solvent gave 9,10-dihydro-10-nitro-9,9'-biphenanthryl (II; R = NO₂) (0.7 g., 80%), m. p. 167° (from ethanol) (Found: C, 83.6; H, 5.25; N, 3.2. C₂₈H₁₉NO₂ requires C, 83.8; H, 4.8; N, 3.5%). The infrared spectrum showed bands at 1550 and 1350 (aliphatic –NO₂ group), 895 (single aromatic C–H group) and 770, 750 and 735 cm.⁻¹ (four adjacent aromatic C–H groups). The ultraviolet spectrum indicated a phenanthrene chromophore; λ_{max}. 2245 (log ε 4.68), 2985 Å (4.06).

Reactions of the Nitro-compound (II; R = NO₂).—(a) When boiled in *p*-cymene, the nitro-compound (II) gave 9,9'-biphenanthryl (90% yield), m. p. and mixed m. p. 186–188°. The nitro-compound was recovered after being kept with hydrogen peroxide or sodium hydroxide in ethanolic acetone, and after boiling with aqueous sulphuric acid (10%) and acetone.

(b) The nitro-compound (II; $R = NO_2$) (1 g.) in ether or tetrahydrofuran was added dropwise to a stirred solution of lithium aluminium hydride (0.3 g., 3 equiv.) in ether (50 ml.) under nitrogen. The mixture was boiled under reflux for $2\frac{1}{2}$ hr., water (10 ml.) in tetrahydrofuran (50 ml.) was added, and the liquid filtered. Evaporation of the filtrate gave 10-*amino-9,10-dihydro-9,9'-biphenanthryl* (0.8 g., 87%), m. p. 124–126° (from light petroleum) (Found: C, 90.75; H, 5.85; N, 3.8. $C_{28}H_{21}N$ requires C, 90.55; H, 5.7; N, 3.8%).

The infrared spectrum showed bands at 1600 (amino group) 895 and 885 (single aromatic C-H group) and 785, 770, 755, and 725 cm^{-1} (four adjacent aromatic C-H groups). The ultraviolet spectrum showed a phenanthrene chromophore: λ_{max} 2270 ($\log \epsilon$ 4.91), 2550 (4.92), 2828 (2.54), 2840 (4.44), and 2955 Å (4.34). This amine was insoluble in dilute aqueous acids and sparingly soluble in concentrated hydrochloric acid. Hydrogen chloride passed into an ethereal solution of the amine gave an oil. The amine was recovered after treatment with excess of sodium nitrite and hydrochloric acid. A sample boiled under reflux in 1,2,4-trichlorobenzene for 1 hr. gave 9,9'-biphenanthryl (52%); in a similar experiment with *p*-cymene as solvent the amine was recovered.

Reaction of the Nitro-nitrate (II; $R = NO_2$, $R' = ONO_2$) *with Base*.—The nitro-nitrate (2.5 g.) was added to a solution from sodium (2.5 g.) in methanol (50 ml.). The solution was warmed briefly and filtered; the filtrate on cooling deposited 9-nitrophenanthrene (1 g.), m. p. and mixed m. p. 115.5–116.5° (from ethanol). Dilution of the mother-liquor with water caused the separation of an oil which solidified; sublimation of the solid at 75°/0.1 mm. gave phenanthrene (0.3 g.), m. p. and mixed m. p. 99–100°.

The same products were obtained in lower yield when the nitro-nitrate in dioxan was treated with alcoholic ammonia, sodium hydroxide, hydrazine hydrate, or lithium aluminium hydride.

Oxidation of the Nitro-nitrate (I; $R = NO_2$, $R' = ONO_2$).—Chromic anhydride (1.5 g.) in water (1 ml.) and acetic acid (1 ml.) was added to the nitro-nitrate (0.5 g.) suspended in acetic acid (10 ml.). The mixture was heated for 2 hr. on a steam-bath and diluted with water; phenanthraquinone (1.9 g., 80%) was deposited, m. p. and mixed m. p. 204–206° (from ether).

Hydrolysis of the Nitro-nitrate (I; $R = NO_2$, $R' = ONO_2$).—Aqueous 10% hydrochloric acid (50 ml.) was added to a solution of the nitro-nitrate (2 g.) in acetone (300 ml.), and the mixture was allowed to stand for 24 hr. Removal of the solvent gave 9,9',10,10'-*tetrahydro-10'-nitro-9,9'-biphenanthryl-10-ol* (1.5 g., 82%), m. p. 214–218° (from acetone) (Found: C, 79.95; H, 5.0; N, 3.25. $C_{28}H_{21}NO_3$ requires C, 80.15; H, 5.05; N, 3.35%). The infrared spectrum showed bands at 1545 and 1360 (nitro-group), 770 (four adjacent aromatic C-H groups), 3500 (H-bonded hydroxyl group) and 2990 cm^{-1} (tertiary aliphatic C-H group). The ultraviolet spectrum showed the presence of a biphenyl chromophore: λ_{max} 2695 Å ($\log \epsilon$ 4.35).

This alcohol was also obtained by treatment of the nitro-nitrate with hydrogen peroxide in acetone, and, mixed with the nitro-compound (II; $R = NO_2$), by heating it with aqueous 25% sulphuric acid in acetone.

Hydrogenolysis of the Nitro-nitrate (I; $R = NO_2$, $R' = ONO_2$).—The nitro-nitrate (1 g.) in tetrahydrofuran (150 ml.) was shaken under hydrogen with Adams catalyst (0.1 g.). Filtration and removal of solvent gave the alcohol (0.9 g., quantitative yield), m. p. 214–218° (from benzene). Similar results were obtained by using acetic acid or ethyl acetate as solvent.

Reactions of the Alcohol (I; $R = NO_2$, $R' = OH$).—(a) The presence of a hydroxyl group, probably secondary, was confirmed by Bordwell's test. The alcohol (I; $R = NO_2$, $R' = OH$) was recovered after it had been heated with alcoholic ammonia, aqueous sodium hydroxide, acetic anhydride with pyridine or sulphuric acid catalyst, phosgene in methylene dichloride, phosphorus tribromide in chloroform, or methanesulphonyl chloride in pyridine.

A sample boiled under reflux in *p*-cymene for 2 hr. gave 9,9'-biphenanthryl (90%); another sample boiled in toluene was recovered.

(b) *Oxidation*. A saturated solution of potassium permanganate in acetone was added to a boiling solution of the alcohol (1 g.) in acetone (100 ml.) until the colour persisted (50 ml.). The mixture was boiled for $2\frac{1}{2}$ hr., ethanol (10 ml.) was added, and the boiling continued for $\frac{1}{2}$ hr. The mixture was cooled and filtered, the filtrate evaporated, and the residue recrystallised from ethanol, giving 10-nitro-9,9'-biphenanthryl (0.1 g., 11%), m. p. and mixed m. p. 284–286°. The mother-liquors on evaporation gave unchanged alcohol (0.7 g., 70%).

(c) *Reduction*. The alcohol (1 g.) in tetrahydrofuran (150 ml.) was added dropwise to a solution of lithium aluminium hydride (0.3 g., 3 equiv.) in tetrahydrofuran (50 ml.) under nitrogen. After 3 hr. under reflux, water (10 ml.) was added, the mixture was filtered, and the

solvent removed, giving 10'-amino-9,9',10,10'-tetrahydro-9,9'-biphenanthryl-10-ol (I; R = NH₂, R' = OH) (0.68 g., 75%), m. p. 126—129° (from light petroleum) (Found: C, 86.45; H, 5.8; N, 3.6. C₂₈H₂₃NO requires C, 86.35; H, 5.95; N, 3.6%). The infrared spectrum showed bands at 3590 (H-bonded hydroxyl group), 3480 and 3380 and 1590 (amino group), 750, 735, and 723 cm.⁻¹ (four adjacent aromatic C-H groups). The ultraviolet specimen showed the presence of a biphenyl chromophore: λ_{max.} 2550 Å (log ε 4.6) and 3405 Å (3.83).

The alcohol (I; R = NO₂, R' = OH) was recovered after attempted reduction with the following: stannous chloride or tin and hydrochloric acid; hydrazine hydrate and palladium charcoal; hydrogen and a platinum or palladium catalyst in a variety of solvents.

9,9',10,10'-Tetrahydro-9,10'-dinitro-9,9'-biphenanthryl (III).—In some preparations of the nitro-nitrate (I; R = NO₂, R' = ONO₂) with oxides of nitrogen ("nitrous fumes," N₂O₃, or N₂O₄ ⇌ 2NO₂), the filtrate, after collection of the nitro-nitrate, when kept for some weeks deposited this dinitro-compound (III) in yields up to 6%. The compound was not isolated in all experiments, and attempts to define the conditions favouring its formation were unsuccessful. It has not been described by investigators other than Schmidt.¹ The yellow compound had m. p. 199—200° (lit.,¹ m. p. 199—200°) from ethanol, raised to 210° by precipitation from dimethyl sulphoxide by ether (Found: C, 74.7; H, 4.15; N, 6.1. Calc. for C₂₈H₂₀N₂O₄: C, 75.0; H, 4.5; N, 6.25%). The infrared spectrum showed bands at 1510, 1545, 1335, and 1350 cm.⁻¹ (aliphatic nitro-groups). The ultraviolet spectrum showed a biphenyl chromophore (λ_{max.} 2485 Å, log ε 4.75).

The dinitro-compound dissolved in an aqueous acetone solution of sodium hydroxide (10%); removal of the solvents *in vacuo* gave a water-soluble residue. When this residue was boiled or dilute acid was added, the dinitro compound was precipitated, m. p. and mixed m. p. 201—203° (from benzene).

The dinitro-compound was recovered after being boiled in a mixture of acetone and dilute (10% or 25%) sulphuric acid for 5 hr.

A sample (0.4 g.) in acetic acid (10 ml.) was oxidised by treatment with chromic anhydride (2 g.) in water (2 ml.) and acetic acid (2 ml.) on a steam-bath for 2 hr. Dilution with water and extraction with benzene gave phenanthraquinone (0.04 g., 11%), m. p. and mixed m. p. 204—207° (from ether).

The dinitro-compound was recovered after attempted reduction by hydrazine hydrate and palladium-charcoal or by hydrogen and platinum.

When the dinitro-compound (0.4 g.) was boiled under reflux for 15 min. or for 1 hr. in 1,2,4-trichlorobenzene (50 ml.), nitrous fumes were evolved; removal of the solvent and crystallisation of the residue from benzene gave 9,10-dihydro-10'-nitro-9,9'-biphenanthryl (IV), m. p. 217—218° (0.3 g., 85%) (Found: C, 83.9; H, 4.9; N, 3.3. C₂₈H₁₉NO₂ requires C, 83.8; H, 4.8; N, 3.5%). The infrared spectrum showed bands at 1505 and 1340 cm.⁻¹ (nitro group), and 760, 745, and 725 cm.⁻¹ (four adjacent aromatic C-H groups). The ultraviolet spectrum showed a phenanthrene chromophore: λ_{max.} 2485 (log ε 5.05) 2555 (5.17) 2770 (4.48) 2875 (4.51) and 2990 Å (4.35). This compound was also formed when the dinitro-compound was boiled in the trichlorobenzene with 10% palladium-charcoal, or heated at 290° with palladium-charcoal without a solvent.

The compound was recovered after attempted salt-formation with sodium hydroxide in aqueous acetone; it was not reduced by hydrazine and palladium-charcoal.

Reaction of Phenanthrene with Dinitrogen Pentoxide.—Dinitrogen pentoxide (6.5 g., 1.25 mol.) was added to a stirred solution of phenanthrene (10 g.) in cyclohexane or chloroform (200 ml.) at 0—5°. Working-up by chromatography on alumina gave phenanthrene (5 g.) and 3-nitro- (2 g.), 4-nitro- (0.5 g.) and 9-nitro-phenanthrene (3.5 g.), and 3-nitrophenanthraquinone (0.3 g.).

Reaction of Phenanthrene with Nitryl Chloride.—Nitryl chloride (50 g., 2.05 mol.) was added slowly to a well-stirred solution of phenanthrene (25 g.) in benzene (125 ml.) at 5—10°. When the addition was complete, the red mixture was kept for 24 hr. and then worked up by chromatography on alumina. The products isolated were 3-nitrophenanthraquinone (1.5 g.), m. p. and mixed m. p. 275—278°; 9-nitrophenanthrene (5 g., 16%), m. p. and mixed m. p. 115—116°; 9,10-dichlorophenanthrene (1 g., 3%) m. p. and mixed m. p. 159—161°; and 9-chloro-10-nitrophenanthrene (9 g., 25%) yellow, m. p. 190—193° (from ethyl acetate followed by sublimation at 130°/0.03 mm.) (Found: C, 64.95; H, 3.2; N, 5.25. C₁₄H₈ClNO₂ requires C, 65.25; H, 3.15; N, 5.45%). This compound showed bands in the infrared spectrum at 1525 and 1345 (nitro-group) 862 (C-Cl group) 750 and 715 cm.⁻¹ (four adjacent aromatic C-H groups).

Its ultraviolet spectrum is closely similar to that of 9-bromo-10-nitrophenanthrene; $\lambda_{\text{max.}}$ 2235 (log ϵ 4.65), 2475 (4.79), 2540 (4.83), 2875 (4.05), and 2995 Å (3.9). 9,10-Dichloro-3-nitrophenanthrene (11 g., 27%), pale yellow, m. p. 240–243° (from benzene or ethanol), was also isolated (Found: C, 57.35; H, 2.6; N, 4.75; Cl, 23.4. $\text{C}_{14}\text{H}_9\text{Cl}_2\text{NO}_2$ requires C, 57.55; H, 2.4; N, 4.8; Cl, 24.3%). Its infrared spectrum showed bands at 1525, 1500, and 1350 (nitro-group) 862 (C–Cl group), 900 (single aromatic C–H group), 829 (two adjacent aromatic C–H groups), 773, 757, 744, and 712 cm^{-1} (four adjacent aromatic C–H groups). The ultraviolet spectrum showed a phenanthrene chromophore: $\lambda_{\text{max.}}$ 2435 (log ϵ 4.73), 2510 (4.79), 3030 (3.59), and 3410 Å (3.92). Oxidation of a sample with chromic anhydride in acetic acid gave intractable products. The orientation of the nitro-group was proved by boiling a sample (85 mg.) in ethanol (40 ml.) with palladium-charcoal (50 mg., 10%) and hydrazine hydrate (1 ml.) under reflux for 1 hr. Filtration, evaporation, and crystallisation from light petroleum (b. p. 60–80°) gave 3-phenanthrylamine (52 mg., 94%), m. p. and mixed m. p. 84–85°. Authentic 3-phenanthrylamine for m. p. and infrared comparison was prepared in 90% yield by the similar reduction of 3-nitrophenanthrene.

In an experiment in which nitril chloride (1 mol.) was added to phenanthrene in benzene below 20°, the nitro-nitrate (I; R = NO₂, R' = ONO₂) (3%) was deposited when the mixture was left overnight; chromatography of the residue then gave the same products as described above. These products, but not the nitrate, were also isolated when methylene dichloride was used as solvent at 0°. When no solvent was used at –16°, the reaction was vigorous and 9-chloro-10-nitrophenanthrene was formed in 50% yield.

9-Methyl-10-nitrophenanthrene.—A stream of dinitrogen tetroxide and oxygen was passed into a solution of 9-methylphenanthrene (5 g.) in benzene (15 ml.) at 20°. When absorption ceased the solution was set aside for 12 hr. and the yellow mononitro-derivative filtered off (1.5 g., 23%), m. p. 172–174° (from benzene) (Found: C, 76.05; H, 4.5; N, 5.7. $\text{C}_{15}\text{H}_{11}\text{NO}_2$ requires C, 75.95; H, 4.7; N, 5.9%). Chromatography on alumina of the evaporated and neutralised filtrate gave more of the *nitro-compound* (1.25 g., total yield 45%). The infrared spectrum of the compound showed bands at 1515 (nitro-group) and 748 and 713 cm^{-1} (four adjacent aromatic C–H groups). The ultraviolet spectrum showed a phenanthrene chromophore: $\lambda_{\text{max.}}$ 2215 (log ϵ 4.7), 2450 (4.84), 2525 (5.47), 2735 (4.25), 2825 (4.12), and 2940 Å (4.08).

In a similar experiment with “nitrous fumes,” the yield of 9-methyl-10-nitrophenanthrene was 30%. When 9-methylphenanthrene in benzene or acetic acid was treated with fuming nitric acid (1.5 mol.) at 15–20°, the yield was 40%.

9-Bromo-10-nitrophenanthrene.—Passage of dinitrogen tetroxide and oxygen through a solution of 9-bromophenanthrene (5 g.) in benzene (15 ml.) at 20–25° gave, after working-up by chromatography on alumina, 9-bromo-10-nitrophenanthrene (1.8 g., 27%), m. p. and mixed m. p. 204–208°, and 9-bromo-3-nitrophenanthrene (1 g.) m. p. 192°, and 3-nitrophenanthraquinone (2.4 g.), m. p. 276–278°. The 9-bromo-10-nitro-compound was also isolated in similar yield, by crystallising from benzene the solid was slowly deposited.

Fuming nitric acid (1.63 ml.; 2 mol.) was added to 9-bromophenanthrene (5 g.) in benzene (5 ml.) at 15–20°, during $\frac{1}{2}$ hr.; the mixture was allowed to stand for $\frac{1}{2}$ hr. and ether (20 ml.) was added. The precipitate was chromatographed on alumina giving 9-bromo-10-nitrophenanthrene (1.9 g., 30%), m. p. as above.

Methyl 9-phenanthroate was largely unchanged (75% recovery) after passage of dinitrogen tetroxide and oxygen through a benzene solution at 20–25° for 2 hr.

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