1109. *Conjugated Cyclic Hydrocarbons. Part VIII.*[1] *The Benzo*[cd]*pyrenium Cation: Synthesis and Reactivity*

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Benzo[*cd*]pyrenium perchlorate has been synthesised and its reactions with nucleophiles have been studied. The results confirm predictions based on Hückel molecular-orbital theory.

MOLECULAR-ORBITAL (MO) theory predicts that the reaction of a conjugated carbonium ion with nucleophiles should occur at the position of highest charge density.[2] Carbonium ions possessing several sites with different charge densities which may compete for the nucleophile are of greatest interest in testing this prediction. In this Paper we describe the synthesis of benzo[*cd*]pyrenium perchlorate (I) in whose cation six positions are available for reaction.*

The benzo[*cd*]pyrenyl systems (IIa, b, and c) are odd-alternant hydrocarbons possessing nine bonding MO's and one zero-energy MO. The zero-energy orbital is empty in the cation, but contains one and two electrons, respectively, in the radical and anion. Charge densities for the benzo[*cd*]pyrenyl ions (IIa and c) have been calculated using the fact [3] that the charge densities of odd-alternant ions are determined entirely by the coefficients of the zero-energy MO. Details are given in Table 1. Four different magnitudes of charge density are found among the positions available for reaction in the cation (IIa). The highest is at position 6 which should, therefore, be the most reactive towards nucleophiles.

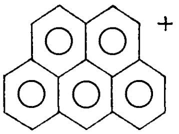
TABLE 1

Charge densities (Hückel MO procedure) in the benzo[*cd*]pyrenyl systems (IIa—c)

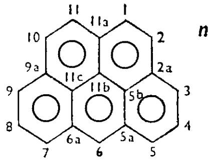
Position: *	2(10)	3(9)	5(7)	6	5b(11c)	11a
Cation (IIa):	+0·0606	+0·1364	+0·1364	+0·2424	+0·0152	+0·0606
Radical (IIb)	0	0	0	0	0	0
Anion (IIc)	−0·0606	−0·1364	−0·1364	−0·2424	−0·0152	−0·0606

* Charge densities zero at all other positions.

(I)



ClO_4^-



(II) a: $n = +$
b: $n = \bullet$
c: $n = -$

Benzo[*cd*]pyrenium perchlorate (I) was synthesised from pyrene by two routes. In the first, the known β-1-pyrenylpropionic acid (III) was prepared by an established method,[4] suitably modified for large-scale work (see Experimental section). Cyclisation of this acid afforded the ketone (IV) which was reduced to the alcohol (V). Dehydration of the alcohol gave a mixture of benzo[*cd*]pyrenes isomeric with and probably containing 3*H*-benzo[*cd*]pyrene (VI), the primary dehydration product. Isomerisations of this kind are well known in the chemistry of the phenalenes.[5] Hydride-abstraction by treatment

* This excludes interior positions and positions at ring junctions.

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[1] Part VII, M. Fraser and D. H. Reid, *J.*, 1963, 1421.

[2] See A. Streitwieser, " Molecular Orbital Theory for Organic Chemists," Wiley and Sons Inc., New York, 1961, p. 378.

[3] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, 1940, **36**, 193; H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

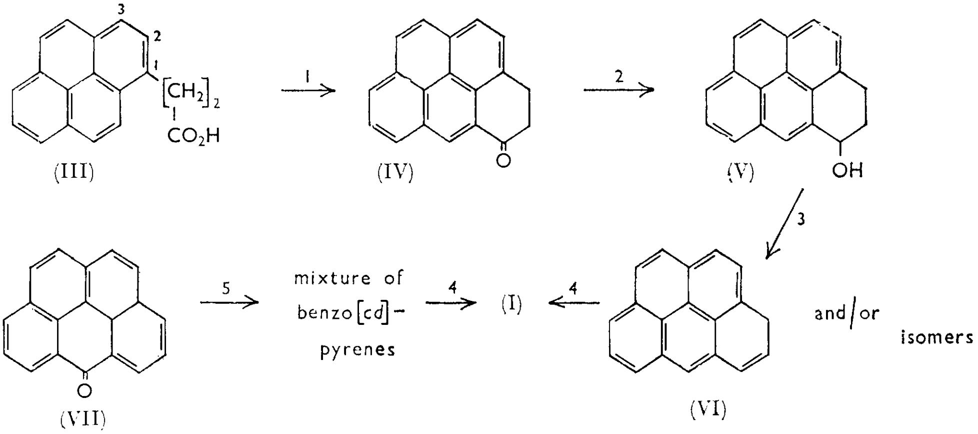
[4] W. E. Bachmann and M. Carmack, *J. Amer. Chem. Soc.*, 1941, **63**, 2496.

[5] V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1240; M. Nakazaki, U.S. Atomic Energy Commission Reports, 1957, UCRL–3700.

of the hydrocarbon mixture with *o*-chloranil and perchloric acid[6] gave benzo[*cd*]pyrenium perchlorate (I) in high yield as stable black needles whose solutions are green.*

In the second route, which is useful for the rapid preparation of small quantities of the perchlorate, the ketone (VII), prepared by the condensation of pyrene with glycerol and sulphuric acid,[7] was reduced with the lithium aluminium hydride–aluminium chloride reagent.[8] A mixture of benzo[*cd*]pyrenes was again obtained whose properties resembled those of the hydrocarbon mixture produced by dehydration of the alcohol (V); when treated with *o*-chloranil and perchloric acid it also gave benzo[*cd*]pyrenium perchlorate.†

The proton magnetic resonance spectrum of benzo[*cd*]pyrenium perchlorate in trifluoracetic acid shows two groups of signals centred at δ 8·62 and 9·25. The cation thus displays aromaticity but does not sustain an abnormally large ring-current.



Reagents: 1, HF. 2, $LiAlH_4$. 3, $HCl-CH_3CO_2H$. 4, *o*-Chloranil–$HClO_4$. 5, $LiAlH_4-AlCl_3$.

Benzo[*cd*]pyrenium perchlorate is indefinitely stable in the absence of moisture. It is hydrolysed irreversibly by water. In a quantitative study, hydrolysis of the perchlorate (I) under nitrogen gave a mixture of the ketone (VII) and a hydrocarbon product. The latter was a mixture of isomeric benzo[*cd*]pyrenes with the same melting range as the hydrocarbon mixture obtained by reduction of the ketone (VII) with lithium aluminium hydride–aluminium chloride; it reacted with *o*-chloranil and perchloric acid to give back benzo[*cd*]pyrenium perchlorate. The ketone (VII) and the hydrocarbon mixture each accounted for 45% of the hydrolysed perchlorate, the remaining 10% being lost in the purification processes. Thus, the hydrolysis of benzo[*cd*]pyrenium perchlorate with water produces an intermediate which disproportionates to an equimolecular mixture of the ketone (VII) and isomeric benzo[*cd*]pyrenes.

The formation of the ketone (VII) establishes that the cation in the salt (I) is attacked initially by water at position 6. We postulate that the carbinol (VIII) is formed which disproportionates to the products by a process of hydride-transfer to the benzo[*cd*]pyrenium cation or a related electrophilic species as shown.

Careful search was made for ketonic hydrolysis products other than the ketone (VII), whose presence would indicate nucleophilic attack elsewhere than at position 6. A yellow compound was detected at low concentration, estimated to be not greater than 0·25% of the total ketonic product. It is possible that part, if not all of this minor product arose

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* The same cation results irrespective of the site from which the hydride ion is lost.

† This excludes interior positions and positions at ring junctions.

[6] D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Letters*, 1961, 530; D. H. Reid and R. G. Sutherland, *J.*, 1963, 3295.

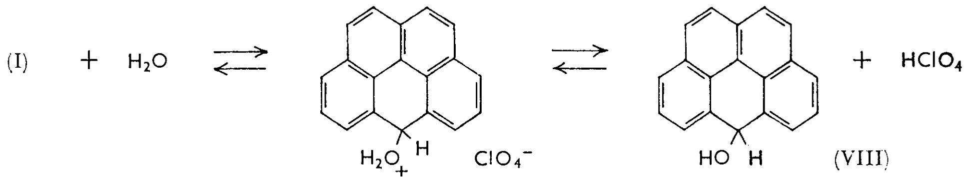
[7] H. Vollmann, H. Becker, M. Correll, and H. Streeck, *Annalen*, 1937, **531**, 1; R. Scholl and K. Meyer, *Ber.*, 1936, **69**, 152.

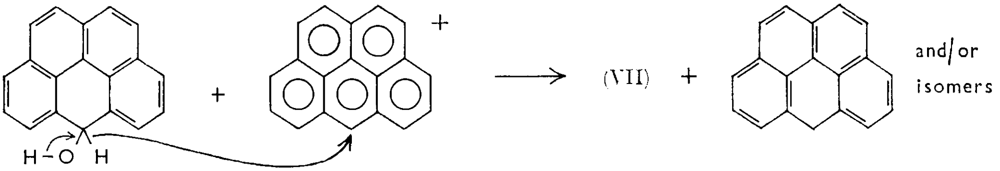
[8] B. R. Brown and A. M. S. White, *J.*, 1957, 3755.

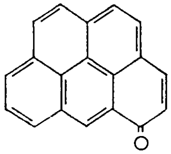
from the oxidation of a component of the hydrocarbon mixture after hydrolysis, and not by attack at an alternative site. This possibility was investigated by repeating the hydrolysis in air. About 1% of the ketonic product was a mixture of approximately equal parts of the ketone (IX) (see below) and the minor yellow product already described. These ketones were separated from the major ketonic product (VII) by utilising their much higher basicity. The yellow ketone must possess structure (X) or (XI). These results demonstrate that nucleophilic attack of the benzo[*cd*]pyrenium cation by water takes place, if not exclusively at position 6, to an extent greater than 99%.

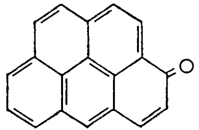
The reaction of benzo[*cd*]pyrenium perchlorate with triphenylphosphine was also examined. This gave an almost quantitative yield of the phosphonium perchlorate (XII) which, when treated with potassium methoxide followed by hydrogen peroxide, yielded the ketone (VII) and triphenylphosphine oxide. Formation of the ketone (VII) demonstrates that triphenylphosphine attacks the benzo[*cd*]pyrenium cation at position 6 and establishes structure (XII) for the phosphonium salt. The intermediate phosphorane (XIII) crystallised as air-sensitive scarlet needles which were not investigated.

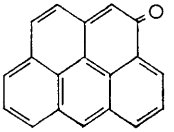
The reference ketone (IX) was obtained by dehydrogenation of its dihydro-derivative (IV) with *o*-chloranil and perchloric acid or triphenylmethyl perchlorate.[9] The primary






(IX)


(X)


(XI)

dehydrogenation product from which the ketone (IX) is obtained by hydrolysis, crystallised from the reaction solution as black needles whose composition corresponded to 2-ketone (IX) : 1 $HClO_4$. We assign to it one of the hydrogen-bridged structures (XIVa or b). Several aldehydes and ketones are known which form similar 2 : 1 salts with perchloric and other strong acids, for example, phenalone,[10] 1-formyl-4,6,8-trimethylazulene,[11] and mesitaldehyde.[12] The structure of the mesitaldehyde–$HClO_4$ salt has been shown to be of the type (XIVa).[13]

It has recently been shown [14] for a series of aromatic carbonyl compounds derived from carbonium ions containing an odd number of carbon atoms and no odd-membered rings, and in which the Coulomb integrals of oxygen in the carbonyl compounds and their

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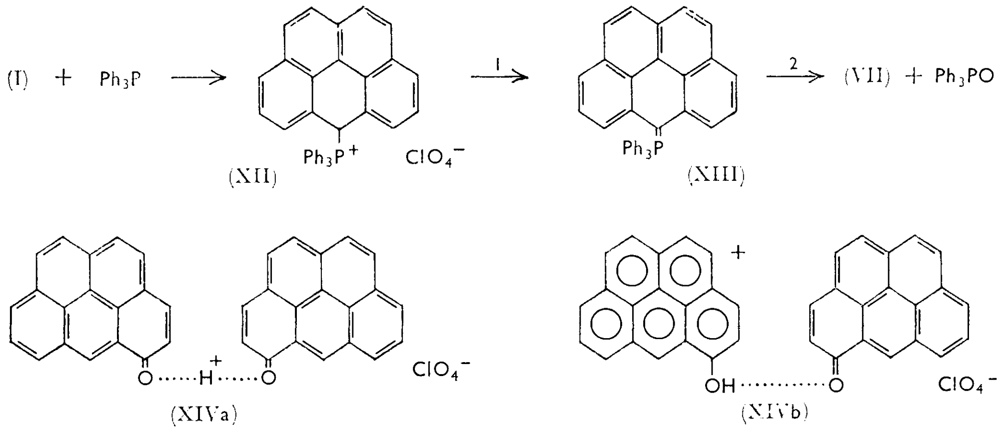
[9] W. Bonthrone and D. H. Reid, *J.*, 1959, 2773.
[10] G. B. Silberman and S. M. Barkov, *Zhur. obshchei Khim.*, 1937, **7**, 1733.
[11] E. C. Kirby and D. H. Reid, unpublished results.
[12] P. C. Myhre, C. D. Fisher, A. T. Nielsen, and W. M. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 29.
[13] C. D. Fisher, L. H. Jensen, and W. M. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 33.
[14] G. Culbertson and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 741.

conjugate acids remain constant, that $-\mathrm{p}K_{\mathrm{BH^+}}$ values should vary linearly with C_{0r}^2, where C_{0r}^2 is the coefficient at atom r of the zero-energy MO of the carbonium ion. This taken with the data in Table 1 indicates that the ketone (IX) should be much more basic than the ketone (VII). Experimentally this is found to be the case. The ketone (IX) dissolves reversibly in concentrated hydrochloric acid to form the green 3-hydroxybenzo[*cd*]pyrenium cation [as in (XIVb)], while the ketone (VII) is completely insoluble. It is also noteworthy that the infrared carbonyl frequency ($CHCl_3$) of the ketone (IX) (1628 cm.$^{-1}$) is considerably lower than that of the ketone (VII) (1651 cm.$^{-1}$). This indicates greater ground-state polarisation of the former, which is usually accompanied by an increase in basicity.



Reagents: 1, KOMe; 2, H_2O_2.

Experimental

Melting points were determined on a Kofler hot-stage apparatus. Ultraviolet spectra were measured with a Unicam S.P. 700 spectrophotometer. Infrared spectra were recorded with a Grubb–Parsons type G.S. 2A instrument. Proton magnetic resonance spectra were measured with a Varian A-60 spectrometer operating at 60 Mc./sec. Tetramethylsilane was used as the internal reference. Chemical shifts (δ) are given in p.p.m. downfield from the T.M.S. signal. Thin-layer chromatography was carried out on Silica-Gel G (Merck).

Materials.—Acetonitrile was purified by boiling it for 1 hr. over phosphoric anhydride, then twice distilled. Light petroleum was of boiling range 40—60°. Perchloric acid refers to 70% w/w perchloric acid of AnalaR grade.

β-1-*Pyrenylpropionic Acid* (III).—1-Hydroxymethylpyrene has been prepared[4] by the catalytic reduction of 1-formylpyrene.[7] The following procedure is convenient for its large-scale preparation. A solution of 1-formylpyrene (80·5 g., 0·35 mole) in benzene (700 ml.) was added to a stirred solution of lithium aluminium hydride (5·99 g., 80% excess) in ether (450 ml.) at such a rate as to maintain gentle boiling. The solution was boiled for 15 min., cooled, and hydrolysed. The mixture was acidified, and the organic layer collected. Part of the product which had crystallised was dissolved in benzene–ether (2 : 1). The combined extracts (4 l.) were washed free from acid, dried (K_2CO_3), and concentrated to *ca.* 250 ml. 1-Hydroxymethylpyrene (76·3 g., 94%) crystallised as pale yellow rhombs, m. p. 122—123° (lit.,[4] 123—124°). This alcohol was converted into 1-chloromethylpyrene (98% yield) as described by Bachmann and Carmack.[4]

1-Chloromethylpyrene (36 g.) was added to a solution of diethyl malonate (71 ml.) in ethanol (500 ml.) in which sodium (7 g.) had been dissolved. The solution was boiled for 10 hr. Solvent was distilled off, and the residue was boiled for 2 hr. with 40% aqueous potassium hydroxide (230 ml.). The cooled solution was diluted with its own volume of water, washed with ether, filtered, and acidified with concentrated hydrochloric acid. α-Carboxy-β-1-pyrenylpropionic acid (35·1 g., 68%) was obtained as colourless crystals, m. p. 190—191° (gas evolved). This acid (31·8 g.) was heated at 190—200° (bath temp.) for 25 min., or until decarboxylation was complete. Crystallisation of the residue from benzene (500 ml.) (charcoal) gave β-1-pyrenylpropionic acid (III) (21 g., 75%) as pale tan plates, m. p. 174—176° (lit.,[4] 178—179°), suitable for cyclisation.

Cyclisation of β-1-*Pyrenylpropionic Acid.*—The acid (13·7 g.) was added to liquid hydrogen fluoride (500 ml.). After 4 hr. at room temperature the solution was poured on to crushed ice (1 kg.). Organic material was extracted into ether (2 × 500 ml.), and the combined extracts were washed successively with water (twice), saturated sodium hydrogen carbonate solution (twice), and water before being dried (Na_2SO_4) and evaporated. The residue in benzene (25 ml.) and ether (25 ml.) was adsorbed on alumina (10 × 4 cm.). Elution with benzene–ether (1 : 1) gave pale yellow eluates which were evaporated at reduced pressure. Crystallisation of the residue from benzene gave 4,5-*dihydro*-5-*oxo*-3H-*benzo*[cd]*pyrene* (IV) (10·2 g., 80%) as pale orange prisms, m. p. 155·5—158°, raised to 157—158° by recrystallisation from benzene–ethanol (1 : 1) (Found: C, 88·7; H, 5·0. $C_{19}H_{12}O$ requires C, 89·0; H, 4·7%).

4,5-*Dihydro*-5-*hydroxy*-3H-*benzo*[cd]*pyrene.*—The foregoing ketone (20·5 g., 80 mmoles) in benzene (480 ml.) was added to a stirred solution of lithium aluminium hydride (1·52 g.) in ether (240 ml.). The mixture was stirred for 1 hr. before being hydrolysed with ice and an excess of dilute sulphuric acid. Part (10·07 g.) of the alcohol crystallised. This was filtered off, washed with water until free from acid, then with ether, and dried. The organic phase and the ether washings were combined, washed free from acid, dried (K_2CO_3), and evaporated. Crystallisation of the residue from benzene (300 ml.) gave colourless needles (7·79 g.), bringing the total yield of 4,5-*dihydro*-5-*hydroxy*-3H-*benzo*[cd]*pyrene* (V) to 17·86 g. (87%). A sample, recrystallised from benzene, had m. p. 165—168° (Found: C, 88·6; H, 6·2. $C_{19}H_{14}O$ requires C, 88·4; H, 5·5%).

Dehydration of 4,5-*Dihydro*-5-*hydroxy*-3H-*benzo*[cd]*pyrene.*—Acetic acid (120 ml.), saturated with anhydrous hydrogen chloride, was added to a solution of the alcohol (10·32 g., 40 mmoles) in acetic acid (120 ml.). The resulting solution was boiled for 5 min., then poured into water. The precipitated solid was extracted with ether (1 l.). The extract was washed successively with water (twice), 15% sodium hydroxide solution (twice), and water, dried (Na_2SO_4), and evaporated. The residue was adsorbed on alumina (12 × 4·2 cm.) from a solution in benzene (75 ml.) and light petroleum (75 ml.). Elution with the same solvent mixture gave colourless eluates (500 ml.). Evaporation afforded a pale yellow residue which was rechromatographed on alumina (12 × 3·2 cm.) with light petroleum–benzene (8 : 1) as eluant. The eluates (800 ml.) were concentrated to 30 ml. at reduced pressure before the addition of boiling ethanol (60 ml.). 3*H*-Benzo[*cd*]pyrene (VI) and/or isomers crystallised as colourless prisms (7·50 g., 78%), m. p. 119—128° (bulk 124—128°) (Found: C, 94·8; H, 5·1. Calc. for $C_{19}H_{12}$: C, 95·0; H, 5·0%). Recrystallisation failed to give a sharp melting point.

Reduction of 6-*Oxo*-6H-*benzo*[cd]*pyrene with Lithium Aluminium Hydride–Aluminium Chloride.*—Crude 6-oxo-6*H*-benzo[*cd*]pyrene, prepared from pyrene, glycerol, and sulphuric acid,[7] was purified by chromatography on alumina with chloroform as eluant. Recrystallisation from benzene gave yellow leaflets, m. p. 250—252°, $\nu_{max.}$ ($CHCl_3$) 1651 cm.$^{-1}$ (C=O). A solution of the ketone (2·54 g., 10 mmoles) in benzene (200 ml.) was added to a stirred solution of lithium aluminium hydride (1·33 g., 35 mmoles) and aluminium chloride (9·35 g., 70 mmoles) in ether (200 ml.). The addition of each drop produced a transient red colour, and the resulting solution was stirred at room temperature for 1 hr. before being poured into an excess of ice-cold dilute sulphuric acid. The organic phase was washed free from acid, dried (Na_2SO_4), and evaporated. The residual oil was chromatographed on alumina (12 × 2·7 cm.) with light petroleum–benzene (2 : 1) as solvent and eluant. Evaporation of the colourless eluates (1500 ml.) at reduced pressure gave 6*H*-benzo[*cd*]pyrene and/or isomers as a pale yellow solid (2340 mg., 97%) which recrystallised from cyclohexane as colourless tablets, m. p. 120—130° (bulk 124—130°). The reported m. p.s of 6*H*-benzo[*cd*]pyrene are 134° [15] and 123—124°.[16]

Benzo[cd]*pyrenium Perchlorate.*—*From* 3H-*benzo*[cd]*pyrene* (VI) *and/or isomers.* A solution of *o*-chloranil (4·92 g., 20 mmoles) and perchloric acid (2 ml.) in acetic acid (50 ml.) at room temperature was added to a boiling solution of the hydrocarbon (4·81 g., 20 mmoles) in acetonitrile (50 ml.). *Benzo*[cd]*pyrenium perchlorate* (I) (6·02 g., 89%) crystallised at once from the

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[15] E. Clar, " Aromatische Köhlenwasserstoffe," Springer Verlag, Berlin, 1952, 2nd edn., p. 453.

[16] A. W. Johnson, *J. Org. Chem.*, 1959, **24**, 833.

green solution as black needles which were filtered, washed with acetic acid followed by dry ether, and dried *in vacuo*. Recrystallisation was from acetonitrile. The perchlorate decomposes gradually above 185° (Found: C, 67·4; H, 3·3; Cl, 10·5. $C_{19}H_{11}ClO_4$ requires C, 67·4; H, 3·3; Cl, 10·5%), $\lambda_{max.}$ (MeCN) 616, 475sh, 434, 318sh, 299sh, 290, 279, 269sh, 245, 236, 218, and 201 mμ (log ε 3·60, 3·94, 4·31, 3·99, 4·22, 4·40, 4·35, 4·27, 4·52, 4·52, 4·70, and 4·80). Tetrachlorocatechol (3·963 g., 80%) was recovered from the mother-liquors.

When a solution of *o*-chloroanil (1230 mg., 5 mmoles) and perchloric acid (0·5 ml.) in acetonitrile (4 ml.) was added to a boiling solution of the hydrocarbon (1201 mg., 5 mmoles) in acetonitrile (16 ml.), the yield was 1260 mg. (74%).

From the hydrocarbon obtained by reduction of 6-*oxo*-6H-*benzo*[cd]*pyrene with lithium aluminium hydride–aluminium chloride.* A solution of *o*-chloranil (2·46 g., 10 mmoles) and perchloric acid (1 ml.) in acetic acid (25 ml.) was added to a boiling solution of the hydrocarbon mixture (2·40 g., 10 mmoles) in acetonitrile (25 ml.). Benzo[*cd*]pyrenium perchlorate (I) (2·950 g., 87%) crystallised as black needles, identical with the product from the preceding experiment.

Hydrolysis of Benzo[cd]*pyrenium Perchlorate under Nitrogen.*—A mixture of water (50 ml.) and acetonitrile (50 ml.) was added to a suspension of the perchlorate (3388 mg., 10 mmoles) in dry benzene (250 ml.) under nitrogen. The mixture was stirred for 1 hr., or until all the salt had solvolysed. A portion (0·25 ml.) of the upper layer was withdrawn, diluted to 1 ml. with benzene, dried (Na_2SO_4), and examined immediately by thin-layer chromatography (t.l.c.) (methylene chloride). The chromatogram showed a large colourless spot (developed in iodine) due to the hydrocarbon mixture, a large yellow spot due to the ketone (VII), and a trace of a yellow strongly adsorbed ketone (X) or (XI). The trace component moved at the same rate as the yellow component of the mixture of ketones [(IX) + (X) or (XI)] obtained in the following experiment. It was estimated to be $<0·25\%$ of the ketonic hydrolysis product on the basis of comparative studies using a sample of the mixture of ketones (IX) + (X) or (XI).

The reaction mixture was diluted with benzene and water. The benzene layer (600 ml.) was washed with water (twice), dried (Na_2SO_4), and evaporated at reduced pressure. The residue in benzene (300 ml.) was adsorbed on alumina (15 × 3·2 cm.). Elution with benzene gave colourless eluates (1000 ml.). Continued elution with chloroform gave yellow eluates (3 l.) from a strongly adsorbed orange-yellow band. The benzene eluates were evaporated at reduced pressure, and the residue in benzene (50 ml.) was rechromatographed on alumina (12 × 2·7 cm.) with benzene as eluant. The colourless eluates were evaporated to low volume at reduced pressure. Boiling ethanol was added. 6*H*-Benzo[*cd*]pyrene and/or isomers crystallised as pale yellow tablets (1070 mg., 45% based on the perchlorate), m. p. 121—127°. Treatment of this hydrocarbon mixture with *o*-chloranil and perchloric acid as described in the preceding experiment gave benzo[*cd*]pyrenium perchlorate (I) (89%) as black needles.

The chloroform eluates were evaporated and the residue was crystallised from benzene (40 ml.). 6-Oxo-6*H*-benzo[*cd*]pyrene (VII) (825 mg.) was obtained as golden-yellow leaflets, m. p. 251—253° (lit.,[15] 253°) (Found: C, 90·5; H, 4·0. Calc. for $C_{19}H_{10}O$: C, 89·8; H, 4·0%), identical (m. p., infrared spectrum, t.l.c.) with the ketone (VII) from the condensation of pyrene with glycerol and sulphuric acid. A further 310 mg. of the ketone were obtained by chromatography of the mother-liquors on alumina (10 × 2·7 cm.) with chloroform–methylene chloride (1 : 3) as eluant. The total yield of the ketone was 1135 mg. (45% based on perchlorate).

Hydrolysis of Benzo[cd]*pyrenium Perchlorate in Air.*—The hydrolysis was carried out in air, but the procedure was otherwise identical with that of the preceding experiment. The benzene layer was evaporated to dryness in order to remove acetonitrile. A solution of the residual solid in benzene was extracted with concentrated hydrochloric acid (3 × 200 ml.), washed free from acid, dried (Na_2SO_4), and concentrated to 300 ml. before being chromatographed in the manner described in the preceding experiment. The eluates afforded 6*H*-benzo[*cd*]pyrene and/or isomers (46%) as pale yellow crystals, m. p. 117—124°, and 6-oxo-6*H*-benzo[*cd*]pyrene (VII) (48%) as golden-yellow leaflets, m. p. 250—252°.

The green acid extracts were washed once with benzene before being diluted with water (1800 ml.) and extracted with chloroform. The extract was washed free from acid, dried (Na_2SO_4), and evaporated. The residue in methylene chloride (30 ml.) was chromatographed on alumina (6 × 1·7 cm.) with methylene chloride as eluant. A trace of the ketone (VII) came through rapidly and was discarded. The succeeding red eluates (300 ml.) from an orange-red band yielded a red solid (13 mg., 1%). Recrystallisation from cyclohexane–methylene chloride (8 : 1) gave a mixture (8 mg.) of approximately equal amounts of 5-oxo-5*H*-benzo[*cd*]pyrene

(IX) (t.l.c. in methylene chloride, pink faster-moving spot) and either 3-oxo-3*H*- (X) or 2-oxo-2*H*-benzo[*cd*]pyrene (XI) (t.l.c., yellow spot) as orange-red needles, m. p. 182—192° (Found: C, 89·5; H, 3·8. Calc. for $C_{19}H_{10}O$: C, 89·8; H, 4·0%).

Reaction of Benzo[cd]*pyrenium Perchlorate with Triphenylphosphine.*—Benzo[*cd*]pyrenium perchlorate (1355 mg., 4 mmoles), triphenylphosphine (1048 mg., 4 mmoles), and acetonitrile (20 ml.) were heated to the boil. Ether (100 ml.) was added gradually to the cooled solution. 6H *Benzo*[cd]*pyren*-6-*yltriphenylphosphonium perchlorate* (XII) (2260 mg., 94%) crystallised as pale brown prisms. Recrystallisation from acetonitrile–ether (1 : 6) and then from acetonitrile gave straw-coloured prisms which decomposed above 185° (Found: C, 73·8; H, 4·7; P, 5·5. $C_{37}H_{26}ClO_4P$ requires C, 73·9; H, 4·4; P, 5·2%).

Oxidation of 6H-*Benzo*[cd]*pyren*-6-*yltriphenylphosphonium Perchlorate with Hydrogen Peroxide–Potassium Methoxide.*—A solution of potassium methoxide (1400 mg., 20 mmoles) in methanol (10 ml.) was run into a stirred solution of the perchlorate (1202 mg., 2 mmoles) in acetonitrile (70 ml.). The solution became deep red and 6*H*-benzo[*cd*]pyren-6-ylidenetriphenylphosphorane (XIII) crystallised as scarlet needles. 30% Hydrogen peroxide (10 ml.) was added in 10 min. to the stirred solution. The solution was gradually heated to the boil and the phosphorane was replaced by a reddish-brown precipitate. After being boiled for 2 min. the cooled solution was poured into water and the organic material was extracted with methylene chloride. The extract (800 ml.) was washed with 5M-hydrochloric acid (twice) and water before being dried (Na_2SO_4) and evaporated. The residue in benzene was chromatographed on alumina (10 × 2·7 cm.). Elution with benzene brought through pale yellow eluates (1750 ml.) which yielded 6-oxo-6*H*-benzo[*cd*]pyrene (VII) (202 mg., 40%) as golden-yellow plates (from benzene), m. p. 250—252°, identical (infrared spectrum, t.l.c.) with the ketone from the hydrolysis of benzo[*cd*]pyrenium perchlorate. Continued elution with chloroform gave orange eluates which upon evaporation yielded an off-white solid (485 mg.). Distillation at 180—200°/0·1 mm. afforded triphenylphosphine oxide as colourless needles or spars (from cyclohexane), m. p. 153·5—156° (lit.,[17] 154—156°). Continued sublimation at 200—300°/0·1 mm. yielded traces of an orange oil which was insoluble in perchloric acid and was discarded.

Dehydrogenation of 4,5-*Dihydro*-5-*oxo*-3H-*benzo*[cd]*pyrene with* o-*Chloranil–Perchloric Acid.*—A solution of *o*-chloranil (984 mg., 4 mmoles) and perchloric acid (0·5 ml.) in acetonitrile (5 ml.) was added to a boiling suspension of 3,4-dihydro-5-oxo-5*H*-benzo[*cd*]pyrene (1024 mg., 4 mmoles) in acetonitrile (20 ml.). The green solution was boiled for 1 min. before being cooled. Gradual addition of ether (75 ml.) precipitated 5-*oxo*-5H-*benzo*[cd]*pyrene hemiperchlorate* (XIVa or b) (1206 mg., 99%). Recrystallisation from acetonitrile gave large black needles which decomposed above 155° (Found: C, 75·0; H, 3·5. $C_{38}H_{21}ClO_6$ requires C, 73·4; H, 3·8%). The hemiperchlorate (300 mg., 99%) was also obtained by the addition of perchloric acid (0·25 ml.) to a boiling solution of 5-oxo-5*H*-benzo[*cd*]pyrene (254 mg., 1 mmole) in acetonitrile (10 ml.) and methylene chloride (10 ml.)

The foregoing hemiperchlorate was shaken with water and methylene chloride (500 ml. each). The methylene chloride extract was washed free from acid, dried (K_2CO_3), and concentrated to 150 ml. The solution was filtered through alumina (10 × 2·7 cm.) with methylene chloride–methanol (10 : 1) as eluant. The eluates were concentrated to 25 ml. and the residual methylene chloride was displaced by boiling ethanol (30 ml.). 5-*Oxo*-5H-*benzo*[cd]*pyrene* (IX) (892 mg., 88% from the ketone) crystallised as garnet-red prisms with a green reflex, m. p. 218·5—221°, unchanged in form or melting point after recrystallisation from acetonitrile (Found: C, 89·7; H, 4·0. $C_{19}H_{10}O$ requires C, 89·8; H, 4·0%), $\nu_{max.}$ ($CHCl_3$) 1628 cm.$^{-1}$ (C=O), $\lambda_{max.}$ (MeOH) 479, 418, 396, 390, 309, 296, 284, 263, 256, 230, and 209 mμ (log ε 4·08, 3·95, 3·73, 3·59, 4·58, 4·42, 4·35, 4·42, 4·35, 4·69, and 4·70). A solution of 5-oxo-5*H*-benzo[*cd*]pyrene in acetic acid containing 4% (v/v) perchloric acid had $\lambda_{max.}$ 622, 466, 408, 314, 274, and 254 mμ (log ε 4·07, 4·16, 4·25, 4·14, 3·87, and 4·00) due to the presence of the 5-hydroxybenzo[*cd*]pyrenium cation.

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[17] G. Wittig and W. Haag, *Annalen*, 1953, **580**, 44.