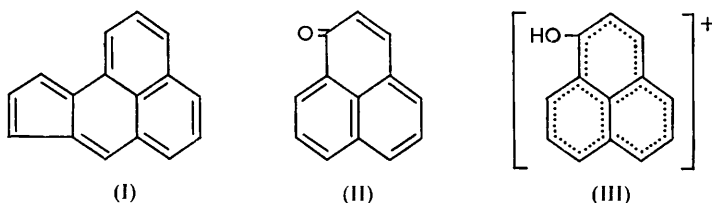


675. The Synthesis of Indeno[2,1-a]perinaphthene.*

By I. M. AITKEN and D. H. REID.

Indeno[2,1-a]perinaphthene (IV) has been synthesised and some of its properties have been studied. The principal findings are: (i) The hydrocarbon is strongly basic; it dissolves reversibly in moderately strong sulphuric acid or anhydrous liquid hydrogen fluoride to form a green cation. (ii) It functions readily as the diene component in Diels-Alder reactions. (iii) Electrophilic substitution takes place readily under mild conditions (the probable position of substitution is discussed). (iv) A new type of reaction by lead tetra-acetate involving intermolecular dehydrogenation is reported.

So far as we are aware no compound containing the ring system of *cyclopenta*[a]perinaphthene (I) has hitherto been synthesised nor is any known to occur naturally. A five-membered ring is known to possess anionic stability when associated with six π -electrons. Further, perinaphthenone (II) itself, in appropriate circumstances, shows considerable cationic character: *e.g.*, the C=O stretching frequency in the infrared spectrum¹ is unusually low (1637 cm^{-1}); and the ketone is abnormally basic,² dissolving reversibly in



concentrated hydrochloric acid. These properties suggest that perinaphthenone has a tendency to become polarised with formation of a stable tricyclic structure of thirteen carbon atoms over which twelve π -electrons are delocalised. This structure exists in the 1-hydroxyperinaphthenylium cation³ (III) which is present in solutions of perinaphthenone

* A preliminary account was read at the 14th Intern. Congr. Pure & Appl. Chem., Zürich, July, 1955.

¹ Cromwell and Hudson, *J. Amer. Chem. Soc.*, 1953, **75**, 872.

² Bamberger and Philip, *Annalen*, 1887, **240**, 178; Cook and Hewett, *J.*, 1934, 365.

³ Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1245; Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1952, 2nd Edn., p. 431.

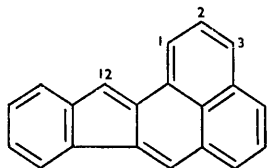
⁴ Reid, Stafford, and Ward, *J.*, 1955, 1193.

⁵ Reid, *Angew. Chem.*, 1955, 761.

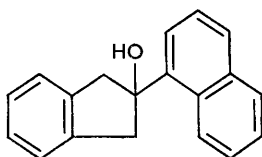
in strong acid. In view of the electronically complementary tendencies of the five-membered ring and the perinaphthene nucleus it was expected that π -electron migration from the perinaphthene moiety to the five-membered ring would prevail to a greater or smaller extent in compounds containing the *cyclopenta*[*a*]perinaphthene ring system. The five-membered ring in such compounds should therefore show considerable nucleophilic reactivity of an order and character found among the azulenes.⁴ To test these conclusions we have begun the synthesis and study of compounds containing the *cyclopenta*[*a*]perinaphthene system.⁵ In this communication the synthesis of indeno[2,1-*a*]perinaphthene (IV), a ring homologue of (I), is described, and a preliminary account of some of its properties is given.

Indan-2-one and 1-naphthylmagnesium bromide gave a mixture of the expected tertiary alcohol (V) and its dehydration product (VI). Dehydration of the mixture was completed by boiling formic-acetic acid. The resulting hydrocarbon (VI) displays monotropy. The metastable form tends to crystallise from impure solutions, and fuses to a clear liquid at 77—79°: the melt then solidifies to a mass of colourless plates, constituting the stable modification, which melt at 90—91°.

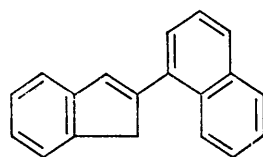
This hydrocarbon condensed with ethyl formate in the presence of potassium methoxide, giving a good yield of the hydroxymethylene compound (VII) which was, however, unstable and could not be isolated pure. Consistently with its tautomeric nature it formed both a benzoate and a 2:4-dinitrophenylhydrazone, which served to characterise it. Owing to its instability, this derivative was cyclised immediately, best by 93% sulphuric acid, the acid concentration being critical. Two highly coloured, benzene-soluble hydrocarbons were obtained in low yield from the cyclisation: one, subsequently shown to be indeno[2,1-*a*]perinaphthene (IV), was found to be strongly basic—and was removed completely



(IV)



(V)



(VI)

by extraction with 77% sulphuric acid; dilution of the green acid extracts caused its precipitation and it formed reddish-brown leaflets, which gave red solutions in benzene. The second hydrocarbon formed purple-black prisms, which in benzene give crimson solutions.

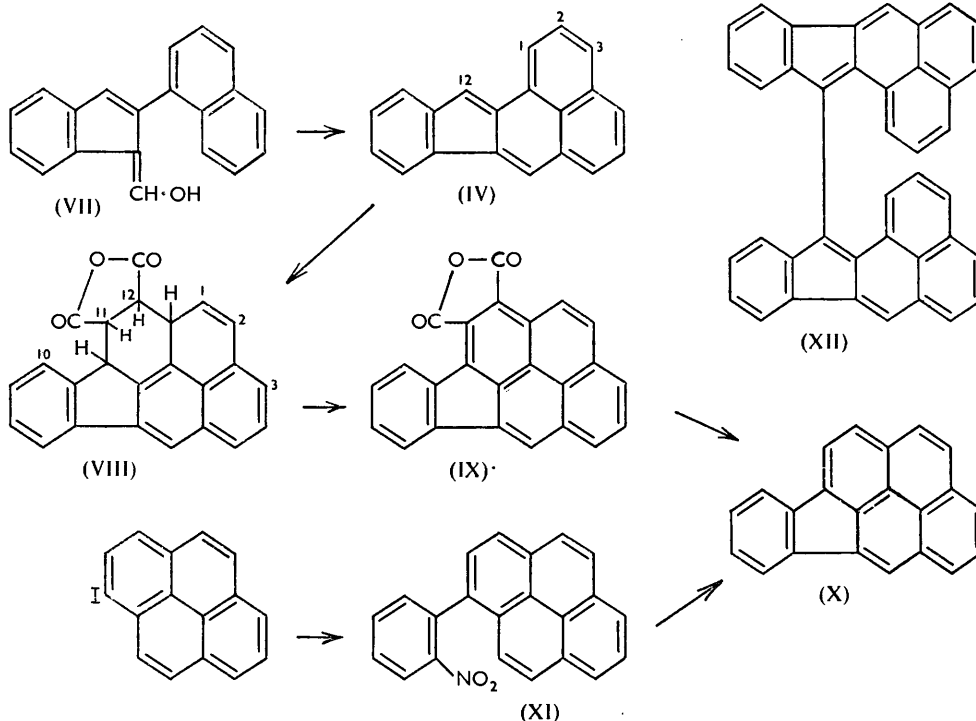
Structural investigation of these hydrocarbons by oxidation failed (indeno[2,1-*a*]perinaphthene was oxidised by chromic anhydride in acetic acid without loss of carbon to an orange diketone of unknown structure).

The basic hydrocarbon was shown to be indeno[2,1-*a*]perinaphthene on the following evidence. It serves readily as the diene component in Diels-Alder reactions: *e.g.*, with maleic anhydride in boiling xylene-acetic acid it gives a colourless adduct (VIII) rapidly and quantitatively. This adduct was dehydrogenated by boiling nitrobenzene and the fully aromatic anhydride (IX) was decarboxylated to the intensely yellow indeno[1,2,3-*cd*]pyrene (X). Independently, a crossed Ullmann reaction between 1-iodopyrene and *o*-bromonitrobenzene gave 1-*o*-nitrophenylpyrene (XI) which, by successive reduction to the corresponding amine, diazotisation, and treatment with copper bronze, was converted into the same hydrocarbon (X). The synthesis of indeno[1,2,3-*cd*]pyrene from 1-(1-hydroxymethylene-2-indenyl)naphthalene and from 1-*o*-nitrophenylpyrene is possible only if cyclisation of the former results in formation of a six-membered ring and ring-closure of 1-*o*-aminophenylpyrene involves the formation of a five-membered ring. The basic hydrocarbon must therefore be indeno[2,1-*a*]perinaphthene (IV).

Indeno[2,1-*a*]perinaphthene forms a complex with trinitrobenzene, crystallising in black needles. The absorption spectra (Fig. 1) of indeno[2,1-*a*]perinaphthene (IV) and

indeno[1,2,3-*cd*]pyrene (X) show close correspondence in the number and intensities of band groups and maxima, but the maxima of the former lie at longer wave-lengths.

The constitution of the purple-black, non-basic hydrocarbon has not yet been established with certainty but the tentative assignment of structure (XII) appears justified by the following results: (i) The molecular weight approximates to twice that of indeno[2,1-*a*]perinaphthene. (ii) The same hydrocarbon is formed in substantial yield when indeno[2,1-*a*]perinaphthene in benzene is treated at room temperature with lead tetra-acetate. (iii) The purple-black hydrocarbon itself, when subjected to the prolonged action of lead tetra-acetate in boiling benzene, is converted into a high-melting green crystalline solid.



Analytical data for this compound agree well with those required by a monoacetoxysterivative of (XII). Thus one molecule of the purple-black hydrocarbon contains two nuclei of indeno[2,1-*a*]perinaphthene. The low basicity of the former, which dissolves only in concentrated sulphuric acid, suggests that the indeno[2,1-*a*]perinaphthene nuclei are attached at the 12-positions, as in structure (XII), since for reasons indicated below we associate the basicity of indeno[2,1-*a*]perinaphthene with its 12-position. The visible absorption spectra of the purple-black hydrocarbon and indeno[2,1-*a*]perinaphthene are given in Fig. 2 (the curve there shown for the former was obtained by plotting $\log_{10} 0.5\epsilon$ against wavelength): their close similarity is consistent with structure (XII).

The experimental evidence presented clearly excludes the possibility of the purple-black hydrocarbon's being benzo[*a*]naphtho[1,2-*e*]pentalene, which would be formed by a cyclisation of (VII) involving the 2-position of the naphthalene moiety. No evidence for the formation of such a cyclisation product was found. Blood and Linstead⁶ have reported that the closely related 1:2-4:5-dibenzopentalene is readily polymerised by traces of strong acid. In view of these findings it is unlikely that any benzo[*a*]naphtho[1,2-*e*]pentalene formed would survive the strongly acid conditions of the cyclisation. The formation of the hydrocarbon (XII) itself under the cyclisation conditions is unusual and

⁶ Blood and Linstead, *J.*, 1952, 2263.

no explanation for its formation can be offered. Its formation by the action of lead tetra-acetate on indeno[2,1-*a*]perinaphthene is noteworthy because it constitutes the only case known where the reagent effects intermolecular dehydrogenation of a hydrocarbon.

The most characteristic property of indeno[2,1-*a*]perinaphthene is its high basicity. This compound therefore represents a new class of basic hydrocarbons of which the

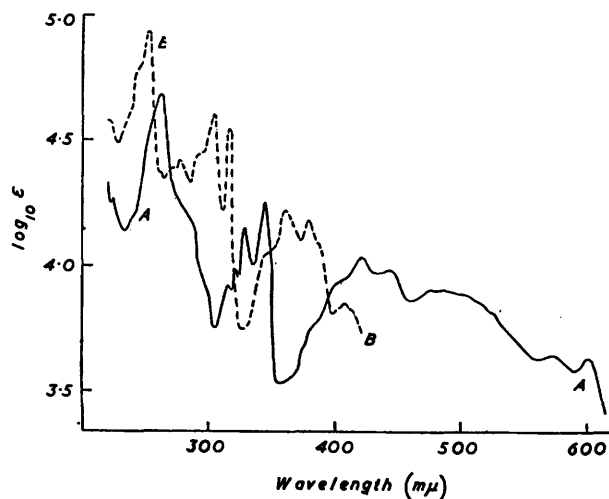


FIG. 1. Absorption spectra of (A) indeno[2,1-*a*]perinaphthene (IV) and (B) indeno[1,2,3-*cd*]pyrene (X) in cyclohexane.

FIG. 2. Absorption spectra of indeno[2,1-*a*]perinaphthene (IV) (A) in benzene, (B) in 77% sulphuric acid, and of (C) di(indeno[2,1-*a*]perinaphthen-12-yl) (XII) in benzene, obtained by plotting $\log_{10} 0.5\epsilon$ against wavelength.

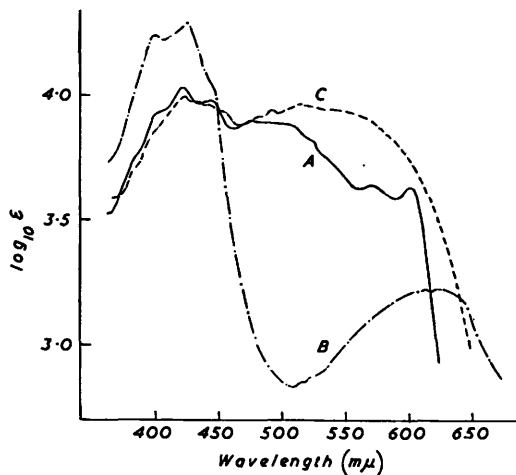
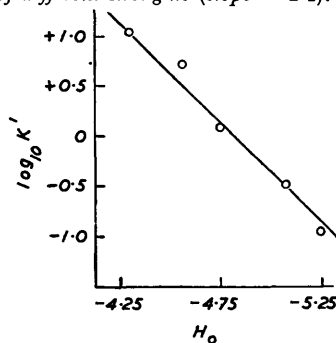


FIG. 3. Plot of $\log_{10} K'$ against H_0 for indeno[2,1-*a*]perinaphthene distributed between cyclohexane and sulphuric acid of different strengths (slope = 2.1).

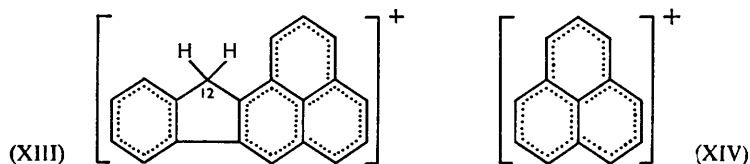


simplest member is the still unknown *cyclopenta*[*a*]perinaphthene (I). The hydrocarbon (IV) dissolves reversibly in strong aqueous sulphuric acid or anhydrous liquid hydrogen fluoride, with formation of a green cation. A measure of the basicity was obtained by the procedure of Plattner, Heilbronner, and Weber⁷ by which the hydrocarbon was partitioned between *cyclohexane* and sulphuric acid of different strengths. Fig. 3 discloses that a linear relation exists between $\log_{10} K'$ (where K' is the apparent partition coefficient)

⁷ Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1949, **32**, 574.

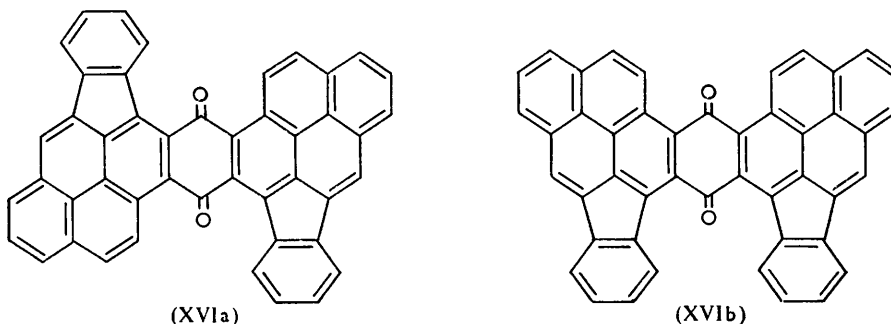
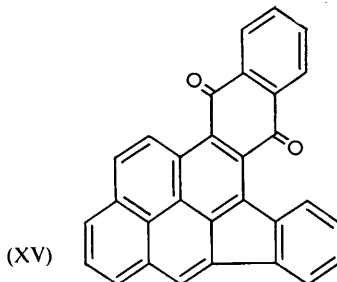
and the Hammett acidity function H_0 ,⁸ and the slope of the straight line approximates closely to two. This is interpreted⁹ as resulting from a salting-in effect on the hydrocarbon base molecules with increasing acidity. The H_0 value found (-4.80) for which K' is unity corresponds to an acid concentration of 64% H_2SO_4 (w/w); this value places indeno[2,1-*a*]perinaphthene alongside the azulenes in order of basicity.⁴

The conjugate acid of indeno[2,1-*a*]perinaphthene is considered to possess structure (XIII) resulting from accession of a proton to $C_{(12)}$. Addition of a proton at this position allows formation, in the perinaphthene moiety, of the π -electron system of the perinaphthenylium cation (XIV) with which considerable stability is associated.



Preliminary experiments on the electrophilic substitution of indeno[2,1-*a*]perinaphthene indicate that the hydrocarbon possesses a nucleophilic reactivity comparable with that of the azulenes. Tetranitromethane¹⁰ in pyridine-ethanol rapidly affords a violet mononitroindeno[2,1-*a*]perinaphthene. The hydrocarbon couples with diazotised *p*-nitroaniline but not with benzenediazonium chloride. The position of substitution in these reactions has not yet been determined experimentally but is also considered to be the 12-position.

The reactions of indeno[2,1-*a*]perinaphthene with suitable dienophiles represent further examples of an aromatic system providing both multiple bonds for the diene addition reaction. Noteworthy is the ready isolation of the primary adduct (VIII) from the reaction with maleic anhydride in non-oxidising media. The reaction of indeno[2,1-*a*]-



perinaphthene with 1 : 4-naphthaquinone in boiling nitrobenzene afforded the expected tetracene derivative (XV). When 1 : 4-benzoquinone was the dienophile a high-melting

⁸ Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, Chap. IX.

⁹ Gold and Tye, *J.*, 1952, 2181.

¹⁰ Schmidt and Fischer, *Ber.*, 1920, 53, 1529.

orange crystalline solid was isolated, resulting from addition of two molecules of the hydrocarbon (IV) to one of 1:4-benzoquinone. This product must possess one of the two possible structures (XVIa and b).

EXPERIMENTAL

M. p.s were determined on a Kofler-type heating-stage. Absorption spectra were measured with a Unicam S.P. 500 instrument. Chromatographic purifications were effected on activated alumina.

1-2'-Indenylnaphthalene (VI).—A solution of indan-2-one (100 g.) in dry ether (300 ml.) was added during 45 min. to the stirred, ice-cooled Grignard reagent prepared from 1-bromonaphthalene (230 g.) and magnesium (28 g.) in anhydrous ether (1 l.). The resulting solution was boiled under reflux for 1 hr. The bulk of the ether was removed by distillation while anhydrous benzene was introduced at such a rate as to maintain the original volume of the solution. This process was terminated when the temperature of the vapour had reached 76°, and the mixture was thereafter boiled under reflux for 6 hr. The cooled solution was poured into excess of ice-cold 4*N*-sulphuric acid, and the separated benzene layer washed with water, dried (Na₂SO₄), and evaporated at reduced pressure. The residual dark oil was separated by distillation into two fractions. The first fraction, boiling range 95—140°/18 mm., consisted chiefly of naphthalene with a small quantity of unchanged indan-2-one and was discarded. The second fraction (60.6 g.) was a viscous yellow oil, b. p. 204—213°/0.9 mm. Elementary analysis showed that it consisted approximately of seven parts of 1-(2-hydroxy-2-indanyl)naphthalene (V) and one part of 1-2'-indenylnaphthalene (VI).

The foregoing mixture in glacial acetic acid (300 ml.) and 98% formic acid (250 ml.) was boiled under reflux for 2 hr. The cooled solution was poured into water and the precipitated oil was taken up in ether. The ether extract was washed successively with water (four times), aqueous sodium hydroxide (twice), and again with water, and finally dried (Na₂SO₄). Evaporation of the solvent left a yellow oil which was dissolved in light petroleum-benzene (8:1) before filtration through a column (9 × 4.2 cm.). A yellow, strongly adsorbed impurity was retained at the top of the column. The almost colourless eluates deposited the *hydrocarbon* (VI) (46.1 g.) in its metastable form as colourless needles which, after recrystallisation from light petroleum, melted at 77—79°. The melt solidifies at 81—84° to a mass of colourless plates which subsequently melt at 90—91° (Found: C, 94.0; H, 6.0. C₁₉H₁₄ requires C, 94.2; H, 5.8%). The *trinitrobenzene complex* crystallised from absolute ethanol as orange elongated prisms, m. p. 142—143° (Found: 12.4. C₁₉H₁₄.C₆H₃O₆N₃ requires N, 12.6%). Solutions of the hydrocarbon fluoresce blue in daylight and ultraviolet light. In a subsequent experiment the crude hydrocarbon was first distilled (b. p. 184—187°/0.7 mm.) before filtration through a column. The stable modification of the hydrocarbon crystallised directly from the concentrated eluates as colourless plates, m. p. 90.5—91°. Ultraviolet absorption spectrum (in *cyclohexane*): λ_{max}. 3100, 2610, 2545, 2490, 2430, 2235, and 2205 Å; log₁₀ ε 4.19, 4.22, 4.31, 4.32, 4.39, 4.70, and 4.63.

1-(1-Hydroxymethylene-2-indenyl)naphthalene (VII).—Dry potassium methoxide (3.2 g.) and ethyl formate (3.3 g.) were added to a solution of 1-2'-indenylnaphthalene (9.7 g.) in anhydrous ether (75 ml.). The resulting mixture was boiled under reflux for 4 hr. and was then poured into water. The alkaline layer was removed, washed once with ether, and acidified with dilute sulphuric acid, and the resulting emulsion was extracted with ether. The extract was washed free from mineral acid, dried (Na₂SO₄), and evaporated. The residual orange-coloured oil, consisting of impure 1-(1-hydroxymethylene-2-indenyl)naphthalene (8.75 g., 81%), did not crystallise; it decomposed slowly on storage and rapidly on attempted vacuum-distillation. In subsequent experiments the crude material was used immediately after preparation. 1-(1-Hydroxymethylene-2-indenyl)naphthalene forms a 2:4-*dinitrophenylhydrazone*, as orange-red prisms (from propionic acid), m. p. 242—244° (Found: N, 11.9. C₂₆H₁₈O₄N₄ requires N, 12.4%), and with sodium ethoxide in ethanol and subsequently benzoyl chloride yields a *benzoate*, as yellow prisms (from acetic acid), m. p. 175—177° (Found: C, 86.3; H, 4.9. C₂₇H₁₈O₂ requires C, 86.6; H, 4.8%).

Ring-closure of 1-(1-Hydroxymethylene-2-indenyl)naphthalene.—A cold mixture of 98% sulphuric acid (100 ml.) and water (10 ml.) was added to a solution of crude 1-(1-hydroxymethylene-2-indenyl)naphthalene (4.3 g.) in benzene (12 ml.) contained in a 250 ml. round-bottomed flask. The mixture was at once shaken vigorously in the stoppered flask for 45 sec. and was then poured on crushed ice (250 g.) in water (1 l.). The mixtures obtained from two

such cyclisation experiments were combined and filtered, and the brown residue was washed successively with water (1 l.), saturated sodium hydrogen carbonate solution (500 ml.), and again with water (250 ml.). The residue was dried at reduced pressure over phosphoric oxide and extracted (Soxhlet) with benzene (500 ml.) until no more coloured material passed into solution. The benzene extract was washed with 10% aqueous sodium hydroxide (twice), then with water, and dried (Na_2SO_4). The solution was concentrated to 100 ml. before filtration through a column (10 × 4.2 cm.) with benzene as eluant. A brown, strongly adsorbed band of organic debris remained at the top of the column. The deep red eluates were concentrated to 500 ml. and extracted with 77% sulphuric acid (3 × 300 ml.). The acid extracts were washed with benzene before dilution with ice-cold water (4 l.). The precipitated brown solid was extracted with ether, and the deep red extract was freed from acid by washing with water and aqueous sodium hydroxide before drying (K_2CO_3) and concentration. The partly crystalline residue was purified by chromatography with benzene as solvent and developer. Evaporation of the eluates to small volume gave indeno[2,1-a]perinaphthene (IV) (710 mg.) as reddish-brown leaflets, m. p. 210—211° (with sublimation) [Found: C, 95.1; H, 4.9%; *M* (Rast), 243. $\text{C}_{20}\text{H}_{12}$ requires C, 95.2; H, 4.8%; *M*, 252]. The *irinitrobenzene complex* crystallised from absolute ethanol as black needles, m. p. 175—176° (Found: N, 8.7. $\text{C}_{20}\text{H}_{12}, \text{C}_6\text{H}_5\text{O}_6\text{N}_3$ requires N, 9.0%). The hydrocarbon, when dissolved in strong acid solutions (77% sulphuric acid or anhydrous liquid hydrogen fluoride), undergoes no appreciable decomposition even after several days.

The benzene solution from which indeno[2,1-a]perinaphthene had been removed by extraction with sulphuric acid was washed free from acid and dried (K_2CO_3) before concentration. Purification of the residue was accomplished by controlled elution with benzene–light petroleum (3 : 2) after adsorption from benzene on a column (9 × 2.7 cm.). The crimson-red eluates on concentration to low volume deposited *di(indeno[2,1-a]perinaphthen-12-yl)* (XII) (210 mg.), as small purple-black prisms, m. p. 294—297° [Found: C, 95.0; H, 4.8%; *M* (Rast), 380. $\text{C}_{40}\text{H}_{22}$ requires C, 95.6; H, 4.4%; *M*, 503]. Attempts to cyclise 1-(1-hydroxymethylene-2-indenyl)naphthalene by other reagents met with failure. Among those tried were the following: anhydrous liquid hydrogen fluoride, hydrogen bromide in acetic acid, phosphoric oxide in benzene, and polyphosphoric acid.

Indeno[1,2,3-cd]pyrene (X).—*First synthesis: from indeno[2,1-a]perinaphthene.* A solution of maleic anhydride (30 mg.) in glacial acetic acid (7 ml.) was added to a boiling solution of indeno[2,1-a]perinaphthene (50 mg.) in xylene (3 ml.) and glacial acetic acid (8 ml.), and the resulting solution was boiled for 4 min. 10b : 11 : 12 : 12a-*Tetrahydroindeno[1,2,3-cd]pyrene-11 : 12-dicarboxylic anhydride* (VIII) crystallised from the cooled solution in almost quantitative yield as colourless needles. The m. p. on a preheated block was approximately 260°. With slow heating the adduct shows no definite m. p. but becomes yellow above 230°, the colour becoming progressively darker up to 400° (Found: C, 82.8; H, 4.1. $\text{C}_{24}\text{H}_{14}\text{O}_3$ requires C, 82.2; H, 4.0%).

The adduct (20 mg.) was boiled in nitrobenzene (5 ml.) for 5 min. The cooled solution deposited *indeno[1,2,3-cd]pyrene-11 : 12-dicarboxylic anhydride* (IX) (15 mg.), which on recrystallisation from chlorobenzene–nitrobenzene (1 : 1) gave golden-yellow needles, m. p. 357—360° (Found: C, 83.0; H, 3.1. $\text{C}_{24}\text{H}_{10}\text{O}_3$ requires C, 83.2; H, 2.9%). Boiling a mixture of indeno[2,1-a]perinaphthene (85 mg.) and maleic anhydride (40 mg.) in nitrobenzene (4 ml.) resulted in direct formation of the fully aromatic anhydride (IX) (73 mg.) as golden-yellow needles, m. p. 358—361°.

The foregoing anhydride (73 mg.) was intimately mixed with soda-lime (4 g.) and heated strongly. *Indeno[1,2,3-cd]pyrene* (X) distilled off and was obtained as bright yellow plates (32 mg.), m. p. 162.5—163.5°, from light petroleum–benzene (10 : 1), after purification on a column (8 × 1.1 cm.) with light petroleum–benzene (1 : 1) as solvent and developer (Found: C, 95.9; H, 4.2. $\text{C}_{22}\text{H}_{12}$ requires C, 95.6; H, 4.4%). The hydrocarbon in solution displays a greenish-yellow fluorescence in daylight and ultraviolet light.

Second synthesis: from 1-iodopyrene. 1-Iodopyrene (2 g.) and *o*-bromonitrobenzene (1.55 g.) were heated at 200—205° and copper bronze (4 g.) was added gradually during 2 hr. The cooled melt was extracted exhaustively with benzene, and the extract, after concentration to low volume, was chromatographed on a column (15 × 2.5 cm.). Initial development with light petroleum–benzene (4 : 1) gave a colourless bottom zone fluorescing blue in ultraviolet light, and from which a small quantity of 1-iodopyrene was recovered. Continued development of the upper orange-yellow zone with light petroleum–benzene (1 : 1) brought through golden-yellow eluates which, after removal of solvent and trituration of the residual oil with ethyl

acetate, afforded 1-*o*-nitrophenylpyrene (XI) (0.875 g., 44%), as golden-yellow needles, m. p. 146.5—147.5° (Found: C, 81.7; H, 3.9; N, 4.1. $C_{22}H_{13}O_2N$ requires C, 81.7; H, 4.1; N, 4.3%).

The foregoing nitro-compound (145 mg.), suspended in glacial acetic acid (25 ml.), was reduced by hydrogen in the presence of 20% palladium-charcoal (100 mg.). Absorption ceased after 1 hr. when the theoretical volume of hydrogen had been taken up. The mixture was filtered free from catalyst and poured into water, and the resulting emulsion was extracted with ether after addition of excess of 20% sodium hydroxide solution. The ether extract was washed with water, dried, and evaporated. The residual brown oil (125 mg.) containing 1-*o*-aminophenylpyrene did not crystallise, and was characterised as its *picrate*, golden-yellow rhombohedra, m. p. 206—207.5° (from ethanol) (Found: C, 64.0; H, 3.3; N, 10.4. $C_{28}H_{18}O_7N_4$ requires C, 64.4; H, 3.5; N, 10.7%).

The crude amine (110 mg.), dissolved in glacial acetic acid (2 ml.), was added to excess of 10% sulphuric acid (3 ml.). Sodium nitrite (40 mg.) in water (1 ml.) was added all at once to the acid solution which immediately became deep red. After 3 min. an excess of urea was added, and after a further 2 min. copper bronze (1 g.) was added. The mixture was then warmed on the water-bath for 10 min. and filtered, and the residue was extracted with boiling benzene. The washed and dried (K_2CO_3) extract was evaporated to low volume and filtered through a column (8 × 2.7 cm.) with benzene-light petroleum (1:1) as developer. After addition of light petroleum the concentrated eluates deposited yellow plates (39 mg., 38%), m. p. 161.5—163°, which did not depress the m. p. of indeno[1,2,3-*cd*]pyrene prepared in the first synthesis and had an identical absorption spectrum. The *picrate*, prepared in benzene or alcohol, showed no definite m. p. but decomposed over the range 150—180° (Found: C, 66.3; H, 3.2; N, 8.4. $C_{22}H_{12}C_6H_3O_7N_3$ requires C, 66.5; H, 3.0; N, 8.3%).

Reactions of Indeno[2,1-a]perinaphthene with Dienophiles.—*With 1:4-naphthaquinone.* The hydrocarbon (110 mg.) and 1:4-naphthaquinone (70 mg.) in nitrobenzene (5 ml.) were boiled for 30 min. The cooled solution deposited indeno[1,2,3-*cd*]naphtho[2',3'-a]pyrene-5:16-quinone (XV) (120 mg.) which crystallised from dimethylformamide as orange needles, m. p. 263—265° (Found: C, 88.7; H, 3.5. $C_{30}H_{14}O_2$ requires C, 88.7; H, 3.5%). The quinone gives a greenish-blue vat with alkaline sodium dithionite.

With 1:4-benzoquinone. The hydrocarbon (100 mg.) and 1:4-benzoquinone (45 mg.) were boiled in nitrobenzene for 15 min. The microcrystalline product (XVIa or b) (90 mg.) separated from the boiling solution and recrystallised from nitrobenzene (50 ml.) as small orange needles, m. p. above 400° (Found: C, 90.9; H, 3.4. $C_{46}H_{20}O_2$ requires C, 91.4; H, 3.3%). It gives no vat with alkaline sodium dithionite.

Oxidation of Indeno[2,1-a]perinaphthene with Lead Tetra-acetate.—An excess of lead tetra-acetate (1.8 g.) was added to a solution of indeno[2,1-a]perinaphthene (200 mg.) in pure dry benzene (50 ml.) and kept at 15° for 1 hr. The solution became deep crimson and at the end of this time gave a negative test (no green coloration with 77% sulphuric acid) for indeno[2,1-a]perinaphthene. It was then poured into water and worked up in the customary manner. The purple-black residue obtained after removal of solvent was passed in benzene through a column (9 × 2.7 cm.). A crimson zone passed down the column rapidly on development with benzene. The concentrated eluates from this zone yielded purple-black prisms (50 mg.), m. p. 293—296°, which did not depress the m. p. of the hydrocarbon (XII) obtained from the cyclisation of 1-(1-hydroxymethylene-2-indenyl)naphthalene and had an identical absorption spectrum (350—650 $m\mu$). Continued washing of the column, ultimately with methanol, brought through violet eluates from which no useful product could be isolated.

Acetoxylation of Di(indeno[2,1-a]perinaphthen-12-yl).—The hydrocarbon (100 mg.) and excess of lead tetra-acetate (1 g.) in pure dry benzene (50 ml.) were boiled under reflux for 2 hr. The cooled solution was poured into water and the resulting mixture was extracted exhaustively with ether and benzene. The green extracts were washed successively with water, saturated sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4). Solvent was removed under reduced pressure and the residue was purified by passage through a column (10 × 2.7 cm.) with benzene-ether (1:1) as eluant. The green eluates yielded 7(?)-acetoxydi(indeno[2,1-a]perinaphthen-12-yl) (30 mg.) which crystallised from xylene as green needles, m. p. >360° (Found: C, 90.4; H, 4.1. $C_{42}H_{24}O_2$ requires C, 90.0; H, 4.3%).

Nitration of Indeno[2,1-a]perinaphthene.—Tetranitromethane (98 mg.) in absolute ethanol (2 ml.) was added to a solution of indeno[2,1-a]perinaphthene (126 mg.) in pure dry pyridine (5 ml.). The initially red solution became purple-violet rapidly. It was kept at 15° for 5 min. and then diluted with ether (250 ml.). The resulting solution was washed free from pyridine and nitroform with hydrochloric acid followed by water, and was dried (Na_2SO_4) before

evaporation. The residue was filtered through a column (6 × 2.7 cm.) with pure ethyl acetate as solvent and developer. On concentration to low volume the violet eluates afforded 12(?)-nitroindeno[2,1-*a*]perinaphthene (22 mg.) as violet prisms, m. p. 186—190° (decomp.) (Found: C, 81.5; H, 3.5; N, 4.8. C₂₀H₁₁O₂N requires C, 80.8; H, 3.7; N, 4.7%).

*Oxidation of Indeno[2,1-*a*]perinaphthene with Chromic Anhydride.*—Chromic anhydride (200 mg.) was added to a suspension of indeno[2,1-*a*]perinaphthene (126 mg.) in glacial acetic acid (20 ml.), and the mixture was boiled for 3 min. The solution was poured into water, and the precipitated orange solid was dissolved in chloroform. The chloroform solution was washed with aqueous sodium hydroxide and water, and dried (Na₂SO₄) before evaporation to dryness. Chromatography of the residue with chloroform–benzene as solvent and developer gave the crude *quinone* which crystallised from dimethylformamide as orange needles (52 mg.), m. p. 283—285°. After recrystallisation from dimethylformamide (twice) and then from chloro-benzene (twice) the compound had constant m. p. 290—292° (Found: C, 85.0; H, 3.7. C₂₀H₁₀O₂ requires C, 85.1; H, 3.6%). The quinone gives a violet-blue vat readily with alkaline sodium dithionite and a greenish-yellow colour with concentrated sulphuric acid.

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