

346. *The Synthesis of Polycyclic Aromatic Hydrocarbons. Part I. A Synthesis of Optically Active 9 : 10-Dihydrodinaphtho(2' : 3'-3 : 4)-(2'' : 3''-5 : 6)phenanthrene, and a New Synthesis of Pentaphene.*

By G. M. BADGER, P. R. JEFFERIES, and R. W. L. KIMBER.

The "intramolecularly overcrowded" 9 : 10-dihydrodinaphthophenanthrene (III) has been prepared by cyclisation of 2 : 2'-bisbromomethyl-1 : 1'-dianthryl (II; R = Br) with phenyl-lithium, and its (+)- and (-)-forms have been similarly prepared from the (+)- and the (-)-form of the bisbromomethyl-compound. The optically active forms of the hydrocarbon have $[\alpha]_D^{25}$ ca. 2000° in benzene and a half-life in boiling xylene of 27 minutes. Dehydrogenation could not be effected without racemisation.

Pentaphene (XI) has likewise been synthesised by cyclisation of 3 : 3'-bisbromomethyl-2 : 2'-dinaphthyl (VIII; R = Br), followed by dehydrogenation.

HALL and TURNER'S elegant method ¹ for the preparation of 9 : 10-dihydrophenanthrene by the action of phenyl-lithium on 2 : 2'-bisbromomethyldiphenyl promises to be of increasing value for the synthesis of more complex polycyclic hydrocarbons. It has already been applied in syntheses of substituted phenanthrenes,² 3 : 4-benzophenanthrene,³ picene,⁴ 3 : 4-5 : 6-dibenzophenanthrene,⁵ and optically active 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene.⁶ As part of a study of "intramolecular overcrowding" ⁷ in polycyclic compounds, this method has now been used to prepare 9 : 10-dihydrodinaphtho(2' : 3'-3 : 4)(2'' : 3''-5 : 6)phenanthrene (III). This molecule is much crowded, and by analogy with related compounds must be considerably distorted from a planar structure, so was expected to exist in highly optically active forms (cf. ref. 6). This has been confirmed. Hall and Turner's method ¹ has also been used in a synthesis of pentaphene (XI) from 3 : 3'-bisbromomethyl-2 : 2'-dinaphthyl (VIII; R = Br).

1 : 1'-Dianthryl-2 : 2'-dicarboxylic acid ⁸ with diazomethane gave the methyl ester (I) which was reduced with lithium aluminium hydride to a diol (II; R = OH) [characterised

¹ Hall and Turner, *Nature*, 1949, **163**, 537; Hall, Leslie, and Turner, *J.*, 1950, 711.

² Hall and Turner, *J.*, 1951, 3072; Bergmann and Pelchowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 2663; Bergmann and Pelchowicz, *J. Org. Chem.*, 1954, **19**, 1387; Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629.

³ Bergmann and Pelchowicz, *J. Org. Chem.*, 1954, **19**, 1383.

⁴ Jefferies, *Chem. and Ind.*, 1955, 1425.

⁵ Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5153.

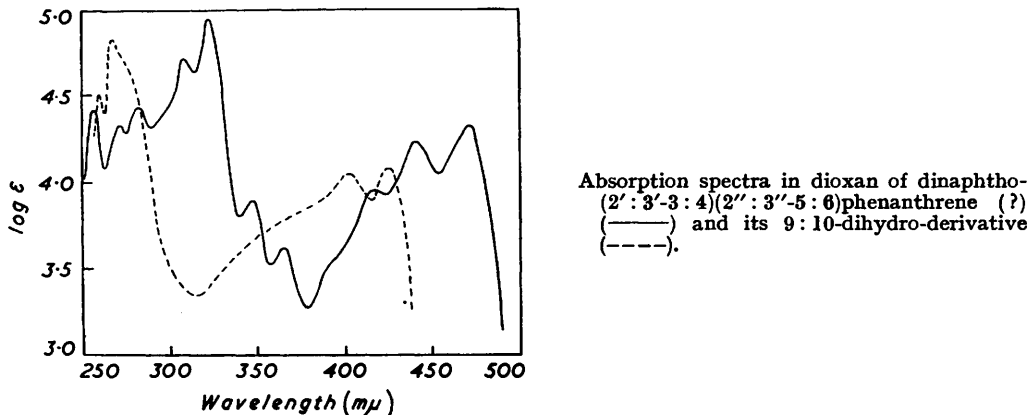
⁶ Hall and Turner, *J.*, 1955, 1242.

⁷ Harnik, Herbststein, Schmidt, and Hirshfeld, *J.*, 1954, 3288.

⁸ Bell and Waring, *J.*, 1949, 1579.

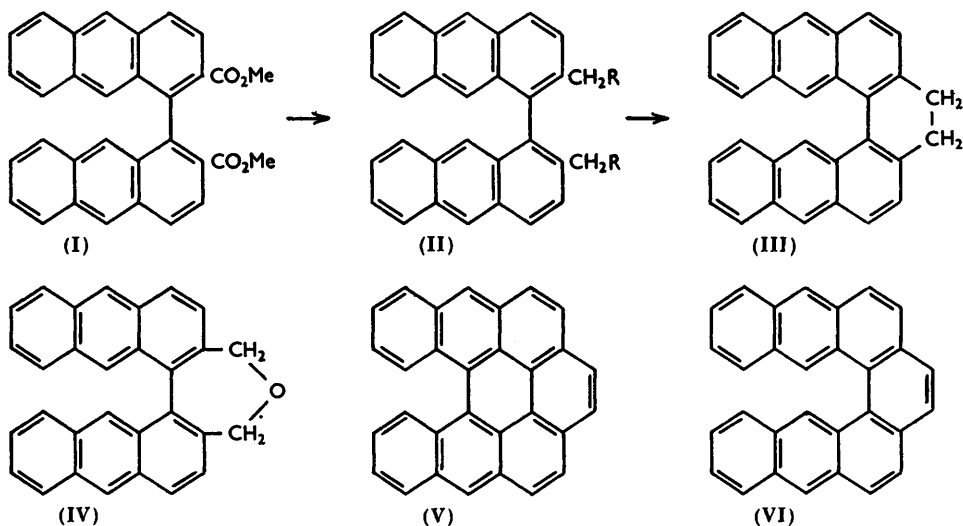
as the acetyl derivative (II; R = OAc)]; this was converted into 2 : 2'-bisbromomethyl-1 : 1'-dianthryl (II; R = Br) with hydrobromic acid in acetic acid, whence phenyllithium in benzene gave the dihydrodinaphthophenanthrene (III) in satisfactory overall yield.

(+)- and (-)-1 : 1'-Dianthryl-2 : 2'-dicarboxylic acid are readily available⁸ and were similarly used. To avoid racemisation, somewhat milder conditions were used for preparation of the bromides, and a small amount of (probably) the cyclic ether (IV) was isolated along with the (-)-dibromide. The (-)-dibromide gave a hydrocarbon (III) having $[\alpha]_D^{25} -2007^\circ \pm 10^\circ$ in benzene, and the (+)-dibromide gave a hydrocarbon with $[\alpha]_D^{25} +1980^\circ \pm 40^\circ$. This very large specific rotation may be compared with that (1500°)



for optically active 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene.⁶ The (-)-form was unchanged after 6 hours in refluxing benzene; but in boiling xylene had a half-life of 27 ± 1 min. (rate constant $2.6 \pm 0.1 \times 10^{-2} \text{ min.}^{-1}$).

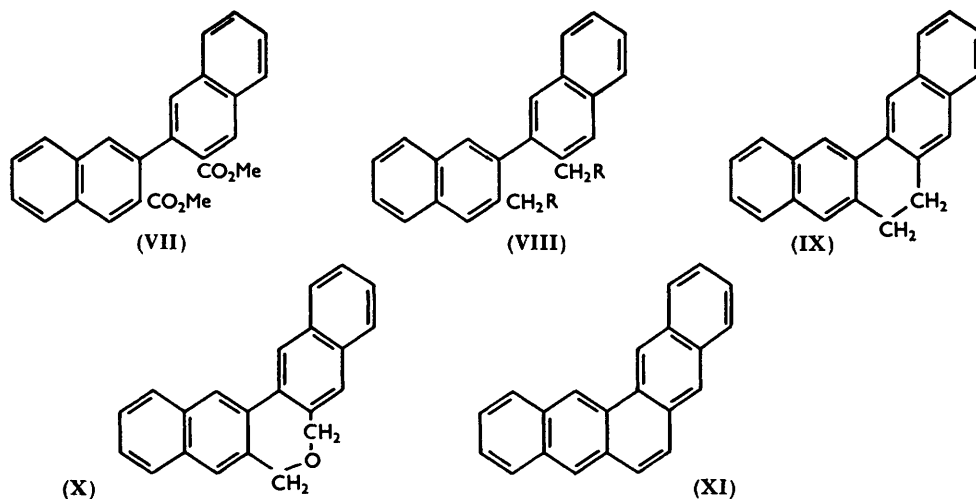
Dehydrogenation of the (\pm)-hydrocarbon with palladium-charcoal in boiling *p*-cymene gave smoothly an aromatic hydrocarbon which, from its absorption spectrum (see Figure)



and other properties, appears to be the expected dinaphthophenanthrene (VI), though the evidence does not exclude its being 1 : 12-5 : 6-7 : 8-tribenzoperylene (V). The latter

hydrocarbon is unknown, although Clar⁹ has given some data for the light absorption of a mixture of *meso*-anthroanthrene and of a hydrocarbon believed to have this structure.

Attempts to dehydrogenate either the racemate or the (–)-form under milder conditions with *N*-bromosuccinimide failed.



For the synthesis of pentaphene (XI), methyl 2:2'-dianthryl-3:3'-dicarboxylate (VII) was reduced with lithium aluminium hydride, and the resulting diol (VIII; R = OH) converted into the bisbromomethyl compound (VIII; R = Br). Some difficulty was experienced in the cyclisation of this product with phenyl-lithium and satisfactory yields were never obtained. Under the most favourable conditions the crude 6:7-dihydro-pentaphene (IX) was contaminated with insoluble material and the cyclic ether (X). The last compound was also prepared by dehydration of the diol (VIII; R = OH), in diphenyl ether, with anhydrous hydrogen chloride.

Dehydrogenation of dihydropentaphene with palladium-charcoal in boiling *p*-cymene gave pentaphene (XI), identical with that described by Clar *et al.*¹⁰ Although the present synthesis gives no higher yield than the earlier methods it is unambiguous.

EXPERIMENTAL

Dimethyl 1:1'-Dianthryl-2:2'-dicarboxylate.—(i) A solution of (±)-1:1'-dianthryl-2:2'-dicarboxylic acid⁸ (4 g.) in dioxan (40 c.c.) was treated with diazomethane (2.5 mols.) in ether at room temperature. After 10 min., the ether was evaporated and water (20 c.c.) added. Recrystallisation from ethanol gave the *ester* (4.25 g., 100%) as pale yellow needles, m. p. 238–239° (Found: C, 81.6; H, 5.0. C₃₂H₂₂O₄ requires C, 81.7; H, 4.7%).

(+)-*Methyl 1:1'-dianthryl-2:2'-dicarboxylate.* After recrystallisation the (+)-*ester* had m. p. 228–230°, [α]_D¹⁸ +382° (c 0.335 in acetone) (Found: C, 81.6; H, 4.7%), and the (–)-*ester*, m. p. 228–230°, [α]_D¹⁸ –387° (c 0.450 in acetone) (Found: C, 82.0; H, 5.0%).

2:2'-Bisbromomethyl-1:1'-dianthryl.—(i) The (±)-methyl ester (4 g.) in ether (400 c.c.) was refluxed with lithium aluminium hydride (5.2 g.) in ether (400 c.c.) for 6 hr. The crude diol (3.3 g., 95%) could not be obtained constant-melting (dehydration during recrystallisation?) and satisfactory analyses were not obtained. (±)-*2:2'-Bisacetoxymethyl-1:1'-dianthryl*, prepared in pyridine with acetic anhydride, formed pale yellow needles, m. p. 232–233°, from light petroleum (b. p. 100–120°) (Found: C, 81.7; H, 5.3. C₃₄H₂₄O₄ requires C, 81.9; H, 5.2%).

The crude diol (1 g.) in boiling glacial acetic acid (25 c.c.) was treated with hydrobromic acid in glacial acetic acid (7.5 c.c.; 50% w/v). After 15 min. a further quantity (5 c.c.) of

⁸ Clar, *Chem. Ber.*, 1949, **82**, 54.

¹⁰ Clar and John, *Ber.*, 1931, **64**, 981; 1930, **63**, 2975; Clar and Stewart, *J.*, 1951, 3215.

hydrobromic acid was added, and heating continued for $\frac{1}{2}$ hr. The product (1.2 g.) was chromatographed in benzene on alumina and recrystallised from ethyl methyl ketone. (\pm)-2 : 2'-*Bisbromomethyl-1 : 1'-dianthryl* was obtained as yellow-orange prisms, m. p. 217—219° (Found : C, 66.9; H, 4.0. $C_{30}H_{20}Br_2$ requires C, 66.7; H, 3.7%).

(ii) Reduction of the (+)-methyl ester in the same way gave a crude diol, $[\alpha]_D^{15} + 460^\circ$, characterised as the (+)-2 : 2'-*bisacetoxymethyl-1 : 1'-dianthryl*. After recrystallisation from light petroleum (b. p. 100—120°) it formed pale yellow prisms, m. p. 180—181°, $[\alpha]_D^{15} + 290^\circ$ (c 0.266 in acetone) (Found : C, 81.8; H, 5.4. $C_{34}H_{26}O_4$ requires C, 81.9; H, 5.2%).

Conversion into the bromo-compound was effected as for the racemate except that the whole of the hydrobromic acid was added at once and the total time of refluxing was only 5 min. (+)-2 : 2'-*Bisbromomethyl-1 : 1'-dianthryl* was obtained as yellow-orange prisms, m. p. 224—226°, $[\alpha]_D^{15} + 195^\circ$ (c 0.230 in C_6H_6) (Found : C, 67.1; H, 3.9%).

(iii) Similarly the (-)-methyl ester gave a crude diol, $[\alpha]_D^{15} - 471^\circ$, which was characterised as the (-)-2 : 2'-*bisacetoxymethyl-1 : 1'-dianthryl*, pale yellow needles (from light petroleum), m. p. 180—181°, $[\alpha]_D^{15} - 290^\circ$ (c 0.248 in acetone) (Found : C, 81.6; H, 5.4%). (-)-2 : 2'-*Bisbromomethyl-1 : 1'-dianthryl* was obtained as yellow orange prisms, m. p. 224—226°, $[\alpha]_D^{15} - 188^\circ$ (c 0.392 in C_6H_6) (Found : C, 66.8; H, 4.2%). Further elution of the column gave *dianthro*-(2' : 1'-3 : 4)(1'' : 2''-5 : 6)*oxepin* (IV) which crystallised from benzene in yellow prisms, m. p. 272—275°, $[\alpha]_D^{15} - 1530^\circ$ (c 0.354 in C_6H_6) (Found : C, 90.6; H, 5.3; O, 4.2. $C_{30}H_{20}O$ requires C, 90.9; H, 5.1; O, 4.0%).

9 : 10-*Dihydrodinaphtho*(2' : 3'-3 : 4)(2'' : 3''-5 : 6)*phenanthrene*.—(i) A solution of phenyl-lithium (4.6 c.c., 1.2 mols.; see below) in anhydrous benzene was added in portions, during 15 min., to a shaken solution of the (\pm)-dibromide (2.2 g.) in anhydrous benzene (20 c.c.) in nitrogen. After being shaken for further 15 min. the mixture was refluxed for $\frac{1}{2}$ hr. Decomposition with water and hydrochloric acid, and recrystallisation of the product from benzene, gave the *dihydro-compound* (1.1 g., 75%) as yellow needles, m. p. 303—305° (Found : C, 94.4; H, 5.3. $C_{30}H_{20}$ requires C, 94.7; H, 5.3%). Its benzene solution had a bright blue fluorescence. Light absorption in dioxan : λ_{max} , 267, 259, 402, and 424 m μ (log ϵ 4.84, 4.51, 4.06, 4.10).

(ii) In the same way the (+)-dibromide was converted into the (+)-*compound*, yellow needles (from benzene), m. p. 295—297°, $[\alpha]_D^{15} + 1980^\circ \pm 40^\circ$ (c 0.072 in C_6H_6) (Found : C, 94.9; H, 5.4%); the (-)-*analogue* had m. p. 295—297°, $[\alpha]_D^{15} - 2007^\circ \pm 10^\circ$ (c 0.142 in C_6H_6) (Found : C, 94.7; H, 5.45%).

(?)-*Dinaphtho*(2' : 3'-3 : 4)(2'' : 3''-5 : 6)*phenanthrene*.—A mixture of the (\pm)-dihydro-dinaphthophenanthrene (0.5 g.), 10% palladium-charcoal (0.4 g.), and *p*-cymene (30 c.c.) was heated under reflux for 4 hr. Removal of the solvent *in vacuo* from the filtered solution and recrystallisation from benzene gave the crude product (0.4 g.), m. p. 290°, which was chromatographed from benzene on alumina and recrystallised from benzene. The *product* was orange needles, m. p. 293—295° (Found : C, 95.3; H, 4.5. $C_{30}H_{18}$ requires C, 95.2; H, 4.8%). Light absorption in dioxan : λ_{max} , 257, 272, 282, 308, 322, 348, 365, 418, 440, and 472 m μ (log ϵ 4.43, 4.35, 4.28, 4.71, 4.96, 3.90, 3.62, 3.95, 4.24, 4.33).

3 : 3'-*Bishydroxymethyl-2 : 2'-dinaphthyl*.—A suspension of methyl 2 : 2'-*dicarboxylate*¹¹ (10 g.) in boiling anhydrous ether (500 c.c.) was added to a boiling suspension of lithium aluminium hydride (13 g.) in ether (500 c.c.), and the mixture refluxed for 2 hr. Decomposition with water and dilute sulphuric acid gave 3 : 3'-*bishydroxymethyl-2 : 2'-dinaphthyl* (7.7 g., 92%), needles (from ethanol), m. p. 228—229° (Found : C, 83.7; H, 6.0. $C_{22}H_{16}O_2$ requires C, 84.1; H, 5.8%). 3 : 3'-*Bisacetoxymethyl-2 : 2'-dinaphthyl*, formed in pyridine with acetic anhydride, crystallised from ethanol in pale yellow needles, m. p. 106—106.5° (Found : C, 78.5; H, 5.8. $C_{26}H_{22}O_4$ requires C, 78.4; H, 5.5%).

3 : 3'-*Bisbromomethyl-2 : 2'-dinaphthyl*.—Hydrobromic acid in glacial acetic acid (15 c.c.; 50% w/v) was added to a boiling solution of the above diol (2 g.) in glacial acetic acid. After 15 minutes' refluxing a further 10 c.c. of hydrobromic acid were added and heating maintained for a further $\frac{1}{2}$ hr. 3 : 3'-*Bisbromomethyl-2 : 2'-dinaphthyl* (2.6 g., 93%) separated on cooling; it crystallised from ethyl methyl ketone in needles, m. p. 165—166° (Found : C, 60.0; H, 3.5. $C_{22}H_{16}Br_2$ requires C, 60.0; H, 3.6%).

6 : 7-*Dihydropentaphene*.—A stock solution of phenyl-lithium was prepared from bromobenzene (22 g.) lithium (3 g.), and ether (80 c.c.), and made up to 100 c.c. with ether.

¹¹ Martin, J., 1941, 679.

Phenyl-lithium solution (8.4 c.c.; 2.2 mols.) was added in portions during 15 min. to 3 : 3'-bisbromomethyl-2 : 2'-dinaphthyl (2.0 g.) in benzene (20 c.c.). After refluxing for $\frac{1}{2}$ hr. the mixture was decomposed with water and dilute hydrochloric acid and filtered. The organic layer was dried and chromatographed on alumina (15 \times 3 cm.). Elution with benzene-hexane (1 : 4; 250 c.c.) and recrystallisation from benzene gave 6 : 7-dihydropentaphene (0.36 g., 30%) as needles, m. p. 140—141° (Found : C, 94.0; H, 5.7. $C_{22}H_{16}$ requires C, 94.3; H, 5.7%). Light absorption in $CHCl_3$: λ_{max} , 264, 279, and 321 $m\mu$ ($\log \epsilon$ 4.45, 4.34, 4.19).

Further elution of the column with benzene-hexane (1 : 1; 250 c.c.) and recrystallisation of the product (50 mg.) from benzene-hexane (1 : 1) gave *dinaphtho*(2' : 3'-3 : 4)(2'' : 3''-5 : 6)-*oxepine* (X) as prisms, m. p. 223—224° (Found : C, 89.0; H, 5.6; O, 5.9. $C_{22}H_{16}O$ requires C, 89.2; H, 5.4; O, 5.4%). The m. p. was not depressed by admixture with a specimen prepared by passing dry hydrogen chloride into a solution of 3 : 3'-bishydroxymethyl-2 : 2'-dinaphthyl (0.5 g.) in diphenyl ether (10 c.c.) at 100°.

Pentaphene.—A mixture of 6 : 7-dihydropentaphene (0.3 g.), 10% palladium-charcoal (0.2 g.), and *p*-cymene (20 c.c.) was refluxed for 4 hr. Evaporation of the filtrate *in vacuo* and recrystallisation of the product from glacial acetic acid and from ethanol gave pentaphene (0.2 g., 67%) as pale greenish-yellow needles, m. p. 255—257° in agreement with the literature (Found : C, 94.6; H, 5.0. Calc. for $C_{22}H_{14}$: C, 94.9; H, 5.0%). The absorption curve was identical with that given by Clar,¹⁰ and the dipicrate had m. p. 184° (lit., m. p. 184°). Oxidation with osmium tetroxide by Cook and Schoental's method¹² gave an unstable diol which was further oxidised with sodium dichromate to *pentaphene-6 : 7-quinone*, red plates, m. p. 326—328° (vac.) (Found : C, 85.3; H, 4.1. $C_{22}H_{12}O_2$ requires C, 85.7; H, 3.9%). Light absorption in $CHCl_3$: λ_{max} , 253, 267, 283, 292, 304, 326, 378, 468, and 488 $m\mu$ ($\log \epsilon$ 4.61, 4.49, 4.49, 4.46, 4.26, 4.45, 3.85, 3.41, 3.39).

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne. We also thank E. I. du Pont de Nemours and Co. for a gift of dimethyldianthraquinonyl, which was used to prepare dianthryldicarboxylic acid.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.

[Received, November 11th, 1956.]

¹² Cook and Schoental, *J.*, 1948, 170.