293. *Alicyclic Studies. Part XV.* Preparation and Reactions of 3,3'-Bi-indenyl and 2,3:2',3'-Dibenzobi(cyclohepta-2,7-dienyl).*

By Yanina Altman and David Ginsburg.

3,3'-Bi-indenyl and 2,3:2',3'-dibenzobi(cyclohepta-2,7-dienyl) have been prepared and their behaviour in Diels–Alder reactions has been investigated.

An improved preparation and Diels–Alder reactions of bi(cyclopent-1-enyl) and bi(cyclohept-1-enyl) have been described.[1] This study reports the extension to the corresponding benzo-fused derivatives.

Reduction of indan-1-one and benzocyclohepten-3-one by the method of Barnett and Lawrence[2] gave 1,1'-bi-indanyl-1,1'-diol and 2,3:2',3'-dibenzobi(cyclopent-3-enyl)-1,1'-diol, in 25% and 10% yield, respectively. Newman's procedure for the reduction of tetralones[3] was found suitable for the preparation of the seven-membered diene in one step in 75% yield but it could not be used, as already noted by Bell and Waring,[4] for the reduction of indan-1-one. However, when the Newman procedure was modified by

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* Part XIV, Altman and Ginsburg, *J.*, 1959, 466.

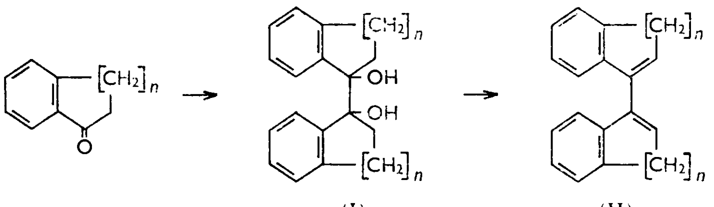
[1] Part XIII, Greidinger and Ginsburg, *J. Org. Chem.*, 1957, **22**, 1406.

[2] Barnett and Lawrence, *J.*, 1935, 1104.

[3] Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 1683.

[4] Bell and Waring, *J.*, 1949, 2689.

decomposition of the excess of aluminium with Rochelle salt under neutral conditions, the corresponding five-membered pinacol (I; $n = 1$) and diene (II; $n = 1$) were obtained in 70% overall yield. [The formulæ for the substances (II) are written in the *cisoid* form as they react in the Diels–Alder reaction. Presumably the *transoid* form is more stable with less steric interference of hydrogen atoms.]



(I) (II)

Dehydration of the pinacol was effected with a mixture of acetic acid and acetic anhydride. The resulting diene (II; $n = 1$) has already been prepared by another route, the yield being first reported [5] to be 48% but later 8%.[6]

Diels–Alder reactions were carried out between the two dienes (II; $n = 1$ and 3) and maleic anhydride, dimethyl acetylenedicarboxylate, and benzoquinone. In contradistinction to our experience with bi(cyclopent-1-enyl) and bi(cyclohept-1-enyl) which reacted exothermically with maleic anhydride, the benzo-fused dienes, as expected, required an excess of dienophile and heating for 3 hr.

The seven-membered adduct (VIII) was aromatised by lead tetra-acetate,[3] but the five-membered adduct (III) withstood these conditions as well as attempted aromatisation by *N*-bromosuccinimide. 5,8-Dihydroindeno[2,1-*c*]fluorene (IV) was obtained, as already reported,[6] by long heating with palladised carbon or by pyrolysis of (III) in the presence of copper powder. Oxidation afforded the hitherto unknown 5,8-dihydro-5,8-dioxoindeno[2,1-*c*]fluorene (V).

The corresponding seven-membered hydrocarbon (IX) was obtained by oxidative decarboxylation [7] with lead dioxide.

Differences in behaviour between the five- and the seven-membered homologues were found also in the reactions with dimethyl acetylenedicarboxylate: (II; $n = 3$) afforded an adduct; the former (II; $n = 1$) surprisingly did not react.

The diene reaction with benzoquinone was carried out by the procedure described by Davies and Porter.[8] Acetic acid as solvent prevents the formation of phenolic products and permits effective separation of quinhydrone from the products. Here, also, the compounds (II; $n = 1$ and 3) behaved differently. The latter ($n = 3$) afforded the tetrahydronaphthaquinone (XIII) or the more highly oxidised compound (XIV) depending on reaction conditions. The compound (II; $n = 1$) reacted much more rapidly and afforded the product formulated as (VI) or the bis-adduct (VII), depending on experimental conditions. The compound (XIII) was readily converted into the dihydric phenol (XV; R = H) or into the diacetate (XV; R = Ac).

Ultraviolet Spectra.—The spectrum of the hydrocarbon (IV) is similar to that of fluorene, except that it contains more fine structure. On the other hand, the spectrum of the analogue (IX) shows three high-intensity maxima in the 220—270 mμ range, lacking the fine structure shown by (IV). The spectrum of compound (IX) shows a striking resemblance to that of 1,2,7,8-tetrahydro-3,4:5,6-dibenzophenanthrene. The absence of coplanarity in the last two compounds as opposed to the apparent planarity of the

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[5] Straus, Kühnel, and Haensel, *Ber.*, 1933, **66**, 1847.

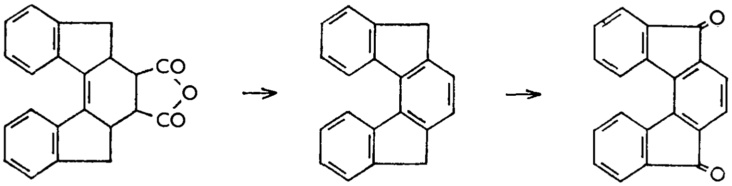
[6] Deuschel, *Helv. Chim. Acta*, 1952, **35**, 1774.

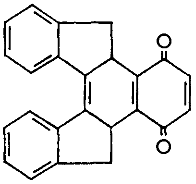
[7] Doering, Farber, and Sayigh, *J. Amer. Chem. Soc.*, 1952, **74**, 4370.

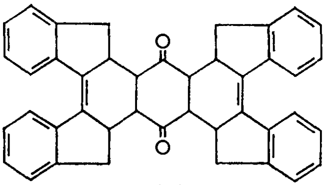
[8] Davies and Porter, *J.*, 1957, 4958, 4961, 4967.

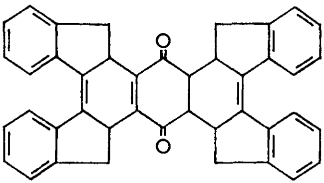
" fluorene " (IV) (this may also be seen in models) may account for the disappearance of the fine structure in the non-planar compounds (see Fig. 1).

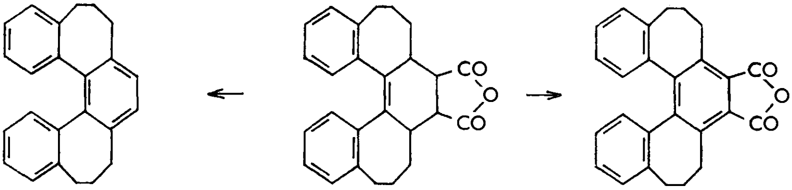
The spectrum of the adduct (VI) clearly shows the typical absorption [9] of a *p*-quinone chromophore ($\lambda_{max.}$ 257; log ε 4·46) and of the *cis*-stilbene [10] ($\lambda_{max.}$ 295; log ε 4·43) at longer wavelength and with higher intensity. The spectrum of the seven-membered homologue (XIV), however, retains only the quinone absorption (*ca.* 250 mμ) with reduced intensity. The *cis*-stilbene absorption appears only as an inflexion at about 300 mμ with greatly reduced intensity (log ε 3·14). This is regarded as further proof of coplanarity (or its absence) in the pentacyclic systems under discussion (see Fig. 2).

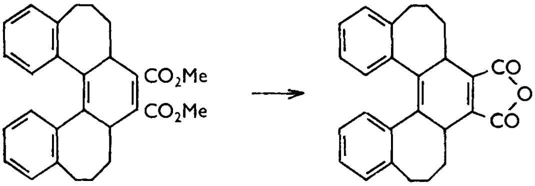

(III) (IV) (V)

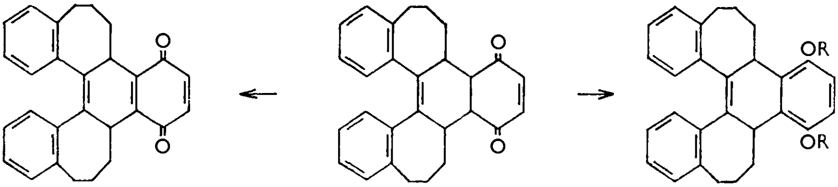

(VI)


(VII)


(VIIa)


(IX) (VIII) (X)


(XI) (XII)


(XIV) (XIII) (XV)

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[9] Braude, *J.*, 1945, 492.
[10] Beale and Roe, *J.*, 1953, 2755.

The typical *cis*-stilbene absorption is also shown in the spectrum of the bis-adduct (VII). The absence of any absorption maximum in the 250 mμ region indicates the

Fig. 1. (IV) (——) *in methylcyclohexane.* (IX) (. . . .) *in methylcyclohexane.* 1,2,7,8-*Tetrahydro*-3,4:5,6-*dibenzophenanthrene* (– – – –) (cf. Part XIV).

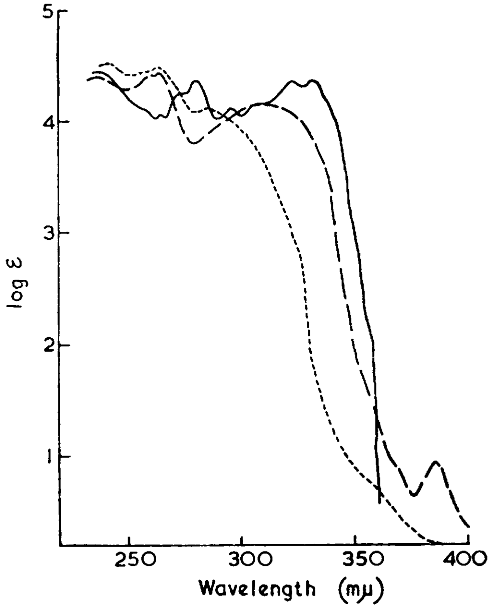


Fig. 2. (VI) (. . . .), (VII) (– – – –), *and* (XIV) (——), *in dioxan.*

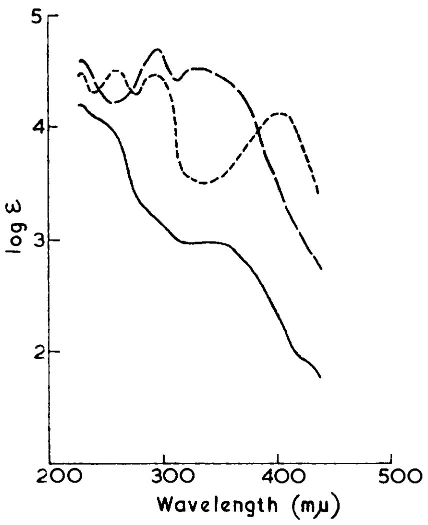
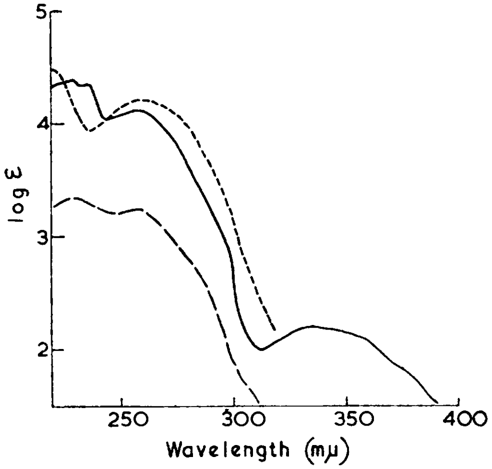


Fig. 3. (II; $n = 1$) (——) *in methylcyclohexane.* (II; $n = 3$) (– – – –) *in methylcyclohexane.* 3,4,3′,4′-*Tetrahydro*-1,1′-*binaphthyl* (. . . .).[15]



absence of a quinonoid system. However, on the basis of existing evidence it is not possible to differentiate unambiguously between structures (VII) and (VIIa). Braude *et al.*[11] report $\lambda_{max.}$ 220, 250, 256 (ε 15,500, 1450, 1400) for system (XVI). Bastron *et al.*[12] report

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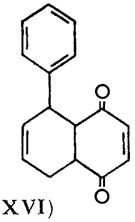
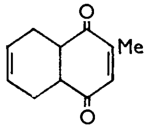
[11] Braude, Jones, and Stern, *J.*, 1947, 1092.

[12] Bastron, Davis, and Butz, *J. Org. Chem.*, 1943, **8**, 515.

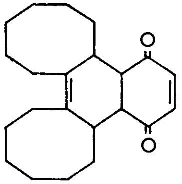
$\lambda_{max.}$ 237, 354 (ε 12,250, 62) for system (XVII). On the other hand, Strumza and Ginsburg[13] found no maximum in the 220—260 mμ region in system (XVIII); and Mandelbaum and Cais[14] found no maximum in this region in system (XIX).



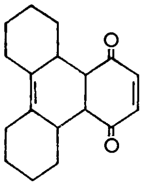
(XVI)



(XVII)



(XVIII)



(XIX)

It is interesting that a large hypochromic effect is shown in the spectrum of the diene (II; $n = 3$) as compared with those of (II; $n = 1$) and of 3,4,3′,4′-tetrahydro-1,1′-binaphthyl[15]* (see Fig. 3).

EXPERIMENTAL

1,1′-*Bi-indanyl*-1,1′-*diol* (I; $n = 1$).—A mixture of freshly scraped aluminium foil (8 g.; 1 cm.^{2} squares, 0·005 inch thick), indan-1-one (25 g.), mercuric chloride (0·5 g.), dry ethanol (200 ml.), and dry benzene (250 ml.) was heated on the steam-bath for 12 hr. away from light (indan-1-one in solution is sensitive to light). After cooling, the excess of aluminium was dissolved in cold 20% Rochelle salt solution (400 ml.) with cooling. The aqueous phase was extracted with ether (3 × 150 ml. portions), and the combined organic phases were washed with Rochelle salt solution until the aqueous phase was clear. After drying (Na_2SO_4) and removal of the solvents, a mixture of methylcyclohexane (30 ml.) and benzene (30 ml.) was added and the solution was refrigerated overnight. The crystalline *pinacol* removed by filtration (9·5 g., 38%) had m. p. 152—154°. The analytical sample (from methylcyclohexane) formed needles; m. p. 156—157° (Found: C, 80·9; H, 6·9; O, 12·1. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8; O, 12·0%), $\nu_{max.}$ (in $CHCl_3$), 3600 cm.$^{-1}$ (OH).

The mother-liquor, on distillation, afforded unchanged indanone, b. p. 70—80°/0·05 mm. (1·2 g., 5%), and 3,3′-bi-indenyl (II; $n = 1$), b. p. 146—148°/0·05 mm. (6·9 g., 32%), a yellow solid. Crystallisation gave yellowish prisms, m. p. 131° (from ethanol) (lit.,[5] m. p. 130·5—131·5°).

When hydrochloric acid was used to dissolve the excess of aluminium, none of the above products was isolated. By the method of Barnett and Lawrence[2] the pinacol was isolated in 25% yield in addition to 10% of unchanged indanone; the reddish residue did not react with maleic anhydride.

3,3′-Bi-indenyl was obtained by dehydration of the diol (13 g.) by acetic acid (22 ml.) and acetic anhydride (22 ml.) on the steam-bath in 1 hr. Water was added to the hot solution until the appearance of a slight turbidity. Refrigeration and filtration afforded crystalline diene (8 g.) and concentration of the mother-liquor gave a second crop (1·5 g.). The hydrocarbon had m. p. 131° (84% yield), $\lambda_{max.}$ (in methylcyclohexane) 228, 236, 257, 340 mμ (log ε 4·39, 4·36, 4·10, 2·17).

5,5a,6,7,7a,8-*Hexahydroindeno*[2,1-*c*]*fluorene*-6,7-*dicarboxylic Anhydride* (III).—The above diene (1·5 g.) and maleic anhydride (5 g.) were heated under reflux in xylene (25 ml.) for 3 hr. The adduct began to be deposited after 15 min. Cooling and filtration gave colourless needles (1·26 g., 59%) of the anhydride, m. p. 310° (lit., m. p. 310°,[5] 300—302°)[6] (Found: C, 79·7; H, 4·95. Calc. for $C_{22}H_{16}O_3$: C, 80·5; H, 4·9%), $\nu_{max.}$ (in KBr) 1860, 1780 cm.$^{-1}$ (C=O of carboxylic anhydride), $\lambda_{max.}$ (in dioxan) 231—232, 242, 252, 292, 304, 331, 346 mμ (log ε 4·15, 4·13, 3·99, 3·95, 3·99, 4·41, 4·41).

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* We thank Dr. M. Cais for discussion of the ultraviolet spectra.

[13] Strumza and Ginsburg, unpublished work.

[14] Mandelbaum and Cais, personal communication.

[15] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951, Spectrum No. 121.

Removal of the solvent from the mother-liquor and trituration of the residue with methanol (which dissolved the excess of maleic anhydride) gave a second isomer as yellow needles (230 mg., 11%), m. p. 262° (from benzene or acetic acid) (lit., m. p. 262°,[5] 255—265 [6]) (Found: C, 80·3; H, 5·0. Calc. for $C_{22}H_{16}O_3$: C, 80·5; H, 4·9%), $\nu_{max.}$ (in KBr) 1870, 1790 cm.$^{-1}$, $\lambda_{max.}$ (in dioxan) 231, 242, 252, 293, 331, 347 mμ (log ε 4·21, 4·09, 3·97, 3·98, 4·43, 4·41).

5,8-*Dihydroindeno*[2,1-*c*]*fluorene* (IV).—A finely powdered mixture of the anhydride (III) (100 mg.), copper powder (100 mg.), barium hydroxide (200 mg.; dried at 400° for 12 hr.), and soda-glass (500 mg.) was heated slowly to 400° and kept at 400° for 1 hr. in an inert atmosphere. The hydrocarbon sublimed. After cooling, the residue was extracted with hot methylcyclohexane, and the combined extracts were passed over a column of acid-washed alumina (5 g.) and eluted with hexane. The yellowish products gave colourless needles of the hydrocarbon, m. p. 144—145° (from ethanol) (lit.,[6] m. p. 140—142°). The yield varied from 10% to 50% and decreased when larger batches were decarboxylated.

Decarboxylation by Deuschel's procedure [6] with palladised carbon at 240°/120 mm. was unsuccessful in our hands. This catalyst (500 mg.) and the dione (V), heated for 8 hr. at 400°/1 atm. (inert gas), gave the hydrocarbon, m. p. 144—145° (80 mg., 20%), $\lambda_{max.}$ (in methylcyclohexane) 245, 262, 277, 304, 314 mμ (log ε 4·07, 4·37, 4·07, 4·33, 4·35).

5,8-*Dihydro*-5,8-*dioxoindeno*[2,1-*c*]*fluorene* (V).—A mixture of the hydrocarbon (IV) (100 mg.), sodium dichromate (336 mg.), and acetic acid (2·5 ml.) was refluxed for 2 hr. After cooling, water and chloroform were added and the coloured chloroform layer was washed with sodium hydrogen carbonate solution and with water until it remained colourless. After drying (Na_2SO_4) and removal of solvent a yellow residue (101 mg.), m. p. 244—274°, was obtained. It was dissolved in benzene (2 ml.) and chloroform (2 ml.), passed over a column of basic alumina (10 g.), and eluted with benzene–chloroform (2 : 1). After a first impure fraction (9 mg.), the *diketone* was obtained (89 mg.) as yellow needles, m. p. 281—283° (from benzene) (Found: C, 85·4; H, 3·6; O, 11·3. $C_{20}H_{10}O_2$ requires C, 85·1; H, 3·6; O, 11·4%), $\nu_{max.}$ (in $CHCl_3$) 1710—1725 cm.$^{-1}$ (C=O), $\lambda_{max.}$ (in dioxan) 282, 311, 367, 390 (mμ) (log ε 4·42, 4·60, 3·34, 3·00).

5,5a,6,9,9b,10-*Hexahydrodi-indeno*[2,1-*a*,1,2-*c*]*naphthalene*-6,9-*dione* (VI).—The diene (II; *n* = 1) (1·8 g.) and *p*-benzoquinone (2·2 g.) were heated in acetic acid (25 ml.) on the steam-bath for 15 min. Filtration of the deposited red crystals and washing with ethanol to remove quinhydrone afforded the *diketone* (700 mg., 41%) as red needles, m. p. 240—242° (decomp.; in evacuated capillary) (from xylene) (Found: C, 85·85; H, 4·65. $C_{24}H_{16}O_2$ requires C, 85·7; H, 4·8%), $\nu_{max.}$ (in KBr) 1653 cm.$^{-1}$ (quinonoid C=O), $\lambda_{max.}$ (in dioxan) 232, 257, 295, 405 mμ (log ε 4·48, 4·46, 4·43, 4·09).

9,9a,9b,10,10a,10b,11,20,20a,20b,21,21a,21b,22-*Tetradecahydrotetraindeno*[2,1-*a*:1′,2′-*c*:2″,1″-*h*:1‴:2‴-*j*]*anthracene*-10,21-*dione* (VII).—A mixture of the diene (II; *n* = 1) (4·2 g.) and *p*-benzoquinone (0·98 g.) was boiled in acetic acid (40 ml.) for 1 hr. After cooling, yellow needles of the *diketone* were deposited, having m. p. 278° (decomp.; in evacuated capillary) (from xylene) (Found: C, 89·2; H, 5·4; O, 5·5. $C_{42}H_{32}O_2$ requires C, 88·7; H, 5·7; O, 5·6%), $\nu_{max.}$ (in KBr) 1680 cm.$^{-1}$ (C=O), $\lambda_{max.}$ (in dioxan) 232, 297, 330 mμ (log ε 4·60, 4·71, 4·57).

2,3:2′,3′-*Dibenzobi*(*cyclohepta*-2,7-*dienyl*) (II; *n* = 3).—A mixture of aluminium foil (6 g.; as above), benzocyclohepten-3-one (20 g.), mercuric chloride (0·5 g.), dry ethanol (80 ml.), and dry benzene (120 ml.) was heated on a steam-bath for 12 hr. After cooling, the excess of aluminium was dissolved in cold 10% hydrochloric acid. The aqueous phase was extracted several times with benzene–ether (1 : 1), and the combined organic phases were washed once with 10% hydrochloric acid. After removal of the solvents, acetic acid (45 ml.) and acetic anhydride (45 ml.) were added to the residue and the solution was refluxed for 3 hr. to complete dehydration of the pinacol. Removal of the solvents at reduced pressure followed by distillation gave unchanged ketone (2 g.), b. p. 75—80°/0·05 mm., and the *diene* (13·5 g., 75%), b. p. 156—160°/0·05 mm. Crystallisation afforded colourless prisms, m. p. 96° (from propan-2-ol) (Found: C, 92·4; H, 7·7. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%); $\lambda_{max.}$ (in methylcyclohexane) 233, 257 mμ (log ε 3·32, 3·21).

2,3:2′,3′-*Dibenzobi*(*cyclohepten*-1-*yl*)-1,1′-*diol* (I; *n* = 3) was isolated when hexane was added to the residue before dehydration, as colourless needles (8 g., 40%), m. p. 214° (from benzene or methylcyclohexane) (Found: C, 81·9; H, 8·4; O, 9·85. $C_{22}H_{26}O_2$ requires C, 81·95; H, 8·1; O, 9·9%), $\nu_{max.}$ (in $CHCl_3$) 3600 cm.$^{-1}$ (OH).

Reduction by the procedure of Barnett and Lawrence [2] gave the pinacol in 10% yield, benzocyclohepten-3-ol, m. p. 103°, in 10% yield (lit.,[16] m. p. 101°), and unchanged ketone (11%). The reddish residue did not react with maleic anhydride.

5,6,7,7a,8,9,9a,10,11,12-*Decahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]*benzene*-8,9-*dicarboxylic Anhydride* (VIII).—The diene (II; *n* = 3) (1·5 g.), when heated on the steam-bath with maleic anhydride (7·5 g.), gave a melt which began depositing crystals after 30 min. After 3 hours' heating, hot acetic acid or acetic anhydride was added to dissolve the excess of maleic anhydride. On cooling, the *anhydride adduct* was obtained (1·35 g., 65%), having m. p. 257° (from acetic anhydride or acetic acid) (Found: C, 81·2; H, 6·5. $C_{26}H_{24}O_3$ requires C, 81·2; H, 6·3%), $\nu_{max.}$ (in $CHCl_3$) 1870, 1780 $cm.^{-1}$ (C=O of carboxylic anhydride), $\lambda_{max.}$ (in dioxan) 229, 275 mμ (log ε 4·18, 4·03).

5,6,7,10,11,12-*Hexahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]*benzene* (IX).—A finely powdered mixture of the anhydride (VIII) (500 mg.) and lead dioxide (1·34 g.; Fisher, technical) in freshly distilled decalin (4 ml.) was heated to 190—200° in an inert atmosphere. Carbon dioxide was evolved during 3 hr. (barium hydroxide solution). The mixture was cooled to 100°, 2,2,4-trimethylpentane (10 ml.) was added, and refluxing maintained for 10 min. The liquid was decanted and this extraction was repeated twice more. Finally the solid was removed and washed with ether. The organic extracts were combined and the solvents removed in a vacuum. The residual oil was triturated with pentane to give a yellow solid. Sublimation at 160°/0·5 mm. gave the colourless *hydrocarbon* (225 mg., 56%), needles, m. p. 194° (from ethanol) (Found: C, 92·95; H, 7·25. $C_{24}H_{22}$ requires C, 92·9; H, 7·1%), $\lambda_{max.}$ (in methylcyclohexane) 221, 245, 265 mμ (log ε 4·53, 4·48, 4·12).

5,6,7,10,11,12-*Hexahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]*benzene*-8,9-*dicarboxylic Anhydride* (X).—A mixture of the anhydride (VIII) (550 mg.), fresh lead tetra-acetate (1·4 g.), acetic acid (7 ml.), and acetic anhydride (7 ml.) was heated at 120° for 2 hr. Water was added dropwise to the hot solution until a slight turbidity appeared. After cooling, yellow crystals, m. p. 244—276°, were deposited. Four recrystallisations raised the m. p. to 284—285° (from acetic anhydride) (390 mg., 72%) (Found: C, 81·4; H, 5·55; O, 13·0. $C_{26}H_{20}O_3$ requires C, 82·0; H, 5·3; O, 12·6%), $\nu_{max.}$ (in $CHCl_3$) 1850, 1770 $cm.^{-1}$ (C=O of carboxylic anhydride), $\lambda_{max.}$ (in dioxan) 269, 337 mμ (log ε 4·51, 4·02).

Dimethyl 5,6,7,7a,9a,10,11,12-*Octahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]*benzene*-8,9-*dicarboxylate* (XI).—A mixture of the diene (II; *n* = 3) (1 g.) and freshly distilled dimethyl acetylenedicarboxylate (5·2 g.) was heated on the steam-bath for 24 hr. The excess of dienophile was removed in a vacuum and the residue was triturated with methanol. The *diester* was obtained as colourless plates, m. p. 225° (from propan-1-ol) (870 mg., 58%) (Found: C, 78·05; H, 7·1. $C_{28}H_{28}O_4$ requires C, 78·5; H, 6·6%), $\nu_{max.}$ (in $CHCl_3$) 1720 $cm.^{-1}$ (C=O of ester).

Hydrolysis of the ester (300 mg.) was effected in aqueous (1·5 ml.)-methanolic (7 ml.) dioxan (7 ml.) by boiling in the presence of potassium hydroxide (1·5 g.) for 15 hr. After the usual working up, the product (240 mg., 90%) had m. p. 272° (needles from acetic acid or n-butyl acetate). Infrared absorption (in $CHCl_3$) at 1850, 1770 $cm.^{-1}$ indicated that the product was 5,6,7,7a,9a,10,11,12-*octahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]*benzene*-8,9-*dicarboxylic anhydride* (XII) (Found: C, 81·0; H, 6·0; O, 13·1. $C_{28}H_{22}O_3$ requires C, 81·65; H, 5·8; O, 12·25%); ultraviolet absorption max. (in dioxan) were at 253, 325 mμ (log ε 4·13, 3·94).

5,6,7,7a,7b,8,11,11a,11b,12,13,14-*Dodecahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]*naphthalene*-8,11-*dione* (XIII) *and* 5,6,7,7a,8,11,11b,12,13,14-*Decahydrodi(benzocyclohepta)*[6,5-*a*:5',6'-*c*]-*naphthalene*-8,11-*dione* (XIV).—A mixture of the diene (II; *n* = 3) (3·6 g.) and *p*-benzoquinone (5·6 g.) was heated in acetic acid (60 ml.) on the steam-bath for 3 hr., then cooled overnight. Quinhydrone was precipitated along with orange crystals of compound (XIV). The product (XIII) was found in the mother-liquor. Washing the precipitate with cold ethanol removed quinhydrone only, and the *adduct* (XIV) gave orange needles (0·5 g., 10%), m. p. 271° (from acetic acid) (Found: C, 85·2; H, 6·4. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%), $\nu_{max.}$ (in $CHCl_3$) 1655, (in KBr) 1650 $cm.^{-1}$ (quinonoid C=O), $\lambda_{max.}$ (in dioxan) 247, 300infl., 338 mμ (log ε 4·08, 3·14, 3·01).

The acetic acid was removed from the mother-liquor, and the residue was dissolved in benzene–hexane (1 : 1). Quinhydrone was precipitated and was removed. The solution was then washed with 5% sodium dithionite solution to convert quinhydrone into quinol, then with 5% sodium hydrogen carbonate solution to remove the latter. After drying (Na_2SO_4) and removal of solvents, the residue was triturated with methanol and gave yellow needles of the *adduct* (XIII) (2·6 g., 54%), m. p. 210° (from propan-1-ol) (Found: C, 84·85; H, 6·9;

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[16] Horn and Rapson, *J.*, 1949, 2426.

O, 8·15. $C_{28}H_{26}O_2$ requires C, 85·2; H, 6·6; O, 8·1%), $\nu_{max.}$ (in $CHCl_3$) 1695 (C=O), (in KBr) 1680 cm.$^{-1}$, $\lambda_{max.}$ (in dioxan) 224, 297infl. mμ (log ε 4·42, 3·00).

Compound (XIII) has a potential enolic function. Boiling with ethanolic sodium ethoxide for 15 min. followed by the usual working up give the *dihydric phenol* (XV; R = H), m. p. 296° (from toluene) (Found: C, 85·0; H, 6·6. $C_{28}H_{26}O_2$ requires C, 85·2; H, 6·6%), $\nu_{max.}$ (in KBr) 3330 cm.$^{-1}$ (OH of phenol) [*diacetate*, m. p. 283—284° (from toluene) (Found: C, 80·1; H, 6·1; O, 13·3. $C_{32}H_{30}O_4$ requires C, 80·3; H, 6·3; O, 13·4%), $\nu_{max.}$ (in $CHCl_3$) 1760 cm.$^{-1}$ (C=O of ester)].

When heated with an excess of *p*-benzoquinone for 8 hr., the monoadduct (XIII) gave the quinone (XIV).

If the time of heating of the diene (II; *n* = 3) with *p*-benzoquinone was increased, *e.g.*, to 8 hr., the quinone (XIV) was obtained in higher yield (30%) at the expense of the monoadduct (33%).

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