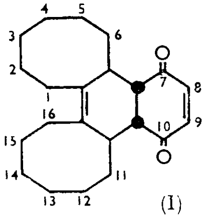
294. *Alicyclic Studies. Part XVI.* The Diels–Alder Reaction of Bi(cyclo-oct-1-enyl) with* p-*Benzoquinone and Steric Interconversions of the Primary Adduct.*†

By Jacob Strumza and David Ginsburg.

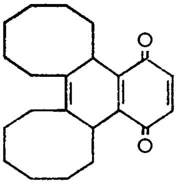
The reaction between bi(cyclo-oct-1-enyl) and *p*-benzoquinone gives a Diels–Alder adduct. Various reactions of the adduct and steric relations between its derivatives are described.

Diels–Alder reactions of symmetrical bicyclic dienes have been described previously.[1] When two equivalents of bi(cyclo-oct-1-enyl) are heated with one of *p*-benzoquinone it is possible to isolate in high yield a 1 : 1 adduct (I) having the usual *cis*-fusion between the two six-membered rings. Spectroscopic and analytical data are consistent with this structure.

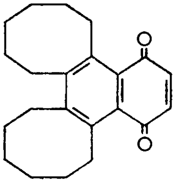
The pure diketone is stable at room temperature but heat or base readily isomerises it to the dihydric phenol (IV).[1] Acetic anhydride and acetic acid convert it into the diacetate (XVII), identical with the product of acetylation of the phenol.



(I)



(II)



(III)

The driving force of aromatisation does not exist in quinonoid systems such as (II) and (III) which may be obtained by allowing an excess of *p*-benzoquinone to react in acetic acid solution [2] either directly with bi(cyclo-oct-1-enyl) or with the adduct (I) or (II), respectively. The infrared absorptions of the carbonyl systems of compounds (II) and (III) (1653 and 1650 cm.$^{-1}$) are in accord with their quinonoid structure. The quinone

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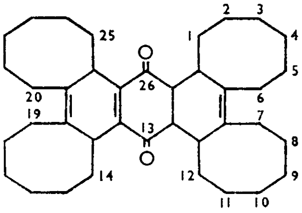
* Part XV, preceding paper.

† Presented at Colloque International de Stereochimie, Montpellier, September, 1959.

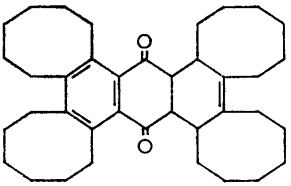
[1] Greidinger and Ginsburg, *J. Org. Chem.*, 1957, **22**, 1406 and papers cited therein.

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

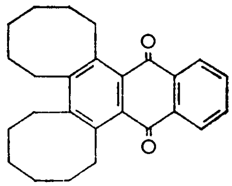
(II) can be reduced to the quinol (IV) by zinc in acetic acid,[3] and the reverse transformation can be accomplished by oxidation with the chromium trioxide–pyridine complex.



(XIX)



(XX)



(XXI)

The activated double bond in the quinones (II) and (III), flanked by two carbonyl functions, adds to another mole of bi(cyclo-oct-1-enyl), giving the two bis-adducts (XIX) and (XX), respectively. Further dehydrogenation of these adducts with an excess of *p*-quinone could not be achieved. An annelated anthraquinone (XXI) was, however, obtained by *p*-quinone dehydrogenation of the bi(cyclo-oct-1-enyl)–naphthaquinone adduct (see Experimental section).

Reduction of the diketone (I) with lithium aluminium hydride gave an unsaturated diol (VII), dehydration of which in 85% phosphoric acid led to a hydrocarbon (XV) that could be further dehydrogenated to give the dodecahydrodicyclo-octa[*a*,*c*]naphthalene (XVI). The 1,4-diacetoxy-derivative (XVIII) of the latter was analogously obtained.

Stereochemical Correlations.—It appeared desirable to establish the steric relations of the six-membered ring portions of the compounds described below in the hope that later, by introduction of functional groups into the eight-membered rings and interaction between the various parts of the molecules, a contribution might be made to the conformation of the eight-membered ring. Accordingly, the following transformations were carried out (cf. reaction chart *).

It has been shown that reduction of the type (I) $\longrightarrow$ (V) with zinc in acetic acid does not affect the fusion of the six-membered rings.[4-6] The product (V) showed saturated carbonyl character ($\nu_{max.}$ 1708 cm.$^{-1}$) in its infrared spectrum. Base epimerised it to the *trans*-fused diketone (IX). Catalytic reduction of either diketone (I) or (V) afforded a *cis*-fused ketol (VI),[6a] and this was epimerised by sodium methoxide to the *trans*-fused ketol (XII), where, however, a double bond had migrated.

Oxidation of the *trans*-ketol (XII) with chromium trioxide in pyridine gave a diketone (XIV). This could be reconverted into its isomer (IX) by rearrangement of the double bond in acidic medium.

Reduction of the diketone (I) with lithium aluminium hydride gave the *cis*-ketol (VI) accompanied by an unsaturated diol (VII) and an unidentified isomer of the latter. The *cis*-fusion in the diol (VII) and its structure are supported by the work of several authors.[4,7,8]

By further reducing the diketone (V) or (VI) with lithium aluminium hydride or by adding one mol. of hydrogen catalytically to the diol (VII), the same *cis*-fused saturated diol (VIII) was obtained.

Although oxidation of the diol (VII) with chromic acid–pyridine gives the quinone (II), both compounds (VI) and (VIII) gave with this reagent the corresponding diketone (V).

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* All the compounds are optically inactive, and braces indicate eight-membered rings.

[3] Cf. Alder and Stein, *Annalen*, 1933, **501**, 247.

[4] Sarett, Lukes, Poos, Robinson, Beyler, Vandegrift, and Arth, *J. Amer. Chem. Soc.*, 1952, **74**, 1393.

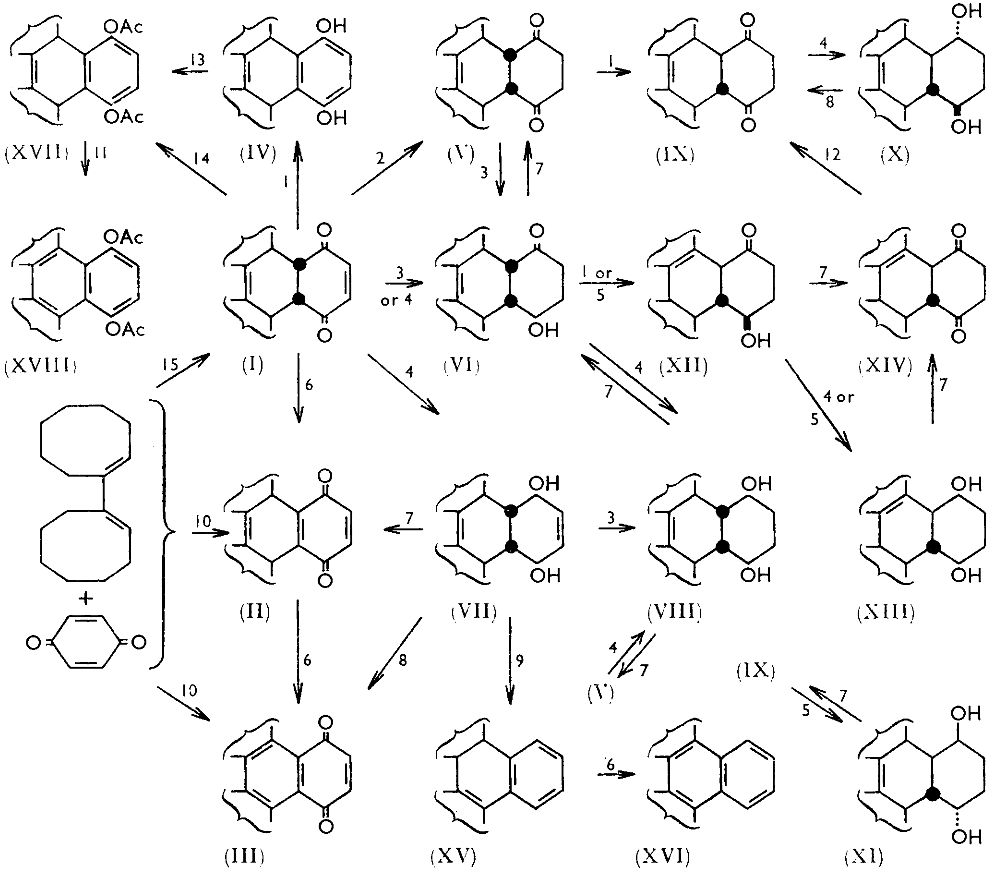
[5] Henbest, Smith, and Thomas, *J.*, 1958, 3293.

[6] Robins and Walker, (*a*) *J.*, 1952, 642, 1610; (*b*) *J.*, 1957, 177; (*c*) *J.*, 1958, 409.

[7] Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.

[8] Robins and Walker, (*a*) *J.*, 1959, 237; (*b*) *J.*, 1954, 3960; (*c*) *J.*, 1955, 1789.

Reduction of the *trans*-diketone (IX) with metal hydrides gave a mixture of diastereoisomeric diols (X) and (XI), formulated as the diequatorial and the diaxial isomers, respectively (see Experimental section). Attempts to obtain the equatorial-axial isomer failed. Metal hydride reduction of the ketol (XII) afforded a third *trans*-fused diol (XIII) which differs, however, from the diols (X) and (XI) in the location of its double bond. The last two, (X) and (XI), were reoxidised with chromic oxide in pyridine or in acetic acid to the same diketone (IX) whilst oxidation of the isomer (XIII) led to a correspondingly isomeric diketone (XIV).



Reagents: 1, NaOMe; 2, Zn–AcOH; 3, H_2–Pt; 4, $LiAlH_4$; 5, $NaBH_4$; 6, benzoquinone–AcOH; 7, CrO_3–pyridine; 8, CrO_3–AcOH; 9, 85% H_3PO_4; 10, AcOH; 11, 30% Pd–C; 12, 2-$C_{10}H_7$·SO_3H; 13, Ac_2O–pyridine; 14, Ac_2O–H^+; 15, Heat.

Since conclusions regarding the configurations of the hydroxyl groups in the above-mentioned diols could not be drawn from infrared data in the 1000 cm.$^{-1}$ region, kinetic experiments were carried out.

Oxidation rates, kindly determined by Dr. J. Schreiber at E.T.H., Zürich, showed a higher value for the diol (XI), in accordance with its diaxial formulation.[9,10] Further, the diacetate of the diol (X), formulated as the diequatorial isomer, was hydrolysed faster than the diacetate of (XI). The diol (X) distinctly showed a higher polar character than (XI), on elution of a mixture of the two isomers from the chromatographic column.[9,11]

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[9] Barton, *Experientia*, 1950, **6**, 316.

[10] Schreiber and Eschenmoser, *Angew. Chem.*, 1955, **67**, 278.

[11] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.

EXPERIMENTAL

$\Delta^{8,16a(16b)}$-*Octadecahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*dione* (I).—Pure *p*-benzoquinone (3·5 g., 0·031 mole) was dissolved in bicyclo-oct-1-enyl (14 g., 0·064 mole) by gentle heating on a steam-bath. Within 5 min., though overheating was avoided, a strong exothermic reaction took place and the red liquid changed to a yellow solid. Trituration with methanol dissolved the excess of diene which was later recovered by distillation at 118—120°/0·2 mm. (3·6 g.); the residue afforded the *diketone* (I) (9·3 g., 89%), m. p. 135° (from methanol) (Found: C, 80·7; H, 9·2; O, 10·6. $C_{22}H_{30}O_2$ requires C, 80·9; H, 9·3; O, 9·8%), $\nu_{max.}$ (in $CHCl_3$) 1675 cm.$^{-1}$ (C=C·C=O), $\lambda_{max.}$ (in dioxan) 328 mμ (log ε 2·78).

When the diketone (I) (0·5 g.) was refluxed in an inert atmosphere with methanolic (100 ml.) sodium methoxide (0·5 g.) for 1 hr. and worked up as usual, colourless needles of 1,2,3,4,5,6,6a,10b,11,12,13,14,15,16-tetradecahydrodicyclo-octa[*a*,*c*]naphthalene-7,10-diol (IV) were obtained (0·3 g., 60%), with m. p. 187° (from benzene) (lit., m. p. 187—188°). The *diacetate* obtained from the diphenol formed colourless prisms, m. p. 155° (from methanol) (Found: C, 75·95; H, 8·6; O, 15·55. $C_{26}H_{34}O_4$ requires C, 76·1; H, 8·3; O, 15·6%).

The diacetate was also obtained directly by heating the adduct (I) (1 g.) with acetic anhydride (20 ml.) containing 3 drops of concentrated sulphuric acid at 90° for 1 hr. After the usual working-up, the diacetate (480 mg.), m. p. 155°, was obtained.

The *dimethyl ether* formed colourless prisms, m. p. 169° (from 2,2,4-trimethylpentane) (Found: C, 81·2; H, 9·6; O, 9·2. $C_{24}H_{34}O_2$ requires C, 81·3; H, 9·7; O, 9·0%).

1,2,3,4,5,6,6a,7,10,10b,11,12,13,14,15,16-*Hexadecahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*dione* (II).—A solution of *p*-benzoquinone (1 g., 0·0092 mole) and bicyclo-oct-1-enyl (0·5 g., 0·0023 mole) in acetic acid (10 ml.) was heated at 100° for 3 hr. After cooling and removal of the black precipitate of quinhydrone, the solvent was removed from the filtrate at reduced pressure and the residue was extracted with benzene (3 × 50 ml.). An equal volume of hexane was added to the extracts and the filtered solution was washed with 40% aqueous sodium hydroxide (40 ml.) containing 5% of sodium dithionite and then with water. The organic solution was dried (Na_2SO_4) and the solvents were removed. Trituration of the dark oily residue gave a brown solid (430 mg.). This gave the *quinone* (II) as brown plates, m. p. 104—105° (from ethanol; carbon), $\nu_{max.}$ (in $CHCl_3$) 1653 cm.$^{-1}$ (quinonoid C=O), $\lambda_{max.}$ (in dioxan) 256, 365 mμ (log ε 4·15, 3·17) (Found: C, 81·5; H, 8·8; O, 10·0. $C_{22}H_{28}O_2$ requires C, 81·4; H, 8·7; O, 9·9%).

The identical quinone (350 mg.) was obtained by dehydrogenating the product (I) (0·5 g.) with *p*-benzoquinone (0·5 g.) in hot acetic acid (5 ml.) for 8 hr. or by oxidising the diphenol (IV) (0·5 g.) with the pyridine (10 ml.)–chromium trioxide (1 g.) complex.

Reduction of the quinone (II) (0·5 g.) with zinc (4 g.) in acetic acid (40 ml.) gave the diphenol (XIV) (250 mg.), identical (admixture) with that described above.

1,2,3,4,5,6,11,12,13,14,15,16-*Dodecahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*dione* (III).—A mixture of pure *p*-benzoquinone (1 g., 0·0092 mole), bicyclo-oct-1-enyl (0·5 g., 0·0023 mole) and acetic acid (10 ml.) was heated at 100° for 8 hr. The mixture was cooled, the precipitate removed, and the filtrate extracted with benzene. An equal volume of hexane was added to the benzene solution and the mixture was washed with alkaline sodium dithionite solution and with water. After drying (Na_2SO_4) and removal of the solvents, trituration with methanol gave a yellow solid (280 mg.), forming golden needles of the *diketone*, m. p. 151—152° (from ethanol, carbon), $\nu_{max.}$ (in $CHCl_3$) 1655 cm.$^{-1}$ (quinonoid C=O), $\lambda_{max.}$ (in dioxan) 260, 381 mμ (log ε 4·28, 3·67) (Found: C, 81·9; H, 8·2; O, 10·0. $C_{22}H_{26}O_2$ requires C, 81·95; H, 8·1; O, 9·9%).

The identical diketone (III) (300 mg.) was obtained by dehydrogenating the product (II) (0·5 g.) with *p*-benzoquinone (2 g.) in acetic acid (5 ml.).

cis-$\Delta^{16a(16b)}$-*Eicosahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*dione* (V).—To a solution of the product (I) (2 g.) in 95% acetic acid (80 ml.) was added in small portions, with stirring during 1 hr., zinc dust (16 g.) that had been previously washed with chloroform and ether. Decolorisation occurred within a few minutes. This mixture was filtered into ice-cold saturated salt solution and this was extracted with ether (500 ml.). The organic layer was washed successively with salt solution and aqueous sodium hydrogen carbonate until free from acid. After drying (Na_2SO_4) and removal of the ether the residue was triturated with pentane, affording colourless cubes (1·7 g., 85%) of the cis-*diketone*, m. p. 108° (from pentane), $\nu_{max.}$ (in $CHCl_3$) 1708 cm.$^{-1}$ (saturated C=O), $\lambda_{max.}$ (in dioxan) 297 mμ (log ε 2·07) (Found: C, 80·4; H, 9·8; O, 9·95.

$C_{22}H_{32}O_2$ requires C, 80·4; H, 9·8; O, 9·7%). The *bis-2,4-dinitrophenylhydrazone* formed brown needles, m. p. 265° (decomp.), from chloroform–methanol (Found: N, 16·1. $C_{34}H_{40}N_8O_8$ requires N, 16·3%).

Epimerisation was effected by adding the diketone (V) (1·2 g.) to a solution prepared from sodium (0·5 g.) and dry methanol (100 ml.) and refluxing the whole in an inert atmosphere for 1 hr. After the usual working-up, the trans-*diketone* (IX) (300 mg., 40%) formed needles, m. p. 145—146° (from hexane). Removal of the solvent from the mother-liquor and refluxing of the residue, m. p. 120—125° (700 mg.), in benzene (50 ml.) with naphthalene-β-sulphonic acid (300 mg.) afforded the same diketone, m. p. 145° (from hexane). It had $\nu_{max.}$ (in $CHCl_3$) 1705 cm.$^{-1}$ (saturated C=O) and $\lambda_{max.}$ (in dioxan) 300 mμ (log ε 1·68) (Found: C, 80·3; H, 9·7; O, 10·6%). The *mono-2,4-dinitrophenylhydrazone* formed yellow needles, m. p. 230° (decomp.), from chloroform–methanol (Found: N, 11·2. $C_{28}H_{36}N_4O_5$ requires N, 11·0%).

cis-$\Delta^{16a(16b)}$-*Eicosahydro-10-hydroxydicyclo-octa*[a,c]*naphthalene-7-one* (VI).—A solution of the product (I) (4 g.) in ethyl acetate (150 ml.) was reduced at atmospheric pressure over Adams catalyst (400 mg.), 2 mol. of hydrogen (320 ml.) being taken up during 3 hr. Removal of catalyst and concentration afforded colourless prisms of the *ketol* (VI) (1·5 g., 38%), m. p. 174° (from methylcyclohexane), $\nu_{max.}$ (in $CHCl_3$) 3550, 1025 (OH), 1710 cm.$^{-1}$ (saturated C=O), $\lambda_{max.}$ (in dioxan) 290 mμ (log ε 1·43) (Found: C, 79·9; H, 10·1; O, 9·5. $C_{22}H_{34}O_2$ requires C, 79·95; H, 10·4; O, 9·7%).

Evaporation of the solvent and trituration of the residual oil with benzene afforded the diphenol (IV) (2·1 g.), m. p. 184° (from benzene). Removal of the benzene and trituration with methanol yielded more of the ketol (VI) (0·25 g.; total yield 43%).

The *ketol monoacetate* formed cubes, m. p. 140° (from ethanol), $\nu_{max.}$ (in $CHCl_3$) 1725 (ester C=O), 1710 cm.$^{-1}$ (saturated C=O) (no OH absorption) (Found: C, 76·9; H, 9·8; O, 13·2. $C_{24}H_{36}O_3$ requires C, 77·4; H, 9·7; O, 12·9%). The *ketol monoacetate 2,4-dinitrophenylhydrazone* formed yellow needles, m. p. 245° (decomp.) from ethyl acetate (Found: C, 65·2; H, 7·4; N, 10·1. $C_{30}H_{40}N_4O_6$ requires C, 65·2; H, 7·3; N, 10·1%).

The identical (mixed m. p. and infrared spectrum) ketol (VI) was obtained (70% yield) by reducing the diketone (V) (100 mg.) in ethyl acetate (10 ml.) in the presence of Adams catalyst (20 mg.) during 3 hr.

Epimerisation was effected by refluxing a solution of the ketol (VI) (1·5 g.) with methanolic (300 ml.) sodium methoxide (prepared from 0·8 g. of sodium) for 1 hr. After the usual working-up the trans-*ketol* (XII) (1·3 g., 87%) was obtained as plates, m. p. 168° (from methylcyclohexane), $\nu_{max.}$ (in $CHCl_3$) 3600 (OH), 1700 cm.$^{-1}$ (saturated C=O), $\lambda_{max.}$ (in dioxan) 290 mμ (log ε 1·52) (Found: C, 79·55; H, 10·3; O, 9·71%). The *mono-2,4-dinitrophenylhydrazone,* orange needles, had m. p. 135° (from ethanol) (Found: C, 66·0; H, 7·4; O, 15·7; N, 10·85. $C_{28}H_{38}N_4O_5$ requires C, 65·9; H, 7·5; O, 15·7; N, 11·0%). The identical derivative was obtained from the ketol (VI). The *monoacetate* from the *trans*-isomer (XII) proved identical with that obtained from (VI) (see above). Evidently epimerisation of (VI) takes place during acetylation and during formation of its 2,4-dinitrophenylhydrazone.

$\Delta^{8,16a(16b)}$-*Octadecahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*diol* (VII).—A solution of product (I) (5 g.) in dry ether (200 ml.) was added during 30 min. to lithium aluminium hydride (7·5 g.) in dry ether (200 ml.) with stirring. The mixture was refluxed for 5 hr. and left overnight. After decomposition by water and dilute sulphuric acid and the usual working-up, trituration with methanol gave colourless crystals (2·42 g.). Five recrystallisations from benzene gave colourless needles of the *diol* (1·95 g.), m. p. 207—208°, $\nu_{max.}$ (in KBr) 3350, 1036 cm.$^{-1}$ (OH) (Found: C, 80·0; H, 10·3; O, 9·7. $C_{22}H_{34}O_2$ requires C, 79·95; H, 10·4; O, 9·7%). The *di*-p-*nitrobenzoate* was obtained as yellowish prisms, m. p. 197—198°, from methylcyclohexane (Found: C, 68·9; H, 6·3; N, 4·4. $C_{36}H_{40}O_8N_2$ requires C, 68·8; H, 6·4; N, 4·5%). The *diacetate,* colourless needles, had m. p. 145—147° (from ethanol) (Found: C, 74·65; H, 9·2; O, 15·8. $C_{26}H_{38}O_4$ requires C, 75·3; H, 9·2; O, 15·4%).

Removal of methanol from the mother-liquor of the diol and addition of methylcyclohexane gave tiny colourless needles of an isomeric *diol* (1·07 g.), m. p. 177—178° (from benzene), $\nu_{max.}$ (in KBr) 1000, 1015, 3330 cm.$^{-1}$ (OH) (Found: C, 79·7; H, 10·2; O, 9·8%). The *di*-p-*nitrobenzoate* formed colourless prisms, m. p. 183°, from methylcyclohexane (Found: C, 68·9; H, 6·7; N, 4·32%), and the *diacetate* cubes, m. p. 136° (from methanol) (Found: C, 75·2; H, 9·0; O, 15·5%).

Removal of the benzene from the recrystallisation mother-liquors of the diol (VII) and chromatography of the residual solid (0·85 g.) in benzene–chloroform (1 : 1; 2 c.c.) over basic alumina (30 g.) afforded, on elution with benzene–chloroform (1 : 1), colourless plates (280 mg.), m. p. 168° (from methylcyclohexane), of the *trans*-ketol (XII). Further elution gave the diol (VII) (510 mg.), m. p. 207° (from benzene).

cis-$\Delta^{16a(16b)}$-*Eicosahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*diol* (VIII).—(*a*) Catalytic reduction at atmospheric pressure of the diol (VII) (0·5 g.) in ethyl acetate (100 ml.) in the presence of Adams catalyst (200 mg.) was complete (88 ml. of hydrogen absorbed) in 50 min. After removal of catalyst and solvent, trituration with methanol gave colourless prisms of the *diol* (VIII) (320 mg.), m. p. 213—214° (from methylcyclohexane), $\nu_{max.}$ (in $CHCl_3$) 3420, 996 cm.$^{-1}$ (OH) (Found: C, 79·4; H, 10·8; O, 9·6. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9; O, 9·6%). The *diacetate* formed colourless prisms, m. p. 176—178° (from ethanol) (Found: C, 74·8; H, 9·8; O, 15·5. $C_{26}H_{40}O_4$ requires C, 75·0; H, 9·7; O, 15·4%).

From the mother-liquor of the diol (VIII), the ketol (VI) (100 mg.) was isolated.

(*b*) Reduction of the ketol (VI) (390 mg.) in dry ether (75 ml.) with lithium aluminium hydride (750 mg.) in dry ether (100 ml.), followed by the usual working-up, gave the identical diol (VIII) (320 mg., 82%).

(*c*) Reduction of the diketone (V) (1 g.) in dry ether (50 ml.) with lithium aluminium hydride (1·5 g.) in dry ether (50 ml.) gave the identical diol (VIII) (840 mg., 84%). Identity of the three products was established by mixed m. p. and infrared spectra.

trans-$\Delta^{16a(16b)}$-*Eicosahydrodicyclo-octa*[a,c]*naphthalene*-7(eq),10(eq)-*diol* (X).—The diketone (IX) (1 g.) in dry ether (100 ml.) was added to lithium aluminium hydride (1·5 g.) in dry ether (100 ml.) and boiling was maintained for 6 hr. After the usual working-up, concentration of the ether solution to a small volume gave white needles of the *diol* (X) (650 mg.), m. p. 215—216° (from 2,2,4-trimethylpentane–xylene), $\nu_{max.}$ (in KBr) 3340, 1040 cm.$^{-1}$ (OH) (Found: C, 79·6; H, 10·7; O, 9·5. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9; O, 9·6%). The *diacetate* was obtained as colourless needles, m. p. 154—155°, from methanol (Found: C, 74·4; H, 9·6; O, 16·05. $C_{26}H_{40}O_4$ requires C, 75·0; H, 9·7; O, 15·4%).

Removal of the ether from the mother-liquor and trituration with methylcyclohexane gave a colourless solid (156 mg.), m. p. 174° (from methylcyclohexane), identified as the diaxial isomer (XI) (see below).

trans-$\Delta^{6a(16b)}$-*Eicosahydrodicyclo-octa*[a,c]*naphthalene*-7,10-*diol* (XIII).—Reduction of the ketol (XII) (1·4 g.) in dry ether (100 ml.) with lithium aluminium hydride (2·1 g.) in dry ether (100 ml.) afforded, in the usual way, colourless prisms of the *diol* (XIII) (1·2 g., 85%), m. p. 178—180° (from methylcyclohexane), $\nu_{max.}$ (in $CHCl_3$) 3600, 1021, 985 cm.$^{-1}$ (OH) (Found: C, 79·55; H, 11·1; O, 9·7. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9; O, 9·6%). The *diacetate*, needles, had m. p. 178—180° (from ethanol) (Found: C, 74·6; H, 9·5; O, 15·9. $C_{26}H_{40}O_4$ requires C, 75·0; H, 9·7; O, 15·4%).

trans-$\Delta^{16a(16b)}$-*Eicosahydrodicyclo-octa*[a,c]*naphthalene*-7(ax),10(ax)-*diol* (XI).—Sodium borohydride (0·7 g.) was added portionwise to a solution of the diketone (IX) (0·7 g.) in methanol (100 ml.) and the mixture left overnight. After the usual working-up the *diol* (XI) (600 mg., 85%) was obtained as colourless prisms, m. p. 174° (from methylcyclohexane), $\nu_{max.}$ (in $CHCl_3$) 3510, 1030 cm.$^{-1}$ (OH) (Found: C, 79·7; H, 10·7; O, 9·6%). Admixture of all possible combinations of (XI), (XIII), and the unidentified isomer of (VII) gave depressions in m. p.

The rhombohedral *diacetate* of compound (XI) had m. p. 105° (from methanol) (Found: C, 74·6; H, 9·6; O, 16·0%).

A portion of the crude reduction product (300 mg.) in benzene–chloroform was chromatographed over acid-washed alumina (15 g.). Elution with benzene–hexane (1 : 1) changing to pure benzene afforded the diol (XI) (207 mg.). Further elution with benzene–chloroform (1 : 1) gave a crude mixture (31 mg.), m. p. 177—185°. Elution with pure chloroform finally gave the isomeric diol (X) (43 mg.).

Saponification of Diacetates of (X) *and* (XI).—A sample of each diacetate (30 mg.) was dissolved in neutral dioxan (3 ml.) and the solution was made up to 10 ml. with 0·1N-sodium hydroxide. Aliquot parts (1 ml.) were titrated at different times with 0·01N-hydrochloric acid at 25·6°, with the results tabulated.

	% Hydrolysed						
Time (min.)	300	570	1350	1770	2760	3210	4230
Diacetate from (X)	10·8	29·0	60·8	65·4	77·8	79·7	84·3
„ „ (XI)	6·1	16·8	47·2	53·5	67·9	71·2	75·3

Oxidation of Diols (X) *and* (XI).—A sample of each diol (0·991 mg.) was dissolved in acetic acid (9 ml.) and oxidised at 20° c with chromic acid (0·800 mg.) in water (1 ml.). We are grateful to Drs. Schreiber and Eschenmoser of E.T.H., Zürich, for the following data: (X), k' 6·3, $t_{1/2}$ 20 min.; (XI) k' 9·4, $t_{1/2}$ 16 min.

Oxidation of Diols.—(*a*) A solution of diol (VII) (0·5 g.) in pyridine (5 ml.) was added to the chromium trioxide–pyridine complex (from 1 g. and 10 ml. respectively). After 24 hr. at room temperature, benzene (20 ml.) was added and the precipitate was removed. An equal volume of ether was added to the filtrate. After washing with dilute hydrochloric acid containing 5% aqueous ferrous sulphate, drying (Na_2SO_4), and removal of solvents, trituration with methanol gave a brown solid (120 mg.), m. p. 104° (from ethanol), identical (mixed m. p.) with the diketone (II). Similar oxidation of the diol, m. p. 177—178°, isomeric with (VII), also gave diketone (II).

(*b*) A solution of the diol (VII) (1·8 g.) in acetic acid (80 ml.) and benzene (20 ml.) was added during 1 hr. to a cooled solution of chromic acid (1·8 g.) in 80% acetic acid (20 ml.) at 5° and left overnight. After the usual working-up and extraction of the oily product three times with boiling hexane, removal of the solvent from this extract and trituration with methanol gave yellow needles (120 mg.), m. p. 152° (from ethanol), identical (mixed m. p.) with the quinone (III). Similar oxidation of the isomeric diol, m. p. 177—178°, gave the same quinone (III).

The following Table summarises analogous oxidations of other diols:

		Oxidant		
Diol	Solvent	CrO_3	C_5H_5N	Products
VIII; 0·5 g.	C_5H_5N; 10 ml.	1 g.	10 ml.	V; 10 mg., 2% VI; 10 mg., 2%
VI; 0·16 g.	C_5H_5N; 5 ml.	0·3 g.	5 ml.	V; 50 mg., 31%
XI; 0·5 g.	C_5H_5N; 10 ml.	1 g.	10 ml.	IX; 100 mg., 20%
X; 0·6 g.	AcOH; 100 mml.	0·6	(80% AcOH; 10 ml.)	IX; 10 mg., 2%

trans-$\Delta^{6a(16b)}$-*Eicosahydrodicyclohepta*[a,c]*naphthalene*-7,10-*dione* (XIV).—Oxidation of the diol (XIII) (0·25 g.) in pyridine (5 ml.) with the pyridine (5 ml.)–chromic acid (0·5 g.) complex as described above gave a yellowish oil. Trituration with methanol afforded white needles of the *diketone* (XIV) (110 mg., 21%), m. p. 124—125° (from methanol; carbon), $\nu_{max.}$ (in $CHCl_3$) 1710 cm.$^{-1}$ (saturated C=O), $\lambda_{max.}$ (in dioxan) 244 mμ (log ε 3·26) (Found: C, 80·3; H, 9·5; O, 9·9. $C_{22}H_{32}O_2$ requires C, 80·4; H, 9·8; O, 9·7%).

The identical diketone (XIV) was obtained by oxidising the ketol (XII) (0·25 g.) in pyridine (5 ml.) with the same reagent.

Diketone (IX) *from its Isomer* (XIV).—Refluxing the $\Delta^{6a(16b)}$-diketone (XIV) (0·4 g.) in benzene (50 ml.) with naphthalene-β-sulphonic acid (0·3 g.) for 2 hr. and washing the cooled solution with aqueous sodium hydrogen carbonate was followed by drying ($MgSO_4$) and removal of the solvent. Trituration with methanol gave white needles (350 mg., 88%), m. p. 145° (from hexane), identical with the *trans*-$\Delta^{16a(16b)}$-diketone (IX) (mixed m. p. and infrared spectra).

1,2,3,4,5,6,6a,6b,11,12,13,14,15,16-*Tetradecahydrodicyclo-octa*[a,c]*naphthalene* (XV).—The diol (VII) (2 g.) was stirred during 4 hr. with 85% phosphoric acid (2 g.) at 100°. Dilution with water, extraction with ether, washing the ether layer with aqueous sodium hydrogen carbonate and water, drying (Na_2SO_4), and removal of the ether gave an oil. Trituration with methylcyclohexane gave solid starting material. Evaporation of the filtrate and addition of 2,2,4-trimethylpentane to the residue gave the colourless ketol (VI) (130 mg.). Concentration of the filtrate therefrom to a small volume and cooling at −10° for a week gave cubes, m. p. 56—57° (from 2,2,4-trimethylpentane). Cooling the mother-liquor at 5° gave another crop of the *hydrocarbon* (XV) (total 0·7 g., 39%), $\lambda_{max.}$ (in cyclohexane [12]) 241, 265, 272, 297 mμ (log ε 4·99, 3·94, 3·97, 3·79) (Found: C, 90·0; H, 10·4. $C_{22}H_{30}$ requires C, 89·7; H, 10·3%).

1,2,3,4,5,6,11,12,13,14,15,16-*Dodecahydrodicyclo-octa*[a,c]*naphthalene* (XVI).—The hydrocarbon (XV) (1 g.) was dehydrogenated in acetic acid (10 ml.) with *p*-benzoquinone (2 g.) at 100° for 8 hr. The black precipitate was removed from the cooled solution and washed with cold methanol, leaving white needles (0·7 g.). Removal of the acetic acid from the filtrate, followed by the usual working-up, gave another crop of the *hydrocarbon* (XVI) (total 0·82 g., 83%), m. p. 139° (from acetic acid), $\lambda_{max.}$ (in cyclohexane [13]) 238, 287, 297 mμ (log ε 4·99, 3·76, 3·81) (Found: C, 90·2; H, 9·5. $C_{22}H_{28}$ requires C, 90·35; H, 9·65%).

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[12] Cf. Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951, No. 129.

[13] Cf. ref. 12, no. 195.

7,10 - *Diacetoxy* - 1,2,3,4,5,6,11,12,13,14,15,16 - *dodecahydrodicyclo* - *octa*[a,c]*naphthalene* (XVIII).—The diacetate (XVII) (0·5 g.) was dehydrogenated by heating it with 30% palladised carbon (200 mg.) at 220—240° for 2 hr. Benzene was added and the catalyst removed by filtration. Removal of benzene at the water-pump and trituration of the residue with hexane gave the yellowish *dodecahydro-diacetate* (XVIII) (200 mg.) as prisms, m. p. 230° (from acetic acid), $\lambda_{max.}$ (in dioxan) 244, 310 mμ (log ε 4·80, 3·93) (Found: C, 76·4; H, 7·9; O, 15·5. $C_{26}H_{32}O_4$ requires C, 76·4; H, 7·9; O, 15·7%).

1,2,3,4,5,6,7,8,9,10,11,12,12a,12b,13,13b,14,15,16,17,18,19,20,21,22,23,24,25,25a,26,26a,26b-*Dotriacontahydrotetracyclo-octa*[a,c,h,j]*anthracene*-13,26-*dione* (XIX).—The diketone (II) (0·5 g., 0·0015 mole) was heated with bicyclo-oct-1-enyl (0·66 g., 0·003 mole) for 30 min. at 100°. A pentane solution of the yellow oily product deposited during 12 hr. at room temperature a yellowish amorphous solid (0·5 g.). The analytical sample of this *diketone* (XIX) formed yellowish prisms, m. p. 197° (from butan-1-ol), $\nu_{max.}$ (in $CHCl_3$) 1680 cm.$^{-1}$ (C=C·C=O) (Found: C, 84·3; H, 9·7; O, 6·0. $C_{38}H_{54}O_2$ requires C, 84·1; H, 10·0; O, 5·9%).

1,2,3,4,5,6,7,8,9,10,11,12,12a,12b,13,14,15,16,17,18,19,20,21,22,23,24,25,26,26a,26b-*Triacontahydrotetracyclo-octa*[a,c,h,j]*anthracene*-13,26-*dione* (XX).—A solution of the diketone (III) (0·5 g., 0·0015 mole) in bicyclo-oct-1-enyl (0·66 g., 0·003 mole) was heated at 100° for 10 min. Trituration with pentane gave a solid (0·88 g.), yielding large yellowish prisms of the *diketone* (XX) (0·8 g.), m. p. 213° (from acetic acid), $\nu_{max.}$ (in $CHCl_3$) 1670 cm.$^{-1}$ (C=C·C=O), $\lambda_{max.}$ (in dioxan) 240μ (log mε 4·43) (Found: C, 84·5; H, 9·6; O, 6·1. $C_{38}H_{52}O_2$ requires C, 84·4; H, 9·7; O, 5·9%).

1,2,3,4,5,6,7,12,13,14,15,16-*Dodecahydrodicyclo-octa*[a,c]*anthracene*-7,12-*dione* (XXI).—1,2,3,4,5,6,6a,6b,7,12,12a,12b,13,14,15,16-Hexadecahydrodicyclo-octa[*a,c*]anthracene-7,12dione-(0·5 g.) was dehydrogenated by *p*-benzoquinone (2 g.) in acetic acid (20 ml.) at 100° for 4 hr. Another portion of benzoquinone (2 g.) was then added and heating continued for 4 hr. The usual working-up gave the *diketone* as yellow needles (200 mg., 40%), m. p. 164° (from acetic acid), $\nu_{max.}$ (in $CHCl_3$) 1665 cm.$^{-1}$ (quinonoid C=O), $\lambda_{max.}$ (in dioxan) 269, 358 mμ (log ε 4·65, 3·82) (Found: C, 84·0; H, 7·7; O, 8·4. $C_{26}H_{28}O_2$ requires C, 83·3; H, 7·6; O, 8·6%).

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