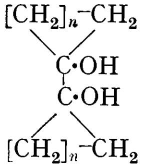
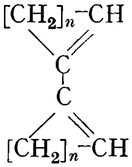
257. *The Derivatives of the Di- and Tetra-polymethylenoanthracenes. Part I.*

By E. de Barry Barnett and Cyril A. Lawrence.

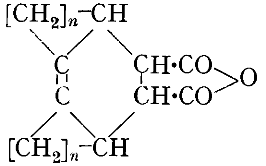
The pinacol condensation of *cyclo*pentanone and *cyclo*hexanone results in *diols* (I) from which conjugated *dienes* (II) are easily obtained by loss of water. These readily undergo the Diels reaction, and with maleic anhydride give (III), and with benzoquinone (IV) and (V), of which the former, but not the latter, readily give acetates (VI).



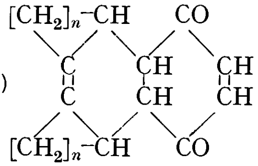
(I.)



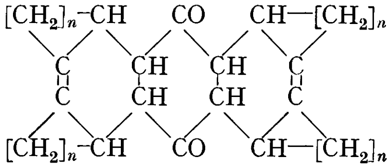
(II.)



(III.)



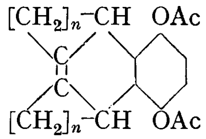
(IV.)

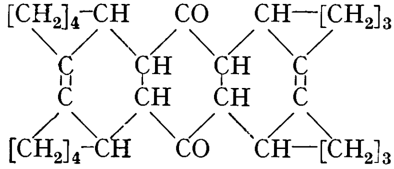


(V.)

By condensing (IV; $n = 3$) with *octahydrodiphenyl* (II; $n = 4$) a *compound* of structure (VII) has been obtained. With α-naphthaquinone, the dienes give *compounds* (VIII), from which *acetates* (IX) are readily obtained. Both compounds of type (VIII) readily undergo oxidation by atmospheric oxygen in alkaline solution, but with this marked difference that, whereas the *dodecahydrodibenzanthraquinone* (VIII, $n = 4$) loses only two atoms of hydrogen to give (X), the corresponding *tetrahydrodi*cyclo*pentenoanthraquinone* *

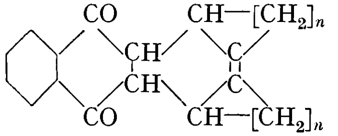
(VI.)

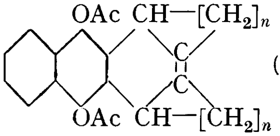




(VII.)

(VIII.)

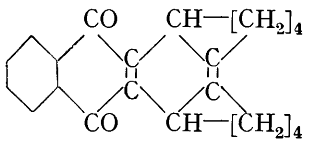


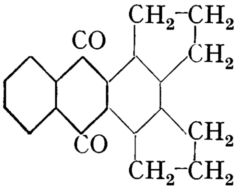


(IX.)

loses four atoms of hydrogen and passes into *di*cyclo*pentenoanthraquinone* (XI), from which 1 : 2 : 3 : 4-*di*cyclo*pentenoanthracene* is readily obtained by reduction.

(X.)



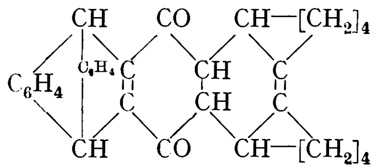


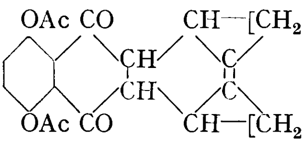
(XI.)

The more readily accessible octahydrodiphenyl has also been condensed with the oxidation product of the adject of anthracene and benzoquinone (Clar, *Ber.*, 1931, **64**, 1684), giving the endocyclic naphthacene *quinone* (XII). No pure substance could be isolated from the reaction product of octahydrodiphenyl and naphthazarin, but (XIII) was obtained from naphthazarin diacetate, although the dye obtained by hydrolysis and oxidation could not be purified.

Attempts to obtain purely aromatic hydrocarbons by the selenium dehydrogenation of some of the above octahydrodiphenyl derivatives were not successful.

(XII.)

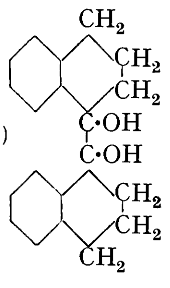


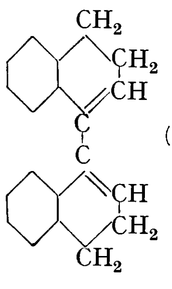


(XIII.)

A *diol* (XIV) was also obtained from 1-ketotetrahydronaphthalene, but the conjugated system in the corresponding *diene* (XV) showed greatly depressed reactivity, and no condensation appeared to take place with benzoquinone or with α-naphthaquinone. Some reaction took place on heating with maleic anhydride, but no pure product could be isolated.

(XIV.)





(XV.)

---

* It is more convenient to name this and similar compounds as derivatives of a hydro*cyclo*pentenoanthracene than as derivatives of a *cyclo*pentanohydroanthracene.

EXPERIMENTAL.

(Compounds were colourless, unless a colour is assigned to them.)

1 : 1′-*Dihydroxy*-1 : 1′-*di*cyclo*pentyl* (I, *n* = 3).—*cyclo*Pentanone (200 g.), coarse aluminium powder (40 g.), mercuric chloride (20 g.), and dry benzene (200 c.c.) were heated on the water-bath for an hour with frequent shaking, and for a further hour after the addition of water (170 c.c.) and benzene (300 c.c.). After filtering the hot mixture and extracting the solid with 300 c.c. of boiling benzene, the united filtrates were concentrated on the water-bath, light petroleum added, and the whole well cooled; yield 63 g., m. p. 109° (cf. Meiser, *Ber.*, 1899, **32**, 2053; Harries and Wagner, *Annalen*, 1915, **410**, 37, both of whom obtained very small yields by reduction with sodium and moist ether).

1 : 1′-*Dihydroxy*-1 : 1′-*di*cyclo*hexyl* (I, *n* = 4).—This was obtained from *cyclo*hexanone (200 g.), aluminium (35 g.), mercuric chloride (14 g.), and benzene (200 c.c.) by the method given above; yield 60 g., m. p. 130° as stated by Zelinsky (*Ber.*, 1901, **34**, 2801), who obtained a very small yield by using sodium and moist ether.

Di-$\Delta^{1:1}$-cyclo*pentene* (II, *n* = 3).—Dihydroxydi*cyclo*pentyl (50 g.) and dehydrated alum (5 g.) were heated at 140—160° until evolution of water had ceased (3—4 hrs.), and the distillate and the extract of the residue were dried with calcium chloride in ethereal solution. After removal of ether, the residue (33 g.) formed a yellow oil, b. p. 208°, but repeated distillation both in a vacuum and at the ordinary pressure failed to give a colourless product, and satisfactory analytical figures could not be obtained.

Di-$\Delta^{1:1}$-cyclo*hexene* (*octahydrodiphenyl*) (II; *n* = 4), similarly obtained (133 g. from 200 g. of diol), had b. p. 245—251°; after recrystallisation from alcohol, the m. p. was 28° (Found : C, 88·7; H, 11·1. $C_{12}H_{18}$ requires C, 88·9; H, 11·1%).

1 : 2 : 3 : 6-*Tetrahydro*-3 : 4 : 5 : 6-*di*cyclo*pentenophthalic Anhydride* (III; *n* = 3).—Di*cyclo*pentene (5 g.) and maleic anhydride (4 g.) were cautiously warmed until reaction took place. After recrystallisation from *cyclo*hexane, the *anhydride* had m. p. 104° (Found : C, 72·3; H, 7·2. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

Dodecahydrophenanthrene-9 : 10-*dicarboxylic Anhydride* (III, *n* = 4).—Octahydrodiphenyl (12 g.) and maleic anhydride (8 g.) were cautiously heated until the lower layer vanished (about 2 mins.). The *anhydride*, washed with light petroleum and recrystallised from *cyclo*hexane, had m. p. 122° (Found : C, 73·7; H, 7·7. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%).

Tetrahydro-5 : 6 : 7 : 8-*di*cyclo*penteno*-1 : 4-*naphthaquinone* (IV, *n* = 3).—Di*cyclo*pentene (4·4 g.) and benzoquinone (3·6 g.) were boiled for an hour with 10 c.c. of methanol, the whole cooled in ice, and the solid recrystallised from methanol and from toluene. The *quinone*, m. p. 124°, was pale yellow (Found : C, 79·2; H, 7·4. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%).

5 : 8-*Dihydro*-5 : 6 : 7 : 8-*di*cyclo*pentenonaphthaquinyl Diacetate* (VI, *n* = 3).—The above quinone (2 g.), acetic anhydride (4 c.c.), and pyridine (10 c.c.) were boiled for 2 hrs., a little water added, and the whole cooled in a freezing mixture. After recrystallisation from methanol (charcoal) and from *cyclo*hexane, the crystals had m. p. 145° (Found: C, 73·5; H, 7·0. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%).

*Octahydrotetra*cyclo*pentenoanthraquinone* (V, *n* = 3).—Equal weights of tetrahydrodi*cyclo*pentenonaphthaquinone (above) and di*cyclo*pentene were boiled for 30 secs., acetone added, and the whole cooled in a freezing mixture. The *quinone* (yield about 10%), recrystallised from *cyclo*hexane, had m. p. 152° (Found : C, 82·9; H, 8·7. $C_{26}H_{32}O_2$ requires C, 82·9; H, 8·6%).

Dodecahydro-5 : 6 : 7 : 8-*dibenz*-1 : 4-*naphthaquinone* (IV, *n* = 4).—Octahydrodiphenyl (4·2 g.) and benzoquinone (2·5 g.) were boiled for 5 hrs. with 15 c.c. of alcohol, the solution cooled in a freezing mixture, and the solid recrystallised from methanol (charcoal). The *product*, m. p. 114°, was pale yellow (Found : C, 80·0; H, 8·3. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%).

Decahydro-5 : 6 : 7 : 8-*dibenznaphthaquinyl Diacetate* (VI, *n* = 4).—The preceding compound (2·0 g.) was boiled for 2 hrs. with acetic anhydride (4 c.c.) and pyridine (10 c.c.), water added, and the solid recrystallised from acetone–alcohol (charcoal) and from toluene; m. p. 161° (Found : C, 74·5; H, 7·6. $C_{22}H_{26}O_4$ requires C, 74·6; H, 7·4%).

Eicositetrahydrotetrabenzanthraquinone (V, *n* = 4).—Octahydrodiphenyl (20 g.) and benzoquinone (6 g.) were heated with shaking until the solution just boiled. The gum which separated on cooling was washed with alcohol and with acetone and recrystallised from toluene and from xylene. The *product* had m. p. 315° (decomp.) (Found : C, 83·0; H, 9·1. $C_{30}H_{40}O_2$ requires C, 83·3; H, 9·2%).

Hexadecahydro-5 : 6 : 7 : 8-*di*cyclo*penteno*-1 : 2 : 3 : 4-*dibenzanthraquinone* (VII).—Tetrahydrodi*cyclo*pentenonaphthaquinone (2·4 g.) and octahydrodiphenyl (2 g.) were cautiously boiled for a few seconds, and the gum formed on cooling was washed with acetone and recrystallised from toluene. The *product* had m. p. 222° after slight sintering (Found : C, 83·0; H, 9·1. $C_{28}H_{36}O_2$ requires C, 83·2; H, 9·0%).

Tetrahydro-1 : 2 : 3 : 4-*di*cyclo*pentenoanthraquinone* (VIII, *n* = 3).—Di*cyclo*pentene (5 g.) and α-naphthaquinone (5·8 g.) were boiled with alcohol (15 c.c.) for an hour, and the crystals obtained on cooling recrystallised from alcohol (charcoal) and then from *cyclo*hexane; m. p. 134° (Found; C, 82·1; H, 6·9. $C_{20}H_{20}O_2$ requires C, 82·2; H, 6·9%).

1 : 4-*Dihydro*-1 : 2 : 3 : 4-*di*cyclo*pentenoanthraquinyl Diacetate* (IX, *n* = 3).—The preceding compound (2·2 g.), acetic anhydride (4 c.c.), and pyridine (10 c.c.) were boiled for 3 hrs., water added, and the washed solid recrystallised from toluene. The *product* had m. p. 195° after some sintering (Found : C, 76·3; H, 6·5. $C_{24}H_{24}O_4$ requires C, 76·3; H, 6·4%).

1 : 2 : 3 : 4-*Di*cyclo*pentenoanthraquinone* (XI).—Air was passed through a suspension of tetrahydrodi*cyclo*pentenoanthraquinone (4 g.) in alcohol (50 c.c.) containing a little caustic potash until the red colour vanished permanently. The *product* (quantitative yield) was recrystallised from anisole. It was pale yellow and had m. p. 253° (Found : C, 83·1; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

1 : 2 : 3 : 4-*Di*cyclo*pentenoanthracene*.—The compound (XI) (2·5 g.), zinc dust (11 g.), caustic soda (11 g.), ammonia (*d* 0·880; 25 c.c.), alcohol (80 c.c.), and water (35 c.c.) were boiled for 6 hrs., cooled, and the solid digested with hydrochloric acid to remove zinc. After recrystallisation from glacial acetic acid and from *cyclo*hexane, the *product*, m. p. 146°, was pale yellow (Found : C, 92·8; H, 7·1. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%).

Dodecahydro-1 : 2 : 3 : 4-*dibenzanthraquinone* (VIII, *n* = 4).—Equal weights of octahydrodiphenyl and α-naphthaquinone were heated until the mixture just boiled. After recrystallisation from xylene and from benzene–light petroleum, the *product* had m. p. 208° (decomp.) (Found : C, 82·5; H, 7·5. $C_{22}H_{24}O_2$ requires C, 82·5; H, 7·5%).

Decahydro-1 : 2 : 3 : 4-*dibenzanthraquinyl Diacetate* (IX, *n* = 4).—The above quinone (3 g.), acetic anhydride (5 c.c.), and pyridine (10 c.c.) were boiled for 2½ hrs., water added, and the solid recrystallised from toluene; m. p. 228° (Found : C, 77·2; H, 6·9. $C_{26}H_{28}O_4$ requires C, 77·2; H, 6·9%).

Decahydro-1 : 2 : 3 : 4-*dibenzanthraquinone* (X).—A suspension of the above quinone (1·5 g.) in alcohol (50 c.c.) and alkali was oxidised as for (XI), and the solid precipitated by water; recrystallised from toluene, it had m. p. 254° and was yellow (Found : C, 83·0; H, 7·1. $C_{22}H_{22}O_2$ requires C, 83·0; H, 6·9%).

5 : 8-*Diacetoxydodecahydro*-1 : 2 : 3 : 4-*dibenzanthraquinone* (XIII).—Naphthazarin diacetate (2·5 g.), octahydrodiphenyl (1·5 g.), and toluene (10 c.c.) were boiled for 2½ hrs., and the toluene then evaporated on the water-bath. After being washed with light petroleum, the residue was recrystallised from *cyclo*hexane; m. p. 173° (Found : C, 71·5; H, 6·7. $C_{26}H_{28}O_6$ requires C, 71·5; H, 6·4%).

endo-9 : 10-o-*Phenylenetetradecahydro*-1 : 2 : 3 : 4-*dibenznaphthacene Quinone* (XII).—Octahydrodiphenyl (3·5 g.) and *endo*-9 : 10-*o*-phenylene-9 : 10-dihydro-1 : 4-anthraquinone [prepared by Clar's method (*loc. cit.*) but with only half the amount of chromium trioxide specified by him] were boiled for 1 hr. with 25 c.c. of xylene. After being kept for a few hours at the ordinary temperature, the solid was washed with xylene and recrystallised from xylene and from anisole. The *product*, m. p. 260—267° (decomp.), was then yellow (Found : C, 85·8; H, 6·8. $C_{32}H_{30}O_2$ requires C, 86·1; H, 6·7%).

1 : 1′-*Dihydroxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-1 : 1′-*dinaphthyl* (XIV).—100 G. of 1-ketotetrahydronaphthalene (prepared by the oxidation of tetralin, D.R.-P. 346,948), 15 g. of coarse aluminium powder, 10 g. of mercuric chloride, and 100 c.c. of dry benzene were boiled for 1 hour, 50 c.c. of water added, and after being boiled for 10 mins., the whole was filtered and the solid extracted with boiling benzene. The united filtrates were concentrated, and the *pinacol* (10 g.) which separated was collected. Two repetitions of the above reduction with the filtrate afforded a further 6 g. of pinacol. After recrystallisation from slightly aqueous alcohol (charcoal) and (for analysis) from benzene, crystals, m. p. 191°, were obtained (Found : C, 81·7; H, 7·7. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%).

3 : 4 : 3′ : 4′-*Tetrahydro*-1 : 1′-*dinaphthyl* (XV).—The above diol (10 g.) and dehydrated alum (1 g.) were heated at 170—190° until no more water was evolved (15—30 mins.). After recrystallisation from aqueous alcohol (charcoal), the *product*, 6 g., had m. p. 140° (Found C, 92·8; H, 7·1. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%).

The authors thank Imperial Chemical Industries, Ltd., for grants.

SIR JOHN CASS TECHNICAL INSTITUTE, JEWRY ST., E.C. 3.

[*Received, May 3rd*, 1935.]