disulfide at room temperature was added 5.5 g. (0.05 mole) of ethyl bromide. Stirring was continued for 1.5 hr. and then the reaction mixture was worked up. The crude product was dissolved in benzene and chromatographed on alumina. Distillation of the benzene followed by two recrystallizations of the product from absolute ethanol resulted in 2.2 g. (16%) of orange needles, m.p. 104–106°.

Anal. Calcd. for $C_{15}H_{12}O_2S_2$: C, 62.50; H, 4.17; S, 22.22. Found: C, 62.37, 62.50; H, 4.37, 4.21; S, 22.33, 22.22.

Methyl dibenzo-p-dioxin-2-dithiocarboxylate (X). To a stirred mixture of 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin, 22 g. (0.16 mole) of aluminum chloride and 100 ml. of carbon disulfide was added 7.1 g. (0.05 mole) of methyl iodide. The mixture was then refluxed for 6.5 hr. and then worked up in the usual manner. After evaporation of the carbon disulfide, the residue was dissolved in benzene and chromatographed on alumina. This did not effect purification, so the crude material was subjected to vacuum sublimation. The unreacted dibenzo-*p*-dioxin sublimed away from the product which was recrystallized twice from ethanol to yield 0.2 g. (1.4%) of orange needles, m.p. 121–123°.

Anal. Calcd. for $C_{14}H_{10}O_2S_2$: S, 23.36. Found: S, 23.73, 23.51.

Diethyl dibenzo-p-dioxin-bis(dithiocarboxylate) (XI). Ethyl chloride was slowly bubbled into 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin, 22 g. (0.16 mole) of aluminum chloride, and 200 ml. of carbon disulfide over a period of 1.5 hr. at room temperature. The usual work-up produced crude material which was recrystallized three times from benzene-ethanol to form 1.7 g. (7%) of dark orange needles, m.p. 174–176°.

Anal. Calcd. for $C_{18}H_{16}O_2S_4$: S, 32.65. Found: S, 32.65, 32.74.

2-Chloromethyldibenzo-p-dioxin (XII). A mixture of 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin, 4 g. (0.13 mole) of paraformaldehyde, 50 ml. of glacial acetic acid, 40 ml. of concentrated hydrochloric acid, and 15 ml. of 85% phosphoric acid was heated at 80° for 10 hr. with stirring. Dilution of the reaction mixture with water followed by suction filtration produced 12.7 g. of crude material. Vacuum-distillation of the crude product yielded 3 g., b.p. 143–144° (0.15 mm.). This material was recrystallized three times from ethanol to form 1.5 g. (13%) of white needles, m.p. 111–113°.

Anal. Calcd. for $C_{13}H_9O_2Cl$: Cl, 15.28. Found: Cl, 15.41, 15.31.

Dibenzo-p-dioxin-2-carboxaldehyde (XIII). An excess of carbon monoxide and hydrogen chloride, obtained by dropping chlorosulfonic acid into formic acid, was bubbled into a mixture of 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin, 23 g. (0.175 mole) of aluminum chloride, 3 g. of cuprous chloride and 50 ml. of benzene for 8 hr. at 40–50°. After hydrolysis and distillation of the benzene layer, the residue was dissolved in methanol and treated with saturated sodium bisulfite solution. The precipitate which formed was washed with ethanol and ether. Treatment of the precipitate with dilute hydrochloric acid produced the product which melted 87–90°. Two recrystallizations from ethanol-water yielded 0.2 g. (2%) of white crystals, m.p. 91–93°.

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.58; H, 3.77. Found: C, 74.40, 74.31; H, 3.54, 3.62.

The 2,4-dinitrophenylhydrazone recrystallized from pyridine-ethanol melted 300–301°.

Anal. Calcd. for $C_{19}H_{12}O_6N_4$: N, 14.29. Found: N, 13.89, 14.00.

Attempted preparation of 2-(α-naphthyl)dibenzo-p-dioxin. A mixture of 11 g. (0.08 mole) of aluminum chloride, 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin, 10 g. (0.08 mole) of quinoline, and 7.3 g. (0.05 mole) of α-fluoronaphthalene were stirred at 150° for 2 hr. Then 7 g. (0.055 mole) more of aluminum chloride was added and the temperature raised to 180° for 2 hr. The purple-black mixture was allowed to cool and hydrolyzed with ice–hydrochloric acid. This was extracted with ether and dried over anhydrous sodium sulfate. The residue, obtained by evaporation of the ether, was vacuum distilled to yield a small amount of α-fluoronaphthalene. By chromatographing the material remaining in the flask after vacuum distillation, 2.5 g. (28%) of starting material was obtained. No product has been isolated.

The other runs using α-bromonaphthalene and *p*-chlorophenol were very similar to that described above except for variations in the solvent.

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AMES, IOWA

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY]

Alicyclic Studies. XIII.[1] Preparation and Reactions of 1,1′-Dicycloalkenyls*

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The preparation of 1,1′-dicyclopentenyl, 1,1′-dicyclohexenyl, 1,1′-dicycloheptenyl, and 1,1′-dicycloöctenyl has been improved. Diels-Alder reactions of these dienes are described.

Diene reactions of 1,1′-dicylopentenyl[1] (Ia) and 1,1′dicylohexenyl[2,3] (Ib) have been described. However, it is clear that particularly in the former case, the diene has not heretofore been obtained pure. The dienes are prepared by dehydration under acidic conditions of the pinacols resulting from pinacol-reduction of cyclopentanone and cyclohexanone, respectively. It has been shown that acidic dehydration of 1,1′-dihydroxy-1,1′-dicyclopentyl gives primarily 2-spirocyclopentanocyclohexanone (II).[4] The yields of Diels-Alder adducts form

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

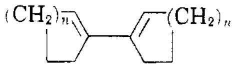
(1) Part XII, Y. Amiel and D. Ginsburg, *Tetrahedron*, 1, 19 (1957).

(2) E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

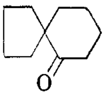
(3) E. E. Gruber and R. Adams, *J. Am. Chem. Soc.*, 57, 2555 (1935).

(4) M. Qudrat-i-Khuda and A. K. Ray, *J. Indian Chem Soc.*, 16, 525 (1939).

1,1′-dicyclopentenyl as described by Barnett and Lawrence[2] show that their diene component could not have contained more than 25 per cent of pure diene even when alum was used to dehydrate the corresponding pinacol. These authors report that they were unable to obtain good analytical results for their diene. When their work was repeated, the infrared spectrum of the product indeed showed that the product of alum dehydration of the pinacol was primarily the spiroketone. The method of choice for this dehydration was found to be through phosphorus oxychloride in pyridine. No rearrangement occurs under these conditions and no carbonyl band is exhibited by the infrared spectrum of the product. The pure diene thus obtained afforded a quantitative yield of adduct with maleic anhydride.



Ia; n = 1
a; n = 2
c; n = 3
d; n = 4



II

Although relatively less of the corresponding spiroketones accompany the dienes Ib, Ic, and Id when they are prepared by acidic dehydration of their pinacols, the phosphorus oxychloride-pyridine method afforded the smoothest means for their preparation.

An alternative method was tried in the case of 1,1′-dicyclooctenyl (Id). 1-Cyclooctylcyclooctene prepared by self-condensation of cyclooctene in the presence of sulfuric acid[5] was brominated with one mole of *N*-bromosuccinimide and the allylic bromide was dehydrobrominated. That the desired symmetrical diene was not thus obtained was shown by the fact that no adduct could be prepared *via* the Diels-Alder reaction with maleic anhydride. Probably a homoannular diene was obtained by bromination-dehydrobromination of 1-cyclooctylcyclooctene. The homoannular product is either 1- or 2-cyclooctylcycloocta-1,3-diene but its structure was not further elucidated.

As stated above, 1,1′-dicyclopentenyl afforded a quantitative yield of adduct with maleic anhydride. All attempts at aromatization of the product gave a central benzenoid ring and no quinonoid arrangement of double bonds throughout the tricyclic (carbocyclic) system could be obtained even from the adduct of the diene with methyl acetylenedicarboxylate. Treatment of the latter substance with excess of *N*-bromosuccinimide followed by dehydrobromination afforded the product with a central benzenoid ring. The same situation obtained in the products of the Diels-Alder reaction of 1,1′-dicycloheptenyl with various dienophiles.

Since the adducts of the dienes with *p*-benzoquinone are cyclohexenediones which can, in principle, readily isomerize to give phenols, the Diels-Alder reaction of 1,1′-dicyclopentenyl with this quinone was carried out under the same conditions as previously reported.[2] It was found from the infrared spectrum of the adduct that it is, indeed, the enedione as formulated. However, when several of the dienes reacted with *p*-benzoquinone in the *absence* of methanol it was clear from the infrared spectrum of one of the products that a phenol had been formed by aromatization of the immediate product of the condensation. The detailed descriptions of these reactions are given in the experimental section.

EXPERIMENTAL

Melting points and boiling points are uncorrected.

1,1′-Dihydroxy-1,1′-dicyclopentyl. This pinacol was prepared by the method of Barnett and Lawrence.[2] The yield was the same as reported and decreased appreciably when magnesium was used instead of aluminum. It had m.p. 109° (from pentane). Lit.[2] m.p. 109°.

1,1′-Dicyclopentenyl (Ia). (*a*) Dehydration of the above pinacol was attempted with oxalic acid in boiling toluene but afforded material which did not react with maleic anhydride. The reported method[2] using anhydrous alum afforded a product, b.p. 205–210°. The condensation of this product with maleic anhydride[2] afforded an adduct in 10–15% yield. The infrared spectrum of the dehydration product exhibited a strong band at 1702 cm.$^{-1}$ (C═O) showing the presence of a large amount of *2-spirocyclopentanocyclohexanone* (II). It gave an orange *2,4-dinitrophenylhydrazone,* m.p. 111–112° (from ethanol).

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: N, 16.86. Found: N, 17.22.

The *spiro*-ketone (7 g.) itself was isolated from the dehydration product (10 g.) through the use of Girard P reagent[6] and the resulting diene from this separation (3 g.) was still slightly contaminated by the spiroketone. The dehydration mixture afforded the above 2,4-dinitrophenylhydrazone in 70–75% yield, again indicating that no more than 25% of diene is present in the mixture.

(b) *By means of phosphorus oxychloride in pyridine.* A mixture of the pinacol (40 g.), phosphorus oxychloride (40 ml.), and dry pyridine (200 ml.) was carefully warmed on the steam bath until a very exothermic reaction occurred, necessitating cooling in an ice bath. When the reaction became moderate, the mixture was warmed on the steam bath for 6 hr. and most of the pyridine was removed at the water pump. Ice cold water was added with cooling to a total volume of *ca.* 250 ml. and the thick mixture was shaken mechanically for 30 min. in order to complete dissolution of the water-soluble compounds. The mixture was extracted with pentane and the pentane extracts were washed with 10% hydrochloric acid, with aqueous sodium bicarbonate, with water, and then dried (sodium sulfate). Removal of the pentane followed by distillation afforded *1,1′-dicyclopentenyl,* b.p. 32°/0.05 mm. (27.5 g.; 84%) as a light yellow mobile liquid. The analytical sample was prepared by dissolving a portion of the diene in dry ether and refluxing the solution over sodium wire until the latter was no longer attacked. The analytical sample had b.p. 34°/0.1 mm., n_D^{19} 1.5251.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.39; H, 10.31.

3,4,5,6-Dicyclopentano-1,2,3,6-tetrahydrophthalic anhydride.

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(5) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 41 (1948).

(6) A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

A mixture of pure 1,1′-dicyclopentenyl (4 g.), maleic anhydride (2.9 g.), and cyclohexane (4 ml.) was warmed gently until the powder melted. Cooling was necessary to control the strongly exothermic reaction. After 2 hr. the mixture solidified. The *anhydride* was removed by filtration (6.5 g.; 94%) and the crude material had m.p. 101°. The analytical sample had m.p. 104° (from cyclohexane). Lit.[2] m.p. 104°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; O, 20.67. Found: C, 72.30; H, 7.15; O, 21.00.

Infrared absorption ($CHCl_3$): 1852 cm.$^{-1}$, 1775 cm.$^{-1}$ (C═O bands of anhydride).

3,4,5,6-Dicyclopentanophthalic anhydride. (*a*) A mixture of the above anhydride (1.95 g.), *N*-bromosuccinimide (2.67 g.; 2 equiv.), and carbon tetrachloride (200 ml.) was heated under reflux for 3 hr. At this point all of the NBS had been converted to succinimide. Anhydrous sodium acetate (1.23 g.) and glacial acetic acid (1.5 ml.) were added and refluxing was continued for an additional 18 hr. The mixture was poured into water and the solid which appeared between the aqueous and organic layers was removed by filtration (250 mg.). The solvents were removed from the organic phase and trituration of the residual bromine-containing oil with a small amount of carbon tetrachloride afforded more solid (350 mg.). The residual oil was not further investigated. Recrystallization of the solid gave the pure *aromatic anhydride*, m.p. 265° (from toluene).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30; O, 21.03. Found: C, 73.51; H, 5.56; O, 21.12.

Infrared absorption (KBr): 1833 cm.$^{-1}$, 1760 cm.$^{-1}$ (C═O bands of anhydride).

Dimethyl 3,4,5,6-dicyclopentano-3,6-dihydrophthalate. A mixture of 1,1′-dicyclopentenyl (6.7 g.) and dimethyl acetylenedicarboxylate (7.1 g.) was warmed on the steam bath. After 15 min. a vigorous reaction set in. Warming was interrupted for 10 min. and then continued for 8 hr. Trituration of the cold reaction mixture with methanol afforded the *ester* (9.7 g.; 70%), m.p. 127° (from methanol).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30; O, 23.16. Found: C, 69.54; H, 6.91; O, 23.63.

A portion of the crude ester was saponified by aqueous methanolic potassium hydroxide. The crude product obtained after removal of the methanol and acidification was recrystallized from acetic acid and from toluene and was identical with the aromatic anhydride described above by mixed m.p. determination.

Aromatization of the diester. A mixture of the above diester (2.76 g.), *N*-bromosuccinimide (2.0 g.) and carbon tetrachloride (50 ml.) was refluxed for 2 hr. After removal of the succinimide and the solvent the crude product was saponified by aqueous methanolic potassium hydroxide. Removal of the methanol, acidification and recrystallization from toluene afforded the aromatic anhydride, identical with that described above by mixed melting point determination.

Reaction of 1,1′-dicyclopentenyl and p-benzoquinone. (*a*) 1,1′-Dicyclopentenyl (7.4 g.; 2 equiv.) and *p*-benzoquinone (3 g.) were mixed at ice-bath temperature and then warmed on the steam bath for 1 hr. The reaction mixture was treated with methyl cyclohexane (100 ml.) and a solid, m.p. 171° (from methylcyclohexane), was obtained. This was *p*-hydroquinone.

The methylcyclohexane solution was concentrated to about one quarter of its original volume and crystals were obtained, m.p. 150° (from methylcyclohexane) (1.9 g.). Infrared absorption (chloroform): broad band 1695–1712 cm.$^{-1}$ (C═O). This must correspond to *1,2,3,4,5,6,7,8-tetracyclopentano-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-anthraquinone* which was also obtained by Barnett and Lawrence,[2] who report m.p. 152° for the product from their mono-adduct of 1,1′-dicyclopentenyl and *p*-benzoquinone with an additional mole of the diene.

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57; O, 8.50. Found: C, 82.76; H, 8.57; O, 8.68.

After evaporation of the methylcyclohexane from the mother liquor an additional portion (4 g.) of the same diketone was obtained, m.p. 150° (from aqueous ethanol or acetone). The overall yield of products was therefore 57%.

(*b*) The same reaction was carried out repeating the conditions of Barnett and Lawrence,[2] in order to determine the infrared spectrum of their mono-adduct: A mixture of the diene (3.3 g.), *p*-benzoquinone (2 equiv.) and methanol (10 ml.) was heated under reflux. The product was *5,6,7,8-dicyclopentano-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione*, m.p. 124° (from methanol) (4 g.). Lit.[2] m.p. 124°. Infrared absorption (chloroform): broad band 1695, 1660 cm.$^{-1}$ (strong band, O═C—C═C—C═O).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49; O, 13.21. Found: C, 79.15; H, 7.46; O, 13.56.

1,2,3,4-Dicyclopentano-1,4,4a,9a-tetrahydro-9,10-anthraquinone. A mixture of the diene (2.2 g.) and 1,4-naphthoquinone (2.7 g.) was warmed on the steam bath. A dark homogeneous melt was obtained immediately and solidified after cooling. Recrystallization afforded the *diketone*, m.p. 130° (from 2-propanol) (3.5 g.; 72%).

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89; O, 10.95. Found: C, 81.86: H. 6.92; O, 11.06.

Infrared absorption ($CHCl_3$): 1682 cm.$^{-1}$ (C═O). Lit.[2] m.p. 134°.

1,1′-Dihydroxy-1,1′-dicycloheptyl. A solution of mercuric chloride (8 g.) in cycloheptanone (100 g.) was added to coarse aluminum powder (16 g.) in dry benzene (150 ml.). After warming on the steam bath for 5–10 min. a strong reaction began and had to be controlled by external cooling. After moderation of the reaction the mixture was refluxed for 12 hr. Benzene was added (150 ml.) and water (60 ml.) was added dropwise during 30 min. The mixture was warmed for an additional 2 hr. with occasional shaking, and filtered. The solid was extracted with benzene (150 ml.) and the combined benzene extracts were distilled at the water pump up to a bath temperature of 150°. Unreacted cycloheptanone (10 g.) was recovered. Pentane was added to the residual oil and the solution was refrigerated overnight. The crystals of pinacol were filtered and washed well with pentane, m.p. 78°.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58; O, 14.14. Found: C, 73.62; H, 11.34; O, 14.28.

The mother liquor was distilled and afforded 1,1′-dicycloheptenyl, b.p. 85–86°/0.01 mm. (15.7 g.) and further portion of pinacol, b.p. 117–118°/0.05 mm. (9 g.). The total yield including diene was 77%. The use of magnesium instead of aluminum gave a lower yield of product.

1,1′-Dicycloheptenyl (Ic). The preferred method for dehydration of the pinacol was by means of phosphorus oxychloride in pyridine as described above for the preparation of 1,1′-dicyclopentenyl. The reaction in this case was less vigorous and requires no external cooling. From the pinacol (25 g.) and phosphorus oxychloride (25 ml.) was obtained the *diene* (19 g.; 90%), b.p. 83–84°/0.05 mm. The infrared spectrum showed no hydroxyl or carbonyl absorption; n^{19}_{D} 1.5223.

Dehydration can be effected in 90% yield by means of oxalic acid or in 82% yield by using the method of Gruber and Adams[3] for the dehydration of 1,1′-dihydroxy-1,1′-dicyclohexyl by means of 10% sulfuric acid. However, both of these products contained *2-spirocycloheptanocyclooctanone*, although in very small amount, and this was characterized as the orange *2,4-dinitrophenylhydrazone*, m.p. 113–114° (from ethanol).

Anal. Calcd. for $C_{20}H_{28}N_4O_4$: N, 14.42. Found: N, 14.70.

For example, 10 g. of pinacol gave 8 g. of product after oxalic acid dehydration and by the use of Girard P reagent, only 100 mg. of *spiro*ketone was isolated.

3,4,5,6-Dicycloheptano-1,2,3,6-tetrahydrophthalic anhydride. A mixture of the diene (5 g.) maleic anhydride (2.6 g.) and methylcyclohexane (5 ml.) was warmed carefully until the powder melted. Slight shaking started a strongly exothermic reaction which was moderated by external cooling. After a few minutes the mixture solidified. After standing overnight the solid was filtered. It had m.p. 157–158° (from methylcyclohexane) (5.1 g.; 68%).

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39; O, 16.64. Found: C, 74.39; H, 8.39; O, 16.81.

Infrared absorption ($CHCl_3$): 1855, 1777 cm.$^{-1}$ (anhydride).

3,4,5,6-Dicycloheptanophthalic anhydride. (*a*) The above adduct (2 g.) was heated with sulfur (0.42 g.) at 245° for 20 min. After crystallization from toluene in the presence of activated carbon a nearly colorless product, m.p. 240° was obtained (0.8 g.). Further recrystallization from toluene raised the m.p. to 254°. (*b*) The adduct (0.29 g.) was dissolved in chloroform (50 ml.) and bromine (0.16 g.) in chloroform (5 ml.) was added. No color change was apparent at room temperature. Refluxing for 2 hr. discharged the bromine color and hydrogen bromide was evolved. The solution was washed with 5% sodium bicarbonate solution and dried (sodium sulfate). The solvent was removed and the residue was recrystallized from carbon tetrachloride, m.p. 253° (0.12 g.). Further recrystallization from toluene yielded snow-white crystals, m.p. 254–255°. (*c*) A mixture of the adduct (1.4 g.), *N*-bromosuccinimide (1.78 g.) and carbon tetrachloride (125 ml.) was refluxed overnight. The mixture was then poured into water and the solid was filtered. The solvent was removed from the organic phase and the residue was triturated with methanol and the solid filtered. The combined solids were recrystallized from toluene and afforded the purest sample of the *aromatic anhydride*, m.p. 256° (0.64 g.) identical with the specimens obtained in (a) and (b) above both by mixed melting point determination.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09; O, 16.88. Found: C, 75.55; H, 6.88; O, 16.86.

Infrared absorption (KBr): 1831, 1762 cm.$^{-1}$ (anhydride).

3,4,5,6-Dicycloheptano-3,6-dihydrophthalic acid. A mixture of the diene (11 g.) and dimethyl acetylenedicarboxylate (8.2 g.) was heated on the steam bath for 8 hr. The product was then heated with aqueous (20 ml.) methanolic (200 ml.) potassium hydroxide (20 g.) for 8 hr. The methanol was removed by distillation, water was added, and the mixture was extracted with ether to remove unsaponified material (5 g.). Acidification of the aqueous phase precipitated a colorless solid (10.3 g.). The product after recrystallization from glacial acetic acid had m.p. 102°.

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74; O, 16.76. Found: C, 75.20; H, 7.68; O, 16.93.

Infrared absorption (chloroform): 1840, 1765 cm.$^{-1}$ (anhydride). This was the *dienic anhydride*. The *acid* could be obtained by aqueous hydrolysis, m.p. 140° (from methylcyclohexane).

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95; O, 21.03. Found: C, 71.33; H, 8.28; O, 20.30.

When the acid was refluxed in methylcyclohexane for 24 hr. it afforded a small amount of the aromatic anhydride, m.p. 256°, and as the major product the dienic anhydride, m.p. 102°. The dienic acid was aromatized in the usual way by treatment with one mole of *N*-bromosuccinimide, yielding the aromatic anhydride, m.p. 256°.

All attempts to isolate products containing more extended conjugation failed. In all cases the aromatic anhydride described above was the only characterizable product. Alternative attempts to add maleic anhydride to brominated 1,1′-dicycloheptenyl in order to introduce bromine atoms in the seven-membered rings in addition to the double bonds in the central six-membered ring, and thence remove them by dehydrobromination, also led to the aromatic anhydride and to an intractable mixture of oily bromoderivatives which could not be resolved.

5,6,7,8-Dicycloheptano-5,8-dihydronaphthalene-1,4-diol. The reaction between 1,1′-dicycloheptenyl (4.3 g.; 2 equiv.) and *p*-benzoquinone (1.2 g.) was carried out exactly as in the case of 1,1′-dicyclopentenyl. The product (2.7 g.; 82%) had m.p. 181° (from wet benzene) and its infrared spectrum showed bands at 3570, 3350 cm.$^{-1}$ (OH). It was therefore the *diphenol*, in the form of its monohydrate.

Anal. Calcd. for $C_{20}H_{26}O_2 \cdot H_2O$: C, 75.91; H, 8.92. Found: C, 76.41; H, 8.90.

Removal of the solvent and addition of 2-propanol afforded the yellow bis-diketone, *1,2,3,4,5,6,7,8-tetracycloheptano-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-anthraquinone* (0.2 g.), m.p. 315° (from dioxane; in preheated bath). The analysis shows the substance to be the bis-diketone but the carbonyl band in the infrared spectrum appeared at abnormally low frequency (1645 cm.$^{-1}$).

Anal. Calcd. for $C_{34}H_{48}O_2$: C, 83.55; H, 9.90; O, 6.55. Found: C, 83.74; H, 9.34; O, 7.10.

The same product was obtained in 20% yield by heating 2 equiv. of diene with 1 equiv. of *p*-benzoquinone in dioxane for 3 hr.

5,6,7,8-Dicycloheptano-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione. 1,1′-Dicycloheptenyl (1.05 g.), *p*-benzoquinone (0.6 g.), and methanol (4 ml.) was heated on the steam bath for 1 hr. Filtration after refrigeration overnight afforded a dark-red solid (0.6 g.). Recrystallization gave the dark-red *diketone*, m.p. 133–134° (from methanol). Infrared absorption ($CHCl_3$): 1660 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78; O, 10.72. Found: C, 80.47; H, 8.19; O, 11.21.

After removal of the solvent the above diphenol, m.p. 181° (0.8 g.) was obtained.

1,2,3,4-Dicycloheptano-1,4,4a,9a-tetrahydro-9,10-anthraquinone. The diene (3.84 g.) and 1,4-naphthoquinone (3.18 g.) afforded the *diketone*, m.p. 105° (from 2-propanol) (6 g.; 86%).

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10; O, 9.18. Found: C, 82.45; H, 8.18; O, 9.31.

Infrared absorption (chloroform): broad band, 1680–1695 cm.$^{-1}$ (C=O).

1,1′-Dihydroxy-1,1′-dicyclooctyl. The pinacol was prepared in a manner exactly analogous to the preparation of its seven-membered ring homolog except that the reflux period was only 9 hr. Cyclooctanone (12 g.) was recovered and the pinacol was obtained after refrigeration overnight in pentane solution (56 g.). It had m.p. 93–94°. Lit.[7] m.p. 93–94°. Distillation afforded 1,1′-dicyclooctenyl, b.p. 113–114°/0.1 mm. (11 g.) and an additional portion of the pinacol (4 g.) (total yield of products 72%).

1,1′-Dicyclooctenyl (Id). (*a*) A mixture of the pinacol (10 g.), oxalic acid (10 g.), and water (20 ml.) was refluxed for 15 hr. at 140°. Pentane extraction followed by distillation afforded the crude diene (8.2 g.) whose infrared spectrum showed the presence of 2-spirocyclooctanocyclononanone (C=O band at 1684 cm.$^{-1}$). The spiroketone (150 mg.) could be isolated through the use of Girard P reagent. (*b*) A mixture of pinacol (75 g.), phosphorus oxychloride (75 ml.), and pyridine (375 ml.) afforded, in the usual way pure *1,1′-dicyclooctenyl*, b.p. 113–114°/0.1 mm.; 118–120°/0.2 mm. (63 g.; quant. yield). Lit.[7] b.p. 122–123°/0.4 mm. The product crystallized spontaneously, m.p. 43°.

3,4,5,6-Dicyclooctano-1,2,3,6-tetrahydrophthalic anhydride. A mixture of 1,1′-dicyclooctenyl (1.09 g.), maleic anhydride (0.40 g.), and methylcyclohexane (1 ml.) gave the adduct, m.p. 155–160° (1.53 g.). The pure anhydride was obtained by recrystallization, m.p. 179–180° (from methylcyclohexane).

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92; O, 15.17. Found: C, 75.65; H, 8.97; O, 15.45.

Infrared absorption ($CHCl_3$): 1852, 1775 cm.$^{-1}$ (anhydride).

3,4,5,6-Dicyclooctanophthalic anhydride. The above anhydride (1.05 g.) was aromatized as usual by refluxing with *N*-bromosuccinimide (1.19 g.; 2 equiv.) in carbon tetrachloride (125 ml.) for 2.5 hr. The colorless *aromatic anhydride* (0.65 g.) had m.p. 199–200° (from toluene).

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(7) L. Ruzicka and A. A. Boekenoogen, *Helv. Chim. Acta,* **14,** 1319 (1931).

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74; O, 15.37. Found: C, 77.30; H, 7.88; O, 15.50.

Infrared absorption (KBr): 1833, 1760 cm.$^{-1}$ (anhydride).

1-Cyclooctylcyclooctene. This product was obtained according to the method described by Reppe *et al.*[5] in 66% yield. It had b.p. 135–140°/2 mm. The cyclooctene which was required as starting material was prepared in 70–80% yield by dehydration of cyclooctanol b.p. 120°/37 mm. with 85% phosphoric acid.[8] It had b.p. 142–146°.

1- or 2-Cyclooctylcycloocta-1,3-diene. A mixture of 1-cyclooctylcyclooctene (4.5 g.), *N*-bromosuccinimide (3.65 g.; 1 equiv.), and carbon tetrachloride (50 ml.) was refluxed for 15 min. The reaction was over in 10 min. The succinimide was filtered, the solvent was removed by distillation and collidine (25 ml.) was added. An immediate precipitation of collidine hydrobromide occurred. The mixture was refluxed for 2 hr. to ensure completion of the dehydrobromination. Filtration of the solution after cooling afforded crystalline collidine hydrobromide (3.8 g.; theory 4 g.). The residual collidine was removed in the usual way and the *diene* was distilled, b.p. 105–110°/0.2 mm. (3.5 g.). No adduct could be obtained from the diene with maleic anhydride.

Dimethyl 3,4,5,6-dicyclooctano-3,6-dihydrophthalate. A mixture of 1,1′-dicyclooctenyl (10.9 g.) and dimethyl acetylenedicarboxylate (7.1 g.) was heated on the steam bath for 8 hr. Trituration of an aliquot (1.5 g.) of the cooled reaction mixture with methanol gave the *ester* (1.2 g.; 80%), m.p. 115° (from methanol).

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95; O, 17.75. Found: C, 72.66; H, 9.04; O, 17.90.

Infrared absorption ($CHCl_3$): broad band, 1710–1735 cm.$^{-1}$ (C=O of ester).

Saponification of the rest of the crude ester afforded the crude acid (15.3 g.), which after recrystallization from glacial acetic acid afforded the *dienic acid*, m.p. 205° (sintering at 200°).

Anal. Calcd. for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49; O, 19.25. Found: C, 71.80; H, 8.07; O, 19.26.

Aromatization with 1 mole of NBS afforded the aromatic anhydride, m.p. 199–200°.

Reaction between 1,1′-dicyclooctenyl and p-benzoquinone. A mixture of the diene (40 g.; 2 equiv.) and *p*-benzoquinone (10 g.) was heated on the steam bath. After 30 min. of heating the liquid mass solidified. After an additional 1 hr. the mixture was again liquid and after one more hour it afforded a yellow crystalline mass. Methylcyclohexane was added and the pink solid (26 g.) was filtered. It formed needles, m.p. 186° (from wet benzene) and was phenolic. (Infrared band at 3330 cm.$^{-1}$). This is therefore *5,6,7,8-dicyclooctano-5,8-dihydronaphthalene-1,4-diol* in the form of its monohydrate.

Anal. Calcd. for $C_{22}H_{30}O_2 \cdot H_2O$: C, 76.70; H, 9.36; O, 13.93. Found: C, 77.11; H, 9.63; O, 13.99.

The solvent was removed from the mother liquor, a small amount of 2-propanol was added, and the solution was refrigerated. The yellow solid was filtered (2 g.) and had m.p. 252° (from dioxane). Infrared absorption ($CHCl_3$): 1710 cm.$^{-1}$ (satd. C=O). This is *1,2,3,4,5,6,7,8-tetracyclooctano-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-anthraquinone.*

Anal. Calcd. for $C_{38}H_{56}O_2$: C, 83.77; H, 10.36. Found: C, 83.09; H, 10.16.

1,2,3,4-Dicyclooctano-1,4,4a,9a-tetrahydro-9,10-anthraquinone. A mixture of the diene (24 g.) and 1,4-naphthoquinone (17.5 g.) was heated on the steam bath for 1 hr. and afforded a brown glassy mass. Trituration with methylcyclohexane afforded a tan solid which was filtered (32 g.; 72%). The dark brown mother liquor deposited a further crop of large transparent rhombs (8 g.). The *diketone* had m.p. 155° (from methylcyclohexane or isopropanol). Infrared absorption (KBr): 1695 cm.$^{-1}$ (C=O adjacent to aromatic ring).

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57; O, 8.50. Found: C, 82.37; H, 8.57; O, 8.85.

1,1′-Dicyclohexenyl (Ib). (Experiment carried out by M. Berdichev). The pinacol from cyclohexanone was prepared in the usual way.[2] Dehydration with phosphorus oxychloride in pyridine as described for the various pinacol homologs afforded the *diene*, b.p. 70–76°/0.05 mm. (95% yield).

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(8) *Cf. Org. Syntheses*, **Coll. Vol. II**, 152 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Reactions of Aromatic Sulfonyl Chlorides with Organocadmium Reagents[*,1]

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Aromatic sulfonyl chlorides react with diarylcadmium reagents to form simple or mixed aryl sulfones in fair yields; sulfinic acids and aryl halides are by-products. Aromatic sulfonyl chlorides react with dialkylcadmium reagents to yield alkyl chlorides and solid products; the latter react with hydrochloric acid to form arylsulfinic acids, and with nitric acid to give *N*,*N*-bis(arenesulfonyl)hydroxylamines.

The interaction of organocadmium reagents with acyl chlorides is an accepted method for preparation of ketones.[3] By analogy, the interaction of the cadmium reagents with sulfonyl chlorides might well be expected to yield sulfones. This reaction, if successful, might become the method of choice for production of mixed sulfones, RSO_2R'.

There appears to be but one published reference to the interaction of a sulfonyl chloride with an organocadmium compound, namely, that of Gilman and Nelson.[4] They reported that from 0.3 mole of benzenesulfonyl chloride and diphenylcadmium (prepared from 0.34 mole of phenylmagnesium bromide and 0.17 mole of anhydrous cadmium chloride), and subsequent acidification of the reac-

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(3) (*a*) J. Cason, *Chem. Revs.*, **40**, 15 (1947). (*b*) D. A. Shirley, *Org. Reactions*, VIII, 28 (1954).

(4) H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 518 (1936).