Cyclic Dienes. XXVII. 1,2,4,5-Tetramethylenecyclohexane[1,2]

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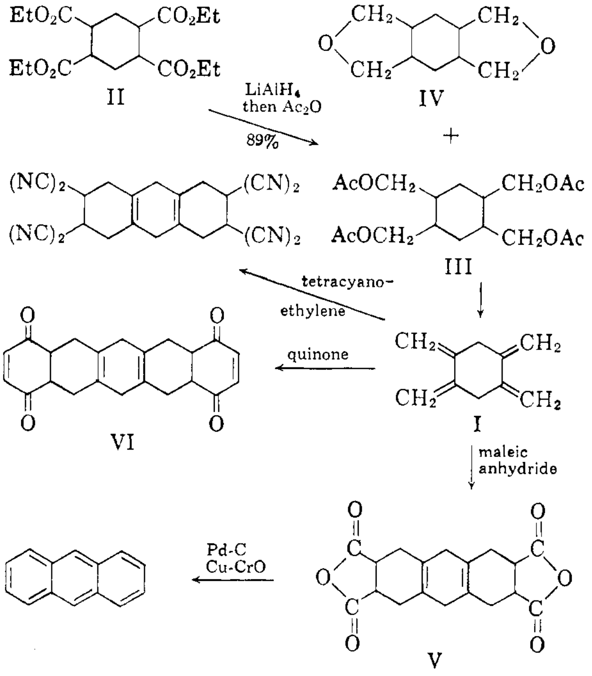
1,2,4,5-Tetramethylenecyclohexane was synthesized in three steps from tetraethyl pyromellitate. The key step was the pyrolysis of a tetraacetate under reduced pressure. The structure of this tetraene was indicated not only by the formation of three solid Diels-Alder adducts, one of which was converted to a known compound, but also by ultraviolet, infrared, and n.m.r. spectral data.

In a research program on Diels-Alder polymers[5] a series of bifunctional or bisdienes, such as 2-vinyl-1,3-butadiene,[6] 2,3-divinyl-1,3-butadiene[7] and bis-(1,3-butadienyl)methyl acetal,[8] has been prepared in this laboratory. An interesting extension of this series is the cyclic bisdiene, 1,2,4,5-tetramethylenecyclohexane (I). Since several articles in this series have illustrated a method for the conversion of carboxyl groups to exocyclic methylene groups, it appeared that pyromellitic acid would be a convenient starting material. When the project was initiated, pyromellitic acid was not commercially available. For that reason a convenient route was developed that involved the oxidation, in a 67% yield, of 1,5-di(chloromethyl)-2,4-dimethylbenzene, which was prepared by the chloromethylation of *m*-xylene. This procedure compares very favorably with the oxidation of charcoal[9] or durene.[10]

In later work commercial pyromellitic acid dihydrate was esterified to give a 92% yield of tetraethyl pyromellitate, which was reduced catalytically to give a 91% yield of tetraethyl hexahydropyromellitate (II). By the method of reductive acetylation developed in this laboratory,[6,11] which involved the reduction with lithium aluminum hydride in the usual manner followed by direct acetylation of the salts of the intermediate tetraol with acetic anhydride, II was converted to 1,2,4,5-(tetraacetoxymethyl)cyclohexane (III) in an 89% yield. From the mixture of stereoisomers could be obtained a pure solid tetraester, but in most cases the mixture of isomers was used. In addition to the tetraester a small amount of what is probably a mixture of decahydrobenzodifuran IV and 5,6-bis(acetoxymethyl)-octahydrobenzofuran was obtained.



When the 1,2,4,5-tetra(acetoxymethyl)cyclohexane (III) was pyrolyzed at atmospheric pressure by the usual techniques at temperatures from 400–650°, a very complex mixture containing benzene, toluene, xylenes, styrene, pseudocumene, methylstyrenes, and dimethylstyrenes was obtained. Even with careful procedures very heavy charring in the pyrolysis tube could not be avoided. Pyrolysis of III in a solvent seemed to reduce the charring but did not appear to improve the yield of tetraene. For this reason, several attempts were made to find a better route to the desired tetraene I. In one attempt, the tetraacetate III was converted to 1,2,4,5-tetrahydroxymethylcyclohexane tetrakis-(methyl carbonate) in an over-all yield of 62% by ester interchange with methanol, followed by treatment of the intermediate tetraol with methyl chloroformate. When this tetracarbonate was pyrolyzed under the usual conditions at 535° and atmospheric pressure, no tetraene was obtained but instead a 69% yield of 1,3,4,5,7,8-decahydrobenzo[1,2-*c*:

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(3) Office of Naval Research Fellow, 1957; Goodyear Tire and Rubber Fellow, 1959–1960; National Cancer Institute Fellow, 1960–1961.

(4) Office of Naval Research Fellow, 1953–1954.

(5) W. J. Bailey, J. Economy, and M. E. Hermes, *J. Org. Chem.*, **27**, 3295 (1962).

(6) W. J. Bailey and J. Economy, *J. Am. Chem. Soc.*, **77**, 1133 (1955).

(7) W. J. Bailey and N. A. Nielsen, *J. Org. Chem.*, **27**, 3088 (1962).

(8) W. J. Bailey and M. E. Hermes, *ibid.*, **27**, 2732 (1962).

(9) E. Phillippi and R. Thalen, *Org. Syntheses*, **10**, 90 (1930).

(10) R. Jacobsen, *Ber.*, **17**, 2516 (1884).

(11) W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, **78**, 2287 (1956).

4,5-*c'*]difuran (IV) plus an 80% yield of dimethyl carbonate were obtained.

Since pyrolysis under reduced pressure gave greatly improved yields in the preparation of 2,3-divinyl-1,3-butadiene,[7] this procedure was applied to the pyrolysis of the tetraacetate III with equally good results. Thus, when III was pyrolyzed at 575° and 60 mm. pressure under conditions such that 64% of four molar equivalents of acetic acid was liberated, an 8% yield of the tetraene was obtained. Repyrolysis of the high boiling residue produced additional tetraene. Even with this reduced pressure pyrolysis small amounts of a large variety of aromatic hydrocarbons were present. For this reason a pure sample of 1,2,4,5-tetramethylenecyclohexane (I) was obtained by preparative gas chromatography.

The structure of the tetraene I was proved by conversion to a known derivative as well as by spectral studies. Thus the treatment of I with maleic anhydride gave the decahydroanthracenetetracarboxylic anhydride V, which was simultaneously dehydrogenated and decarboxylated to produce anthracene. When the tetraene was treated with an excess of *p*-benzoquinone, the tetradecahydropentacene derivative VI was produced. The bifunctional dienophile VI should be of use in Diels-Alder polymerization as well as for the synthesis of linear condensed polynuclear aromatic hydrocarbons. Similarly, treatment of I with tetracyanoethylene gave the diadduct VIII.

The 1,2,4,5-tetramethylenecyclohexane possessed an $\epsilon_{\max}$ at 224 mμ which, although at a lower wave length than predicted by Woodward's rules,[12] is not far from the 220-mμ maximum found for 1,2-dimethylenecyclohexane[13] which has its methylene groups somewhat askew. The n.m.r. spectrum indicated the presence of only two types of hydrogen atoms, those on a terminal methylene group and those on a ring methylene group. The infrared absorption spectrum was also in agreement with the assigned structure.

The use of this interesting bifunctional diene to produce Diels-Alder polymers and polynuclear hydrocarbons will be reported separately.

Experimental[14]

Pyromellitic Acid.—In a 12-l., three-necked flask, equipped with a stirrer and a condenser, were placed 406 g. (2 moles) of 1,5-di(chloromethyl)-2,4-dimethylbenzene, m.p. 96–98° (reported[15] m.p. 99°), which was prepared by the chloromethylation of *m*-xylene according to the procedure of Braun and Welles, 6000 ml. of water, 50 g. of sodium hydroxide, and 365 g. of potassium permanganate. After this mixture had been heated at 80° for 24 hr. and all the potassium permanganate had been reduced to manganese dioxide, an additional 300 g. of potassium permanganate together with 50 g. of sodium hydroxide was added. (The temperature of the reaction mixture was reduced to 65° during the second addition since considerable heat was generated almost immediately.) When the mixture gave a negative permanganate test, an additional 2100 g. of potassium permanganate was added over a 5-day period in 100-g. portions, each accompanied by 25 g. of sodium hydroxide. After the reaction mixture had been heated under reflux for an additional 24 hr., the excess permanganate was decomposed with ethanol. The manganese dioxide was removed by filtration, and the filtrate was acidified with acetic acid. After an excess of a boiling saturated solution of barium chloride had been added, the resulting barium pyromellitate was removed by filtration, washed, dried and then dissolved in 20 times its weight of boiling 3 *N* sulfuric acid. When the filtrate from the barium sulfate mixture was concentrated to about 4 l., 390 g. (67%) of large flakes of pyromellitic acid dihydrate, m.p. 259° (reported[9] m.p. 262°), was obtained.

Tetraethyl Hexahydropyromellitate.—By use of the azeotropic esterification procedure 870.5 g. (3 moles) of pyromellitic acid dihydrate was esterified with 2000 ml. of absolute ethanol, 7000 ml. of benzene, and 10.5 ml. of concentrated sulfuric acid. Distillation through a 10-in., helix-packed column in the presence of Raney nickel catalyst gave 1108 g. (92%) of tetraethyl pyromellitate, b.p. 185° (0.2 mm.), m.p. 55°.

In a 1640-ml. high pressure hydrogenation vessel were placed 522 g. (1.30 moles) of powdered tetraethyl pyromellitate and approximately 50 g. of freshly prepared W-2 Raney nickel catalyst under an atmosphere of hydrogen at 3100 lb. per square inch. After the theoretical amount of hydrogen had been consumed (1960 p.s.i. at 180°) and the vessel had cooled, the catalyst was removed by suction filtration through Celite. Distillation of the filtrate through a 10-in. Vigreux column gave 485 g. (91%) of tetraethyl hexahydropyromellitate, b.p. 204° (2.5 mm.), $n^{25}\text{D}$ 1.4633.

Anal. Calcd. for $C_{18}H_{28}O_8$: C, 58.04; H, 7.57. Found: C, 58.01; H, 7.39.

1,2,4,5-Tetra(acetoxymethyl)cyclohexane.—To a 12-l., three-necked flask, equipped with a mechanical stirrer, a reflux condenser and a dropping funnel, and containing 205 g. (5.4 moles) of lithium aluminum hydride in 5 l. of dry ether, was added dropwise 501 g. (1.23 moles) of tetraethyl hexahydropyromellitate dissolved in 1.5 l. of dry ether. After the reaction mixture was heated under reflux with stirring for 3 days, the ether solvent was removed through a modified Dean-Stark trap and was intermittently replaced by 4 l. of distilled and dried *n*-butyl ether over a 12-hr. period. After 675 ml. of glacial acetic acid was added dropwise at a rate sufficient to maintain gentle reflux, 5 l. of acetic anhydride was added to the mixture which was heated under reflux. The mixture became so thick that stirring had to be discontinued, but after the mixture was refluxed gently for 30 hr., the slurry became thin enough so that stirring could be resumed. The acetylation was then continued for 30 days by heating under reflux with stirring. At the end of this period, the salts were removed by filtration and the filtrate was concentrated by removal of the butyl ether, acetic acid, and acetic anhydride by distillation under reduced pressure. The dark residue was diluted with chloroform and the resulting solution was washed consecutively with water, a saturated sodium bicarbonate solution, and a saturated sodium chloride solution. After the chloroform solution was dried over magnesium sulfate, the chloroform was removed by evaporation under partial vacuum. The residue was distilled through a 10-inch Vigreux column to yield 406 g. (89%) of 1,2,4,5-tetra(acetoxymethyl)cyclohexane, b.p. 198° (0.9 mm.), $n^{25}\text{D}$ 1.4737.

Anal. Calcd. for $C_{18}H_{28}O_8$: C, 58.04; H, 7.57. Found: C, 57.94; H, 7.44.

The distilled tetraacetate crystallized to an oily solid on standing. Extraction with petroleum ether (b.p. 60–90°)

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(12) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941).

(13) W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

(14) The authors are grateful to Dr. Franz Kasler, Mrs. Kathryn Baylouny, and Mrs. Christine Nielsen for the microanalyses and to Dr. E. Becker of the National Institutes of Health for the n.m.r. spectrum.

(15) J. V. Braun and J. Welles, *Ber.*, **67B**, 1094 (1934).

at room temperature gave a white solid, while a viscous oil was obtained by evaporation of the solvent washes. The oily material represented approximately 15 to 20% of the distilled tetraacetate. Recrystallization of the solid tetraacetate from petroleum ether (b.p. 30–60°) gave an analytically pure sample, m.p. 79.5–80.5°.

Anal. Calcd. for $C_{18}H_{28}O_8$: C, 58.04; H, 7.57. Found: C, 58.15; H, 7.51.

Careful distillation and fractionation of the residual oil through a 21-inch Podbielniak column gave a sample of the liquid isomer (or isomers) of 1,2,4,5-tetra(acetoxymethyl) cyclohexane in the form of a yellow, viscous oil, b.p. 180° (0.15 mm.), n^{24}D 1.4730.

Anal. Calcd. for $C_{18}H_{28}O_8$: C, 58.04; H, 7.57. Found: C, 58.30; H, 7.77.

The infrared spectra of the solid and liquid isomer mixtures reported above are virtually identical.

A successful reduction also was accomplished by the addition of 1002 g. (2.45 moles) of tetraethyl hexahydropyromellitate dissolved in 1.5 l. of dry ether to 409 g. (10.8 moles) of lithium aluminum hydride in 5 l. of dry ether over a 12-hr. period. After the resulting mixture was heated under reflux for 16 days, the ether solvent was replaced by 4 l. of *n*-butyl ether, as described previously, and the excess lithium aluminum hydride was decomposed by the addition of 1350 ml. of glacial acetic acid. The mixture containing the reduced product was divided approximately equally between two 12-l. flasks and each portion was subsequently acetylated according to the procedure given previously. Redistillation of the forerun obtained from this combined acetylated product gave 99.2 g. of what is assumed to be crude decahydrobenzo[1,2-*c*:4,5-*c*′]difuran, b.p. 45–49° (0.07 mm.), n^{25}D 1.4940, and 28.1 g. of what is assumed to be crude 5,6-bis(acetoxymethyl)octahydrobenzo[*c*]furan, b.p. 118–128° (0.15 mm.), n^{25}D 1.4838.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.38; H, 9.58. Found: C, 71.10; H, 9.65. Calcd. for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.61; H, 8.27.

1,2,4,5-Tetra(hydroxymethyl)cyclohexane tetrakis(methyl carbonate).—After a solution of 0.50 g. of sodium in 200 ml. of methanol plus 140 g. (0.377 mole) of 1,2,4,5-tetra(acetoxymethyl)cyclohexane was heated under reflux for 12 hr., 139.5 g. (100%) of a methanol–methyl acetate azeotrope was removed by slow distillation through a 12-in., helix-packed column over a 36-hr. period. The excess methanol was removed by distillation under reduced pressure to yield the crude 1,2,4,5-tetra(hydroxymethyl)cyclohexane, which was not purified.

To 66.2 g. (0.335 mole) of the crude 1,2,4,5-tetra(hydroxymethyl)cyclohexane in 350 ml. of dry chloroform and 220 g. of dry pyridine at 0° was added 187.2 g. (2.04 moles) of methyl chloroformate, dropwise over a period of 12 hr. After the reaction had been stirred for an additional 12 hr. at 0°, the solution was extracted consecutively with water, dilute hydrochloric acid, a saturated sodium bicarbonate solution, and a saturated sodium chloride solution. After the solution had been dried over a mixture of anhydrous potassium carbonate and Drierite, the chloroform was removed by distillation under reduced pressure. The residue was recrystallized from a mixture of chloroform and cyclohexane to yield 88 g. (62%) of 1,2,4,5-tetrahydroxymethylcyclohexane tetrakis(methyl carbonate), m.p. 109–112°.

Anal. Calcd. for $C_{18}H_{28}O_{12}$: C, 49.54; H, 6.43. Found: C, 49.57; H, 6.32.

1,3,4,5,7,8-Decahydrobenzo[1,2-*c*:4,5-*c*′]difuran.—At the rate of 0.67 g. per minute, 30 g. (0.0688 mole) of molten 1,2,4,5-tetra(hydroxymethyl)cyclohexane tetrakis(methyl carbonate) was added dropwise to the Vycor pyrolysis tube packed with helices and heated at 535°. While oxygen-free nitrogen was passed through the system, the liquid pyrolysate was collected in a flask cooled in Dry Ice while 5.0 g. (85%) of carbon dioxide was absorbed in a weighed Ascarite tube. Distillation of the pyrolysate through a 12-inch, helix-packed column gave 8.0 g. (69%) of 1,3,4,5,7,8-decahydrobenzo[1,2-*c*:4,5-*c*′]difuran, b.p. 87–89° (2 mm.), n^{25}D 1.4928, and 10 g. (80%) of dimethyl carbonate, b.p. 89–91°, n^{25}D 1.3711 (reported[16] b.p. 90–91°, n^{20}D 1.3687.)

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.38; H, 9.58. Found: C, 71.16; H, 9.25.

Vacuum Pyrolysis of 1,2,4,5-Tetra(acetoxymethyl)cyclohexane.—The apparatus previously described[7] was flushed with a steady stream of oxygen-free nitrogen as the furnace temperature was slowly raised to 575°. After the flow of oxygen-free nitrogen was discontinued prior to the partial evacuation of the system by means of a vacuum pump to maintain a pressure of 58 to 63 mm., 15 g. (0.0403 mole) of 1,2,4,5-tetra(acetoxymethyl)cyclohexane was pyrolyzed dropwise over a 17-min. period at 575° under conditions that produced very light charring. The 14.4 g. of yellow pyrolysate, collected in a flask cooled in a Dry Ice bath, was flash-distilled at room temperature over a 35-min. period under a pressure of 0.25 mm. and then finally at 55° (hot water bath) over a 3-min. period under the same pressure.

The 6.9 g. (or 6.8 ml.) of yellow flash distillate thus obtained was extracted successively with an aqueous sodium chloride solution and a saturated sodium bicarbonate solution to leave an organic residue of 0.9 ml. which was dried over anhydrous potassium carbonate and stored in Dry Ice. (The 5.9 ml. of acetic acid removed in this manner represents approximately 64% of four molar equivalents of acetic acid.) Preliminary analyses of this fraction on an 84 × 5/16-inch chromatographic column packed with 20% by weight of Apiezon N stopcock grease on 30–60 mesh Chromosorb at a temperature of 160° under a helium flow of 1.1 ml. per second indicated the complexity of the pyrolysate mixture. Comparison of the retention times of several of the approximately 15 to 20 compounds present with those of known hydrocarbons injected into the same column under the same conditions indicated that benzene, toluene, and the isomeric xylenes were present in the mixture. Collection of the peaks which were believed to be benzene, toluene, *m*- and *p*-xylene (unresolved mixture), and *o*-xylene was made later from a Carbowax column and the ultraviolet absorption spectra of the experimental materials agreed with those determined for the authentic compounds. When authentic mesitylene, which did not appear to be present in the pyrolysate itself, was injected as a representative of a liquid hydrocarbon close to tetramethylenecyclohexane in molecular weight, it was found that the most prominent peak had a retention time just 1.8 min. greater than the authentic mesitylene. The material that represented this peak was collected from the chromatographic column by means of a semimicro collector. The pale yellow liquid obtained in this manner was dissolved in a small quantity of peroxide-free ether, reinjected, and recollected as a single peak. The recollected material gave precipitates with ethereal solutions of maleic anhydride, benzoquinone, and tetracyanoethylene and also gave a chemical analysis corresponding to a $C_{10}H_{12}$ hydrocarbon. However, when this liquid, which represented a single peak on the Apiezon N column, was reinjected into either Carbowax 1500 or Carbowax 20-M columns (both 20% by weight on 30–60 mesh Chromosorb) at 155°, three peaks were obtained. The first of these peaks had a retention time slightly greater than that of authentic mesitylene injected into either column, and the collected material gave a chemical analysis corresponding to a C_9H_{12} hydrocarbon which was identified as pseudocumene by comparison of the ultraviolet and infrared absorption spectra of the collected material with those spectra[17] reported for authentic pseudocumene. The material that represented the third peak gave an analysis corresponding to a C_9H_{10} hydrocarbon,

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[16] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, 1953, p. 289.

[17] "Catalog of Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D. C., spectra No. 127, 141, and 163; and "Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., spectrum No. 1038.

of which the infrared absorption spectrum indicated the presence of a vinyl group and the ultraviolet absorption spectrum was of the styrene absorption type. The ultraviolet absorption spectra reported[18,19] for the ring monomethylated styrenes (C_9H_{10}) are similar, if not identical, to each other and agree well with the experimentally determined spectrum of the C_9H_{10} component which exhibited a principal absorption maximum at 251 mμ and three weaker maxima at 275, 285, and 295 mμ, respectively. The spectral data suggest that this material may be a mixture of all three possible isomers. Of the three major peaks obtained on the Carbowax columns, the second (middle) was quite small in comparison to the other two when pyrolysis was accompanied by heaving charring. This material was collected in a later experiment from a Carbowax 20-M column, and reinjection of a peroxide-free ether solution of the collected material gave a single peak corresponding to 1,2,4,5-tetramethylenecyclohexane.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.05; H, 9.16.

When the extracted flash distillate obtained from the vacuum pyrolysis was examined on a 23-ft. coil column packed with 20% by weight of Carbowax 20-M on 30–60 mesh Chromosorb, it was found that the desired tetraene represented approximately 52% of the injected mixture or a yield on pyrolysis of approximately 8%.

An infrared absorption spectrum of 1,2,4,5-tetramethylenecyclohexane was obtained by use of a Beckman IR-5 infrared spectrophotometer. Prominent bands were located at 3085, 2950, 2855, 1648, 1610, 1422, 1282, 890, and 750 $cm.^{-1}$ respectively.

When the ultraviolet absorption spectrum of 1,2,4,5-tetramethylenecyclohexane was determined with a Beckman Model DK-1 spectrophotometer, a sample of 3.33×10^{-5} *M* concentration in isoöctane exhibited a broad absorption maximum (3-min. scanning time) which had an absorbance of 0.35 at 224 mμ corresponding to a molar extinction coefficient of 10,500.

A n.m.r. spectrum was determined by use of a Varian HR60 n.m.r. spectrometer for a sample of 1,2,4,5-tetramethylenecyclohexane which had been recollected twice from a Carbowax 20-M column. Approximately 5 to 10 mg. of the pure tetraene was dissolved in *ca.* 0.4 ml. of carbon tetrachloride that contained a small quantity of tetramethylsilane to serve as an internal standard. The spectrum of the very dilute solution possessed a low signal-to-noise ratio but nevertheless exhibited four distinct peaks (the 4th being somewhat smaller than the first three) at 4.91, 5.30, 6.96, and 7.77 p.p.m. deviation from the tetramethylsilane peak taken as 10. The peaks at 4.91 and 5.30 are in the region for hydrogens on a terminal methylene grouping, while the peaks at 6.96 and 7.77 correspond to the region of ring methylene response. Although the determination of the ratio of the areas under the peaks was difficult, this ratio was approximated to be 1.6 to 1, where reference is made to the ratio of the peaks representing the exomethylenic hydrogen atoms to those representing the ring-methylenic hydrogen atoms. If the last peak, which was considerably smaller than the first three, is not considered, the ratio of the two remaining peaks in the exomethylenic hydrogen area to the one peak in the ring-methylenic hydrogen area becomes very nearly 2 to 1. It is significant that no peaks were found in the regions which are attributed to aromatic-type protons and methyl-type protons, respectively. A portion of the carbon tetrachloride solution on which the spectrum was determined was injected into a Carbowax 20-M column and the resulting chromatograph exhibited three peaks corresponding to the tetraene, carbon tetrachloride, and tetramethylsilane.

$\Delta^{4a(9a),10a(8a)}$-Decahydroanthracene-2,3,6,7-tetracarboxylic Dianhydride.—Approximately 21 mg. of crude 1,2,4,5-tetramethylenecyclohexane, re-collected from the Apiezon N column, was added to *ca.* 2 ml. of dry, distilled ether in which there was dissolved a fourfold molar excess of freshly sublimed maleic anhydride. The white diadduct began to precipitate after several minutes. After the reaction mixture was allowed to stand at room temperature for 2 days, the precipitated diadduct was washed and centrifuged with dry, distilled ether until no more maleic anhydride was present in the decanted washes. The dried diadduct (14 mg.) was recrystallized from freshly distilled and dried 2-butanone to give a white solid, m.p. 389–391° (dec.) (determined in a sealed capillary on a high temperature block.)

Anal. Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.80; H, 5.21.

Simultaneous dehydrogenation and decarboxylation of 50 mg. (0.00015 mole) of the $\Delta^{4a(9a),10a(8a)}$-decahydroanthracene-2,3,6,7-tetracarboxylic dianhydride was carried out in the presence of 0.1 g. of 5% palladium-on-carbon and 0.1 g. of copper–chromite catalyst. When the mixture was heated at 270° for 3 hr., 5 mg. (19%) of crude anthracene, m.p. 201–206° (reported[20] m.p. 216°), had sublimed to the cold finger. A mixed melting point determination with an authentic sample of anthracene, m.p. 213–215°, showed a melting point of 209–212°.

$\Delta^{2,3;5a(13a);6a(12a);9,10}$-Tetradecahydropentacene-1,4,8,11-tetraone.—A 20-mg. sample of crude 1,2,4,5-tetramethylenecyclohexane, which was re-collected from an Apiezon N column, was dissolved in a small portion of dry, freshly distilled ether and the resulting solution was added slowly to a saturated solution of sublimed benzoquinone in *ca.* 2 ml. of dry, distilled ether. A fine precipitate of the diadduct began to form after 5 min. After the reaction mixture was allowed to stand at room temperature for 1 day, the precipitated diadduct was washed with fresh portions of dry, distilled ether until no more benzoquinone was present in the decanted ether extracts.

The pale yellow diadduct, which was insoluble in the cold, common organic solvents, was dried under vacuum in an Abderhalden drying pistol with refluxing acetone in the outer chamber to obtain 15 mg. of $\Delta^{2,3,5a(13a);6a(12a);9,10}$-tetradecahydropentacene-1,4,8,11-tetraone, m.p. 333–338° (dec.) (sealed capillary).

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.83; H, 5.78. Found: C, 75.53; H, 5.50.

2,2,3,3,6,6,7,7-Octacyano-$\Delta^{4a(9a),8a(10a)}$-decahydroanthracene.—A 20-mg. sample of crude 1,2,4,5-tetramethylenecyclohexane, which was re-collected from an Apiezon N column, was dissolved in a small portion of dry, distilled ether. When the resulting ethereal solution was added slowly to *ca.* 2 ml. of a saturated solution of sublimed tetracyanoethylene in dry, distilled ether, a red color developed and the diadduct precipitated immediately. After the reaction mixture was allowed to stand at room temperature for 1 or 2 days, the precipitate was washed with fresh portions of dry, distilled ether until no more tetracyanoethylene was present in the decanted ether extracts. The pale yellow diadduct was dried under vacuum in an Abderhalden drying pistol with refluxing acetone in the outer chamber to give 18 mg. of the octacyano compound which did not exhibit sharp melting but decomposed at 330–340° (sealed capillary).

Anal. Calcd. for $C_{22}H_{12}N_8$: C, 68.03; H, 3.12; N, 28.85. Found: C, 68.17; H, 3.38; N, 28.92.

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(18) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum No. 26.

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(20) A. Reissert, *Ber.*, **23**, 2245 (1890).