Ketodinitrile 11 in Form 11b.—Corey and Sneen[11] do not furnish the cartesian coordinates of the atoms in a boat conformation of the cyclohexylidene ring, therefore the directional moments k_ix_i, k_iy_i and k_iz_i of the C-7 nitrile group for this form were determined from measurements on a Dreiding model. An orthogonal coordinate system was constructed with string and the C-7 carbon atom of the model for form **11b** was inserted at the origin such that the coordinate system with respect to the remaining atoms was identical with that employed by Corey and Sneen.[11] The angles the C-7 nitrile group made with the x, y and z axes were carefully measured to be 83, 40 and 52°, respectively. The product of the cosine of the angle times the nitrile group moment gave a new set of directional moments for the C-7 nitrile group in this conformation: 0.46, −2.89 and 2.32 D for the x, y and z coordinates, respectively. These data along with the directional moments of the carbonyl group and the axial nitrile group on carbon c allowed a calculation of 8.1 D for the dipole moment of **11b**.

C. **Experimental Dipole Moment Values.**—The DM01 dipolemeter manufactured by Wissenshaftlich-Technische Werkstatten was used for the dielectric constant measurements (ϵ_{12}) at various weight fraction (weight of sample/weight of solution) concentrations (ω_{12}). This apparatus was thermostated to 25 ± 0.01° and has been described elsewhere.[34] Measurements were made in benzene, n_{5460}^{25} 1.49790, d^{25} 0.87368, ϵ_1^{25} 2.2725. Refractive indices (ΔN_{12}) were measured at the same concentrations (ω_{12}) in a 2.5-cm cell on a Rayleigh interferometer operating at 25° on a wavelength of 0.546×10^{-4} cm. This instrument is described elsewhere.[35] The ϵ_{12}, ΔN_{12} and ω_{12} values are presented in Table III.

The calculations were made essentially by the method of Halverstadt and Kumler[36] as modified by Guggenheim,[37] and are fully described by Smith.[38] Details for the calculation of ν are given by Bauer, Kajans and Lewin.[35] The values for α, ν, M_2, μP_2 and μ_2 are listed in Table IV.

Registry No.—Cyanide ion, 57-12-5; **2**, 19291-93-1; **4**, 19291-94-2; **5**, 19291-95-3; **6**, 19291-96-4; **7**, 19291-97-5; **8**, 19291-98-6; **9**, 19291-99-7; **10**, 19292-00-3; **11**, 19292-01-4; **12**, 19292-02-5; **13**, 19292-03-6; **14**, 19292-04-7; **15**, 19292-17-2; **16**, 19292-05-8; **17**, 19292-06-9.

Acknowledgment.—The authors are most grateful to Jean-Marie Lehn, Institut de Chimie, Universite de Strasbourg, France, for supplying the experimental dipole moment data.

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[34] N. L. Allinger, H. M. Blatter, M. A. DaRooge, and L. A. Freiberg, *J. Org. Chem.*, **26**, 2550 (1961).

[35] N. Bauer, K. Kajans, and S. Z. Lewin, "Physical Methods of Organic Chemistry," Vol. I, Part 2, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1960, pp 1254–1270.

[36] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

[37] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[38] J. W. Smith, "Electric Dipole Moments," Butterworth and Co., Ltd., London, 1955.

Dienones Derived from 5-Methoxy[2.2]metacyclophanes[1]

V. BOEKELHEIDE, C. RAMEY, E. STURM, T. MIYASAKA, AND B. A. HESS, JR.

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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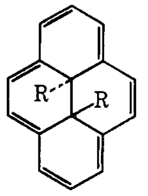
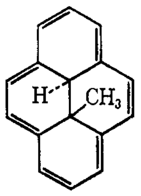
Treatment of 5,13-dimethoxy[2.2]metacyclophane (**4**) under the conditions of the Rieche reaction gives predominantly the corresponding 8-formyl derivative (**5**). Attempts to convert **5** into a methylene-bridged *cis*-[2.2]metacyclophane were unsuccessful. However, **5** could be converted into the corresponding 8-methyl derivative (**7**) and this in turn was oxidized to the corresponding dienone (**8**). Also, it has been shown through the preparation of 5-methoxy-8-methyl[2.2]metacyclophane (**11**) that the Wurtz reaction can be used effectively to prepare "mixed dimeric" products. Oxidation of **11** gave the corresponding dienone **12** and treatment of **12** with acetic anhydride and perchloric acid readily effected a dienone–phenol type of rearrangement to give 2-acetoxy-3-methyl-4,5,9,10-tetrahydropyrene (**13**).

The synthesis of *trans*-15,16-dimethyldihydropyrene[2,3] (**1**) and *trans*-15,16-diethyldihydropyrene[4] (**2**) have demonstrated the possibility of preparing aromatic molecules having substituents within the cavity of the aromatic π cloud of electrons. In a continuation of this study one of the molecules of high interest would be the corresponding *trans*-15-methyldihydropyrene (**3**). Having hydrogen as one of the substituents in the cavity of the π cloud would open the possibility of removal of the "internal" hydrogen to form the corresponding anion, cation, or radical. Such species would not only be inherently interesting but might allow the direct introduction of various other substituents. Also, if the internally substituted hydrogen were labile, it might allow its equilibration to the still unknown *cis*-15,16-dihydropyrene system. For these reasons we undertook a study of the synthesis of *trans*-15-methyldihydropyrene (**3**).



1, R = CH_3
2, R = C_2H_5



3

The synthetic approach envisioned was modeled closely to the route proven successful for **1** and **2**. This required in the first instance the synthesis of 5,13-dimethoxy-8-methyl[2.2]metacyclophane (**7**). Since the Wurtz reaction, which is the standard procedure for preparing [2.2]metacyclophanes, is normally utilized only for the synthesis of symmetrical molecules, a modification of this approach was necessary. One possibility was to subject the readily available 5,13-dimethoxy[2.2]metacyclophane[5] (**4**) to electrophilic substitution in the hope that substitution would occur at the 8 position in reasonable yield. Actually, examination of models or a projection drawing such as

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[1] This work was supported in part by the Office of Naval Research and in part by the National Science Foundation.

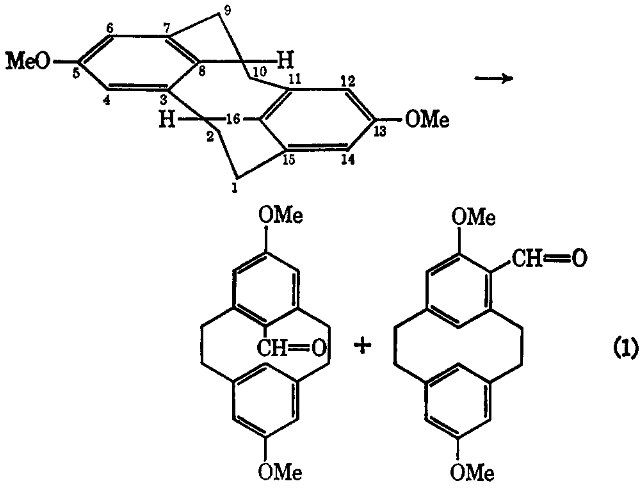
[2] V. Boekelheide and J. B. Phillips, *Proc. Natl. Acad. Sci. U. S.*, **51**, 550 (1964).

[3] V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.*, **89**, 1695 (1967).

[4] V. Boekelheide and T. Miyasaka, *ibid.*, **89**, 1709 (1967).

[5] V. Boekelheide and R. W. Griffin, Jr., *J. Org. Chem.*, **34**, 1960 (1969).

4 clearly suggests that the 8 position is less sterically hindered than the other positions available for reaction. In fact, when **4** was subjected to the conditions of the Rieche procedure[6] there was formed in high yield a mixture of the two aldehydes, **5** and **6** (eq 1), in a ratio of 3:1, as estimated from the nmr spectrum of the mixture. Thus, as predicted, the "internal" 8 position undergoes substitution more readily than the "external" positions even though the external positions are twice as abundant.

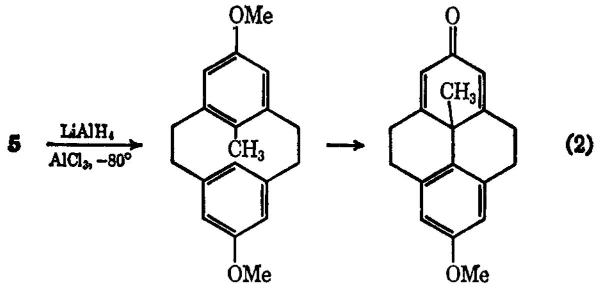


5 **6**

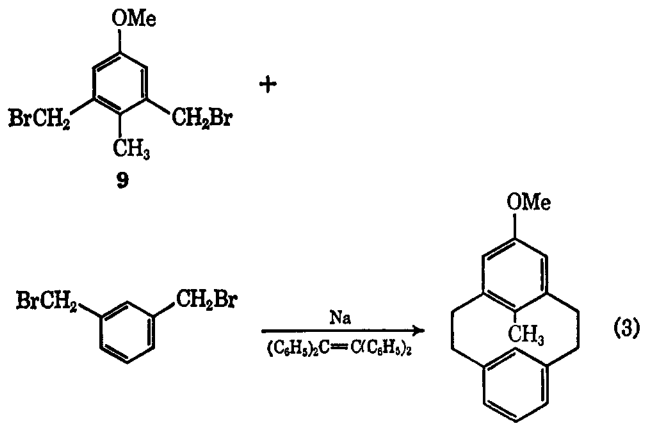
The separation and purification of the two aldehydes **5** and **6** was readily accomplished by chromatography over alumina. Their identification was apparent from examination of their nmr spectra. Substituents at the 8 and 16 positions of [2.2]metacyclophanes are directly over the face of the opposite aromatic ring and show unusual chemical shifts because of the ring current in the opposite aromatic ring. Thus, the signal for the 8 and 16 protons of **4** occurs at τ 5.99, a shift of almost 3 ppm to higher field than the normal region for a benzenoid proton.[5] Similarly, a comparison of **5** and **6** shows that, whereas the signal for the aldehyde proton of **6** is normal, occurring at τ −0.60, the signal for the aldehyde proton of **5** occurs at 1.22, exhibiting the strong shift to higher field to be expected for a proton exposed to the ring current of the opposite aromatic ring.

Reduction of **5** by means of a lithium aluminum hydride–aluminum chloride mixture at −80° proceeded smoothly in good yield to give the desired 5,13-dimethoxy-8-methyl[2.2]metacyclophane (**7**). In previous studies,[2–4] oxidation of various substituted 5,13-dimethoxy[2.2]metacyclophanes occurred readily in good yield to give the corresponding bisdienones. However, when **7** was subjected to the usual chromic acid oxidation procedure, an unstable product was isolated whose nmr spectrum was in accord with structure **8** (eq 2). Attempts to convert **8** into a stable derivative or to utilize it in subsequent steps of the reaction scheme were not fruitful.

In view of the fact that oxidation of **7** gave a monodienone with retention of the other aromatic ring, our attention turned to possible modifications of our approach that would allow us to take advantage of this mode of oxidation. A likely molecule for this purpose was the analogous 5-methoxy-8-methyl[2.2]metacyclophane (**11**). However, to employ the Wurtz reaction in a synthesis of **11** seemed feasible only if the Wurtz reaction could be modified to be effective for preparing "mixed dimeric" products. Fortunately, the two partners, **9** and **10**, needed for studying such a mixed dimerization were at hand.[3] Obviously, the formation of symmetrical dimers could not be avoided completely. However, since *m*-xylyl dibromide is commercially available, it was used in twofold excess to allow more efficient use of the more costly 3,5-bis(bromomethyl)-4-methylanisole (**9**).[3] As expected, the Wurtz reaction under these conditions gave all three possible dimers but these could readily be separated by column chromatography over alumina. The desired "mixed dimer" (**11**) was isolated in 19% yield (eq 3), based on the amount of **9** employed. This is quite favorable when compared with the usual yields of symmetrical [2.2]metacyclophanes obtained by the Wurtz reaction and establishes the merit of such mixed dimerization experiments.



7 **8**



9 **10** **11**

Chromic acid oxidation of **11** proceeded readily to give the corresponding dienone **12** (eq 4) as stable white needles in 50% yield. However, attempts to introduce further unsaturation either by reaction with N-bromosuccinimide or with 2,3-dichloro-5,6-dicyanoquinone were unsuccessful, resulting in mixtures of unstable products in poor yield.

The dienone **12** is somewhat unusual in that for it to undergo a dienone–phenol rearrangement double migration of the methyl group is required. It might be expected, therefore, that the dienone–phenol rearrangement would not occur so readily in this case. In fact, when **12** was treated with a solution of perchloric acid in acetic acid at 0°, rearrangement to **13** was complete in a few minutes.

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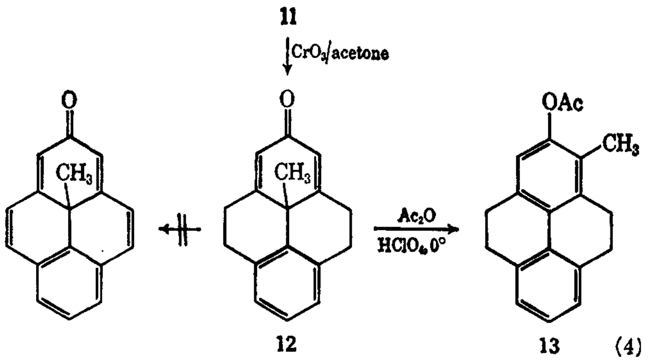
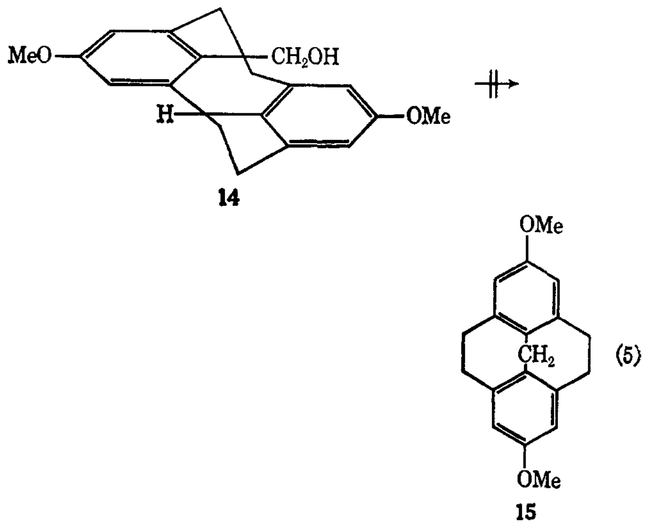
(6) A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).



(4)

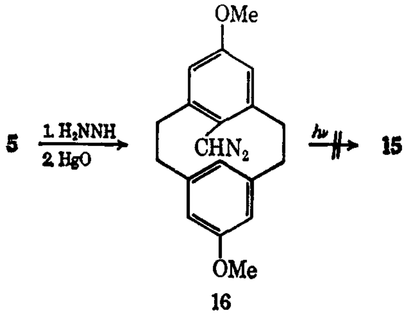
As shown by formula **4** the [2.2]metacyclophanes have a stepwise geometry and X-ray crystallographic analysis of both [2.2]metacyclophane[7] and 8,16-dimethyl[2.2]metacyclophane[8] show the internal carbon atoms at the 8 and 16 positions to be only about 2.8 Å apart. The fact that oxidation[3-5] and electrophilic substitution[9] of these molecules occur with bond formation between the 8 and 16 positions demonstrates that the chemical properties of the [2.2]metacyclophanes are strongly dependent on their special geometry. In view of this it was of interest to explore the question of whether ready interaction might also occur between the aromatic 16 position and a suitably substituted benzylic carbon at C-8. Such a hypothetical reaction is illustrated by the conversion of **14** into **15** (eq 5) and, if successful, would provide an easy route from *trans*-[2.2]metacyclophanes to methylene-bridged *cis*-[2.2]-metacyclophanes. Examination of models suggests that **14** can meet the spatial requirements necessary for either SN1 or SN2 displacement reactions which would give rise to **15**.



(5)

Reduction of the aldehyde mixture (**5** and **6**) from the Rieche reaction with sodium borohydride led to a mixture of the corresponding alcohols which, after chromatography over silica gel, gave the desired alcohol **14** in good yield. Several attempts were made to bring about the conversion of **14** into **15** using such conditions as boron trifluoride in ether or toluenesulfonic acid in formic acid, but nothing useful could be isolated that had physical properties corresponding to those to be expected for a methylene-bridged *cis*-[2.2]metacyclophane.[10]

Alternatively, the possibility of effecting the desired transannular ring closure by a carbene insertion reaction was explored. Conversion of **5** into its hydrazone followed by oxidation with mercuric oxide gave the corresponding diazo derivative **16** (eq 6). Irradiation of an ether solution of **16**, as the crude product, caused loss of the diazo absorption band at 2060 cm^{-1}, but nothing recognizable could be isolated from the reaction mixture.



(6)

Experimental Section[11]

5,13-Dimethoxy-8-formyl[2.2]metacyclophane (5).—To a solution of 500 mg of 5,13-dimethoxy[2.2]metacyclophane[5] (**4**) in 10 ml of methylene chloride held at 0° under a nitrogen atmosphere there was added dropwise with stirring 294 mg of dichloromethyl *n*-butyl ether.[6] The solution was then allowed to warm to room temperature and stand with continued stirring for 5 hr. It was poured into ice water and the aqueous solution was extracted with ether. After the ether extract had been dried, it was concentrated to give a solid residue. Analysis of the nmr spectrum of this solid residue indicated it to be a 3:1 mixture of **5** and **6**. To separate the two aldehydes the mixture was taken up in benzene and chromatographed over neutral alumina (Woelm, activity II). The first fractions of eluate gave 110 mg of white crystals, mp 214–216°, whose nmr spectrum [singlet at τ −0.60 (1 H), multiplet at 3.5 (3 H), broadened singlet at 5.93 (2 H), and singlets at 6.1 and 6.2 (3 H each), and doublets at 7.0 and 7.9 (8 H)] is in accord with **6**. From the eluate directly following there was isolated 321 mg (58%) of crystals corresponding to **5**. After recrystallization from a benzene–chloroform mixture, **5** was obtained as white crystals: mp 157–159°; nmr (CDCl$_3$) singlet at τ 1.22 (1 H), multiplet at 3.37 (4 H), singlet at 6.01 (1 H), singlets at 6.16 and 6.24 (3 H each), and multiplet at 6.4–8.2 (8 H).

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.94; H, 6.75.

5,13-Dimethoxy-8-methyl[2.2]metacyclophane (7).—To 30 ml of a solution of lithium aluminum hydride–aluminum chloride reagent (prepared by boiling a solution of 6 g of aluminum chloride and 2 g of lithium aluminum hydride in 200 ml of ether for 2 hr and then decanting the solution from the residue) held at −80° a solution of 159 mg of 5,13-dimethoxy-8-formyl-[2.2]metacyclophane (**5**) in 5 ml of ether was added dropwise with stirring. The mixture was then stirred an additional 2 hr at −80° and allowed to warm to room temperature. The excess reducing agent was destroyed by cautious addition of moist ether followed by a saturated aqueous solution of sodium sulfate.

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[7] C. J. Brown, *J. Chem. Soc.*, 3278 (1953).

[8] A. W. Hanson, *Acta Cryst.*, **15**, 956 (1962).

[9] (a) N. L. Allinger, M. A. Da Rooge, and R. B. Hermann, *J. Amer. Chem. Soc.*, **83**, 1974 (1961); (b) N. L. Allinger, B. J. Gordon, S-E Hu, and R. A. Ford, *J. Org. Chem.*, **32**, 2272 (1967).

[10] H. B. Renfroe, J. A. Gurney, and L. A. R. Hall, *J. Amer. Chem. Soc.*, **89**, 5304 (1967).

[11] Analyses were performed by Micro-Tech Laboratories and Pascher and Pascher Laboratories. Spectra were obtained using a Varian A-60 nmr, Cary 15, and Beckman IR-5 spectrometers. We thank the National Science Foundation for providing the funds for the Varian A-60.

After removal of the precipitate by filtration, the filtrate was dried over magnesium sulfate and concentrated. Recrystallization of the resulting solid from methanol gave 90 mg of white cubes: mp 97.5–98.5°; nmr ($CDCl_3$) multiplet at τ 3.32–3.38 (4 H), singlets at 6.19 and 6.25 (3 H each), singlet at 6.41 (1 H), multiplet at 6.9–8.0 (8 H), and singlet at 9.41 (3 H).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 81.11; H, 7.77.

Chromic Acid Oxidation of 7.—To a solution of 50 mg of 5,13-dimethoxy-8-methyl[2.2]metacyclophane (**7**) in 5 ml of acetone held at 0° there was added dropwise with stirring 0.05 ml of a 9 *M* solution of chromium trioxide in concentrated sulfuric acid. The solution was stirred at 0° until precipitation occurred and then, after an additional 5 min, the mixture was poured into 20 ml of ice water. The aqueous suspension was extracted with three 30 ml portions of methylene chloride; the methylene chloride extracts were combined, dried, and concentrated. The red-brown oily residue was taken up in a 1:1 mixture of benzene–methylene chloride and chromatographed over neutral alumina (Woelm, activity II). From the eluate there was isolated a yellow oil: ir $\lambda_{\max}^{CHCl_3}$ 5.95, 6.08, 6.17, 8.63, 9.50, and 10.97 μ; nmr ($CDCl_3$) singlet at τ 3.54 (2 H), singlet at 3.97 (2 H), singlet at 6.26 (3 H), multiplet at 6.75–7.50 (8 H), and singlet at 8.45 (3 H). On standing the oil underwent resinification and it was not possible to prepare a pure sample for analysis.

5-Methoxy-8-methyl[2.2]metacyclophane (**11**).—A solution of 15.4 g of 3,5-bis(bromomethyl)-4-methylanisole[3] (**9**) and 26.4 g of *m*-xylyl dibromide in 1.0 l. of dry tetrahydrofuran was added through a Hershberg dropping funnel over a period of 48 hr to a rapidly stirred suspension of 20.0 g of sodium granules and 2.0 g of tetraphenylethylene in 1.0 l. of tetrahydrofuran at room temperature under a nitrogen atmosphere. At the end of the addition the excess sodium was removed by filtration of the mixture through glass wool. The resulting milky-white suspension was then filtered through Celite and concentrated under reduced pressure. The yellow, sticky residue was taken up in 1:1 mixture of benzene–*n*-pentane and chromatographed over 500 g of neutral alumina (Woelm, activity I). From the first eluate fractions there was isolated a mixture of tetraphenylethane and [2.2]metacyclophane. From the next eluate fraction there was isolated 2.4 g (19%) of white solid having spectral properties in accord with **11**. In the final eluate fraction there was a small quantity of 5,13-dimethoxy-8,16-dimethyl[2.2]metacyclophane.[3] Crystallization of **11** from a benzene–methanol mixture gave white cubes: mp 93–95°; nmr ($CDCl_3$) multiplet at τ 2.80–3.00 (3 H), singlet at 3.33 (2 H), broad singlet at 6.05 (1 H), singlet at 6.19 (3 H), multiplet at 6.8–8.0 (8 H), and singlet at 9.51 (3 H).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.09; H, 8.04.

2-Keto-15-methyl-2,4,5,9,10,15-hexahydropyrene (**12**).—To a stirred solution of 250 mg of 5-methoxy-8-methyl[2.2]metacyclophane (**11**) in 50 ml of acetone held at 0° there was added dropwise 0.7 ml of an 8 *M* solution of chromium trioxide in concentrated sulfuric acid over a period of 1 hr. The mixture was then stirred for an additional hour at 0° before being poured into 50 ml of ice water. The aqueous solution was extracted with three 50-ml portions of methylene chloride, and then the combined methylene chloride extracts were washed successively with water, aqueous sodium bicarbonate, and water. After the methylene chloride extract had been dried, it was concentrated giving a yellow gummy residue. This was taken up in benzene and transferred to a silica gel column. Elution of the column with a 3:1 benzene–chloroform mixture afforded 119 mg of pale yellow crystals, mp 105–106°. Treatment with charcoal followed by recrystallization from hexane gave white needles: mp 106–107°; ir $\lambda_{\max}^{CHCl_3}$ 6.01 and 6.17 μ; nmr ($CDCl_3$) broad singlet at τ 2.98 (3 H), singlet at 3.81 (2 H), multiplet at 6.6–7.6 (8 H), and singlet at 8.51 (3 H).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.53; H, 6.80.

2-Acetoxy-1-methyl-4,5,9,10-tetrahydropyrene (**13**).—To a solution of 50 mg of 2-keto-15-methyl-2,4,5,9,10,15-hexahydropyrene (**12**) in 25 ml of carbon tetrachloride held at 0° there was added dropwise with stirring a solution of 3 drops of 70% perchloric acid in 1.0 ml of acetic anhydride. The reaction mixture rapidly turned yellow-orange and then faded to a light yellow. The solution was stirred at 0° for 10 min and then poured into 50 ml of water. The organic layer was separated and washed successively with water, a 5% aqueous solution of sodium bicarbonate, and water. It was then dried and concentrated to give a white solid. This was sublimed at 120° (0.5 mm), yielding 45 mg of fine white needles: mp 167–168°; ir $\nu_{\max}^{CHCl_3}$ 1740, 1444, 1360, 1200, 1172, and 1068 cm^{-1}; nmr (CDC_3) singlet at τ 2.94 (3 H), singlet at 3.22 (1 H), singlet at 7.17 (8 H), singlet at 7.69 (3 H), and singlet at 7.89 (3 H).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.03; H, 6.76.

5,13-Dimethoxy-8-hydroxymethyl[2.2]metacyclophane (**14**).—To a solution of 380 mg of the aldehyde mixture (**5** and **6**) from the Rieche reaction in 100 ml of methanol there was added dropwise at room temperature a solution of 400 mg of sodium borohydride in 5 ml of methanol. After the mixture had been stirred at room temperature overnight, 10 ml of a 10% aqueous sodium hydroxide solution was added and the mixture was boiled under reflux for 0.5 hr. Concentration of the mixture gave a white solid which was taken up in methylene chloride and chromatographed over neutral alumina (Woelm, activity II). From the first eluate fractions there was isolated 267 mg of white crystals: mp 163–164°; uv $\lambda_{\max}^{EtOH}$ 247 mμ (ϵ 10,200) and 292 (2760); ir $\nu_{\max}^{KBr}$ 3560, 1020, 993, 846, and 717 cm^{-1}; nmr ($CDCl_3$) singlet at τ 3.39 (4 H), singlets at 6.20 and 6.27 (3 H each), singlet at 6.41 (1 H), multiplet at 6.90–7.92 (10 H), and singlet at 9.15 (1 H, broadening on dilution indicating it to be the hydroxyl proton). Reduction of a portion of these crystals at −80° with a lithium aluminum hydride–aluminum chloride mixture proceeded in good yield to give a sample of **7**, identical in all respects with the product of the preparation described earlier. Thus the structure of **14** is established.

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.31; H, 7.58.

In the above experiment after elution of the silica gel column with methylene chloride, further elution with chloroform afforded 90 mg of white crystals, mp 202–204°, whose spectral properties are in accord with those to be expected for 5,13-dimethoxy-4-hydroxymethyl[2.2]metacyclophane.

Conversion of 5 into 16 and the Irradiation of 16.—A solution of 180 mg of 5,13-dimethoxy-8-formyl[2.2]metacyclophane and 120 mg of 100% hydrazine hydrate in 2 ml of absolute ethanol was boiled under reflux for 2 hr. It was then concentrated under reduced pressure leaving a solid residue. This was dissolved in 5 ml of tetrahydrofuran and 600 mg of sodium sulfate and 10 drops of a saturated alcoholic solution of potassium hydroxide were added. After the mixture had been cooled to 0°, 210 mg of yellow mercuric oxide was added. The mixture was then allowed to warm to room temperature and to stand with stirring for 4 hr. The solution was then concentrated, the residue was taken up in ether, and the ether solution was centrifuged. Examination of the clear ether solution in the ir showed the distinctive diazo absorption band at 2060 cm^{-1} and absence of carbonyl absorption. The ether solution was then diluted to a volume of 100 ml and irradiated under a nitrogen atmosphere with a 150-W Hanovia lamp using a Pyrex filter. The color of the solution changed from orange to a light yellow over a period of 3 hr. After concentration, the residue was taken up in chloroform and examination in the ir showed the complete disappearance of absorption at 2060 cm^{-1}. Removal of the chloroform followed by chromatography over neutral alumina (Woelm, activity I) using benzene for elution gave 100 mg of a yellow oil. This oil showed only a single spot on thin layer chromatography over silica gel. However, its nmr spectrum was complex and not at all in accord with that to be expected for a methylene-bridged *cis*-[2.2]metacyclophane.[10]

Registry No.—5, 19289-32-8; **7,** 19289-33-9; **11,** 19289-34-0; **12,** 19289-35-1; **13,** 19289-36-2; **14,** 19289-37-3.