[3.2]Metacyclophanes. Conformational Studies

Rodger W. Griffin Jr.,[1a] and Robert A. Coburn[1b]

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received March 4, 1967*

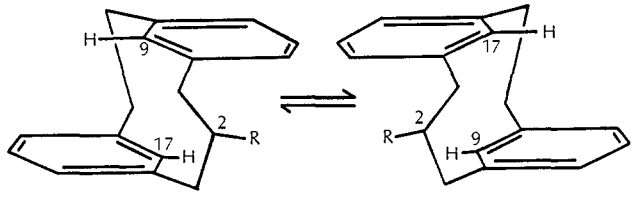
Abstract: The energy barriers to ring inversion of the 11-membered aromatic–aliphatic rings in a number of 2-substituted [3.2]metacyclophanes were determined from the temperature dependence of their proton magnetic resonance spectra. The energy barriers to ring inversion were found to be dependent upon the steric nature of the 2-substituent and lie between 15.8 and 19.1 kcal/mole in the temperature range 60–120°. Bulky 2 substituents were found to produce conformational changes in 2-monosubstituted derivatives with respect to 2,2-symmetrically disubstituted derivatives. A half-life at 0° of 2.4 sec for the stable conformers of [3.2]metacyclophane-2-carboxylic acid is predicted from the activation energy parameters for ring inversion obtained from the nmr data. In comparison, [2.2]metacyclophane is estimated to have a barrier to ring inversion of greater than 26–28 kcal/mole.

The unique geometry of the [2.2]metacyclophane system which results in the crowding of two aromatic rings[2] leads to a number of interesting physical and chemical properties. These include transannular effects and reactions,[2b] unusual aspects in the proton magnetic resonance spectrum,[3] and strain and rigidity in the ten-membered aromatic–aliphatic ring resulting in a very unreactive benzylic position.[4]

These interesting properties have prompted the synthesis of [3.2]metacyclophanes and the study of their physical and chemical properties. We report here the results of conformational studies of a number of 2-substituted [3.2]metacyclophanes.

Method

The compounds examined were obtained from diethyl [3.2]metacyclophane-2,2-dicarboxylate whose synthesis has been reported earlier.[5] The 9,17-proton magnetic resonance frequency in [3.2]metacyclophanes exhibits a diamagnetic shift of *ca.* 2.1 ppm relative to that of the other methine protons. In symmetrically 2,2-disubstituted derivatives this signal appears as a singlet broadened slightly by weak coupling with the *meta* and *para* protons. However, in 2-monosubstituted [3.2]metacyclophanes the 9,17 protons exhibit different chemical shifts. A number of 2-monosubstituted derivatives were synthesized from diethyl [3.2]metacyclophane-2,2-dicarboxylate in order to determine the origin of the chemical shift difference.



Ring inversion in 2-monosubstituted [3.2]metacyclophanes exchanges the 9 and 17 positions with respect to the substituent. The temperature dependence of the line positions of the 9,17-proton magnetic resonance was used to determine ring inversion rates in the range of "intermediate exchange rates."[6,7] The method employed was that of Gutowsky and Holm[8a] in which signals from two noninteracting protons of different chemical shift coalesce to a single line by the exchange of their environments; $k_i = \pi\sqrt{(\nu^2 - \Delta_i^2)/2}$. The rate of exchange at temperature T_i can be estimated from the frequency separation at the temperature (Δ_i) and the frequency separation under conditions of no exchange (ν). The separation frequency under conditions of no appreciable exchange was obtained by progressively lowering the temperature until no further increase in separation frequency was observed. A correction for overlap of components was unnecessary due to the large frequency separations relative to the observed line widths. The estimated systematic error in this method was found to be less than the experimental error for this system.[8b] The weak coupling of the 9,17 protons to the remaining aromatic protons hindered application of the line shape and line broadening techniques to obtain additional kinetic data.

Results

Listed in Table I are the maximum frequency separations of the 9,17-proton magnetic resonance signals of a number of 2-monosubstituted [3.2]metacyclophanes, obtained by progressively lowering the sample temperature. By raising the temperature these frequency separations fell to zero, in all cases, as ring inversion became rapid. Regardless of the exact origin of these chemical shift differences, the separation frequencies provided kinetic data for the ring inversion. Although the broad unresolved bridging methylene protons'

(1) (a) Author to whom inquiries may be addressed: Division of Natural Sciences, New College, Sarasota, Fla. 33578. (b) Taken from the Ph.D. thesis submitted by R. A. Coburn to Harvard University, 1966. Acknowledgment is made to the National Institutes of Health for partial support of this work.

(2) (a) C. J. Brown, *J. Chem. Soc.*, 3278 (1953); (b) N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J. Am. Chem. Soc.*, **83**, 1974 (1961). The authors of these papers explain the distortions reported in this molecule to be due to repulsions between benzenoid rings. However, it seems anomalous that four bond angles should be distorted by 15° while four others also available for the relief of strain suffer no deformation whatever.

(3) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *ibid.*, **82**, 6302 (1960).

(4) R. W. Griffin, Jr., *Chem. Rev.*, **63**, 45 (1963).

(5) R. W. Griffin, Jr., and R. A. Coburn, *Tetrahedron Letters*, 2571 (1964).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., p 218.

(7) A number of examples of the application of this method are available: (a) K. G. Untch and R. J. Kurland, *J. Am. Chem. Soc.*, **85**, 346 (1963); (b) P. Radlick and S. Winstein, *ibid.*, **85**, 344 (1963); (c) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962).

(8) (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

resonance signals became greatly simplified at higher temperature, the poor definition of the spectra at low temperature limited their usefulness in providing kinetic data.

Table I. Frequency Separations between 9- and 17-Proton Magnetic Resonance Signals in Various 2-Monosubstituted [3.2]Metacyclophanes

Compd	2-Substituent	ν, Hz
1	CN	4.5
2	CO_2H	19.8
3	CO_2CH_3	23.0
4	COCl	25
5	$CONH_2$	35
6	$CONEt_2$	35
7	CON-*i*-Pr_2	37
8	$C(CH_3)_2OH$	70
9	$C(Ph)_2OH$	77

Figure 1 represents plots of the kinetic data for methyl [3.2]metacyclophane-2-carboxylate and [3.2]-metacyclophane-2-carboxylic acid. The coalesence temperatures for the ester and acid were 59.3 and 53.9°, respectively. Rates of ring inversion were determined in the temperature range of 40–60°. Table II contains the activation energy parameters for the ring inversion of ester **3** and acid **2**.[9] The energy barriers to ring inversion in alcohols **8** and **9** were determined from the rate of inversion at the temperature which their 9,17-proton signals coalesce using the absolute rate theory.[10,11]

Table II. Energies of Activation for Ring Inversion in a Number of 2-Monosubstituted [3.2]Metacyclophanes

Compd	2-Substituent	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}_{60°}$, kcal/mole
2	CO_2H	15.81 ± 0.2	−2.9	16.8 ± 0.2
3	CO_2CH_3	16.06 ± 0.2	−2.4	16.8 ± 0.2
8	$C(CH_3)_2OH$			16.2 ± 0.3
9	$C(Ph)_2OH$			15.7 ± 0.3

Attempts were made to resolve [3.2]metacyclophane-2-carboxylic acid using various optically active amine bases (brucine, strychnine, cinchonine, and *d*-α-methylbenzylamine) in a number of solvent systems. No evidence of a successful resolution could be obtained. The stable conformers of [3.2]metacyclophane-2-carboxylic acid were predicted to have a mean half-life at 0° of 2.4 sec based upon the activation energy parameters derived from the nmr data.

2-Benzhydrylidene[3.2]metacyclophane was prepared from methyl [3.2]metacyclophane-2-carboxylate and was found to exhibit bridging methylene proton resonance frequencies sufficiently separated to allow observation of the simultaneous collapse of the AB (three-membered bridge) and A_2B_2[12] (two-membered bridge) systems upon heating. Although not strictly an AX system, the AB system (ν = 39 cps, J = 10 cps) provided a good estimate of the rate of ring inversion at its coalescence temperature. This temperature was, within experimental error, the same as the coalescence temperature for the A_2B_2 system. The energy barrier to ring inversion,[11] 17.3 ± 0.3 kcal/mole at 72°, was expected to be less than that for symmetrically 2,2-disubstituted [3.2]-metacyclophanes due to relaxation in strain upon substitution of a trigonally hybridized carbon atom for a tetrahedral ring member.

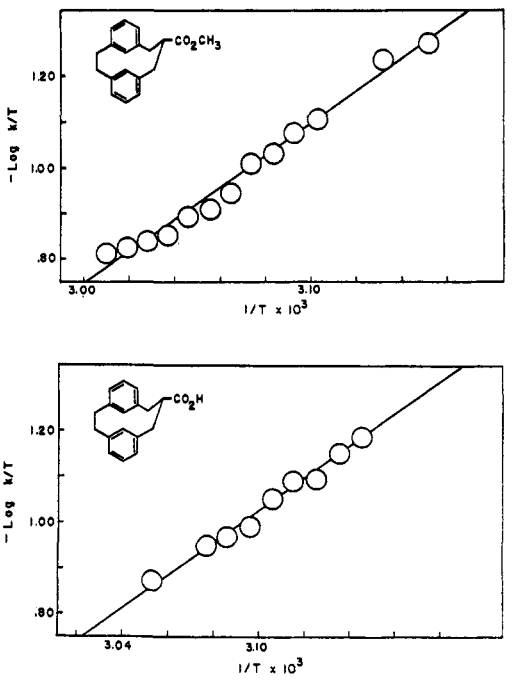


Figure 1. Plots of ring inversion rate data for methyl [3.2]metacyclophane-2-carboxylate and [3.2]metacyclophane-2-carboxylic acid.

The nmr spectrum of [2.2]metacyclophane previously described[2] and studied in detail[13] remains unchanged over the temperature range 20–200°. This allows an estimate of the lower limit of the energy barrier to ring inversion for [2.2]metacyclophane of 26–28 kcal/mole.

Discussion

The magnitude of the chemical shift difference between the 9 and 17 protons and the remote location of the substituents indicate that this difference does not arise from an induced modification in the nature of the carbon–hydrogen bond. This difference most likely arises from a modification of the secondary diamagnetic field experienced by the 9,17 protons which results from the "induced ring current" in the benzenoid rings.[14] This

(9) F. W. Cagle, Jr., and H. Eyring, *J. Am. Chem. Soc.*, 73, 5628 (1951); a least-squares treatment was applied. Sample calculations show that the probable error in $\Delta H^{\ddagger}$ which is introduced by the uncertainty in ν exceeds, by an order of magnitude, that which is introduced by the uncertainty in T (±1°) or Δ (±0.2 Hz).

(10) The values of $\Delta F^{\ddagger}$ for compounds **8** and **9** could not be determined in the same manner as those for compounds **2** and **3**. In one case solubility problems and in the other case uncertainties due to line width precluded a determination of ν with sufficient accuracy to justify application of the former method. Small errors in ν were found to produce gross errors in $\Delta F^{\ddagger}$.

(11) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 195.

(12) Rotation about the C_{10}–C_{11} bond caused by the three-membered bridge may result in this system being more properly labeled as an ABXY system.

(13) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, 37, 120 (1962).

(14) Regardless of the origin of the anisotropic magnetic effects in benzenoid hydrocarbons arising from a ring current (see R. J. Abraham and W. W. Thomas, *J. Chem. Soc.*, 127 (1966)), or arising partially (J. A. Pople, *J. Chem. Phys.*, **41**, 2559 (1964)), or totally (J. I. Musher, *ibid.*, **43**, 4081 (1965)) from localized electrons, the above arguments are valid. The ring current based on calculations of C. E. Johnson and

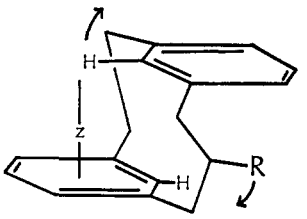


Figure 2. Effect of bulky 2-substituent on the conformation of 2-monosubstituted [3.2]metacyclophane.

diamagnetic field produces a shift of the 9,17-protons' resonance signals by *ca.* 125 Hz to higher field from the normal aromatic proton resonance frequency.

This change in the diamagnetic field effect can be brought about by a change in the 9,17-protons' positions in the induced field or by a modification of the field itself. The former situation would occur with any conformational change which moved the C_9–H and C_{17}–H bond axes out of parallel planes. This would destroy an element of symmetry in the molecule which allows the 9,17 protons in symmetrically 2,2-disubstituted [3.2]metacyclophanes to experience identical electronic environments. The second explanation would require that the substituent modify the induced diamagnetic field of the benzenoid rings by, perhaps, an inductive field perturbation of the aromatic rings or by an anisotropic contribution of its own to the secondary magnetic field experienced by the 9,17 protons.

The results tabulated in Table I suggest that steric effects play a primary role in the origin of the frequency separations between 9,17 proton signals in 2-monosubstituted [3.2]metacyclophanes. The smallest shift difference occurs in nitrile **1** from which one would expect a large anisotropic effect (with the proper orientation). The same is true of diphenyl alcohol **9** which exhibits a frequency separation very similar to that of dimethyl alcohol **8**. These results argue against an anisotropic effect by the substituent while the magnitude of the separations, especially in the case of the alcohols, seems to be much greater than that which would arise by an inductive effect by the substituent on the benzenoid rings.

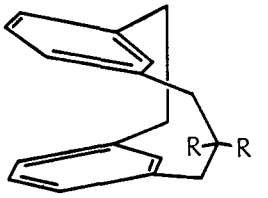
If the derivatives are classified according to the steric nature of their substituent (CX, CX_2, CX_3), the frequency separations between 9- and 17-proton signals of members within each group are similar. Furthermore, the magnitude of the frequency separation correlates with the degree of branching in the α position of the substituent.

A steric interaction between the substituent and the nearest benzenoid ring would be relieved by the substituent assuming a pseudo-equatorial position with respect to the 11-membered aromatic–aliphatic ring. Such a movement produces a change in attitude between the two benzenoid rings when torsional strain is minimized. Thus, the 9,17 protons change their positions relative to the centers of their nonbonded benzenoid rings in a dissymmetric fashion (Figure 2). Due to the large field gradient in the induced secondary diamagnetic field in the region in which the 9,17 protons are found (as evidenced by the magnitude of the observed diamagnetic shift), the conformational change necessary to produce even the largest of the observed frequency separations would not need to be great.[15]

One may expect a lower enthalpy of activation for ring inversion to result from any appreciable destabilization of the ground-state conformer produced by steric interactions as long as these interactions are absent in the transition state. The energy barriers to ring inversion in the two metacyclophanes **8** and **9**, containing the substituents which produce the largest conformational change, show a small (in comparison to the reliability of the data) but significant decrease. Since the enthalpies of activation for these compounds are not known, it can only be hypothesized that these lower energy barriers result from a lower enthalpy of activation caused by the steric interactions of the substituents. But the similarity of the compared systems and the expected reverse effect of any change in entropy of activation make this a reasonable assumption. This suggests that these steric interactions lead to a conformational change, in the 2-monosubstituted [3.2]metacyclophanes, which a symmetrically 2,2-disubstituted [3.2]metacyclophane would have to effect while undergoing a ring inversion. Diethyl [3.2]metacyclophane-2,2-dicarboxylate-d_4 was previously estimated to possess an energy barrier of 19.1 ± 0.5 kcal/mole at 112.4°.[5]

Conclusions

The repulsive strain between aromatic rings in [2.2]paracyclophane has been estimated to be 16 kcal/mole,[16] although this appears to be a conservative estimate in view of the 18-kcal/mole strain energy calculated for [2.2]metacyclophane which has fewer steric interactions.[2b] This type of strain in the *cis* ring conformation **10** would be less due to the greater separation allowed between benzenoid rings. In view of the energy barriers to ring inversion for a number of [3.2]metacyclophanes (16–19 kcal/mole), **10** cannot be excluded as a possible intermediate since its standard free energy level may well be below this energy barrier. The possibility remains, however, that the activation energy necessary to achieve this *cis* conformation is higher than that required to effect the ring inversion. Lack of knowledge concerning the transition-state geometry hinders solution of this question.



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Experimental Section

Melting points were determined with a Fisher-Johns melting point apparatus and are corrected. Petroleum ether refers to Fisher Certified Reagent Grade petroleum ether (bp 40–60°). Ultraviolet spectra were recorded with a Cary spectrophotometer,

F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958), describe qualitatively but not quantitatively the nmr data for a number of [*m.n*]metacyclophanes: R. A. Coburn, Ph.D. Thesis, Harvard University, 1966.

(15) Calculations based on the data of Johnson and Bovey,[14] the observed diamagnetic shift, and a model incorporating some of the strain observed in [2.2]metacyclophane predict that a displacement of H_9 of only 0.2–0.5 A along the *z* axis (Figure 2) would be necessary to produce the observed separation frequencies.

(16) B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, p 359.

Model 11M. Infrared spectra were obtained with a Perkin-Elmer grating spectrophotometer, Model 237. Nmr spectra were recorded in deuteriochloroform, unless otherwise noted, with a Varian A-60 nmr spectrometer equipped with a V-6040 nmr variable-temperature controller. Tetramethylsilane was used as the internal standard (0 ppm). Frequency separations were determined by locating the two signals within 0.04 Hz using the audio-frequency-side-band technique.[17]

[3.2]Metacyclophane-2-carboxylic Acid (2). Diethyl [3.2]metacyclophane-2,2-dicarboxylate[4] (600 mg, 1.64 mmoles) was added to a 50% aqueous potassium hydroxide solution (5 ml), and the mixture was refluxed for 4 hr. The cooled solution was diluted with water to 40 ml and washed with ether (10 ml). The aqueous solution was acidified and extracted with five 10-ml portions of ether. The combined ether extract was washed with distilled water and saturated salt solution and dried over anhydrous magnesium sulfate. Evaporation of the ether left 397 mg of [3.2]metacyclophane-2,2-dicarboxylic acid, mp 163–164° dec. This material was heated in an oil bath at 180° until the evolution of gas ceased. Recrystallization of the residue from ether–petroleum ether afforded 324 mg (74% yield) of **2** as white crystals, mp 163–164.5°, λ_{max}^{EtOH} 208 (log ϵ 4.57) and 269 mμ (log ϵ 2.59). Its infrared spectrum (KBr pellet) showed absorption at 5.93 and 3.4 μ typical of carboxylic acids. The nmr spectrum recorded at −50° showed an unresolved nine-proton multiplet at 2–3.5 ppm (bridging methylene protons), two one-proton singlets at 5.0 and 5.3 ppm (9,17 protons), a six-proton multiplet at 7.4 ppm (remaining aromatic protons), and a one-proton singlet at 11.9 ppm (carboxyl group proton).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.36; H, 6.85.

Attempted Resolution of [3.2]Metacyclophane-2-carboxylic Acid (2). [3.2]Metacyclophane-2-carboxylic acid was treated with 1.2 equiv of optically active amine (brucine, strychnine, or cinchonine) in ether. The resulting solution was cooled for 12 hr in a Dry Ice–acetone bath. An oil slowly formed which could not be induced to crystallize. This procedure was repeated in chloroform, tetrahydrofuran, and 1:1 benzene–ether with the same results. A crystalline salt was obtained when *d*-α-methylbenzylamine[18] was employed in dry acetone. However, no mutarotation or contribution to the optical activity from the cation could be detected in solutions of the recrystallized salt. A sample of **2** recovered from the salt was optically inactive.

Methyl [3.2]Metacyclophane-2-carboxylate (3). A dry, distilled solution of diazomethane in ether was slowly added to a solution of **2** (366 mg, 1.37 mmoles) in tetrahydrofuran until a yellow color persisted. Evaporation of solvent left 384 mg (100% yield) of **3** as a colorless oil which could not be induced to crystallize even after chromatography on silica gel. Its nmr spectrum taken in carbon tetrachloride was similar to that of **2** except for the absence of the one-proton singlet at 11.9 ppm and the addition of a three-proton singlet at 3.7 ppm (OCH_3). Strong carbonyl absorption at 5.78 μ is noted in the infrared.

[3.2]Metacyclophane-2-carbonyl Chloride (4). A mixture of **2** (100 mg, 0.376 mmole), benzene (1 ml), and thionyl chloride (0.25 ml) was refluxed for 1 hr. The solvent was distilled and replaced with 2 ml of dry benzene. The solvent was again distilled, and the residual oil was warmed on a steam bath under reduced pressure for 1 hr. There was obtained 110 mg of **4** as a colorless oil which was used without further purification to prepare the amides. Its nmr spectrum was very similar to that of **2** but lacked the singlet at 11.9 ppm.

[3.2]Metacyclophane-2-carboxamide (5). A solution of **4** (110 mg) in dry acetone (5 ml) was slowly added to concentrated aqueous ammonia (2 ml). After several minutes a white precipitate formed which was collected, washed with water, and recrystallized from methanol. There resulted 50 mg of **5** as white crystals; mp 214.5–215.5°, $\lambda_{max}^{CCl_4}$ 6.15 μ. Its nmr spectrum taken in deuteriochloroform is similar to that of **4** but with a broad two-proton singlet at 5.73 ppm identified as the amide protons' signal by its absence from the spectrum taken in methanol-d_4 (with a trace of sodium methoxide added).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.79; H, 7.33; N, 5.45.

N,N-Diethyl[3.2]metacyclophane-2-carboxamide (6). A procedure identical with that described above employing diethylamine instead of ammonia was used. There resulted 157 mg (81% yield) of **6** as a colorless oil. A sample crystallized from methanol in a Dry Ice–acetone bath, but melted below room temperature; λ_{max}^{neat} 6.10 μ. The nmr spectrum was similar to that of amide **5** but lacked the amide protons' signal. A triplet at 1.15 ppm and a quartet at 3.3 ppm were assigned to the ethyl groups.

Anal. Calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 81.60; H, 8.62; N, 4.25.

N,N-Diisopropyl[3.2]metacyclophane-2-carboxamide (7). A procedure identical with that described above employing diisopropylamine was used. These was obtained 161 mg (76% yield) of **7** as white crystals, mp 82–83.5°.

Anal. Calcd for $C_{24}H_{31}NO$: C, 82.48; H, 8.94; N, 4.01. Found: C, 82.23; H, 8.98; N, 4.13.

2-Cyano[3.2]metacyclophane (1). A mixture of **5** (50 mg, 0.188 mmole), benzene (1 ml), and thionyl chloride (0.5 ml) was refluxed for 3 hr. The solvent was evaporated and carbon tetrachloride (one drop) and petroleum ether (ten drops) were added to the resulting oil. A small amount of amide **5** precipitated and was removed by filtration. The filtrate was cooled giving white crystals which were collected and recrystallized from petroleum ether. There was obtained 28 mg (68% yield) of **1** as white needles, mp 88–89°, $\lambda_{max}^{CCl_4}$ 4.46 μ.

Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.64; H, 6.87; N, 5.68.

Dimethyl-2-[3.2]metacyclophanemethanol (8). Ester **3** (384 mg, 1.37 mmoles) in dry ether (10 ml) was slowly added to 10 ml of 0.42 *N* methyllithium solution maintained at 0° in an ice bath. The mixture was stirred for 1 hr, then refluxed for 30 min. The reaction mixture was cooled and saturated ammonium chloride solution (10 ml) was added. The separated ether layer was washed with distilled water and saturated salt solution, and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 379 mg (98% yield) of **8** as white crystals, mp 138–141°. A sample was recrystallized from methanol for analysis, mp 142–143.5°, $\lambda_{max}^{CCl_4}$ 2.78 μ. The nmr spectrum taken at room temperature in carbon tetrachloride showed signals at 4.62 and 5.65 ppm assigned to the 9,17 protons.

Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.68; H, 8.59.

Diphenyl-2-[3.2]metacyclophanemethanol (9). An analogous procedure to that described above for the preparation of **8** but employing a 3 *N* phenyllithium solution was used. The crude product was chromatographed on 2 g of alumina (Merck). Elution with 5% ether in benzene gave 113 mg (75% yield) of **9** as white needles, mp 146–147.5°, $\lambda_{max}^{CCl_4}$ 2.76 μ. The nmr spectrum taken at room temperature in carbon tetrachloride exhibited signals at 4.5 and 5.6 ppm assigned to the 9,17 protons.

Anal. Calcd for $C_{30}H_{28}O$: C, 89.07; H, 6.98. Found: C, 88.76; H, 6.95.

2-Benzhydrylidene[3.2]metacyclophane. A solution of **9** (117 mg, 0.29 mmole) in glacial acetic acid (2 ml) and acetic anhydride (1 ml) was refluxed for 6 hr. Evaporation of solvent at reduced pressure gave a colorless oil which crystallized on standing. Recrystallization from ether–petroleum ether gave 60 mg (50% yield) of 2-benzhydrylidene[3.2]metacyclophane as white needles, mp 172–173°, $\lambda_{max}^{CCl_4}$ 6.2 μ, λ_{max}^{EtOH} 205 (log ϵ 4.07) and 245 mμ (log ϵ 3.57). The nmr spectrum taken in carbon tetrachloride showed a two-proton singlet at 5.00 ppm assigned to the 9,17 protons.

Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.03; H, 6.73.

(17) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(18) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 506.