Table IX

Expt	Mass film in vacuo, g	ΔR_o, ohm	Δt, °K	q_i, J	q_t, J	q_n, J	E_o, J deg^{-1}	$-\Delta E_{B/m}$,^{a} J g^{-1}
1	0.616070	0.172328	1.703355	3.01	94.52	4.02	3.96	46,310
2	0.527113	0.148468	1.466834	3.31	90.29	3.97	3.43	46,660
3	0.557100	0.156014	1.542409	3.56	96.61	5.15	3.59	46,350
								Av 46,440 ± 110

The several values were averaged and the standard deviation was calculated. Densities were taken from Beilstein or estimated. As the heat contributed by the film was only ~10% of the total, we did not make a separate correction for the heat capacity of the film.

Enthalpies of Vaporization. Vapor pressures were measured by use of a sickle cell, a differential pressure measuring device (glass Bourdon gauge).[18,19] The sickle cell pressure indicator pointer is displaced from its null point when a pressure difference exists between the open and closed parts of the cell to bring the measuring pointer to its null position, thus equalizing the pressure in both parts of the system. The pressure in the open part is then read by a McLeod gauge or mercury manometer and is taken as the pressure of the closed part of the system.

Measurements were made by attaching the 225-ml cell to a vacuum system and bringing both parts of the cell to a pressure of 10^{-5} mm. The cell was then brought to atmosphereic pressure by adding dry nitrogen to both parts. The specimen was introduced into the cell and frozen by immersing in a mixture of Dry Ice–acetone. While the specimen remained frozen, both sections of the cell were evacuated to a pressure of 10^{-5} mm and the sample entrance port was sealed off. The cell was then allowed to reach room temperature and was placed into a controlled bath of Dow-Corning 550 silicone oil. The temperature of the bath was then brought to a constant temperature of 30 ± 0.05° and allowed to stand for 20–25 min. The pressure of the open part of the system

was adjusted to match the pressure of the closed part of the system by admitting dry air. This brought the measuring pointer of the sickle cell to its null point and the pressure of the open part of the system was read. Additional pressures were read in increments of 15–20° up to the boiling point of the specimen under investigation. Enthalpies of vaporization were calculated from

$$\Delta H_v = \left[\frac{\log P_2 - \log P_1}{1/T_2 - 1/T_1}\right] 2.303R$$

There were no discontinuities in the vapor pressure plots for the solid hydrocarbons at the melting points. Plots were linear over the range studied. The vapor pressure data are collected in Tables I–V.

A variety of compounds for which we obtained satisfactory agreement with literature values is given in ref 12.

(18) F. Daniels, *J. Amer. Chem. Soc.*, **50**, 1115 (1928).
(19) A. W. Laubengayer and F. B. Schermer, *ibid.*, **62**, 1578 (1940).

[2.2.2](1,3,5)Cyclophane and Its Derivatives. An Extreme Example of Face-to-Face Crowding of Aromatic Rings[1]

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Abstract: The reaction of 1,3,5-tris(bromomethyl)benzene with sodium sulfide yields 2,11,20-trithia[3.3.3](1,3,5)-cyclophane (6) which, on subjection to a Stevens rearrangement followed by a Hofmann elimination, leads to [2.2.2](1,3,5)cyclophane-1,9,17-triene (11). The average distance between the two aromatic rings of 11 is only 2.80 Å and represents the most extreme example of face to face crowding of two aromatic rings presently known. The physical and chemical properties of 11 and its derivatives are discussed. The chemical effects of this interfacial crowding are especially evident in the facile conversion of 15 to the novel cage structure 24.

Recently, we have described a procedure for the transformation of a sulfide linkage to a carbon–carbon double bond.[3] This involved a Stevens rearrangement followed by a Hofmann elimination and has been utilized for syntheses of *cis*- and *trans*-15,16-dimethyldihydropyrene,[3,4] *trans*-15,16-dihydropyrene,[5]

[2.2]metaparacyclophane-1,9-diene,[6] and [2.2](2,6)pyridinophane-1,9-diene.[7] As a further test of the generality of this synthetic method, we have now investigated its application for the synthesis of [2.2.2](1,3,5)-cyclophanes.[8]

In an interesting approach to cyclophane chemistry Hubert has previously shown that trimerization of diacetylenes, such as 1, using a Ziegler catalyst yields tris-bridged (1,3,5)cyclophanes of the general formula

(1) We thank the National Science Foundation for their support of this investigation.
(2) National Science Foundation Predoctoral Fellow, 1968–1970.
(3) R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1197 (1970).
(4) R. H. Mitchell and V. Boekelheide, *Chem. Commun.*, 1555 (1970).
(5) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3510 (1970).

(6) V. Boekelheide and P. H. Anderson, *Tetrahedron Lett.*, 1207 (1970).
(7) V. Boekelheide and J. A. Lawson, *Chem. Commun.*, 1558 (1970).
(8) For a preliminary communication of these results, see V. Boekelheide and R. A. Hollins, *J. Amer. Chem. Soc.*, **92**, 3512 (1970).

given by 2.[9] Although this procedure is satisfactory

1

2

3

4

5
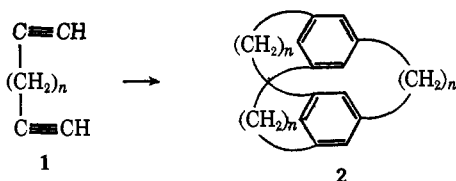
for the examples where $n = 3$ or larger, it fails for the most interesting case where $n = 2$.

Until now the [2.2]paracyclophanes have represented the extreme example of interfacial crowding of two aromatic rings. As summarized in Figure 1, the X-ray crystallographic analysis of [2.2]paracyclophane-1,9-diene shows the two aromatic rings to be bent very considerably from planarity, but even so the central carbons of the two rings are only 3.14 Å apart.[10] This is in contrast to the normal stacking distance of aromatic rings in crystals of about 3.4 Å.[11] This strong interfacial crowding of the two aromatic rings of [2.2]paracyclophane is responsible in large measure for the unusual chemistry of this class of compounds, which has been studied so extensively and elegantly by Professor Cram.[12] However, it is clearly evident from molecular models that, if the two benzene rings are brought face to face with three two-carbon bridges located at the 1, 3, and 5 positions, deformation of the benzene rings becomes more difficult than with the [2.2]paracyclophanes and so the interfacial crowding is more intense.

It was for the purpose of looking into the physical and chemical properties of such tris-bridged cyclophanes having this exceptionally strong interfacial crowding that the present study was undertaken. It had been shown in three different laboratories that 2,11-dithia[3.3]metacyclophane undergoes easy conformational flipping between an anti arrangement (3) of the aromatic rings and a syn arrangement (4).[5,13,14] Thus, if suitable functionality were provided, as shown by 4, ring closure to a (1, 3, 5) tris-bridged cyclophane such as 5 should be possible.

Since the synthesis of 2,11-dithia[3.3]metacyclophane (3, X = H) is readily accomplished by the reaction of m-xylylene dibromide with sodium sulfide,[5,13,14] the obvious example for testing this idea was the reaction of 1,3,5-tris(bromomethyl)benzene with sodium sulfide. The [3.3]metacyclophane (3, X = CH₂Br) first formed should freely undergo conformational flipping to provide equilibrium concentrations of 4 (X = CH₂Br), which on further reaction with sodium sulfide would give 2,11,20-trithia[3.3.3](1,3,5)cyclophane (6). In fact the reaction proceeded as expected in 24% yield to give 6. Alternatively, of course, treatment of 1,3,5-tris(bromomethyl)benzene with 1,3,5-tris(mercaptomethyl)benzene should also give 6, and Vögtle has shown this reaction to be successful, but in only 5.3% yield.[15]

The room-temperature nmr spectrum of 6 shows the benzylic proton resonance as a singlet at τ 6.17, indicating a rapid conformational flipping of the sulfur atoms. More remarkably, the X-ray crystallographic analysis of 6 shows a disordering of one of the sulfur atoms which may be interpreted as the result of a dynamic conformational flipping of that sulfur atom in the crystal state.[16] The benzene rings of 6 are planar and separated by a distance of 3.2 Å.[16]

Treatment of 6 with dimethoxycarbonium fluoroborate[17] gave the corresponding tris-sulfonium salt as a mixture of stereoisomers but in essentially quantitative yield. When 7 was allowed to react with sodium hydride in tetrahydrofuran, ring contraction via a triple Stevens rearrangement occurred to give 8 as a mixture of stereoisomers in 42% yield. Accompanying 8 was the corresponding ring-opened derivative 9, formed in 12% yield. A second methylation of 8 gave the corresponding tris-sulfonium salt 10 in quantitative yield which, on reaction with sodium hydride in boiling tetrahydrofuran, underwent a triple Hofmann elimination to form [2.2.2](1,3,5)cyclophane-1,9,17-triene (11) in 71% yield.

The tris-bridged triene 11 is a white crystalline solid, mp 203–204°. Its nmr spectrum shows only two singlets of equal intensity at τ 2.63 and 3.76. The answer to the question of which signal corresponds to the six aromatic protons and which to the six vinylic protons was not obvious. To establish this point the synthesis was repeated employing 1,3,5-tris(bromomethyl)benzene in which the benzylic hydrogens were replaced with deuterium. The resulting product 11, now having the vinylic hydrogens replaced by deuterium, showed only the singlet at τ 3.76. Thus, the highfield signal is due to the aromatic protons, whereas the low-field signal relates to the vinylic protons.

The data from the X-ray crystallographic analysis of [2.2.2](1,3,5)cyclophane-1,9,17-triene (11) are summarized in Figure 1.[18] The bond lengths of the aromatic double bonds, vinyl double bonds, and carbon–carbon single bonds are all quite normal. The benzene rings are distorted slightly from planar with an

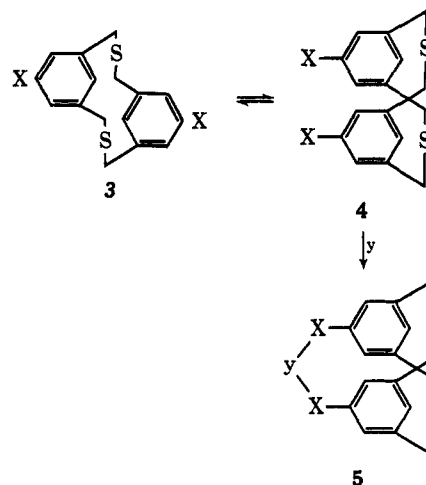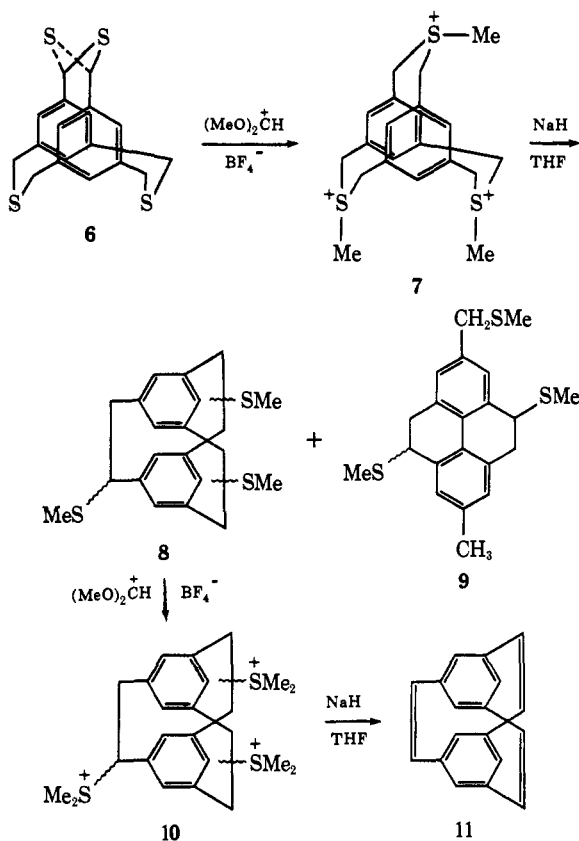(9) A. J. Hubert, J. Chem. Soc., 3160 (1965); J. Chem. Soc. C, 6, 11, 13 (1967).

(10) C. L. Coulter and K. N. Trueblood, Acta Crystallogr., 16, 667 (1963).

(11) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, p 213.

(12) For a recent summary of activities in this area, see D. J. Cram and J. M. Cram, Accounts Chem. Res., 4, 204 (1971).

(13) T. Sato, M. Wakabayashi, M. Kainosho, and K. Hata, Tetrahedron Lett., 4185 (1968).

(14) F. Vögtle and L. Schunder, Chem. Ber., 102, 2677 (1969).

(15) F. Vögtle, Justus Liebigs Ann. Chem., 735, 193 (1970). By a similar reaction scheme, F. Vögtle and P. Neumann [Chem. Commun., 1464 (1970)] have also prepared a 2,11,20-triaza[3.3.3](1,3,5)cyclophane derivative.

(16) A. W. Hanson and E. W. Macauly, Acta Crystallogr., Sect. B, 28, 1255 (1972).

(17) R. F. Borch, J. Org. Chem., 34, 627 (1969).

(18) A. W. Hanson, Acta Crystallogr., Sect. B, 28, 2287 (1972).

a = 1.396 Å (range 1.389-1.402 Å)
b = 1.502 Å (range 1.498-1.504 Å)
c = 1.340 Å (range 1.335-1.347 Å)

Figure 1. A summary of the X-ray crystallographic analyses of [2.2]paracyclophane-1,9-diene[10] (left-hand figure) and [2.2.2]-(1,3,5)cyclophane-1,9-diene[18] (right-hand figures). Open circles represent hydrogen atoms.

overall chair-type conformation. The distance between the two benzene rings at bridge points is only 2.74 Å, whereas the distance between the rings at non-bridging carbons is 2.86 Å. Thus, the two benzene rings show appreciably greater face to face crowding than in the [2.2]paracyclophanes. It is interesting to note that, similar to the case of [2.2]paracyclophane-1,9-diene,[10] the bond angle of the aromatic carbon–hydrogen bond is not as would be expected but rather brings the hydrogens much closer to the center area between the two rings. Assuming the usual carbon–hydrogen bond angles, the separation of hydrogen atoms from the two aromatic rings would be expected to be about 3.01 Å, whereas in fact the separation is only 2.52 Å.[18] It might be thought that this change in carbon–hydrogen bond angle is a result of some rehybridization of the aromatic ring carbons giving them more sp[3] character. This would seem a logical way of allowing greater π-electron density outside of the rings and decreasing the π-electron density in the crowded area between the two rings. However, such rehybridization should be reflected in the ^{13}C–H coupling constants. The ^{13}C–H coupling constants measured for 11 show $J_{^{13}C-H}$ = 162 Hz for the aromatic protons and $J_{^{13}C-H}$ = 164 for the vinyl protons, which is quite normal and provides no evidence at all in support of such a rehybridization theory.[19]

An anomalous spectral property of [2.2]paracyclophane is the long wavelength band it exhibits at 302 nm. This has been attributed to an interaction of the two benzene rings and has been the subject of some theoretical discussion.[20] The ultraviolet spectrum of

(19) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 233–236.
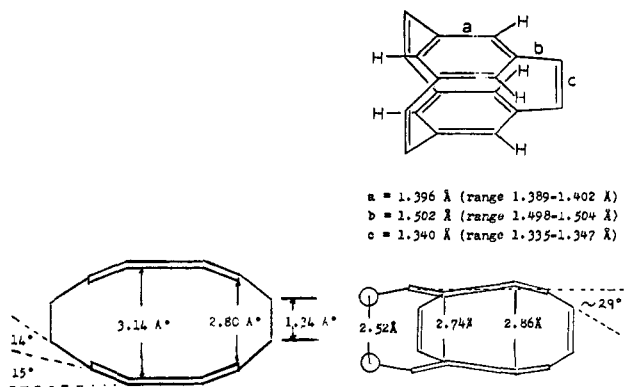(20) See R. Gleiter, Tetrahedron Lett., 4453 (1969), and references to earlier work cited therein.

11 shows absorption maxima at 252 nm (ϵ 1960) and 325 (90). As will be discussed later, the vinylic bridges of 11 can be successively reduced and, as they are, there is a regular, progressive shift of this long wavelength band toward the blue. Thus, [2.2.2]-(1,3,5)cyclophane (15) shows this band at 312 nm.

As noted earlier, the Stevens rearrangement of 7 gave both the expected product 8 and the tetrahydropyrene derivative 9. A great deal of work has been done in the past several years,[21] which has established that many Stevens rearrangements of ammonium and sulfonium salts exhibit chemically induced dynamic nuclear polarization and so, at least in part, the mechanism of the Stevens rearrangement must involve diradical intermediates. In the case of the Stevens rearrangement of 7, a diradical intermediate such as 12 might readily undergo a conformational flip to 13 to relieve strain and this, in turn, would be expected to tautomerize to 9. The structure of 9, incidentally,
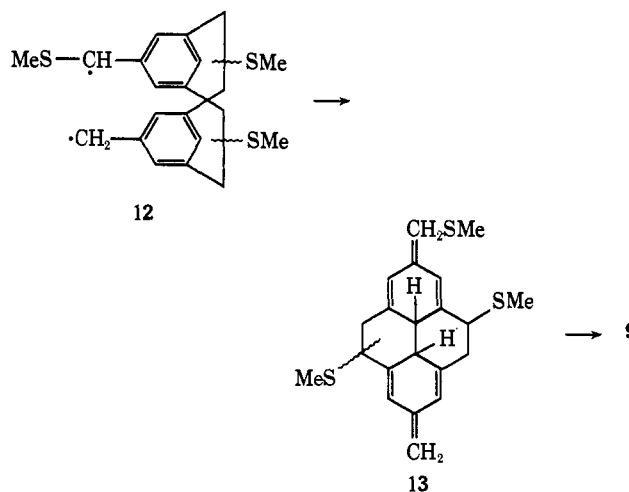
was established by desulfurization using sodium and liquid ammonia to give 2,7-dimethyl-4,5,7,10-tetrahydropyrene which, on treatment with dichlorodicyanoquinone, gave in quantitative yield 2,7-dimethylpyrene, identical in all its properties with a known specimen.

(21) A. R. Lepley, Chem. Commun., 1460 (1969), and earlier papers; U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, Tetrahedron Lett., 3415 (1969).

However, it is an interesting point that whether the Stevens rearrangement of **7** gives the normal product **8** or a pyrene derivative is very much solvent dependent. When **7** was treated with sodium hydride in dimethyl sulfoxide rather than tetrahydrofuran, the only product to be isolated was the pyrene derivative **14**, which formed in 35% yield. Since **9** is converted to **14** in

$$7 \xrightarrow[\text{DMSO}]{\text{NaH}} \quad \xleftarrow[\text{DMSO}]{\text{NaH}} 9$$

14
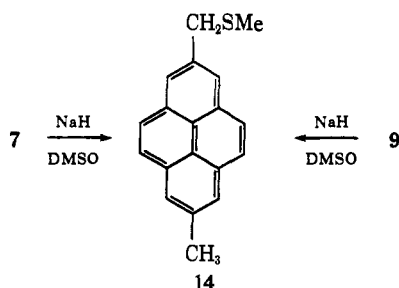
75% yield by reaction with sodium hydride in dimethyl sulfoxide, it seems likely that **9** is an intermediate in the formation of **14**. Just why ring opening should be favored by a more polar solvent is not clear. Again, the structure of **14** was established by Raney nickel desulfurization to give the known 2,7-dimethylpyrene.

The first chemical study of [2.2.2](1,3,5)cyclophane-1,9,17-triene (**11**) was its catalytic hydrogenation. Reduction of **11** using a platinum catalyst with ethyl acetate as solvent gave [2.2.2](1,3,5)cyclophane (**15**) in quantitative yield. The signal for the aromatic protons of **15** occurs at τ 4.27, showing the strong shielding effect of the neighboring benzene ring. The effect here is appreciably stronger than in [2.2]paracyclophane, where the signal for the aromatic protons appears at τ 3.63.[22] Since the catalytic hydrogenation of **11** must proceed through the corresponding dihydro and tetrahydro derivatives, it was of interest to examine the partial hydrogenation of **11** in order to obain these derivatives, **16** and **17**, as well. If it is assumed that


16 **17** **15**
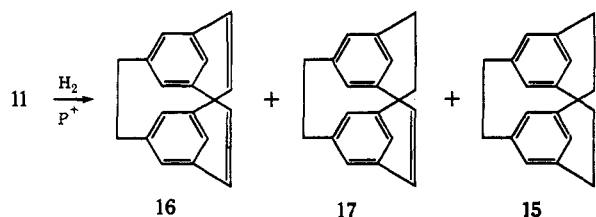
the relative rates of hydrogenation of **11**, **16**, and **17** are equal but statistically governed by the number of available double bonds, a computer simulation of the relative concentration–time relationship of each of the constituents during hydrogenation can be made.[23] However, the experimental data do not agree at all with such a computer simulation. In order to obtain agreement between the experimental values and the computer simulation, it was necessary to assume that the relative rates of hydrogenation of **11**, **16**, and **17** vary in the ratio of 1:2:2.5. This is exactly contradictory to what would be predicted *a priori* based on arguments of relief of steric strain. It may be that this is an unusual entropy effect, but, if so, it is not obvious.

(22) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Amer. Chem. Soc.*, **85**, 1088 (1963).

(23) We thank Dr. R. S. Cooke for his help in making these computer simulations and interpretations.

Cram and his colleagues have made extensive studies of the relative π basicities of cyclophanes using the long wavelength charge transfer bands of the corresponding tetracyanoethylene (TCNE) complexes as the basis for correlation.[24] When the TCNE complexes of **11**, **16**, **17**, and **15** were prepared and measured, it was found that a plot of the long wavelength bands against the number of bridging double bonds gave a straight line with the order of relative π basicities being **15** > **17** > **16** > **11**. The long wavelength charge transfer band of **15** in dichloromethane solution is at 568 nm, indicating a greater π basicity than for [2.2]paracyclophane (521 nm). This is probably as expected since in **15** the two benzene rings are more nearly planar and in closer proximity. However, the fact that [3.3]paracyclophane shows a still greater π basicity (599 nm) emphasizes that this measurement is a summation of effects of which aromatic ring planarity and proximity are only two contributing factors.

Although the vinyl double bonds of **11** are orthogonal to the π clouds of the benzene rings and so are not expected to show conjugative interaction, it was felt that the bent bonds of the corresponding cyclopropane derivative might show a strong interaction with the benzene π clouds. Unfortunately, despite our best efforts, we have been unable to effect addition of carbenes or carbenoid reagents to **11**. The only instance of success was when **11** was allowed to stand in an ethereal solution of diazomethane for 10 days. This gave the pyrazoline derivative **18**. How-

$$11 \xrightarrow{\text{CH}_2\text{N}_2}$$

18
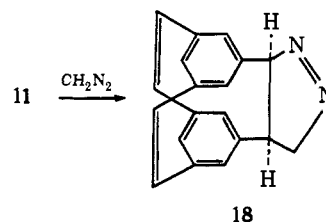
ever, neither irradiation nor pyrolysis of **58** gave any of the desired cyclopropane analog.

Inasmuch as *syn*-[2.2]metacyclophanes are exceedingly rare,[4] an attempt was made to see whether cleavage of one of the bridges in these tris-bridged cyclophanes would yield an isolable *syn*-[2.2]metacyclophane derivative. Treatment of **11** with osmium tetroxide and sodium periodate gave pyrene-2,7-dicarboxaldehyde (**19**) in 84% yield, presumably *via* an intermediate 15,16-dihydropyrene derivative.

$$11 \xrightarrow[\text{NaIO}_4]{\text{OsO}_4}$$

19
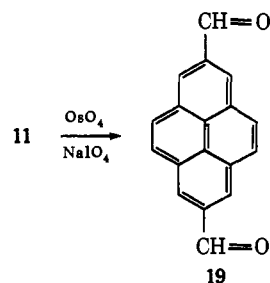
When the monoolefin **17** was treated with osmium tetroxide and sodium periodate in tetrahydrofuran,

(24) D. J. Cram and R. H. Bauer, *J. Amer. Chem. Soc.*, **81**, 5971 (1959); see also R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

there was formed the *anti*-[2.2]metacyclophane-5,13-dicarboxaldehyde (**20**) in 54% yield. Similarly, when

20
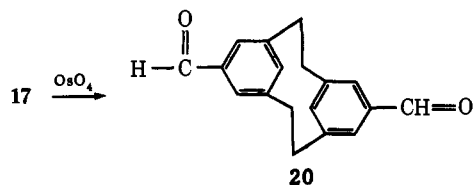
17 was treated with osmium tetroxide alone in pyridine solution at room temperature, the product was **20**. Thus, whereas the barrier to conformational flipping from anti to syn in [2.2]metacyclophane has been set as being greater than 27 kcal/mol based on nmr temperature-dependence studies,[13,25,26] the corresponding barrier for conformational flip from *syn*- to *anti*[2.2]metacyclophane-5,13-dicarboxaldehyde must be very small indeed.

In order to have adequate quantities of [2.2.2](1,3,5)-cyclophane for chemical study, an alternate synthesis was also devised. The trisulfone **21** was prepared

21
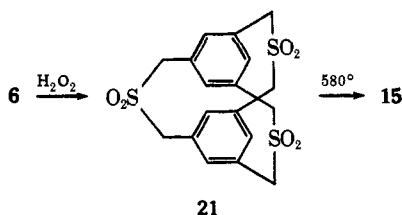
from the corresponding trisulfide **6** in quantitative yield following Vogtle's procedure.[15] Pyrolysis of **21**, under conditions similar to those described by Matthias and Staab for sulfone pyrolyses in general,[27] led to the formation of **15** in 20% yield. However, in view of the few steps involved and the convenience of operation, this is the preferred route for preparing [2.2.2](1,3,5)cyclophane.

The Birch reduction of [2.2.2](1,3,5)cyclophane proceeded smoothly to give a single product in 50% yield. The nmr spectral data show the vinyl protons as two slightly broadened singlets at τ 4.60 and 4.71, with the methylene and methine protons as complex signals in the region of τ 7.24 and 8.20. We have, therefore, tentatively assigned structure **22** to this

22
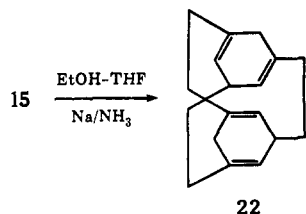
product. Although the ultraviolet spectrum of **22** shows only end absorption, this extends to about 270 nm, indicating the strong transannular interactions of the isolated olefinic bonds. When the Birch reduction was repeated under slightly different conditions (less proton source and more sodium metal), the reaction took a completely different course and gave only *trans*-5,13-dimethyl[2.2]metacyclophane. This

result is analogous to that observed by Marshall and Folsom in a modified Birch reduction of [2.2]paracyclophane.[28]

The Friedel–Crafts acylation of [2.2.2](1,3,5)cyclophane proceeded extremely rapidly using acetyl chloride and aluminum chloride to give the monoacetyl derivative **23**. The aromatic proton on the opposite

23
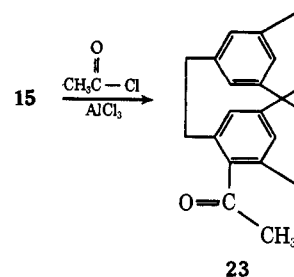
ring but directly across from the acetyl group appears as a triplet at τ 3.97, whereas the other aromatic protons are upfield at τ 4.26 and 4.30.

When an attempt was made to formylate **15** using a mixture of anhydrous hydrogen chloride, sodium cyanide, and zinc chloride, a product mixture resulted showing no aldehydic, aromatic, or olefinic protons. In view of this surprising result, **15** was allowed to react with anhydrous hydrogen chloride and aluminum chloride in methylene chloride at 0° for a short time. Again the product mixture showed no trace of aromatic or olefinic protons. Mass spectral data indicated the product to be a mixture in which H_xCl_{6-x} units had been added to **15**. However, when this product mixture was treated with lithium and *tert*-butyl alcohol in boiling tetrahydrofuran to effect reductive removal of all organic chloride, a single crystalline product resulted in 49% overall yield from **15**. The spectral properties of this crystalline product are very simple and in full accord with its having the novel cage structure **24**. Thus, the nmr spectrum of **24** shows only three signals: τ 8.33 (m, 6 H, –CH–), 8.43 (t, 12 H, –CH$_2$–, J = 1.25 Hz), and 9.01 (m, 6 H, –CH–). The infrared spectrum of **24** exhibits absorption bands at 2920, 2880, 1460, 1440, and 1304 cm^{-1}, with the 1440-cm^{-1} band probably being an overtone of the 2880-cm^{-1} band.

25   **26**

27

Prior to the synthesis of **15** we had anticipated that such a molecule with extreme face-to-face crowding

(25) R. W. Griffin, Jr., and R. A. Coburn, *ibid.*, **89**, 4638 (1967).
(26) F. Vogtle, *Tetrahedron Lett.*, 3623 (1968).
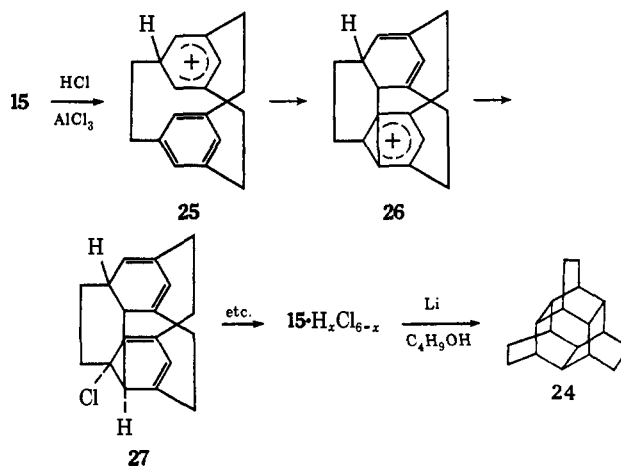(27) H. Matthias and H. A. Staab, *ibid.*, 3585 (1970).
(28) J. L. Marshall and T. K. Folsom, *ibid.*, 757 (1971).

of the benzene rings would probably show a variety of unusual transannular chemical reactions. The transformation of **15** to the novel cage structure **24** is the first clear-cut example of this type of anticipated transannular interaction. A likely reaction path to explain the transformation would be first protonation to give **25** which, by transannular bond formation, would give the new carbonium ion **26**. This could then acquire a chloride ion yielding **27** which, in turn, is set up to repeat the process. The fact that the product is both a stereoisomeric mixture as well as containing a variable number of chlorine atoms is not surprising. The scrambling of halogens in the presence of aluminum chloride is well known.[29] The interesting fact is that, on removal of all organic halogen, a single crystalline compound results, indicating that only one type of cage structure has been formed. This cage structure, as shown by **24**, is based on bicyclo-[2.2.2]octane as the unit and has all of its hydrogen atoms eclipsed. Whether, under more drastic treatment with aluminum chloride, **24** would rearrange to some other thermodynamically more stable cage structure has not been determined.

Experimental Section[30]

2,11,20-Trithia[3.3.3](1,3,5)cyclophane, 6. To prepare the starting material, 1,3,5-tricarbomethoxybenzene was reduced with diisobutylaluminum hydride in benzene to give 1,3,5-tris(hydroxymethyl)benzene in 94% yield as colorless prisms, mp 76–77°.[31] This, on treatment with phosphorus tribromide in ether, gave 1,3,5-tris(bromomethyl)benzene in 96% yield as white needles, mp 92–93° (lit.[31] mp 93°). A solution of 4.2 g of 1,3,5-tris(bromomethyl)benzene in 300 ml of benzene was added simultaneously, using constant-addition-rate dropping funnels, with a solution of 4.3 g of sodium sulfide nonahydrate in 300 ml of 90% aqueous ethanol to 1 l. of rapidly stirred absolute ethanol over a 3-hr period. The solid material, which had separated, was collected by filtration, redissolved in dichloromethane, and again filtered. Concentration of the dichloromethane filtrate gave a tan solid. This was taken up in an 80% benzene–petroleum ether (30–60°) solution and chromatographed over silica gel. The main eluate fraction gave a white solid which, after recrystallization from cyclohexane, yielded 455 mg (24%) of fine white needles: mp 254–255°; ir (CHCl₃) 3000 and 2930 cm⁻¹; uv (absolute EtOH) 241 nm (ϵ 6190); nmr (CDCl₃) τ 3.10 (s, 6 H, ArH) and 6.17 (s, 12 H, ArCH₂); mass spectrum, m/e 330 (M⁺).

Anal. Calcd for C₁₈H₁₈S₃: C, 65.40; H, 5.49; S, 29.11. Found: C, 65.39; H, 5.29; S, 28.96.

Tris(methylsulfonium) Fluoroborate Salt (7). A solution of 215 mg of **6** in 3 ml of dichloromethane was added slowly to 1 ml of dimethoxycarbonium fluoroborate reagent[17] at −30°. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred overnight. It was then diluted with 30 ml of ethyl acetate and stirred an additional 0.5 hr. The white solid was collected by filtration and washed successively with ethyl acetate and then ether. It weighed 415 mg (100%). A sample recrystallized from water gave fine white needles; mp 270° dec; nmr (DMSO-d₆) broad singlets at τ 2.66, 2.80, and 2.96 (6 H, ArH), broad singlet at 4.96–5.21 (12 H, ArCH₂), and singlets at 6.90 and 6.94 (9 H, SCH₃).

Anal. Calcd for C₂₁H₂₇S₃B₃F₁₂: C, 39.64; H, 4.28; S, 15.13. Found: C, 39.75; H, 4.39; S, 15.19.

Methyl (7-Methylpyren-2-yl)methyl Sulfide (14). A solution of 197 mg of **7** in 1 ml of dimethyl sulfoxide was added to 72 mg of

washed sodium hydride in 1 ml of dimethyl sulfoxide and stirred for 0.5 hr. Excess sodium hydride was then destroyed by addition of water; the mixture was made acidic with dilute hydrochloric acid and then neutralized with sodium bicarbonate. Extraction of the solution with dichloromethane gave a pale yellow oil. This was chromatographed over silica gel using a 25% benzene–petroleum ether (bp 30–60°) solution for elution. The main eluate fraction gave 30 mg (35%) of long white needles: mp 134.0–134.5°; uv (absolute EtOH) 238 nm (ϵ 156,000), 249 (149,000), 267 (93,000), 279.5 (100,000), 308 (56,200), 322 (60,200), and 338.5 (67,000); nmr (CDCl₃) τ 1.92 (s, 2 H, ArH), 202 (s, 6 H, ArH), 5.92 (s, 2 H, ArCH₂), 7.23 (s, 3 H, ArCH₃), and 7.96 (s, 3 H, SCH₂).

Anal. Calcd for C₁₉H₁₆S: mol wt, 276.097. Found (high resolution mass spectrum): mol wt, 276.096.

Desulfurization of 14 to 2,7-Dimethylpyrene. A mixture of 15 mg of **14** and 100 mg of Raney nickel in 40 ml of absolute ethanol was stirred at room temperature for 1.5 hr. After filtration, the filtrate was concentrated to give a white solid. This was chromatographed over silica gel using petroleum ether (30–60°) as eluent. The white solid obtained from the main eluate fraction was recrystallized from cyclohexane to give white needles: mp 234–237° (lit.[32] mp 238°); nmr (CDCl₃) τ 1.92 (s, 8 H, ArH) and 7.17 (s, 6 H, CH₃); identical in all respects with a known specimen of 2,7-dimethylpyrene.

Reaction of 7 with Sodium Hydride in Tetrahydrofuran to Give 8 and 9. A mixture of 5.0 g of **7** and 1.02 g of washed sodium hydride in 100 ml of tetrahydrofuran was stirred at room temperature for 24 hr. Water was added to destroy the excess sodium hydride, the mixture was filtered, and the filtrate was concentrated. The resulting yellow oil was chromatographed over silica gel using a 20% benzene–petroleum ether (30–60°) solution for elution. Concentration of the eluate gave 1.23 g (42%) of **8** as a colorless oil: nmr (CDCl₃) τ 3.45–3.65 (m, ArH), 4.02–4.32 (m, ArH), 5.67–6.23 (m, ArCH), 6.32–6.95 (m, ArCH₂), 7.45–8.08 (m, ArCH₂), and 7.85 (s, 9 H, SCH₃).

Anal. Calcd for C₂₁H₂₄S₃: mol wt, 372.104. Found (high resolution mass spectrum): mol wt, 372.100.

Further elution of the silica gel column in the above experiment using a 50% benzene–petroleum ether (30–60°) mixture for elution gave 340 mg (12%) of **9** as a pale yellow oil: uv (cyclohexane) 263 nm (ϵ 10,300), 282 (16,000), 292 (19,800), and 306 (14,600); nmr (CDCl₃) τ 2.93 (s, 2 H, ArH), 303 (s, 2 H, ArH), 5.83–6.05 (m, 2 H, ArCH), 6.35 (s, 2 H, ArCH₂S), 6.62–6.93 (m, 4 H, ArCH₂), 7.65 (s, 3 H, ArCH₃), 7.98 (s, 3 H, SCH₃), 8.07 (s. 3 H, SCH₃), and 8.16 (s, 3 H, SCH₃).

Anal. Calcd for C₂₁H₂₄S₃: mol wt, 372.104. Found (high resolution mass spectrum): mol wt, 372.109.

The desulfurization of **9** to give 2,7-dimethyl-4,5,9,10-tetrahydropyrene was carried out by dissolving 40 mg of **9** in 5 ml of dry ether and adding this to a blue solution of 100 mg of sodium in 30 ml of liquid ammonia. After the solution had been stirred for 2 min, solid ammonium chloride was added to discharge the blue color. When the ammonia had evaporated, water was added and the mixture was extracted with ether. Concentration of the ether extracts gave a pale yellow solid which was chromatographed over silica gel using petroleum ether (30–60°) for elution. The main eluate fraction gave a white solid which, after recrystallization from petroleum ether (30–60°), afforded 16 mg (64%) of 2,7-dimethyl-4,5,9,10-tetrahydropyrene as white crystals: mp 244–246° (lit.[33] mp 146.5–148°); nmr (CDCl₃) τ 3.13 (s, 4 H, ArH), 7.18 (s, 8 H, ArCH₂), and 7.68 (s, 6 H, ArCH₃).

Anal. Calcd for C₁₈H₁₈: mol wt, 234.141. Found (high resolution mass spectrum): mol wt, 234.140.

Oxidation of 2,7-dimethyl-4,5,9,10-tetrahydropyrene to 2,7-dimethylpyrene was accomplished by boiling a solution of 10 mg of 2,7-dimethyl-4,5,9,10-tetrahydropyrene and 20 mg of dichlorodicyanoquinone in 5 ml of benzene under reflux for 8 hr. After filtration of the reaction mixture, the filtrate was concentrated to give a white solid. This was chromatographed over silica gel using benzene as eluent. This gave 10 mg (100%) of crystalline 2,7-dimethylpyrene, identical in all respects with a known specimen and with the sample described earlier.

[2.2.2](1,3,5)Cyclophane-1,9,17-triene (11). A solution of 545 mg of **8** in 25 ml of dichloromethane was added slowly to 2.25 ml of the dimethoxycarbonium fluoroborate reagent[17] with stirring at −30°. When the addition was complete, the solution was stirred

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(30) Elemental and mass spectral analyses were determined by Dr. S. Rottschaefer of the University of Oregon Microanalytical Laboratories. Ultraviolet and visible spectra were measured with a Cary Model 15, infrared spectra with a Beckman IR-7, and nmr spectra with either a Varian A-60, H.A.-100 or an XL-100. We thank the National Science Foundation for the funds providing the Varian XL-100.

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for an additional 3 hr at room temperature. After decantation of the dichloromethane and addition of 100 ml of ethyl acetate, the mixture was stirred at room temperature for another 12 hr. The resulting solid was collected by filtration and washed successively with ethyl acetate and then ether. The salt, 10, weighed 1.0 g (100%) but smelled strongly of dimethyl sulfide. Therefore, it was used immediately in the Hofmann elimination step. A suspension of 0.90 g of 10 and 0.90 g of washed sodium hydride in 150 ml of tetrahydrofuran was stirred while boiling under reflux for 4 hr. The mixture was then filtered and the filtrate concentrated to give a yellow oil. Chromatography of this oil over silica gel using petroleum ether (30–60°) as eluent gave 252 mg (71%) of a white solid. Recrystallization of a sample from cyclohexane yielded 11 as white platelets: mp 203–204° dec; ir (CDCl₃) 689 and 3000 cm⁻¹; uv (absolute EtOH) 252 nm (ϵ 1960) and 325 (90); nmr (CDCl₃) τ 2.63 (s, 6 H, —CH=CH—) and 3.76 (s, 6 H, Ar H); mass spectrum, m/e 228 (M⁺).

Anal. Calcd for $C_{18}H_{12}$: C, 94.69; H, 5.31. Found: C, 94.70; H, 5.47.

[2.2.2](1,3,5)Cyclophane (15). A mixture of 56 mg of 11 and 100 mg of prereduced platinum oxide catalyst in 15 ml of ethyl acetate was subjected to hydrogenation at room temperature and atmospheric pressure for 3 hr. After removal of the catalyst and solvent, the crystalline residue was taken up in ethyl acetate and recrystallized to give 57 mg (100%) of white crystals: mp 204–206° dec; uv (hexane) 258 nm (ϵ 1200) and 312 (96); nmr (CDCl₃) τ 4.27 (s, 6 H, ArH) and 7.25 (s, 12 H, ArCH₂); mass spectrum, m/e 234.131 (M⁺, mol wt calcd, 234.131).

Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.75. Found: C, 92.15; H, 7.81.

Partial Hydrogenation of 11 to Give 15, 16, and 17. A mixture of 228 mg of [2.2.2](1,3,5)cyclophane-1,9,17-triene (11) and 30 mg of prereduced platinum oxide in 25 ml of ethyl acetate was subjected to hydrogenation at room temperature and atmospheric pressure until 33.6 ml (50% of theoretical for saturation of the olefinic bonds) of hydrogen had been absorbed. After removal of the catalyst and solvent, the residual solid was analyzed by solution nmr and found to consist of 29% of 11, 22% of 16, 17% of 17, and 32% of 15. Preparative separation of the four components could be accomplished by chromatography over silica gel using petroleum ether for elution. The first substance to be eluted was the starting material 11. The second substance to be eluted was the diene 16 and it was obtained, after recrystallization from petroleum ether (30–60°), as white crystals: mp 172.5–173.0°; uv (cyclohexane) 245 nm (sh, ϵ 2250), 281 (sh, 603), and 322 (84); nmr (CDCl₃) τ 2.83 (s, 4 H, —CH=CH—), 3.80 (t, 2 H, $J = 1.5$ Hz, ArH), 4.16 (d, 4 H, $J = 1.5$ Hz, ArH), 7.18 (s, 4 H, ArCH₂).

Anal. Calcd for $C_{18}H_{14}$: C, 93.86; H, 6.14. Found: C, 93.63; H, 6.27.

The third substance to be eluted was the monoene 17. After recrystallization from petroleum ether, it gave white crystals: mp 182.0–182.5° dec; uv (cyclohexane) 281 nm (sh, ϵ 590) and 317.5 (90); nmr (CDCl₃) τ 2.90 (s, 2 H, —CH=CH—), 4.08 (d, 4 H, $J = 1.5$ Hz, ArH), 4.38 (t, 2 H, $J = 1.5$ Hz, ArH), 7.23 (s, 8 H, ArCH₂).

Anal. Calcd for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.97; H, 6.95.

The fourth substance to be eluted was [2.2.2](1,3,5)cyclophane (15), identical in all respects with the specimen described earlier.

TCNE Complexes of Compounds 11, 15, 16, and 17. The TCNE complexes were not actually isolated. Rather, equimolar mixtures of TCNE and the cyclophane in dichloromethane were examined in the ultraviolet for the long wavelength charge transfer band. The absorption bands measured for these solutions were: 11-TCNE, 543 nm; 16-TCNE, 553 nm; 17-TCNE, 559 nm; and 15-TCNE, 568 nm.

Pyrolysis of 2,11,20-Trithia[3.3.3](1,3,5)cyclophane Trisulfone (21). The trisulfone 21 was prepared from 6 in quantitative yield following the procedure of Vogtle.[16] The pyrolysis was carried out following the general procedure of Matthias and Staab[27] using a nitrogen bleed and a pyrolysis temperature of 580° at 0.1 mm. Typically, runs of 50 to 100 mg were made with the pure [2.2.2]-(1,3,5)cyclophane being isolated in about 20% yield.

Osmium Tetroxide Oxidation of 17 to Give 20. To a solution of 23 mg of 17 in a mixture of 0.1 ml of water and 3 ml of tetrahydrofuran was added 10 μl of a solution prepared by dissolving 0.5 g of osmium tetroxide in 10 ml of tetrahydrofuran. After 1 min, 48 mg of sodium periodate was added and the mixture was stirred at room temperature for 1.5 hr. After the addition of 5 ml of water, the mixture was extracted twice with 20-ml portions of ether. The

ether extracts were washed successively with aqueous hydrogen sulfide and 1 N aqueous sodium bicarbonate. When the ether layer had been filtered and dried, it was concentrated to give a tan solid. This was chromatographed over silica gel using dichloromethane as eluent to give 14 mg (54%) of 20 as white crystals: mp 245–246°; ir (CHCl₃) 1690 cm⁻¹ (C=O); nmr (CDCl₃) τ −0.07 (s, 2 H, —CH=O), 2.37 (d, 4 H, $J = 1.5$ Hz, ArH), 5.47 (t, 2 H, ArH), and 7.23 (AA'BB', 8 H, ArCH₂); mass spectrum, m/e 264 (M⁺). The large upfield chemical shift (τ 5.47) for the 8- and 16-aromatic protons is clear evidence for the *anti*-[2.2]meta-cyclophane structure 20.

Anal. Calcd for $C_{18}H_{16}O_{2}$: C, 81.72; H, 6.10. Found: C, 81.54; H, 6.11.

When a similar experiment was tried using pyridine as solvent, omitting the sodium periodate, and working up by addition of sodium bisulfite, the product again was the *anti*-[2.2]metacyclo-phane-5,13-dicarboxaldehyde, 20.

Osmium Tetroxide Oxidation of 11 to Give 2,7-Pyrenedicarboxal-dehyde (19). To a solution of 9 mg of 11 in a mixture of 5 ml of tetrahydrofuran containing one drop of water was added one drop of a solution prepared by dissolving 0.5 g of osmium tetroxide in 10 ml of tetrahydrofuran. To this was added 50 mg of sodium periodate with stirring. After 5 min, the mixture was poured into 10 ml of water and extracted with chloroform. After the chloroform extracts had been dried and concentrated, the residual solid was chromatographed over silica gel using chloroform for elution. From the main eluate fraction there was isolated 9 mg (84%) of 2,7-pyrenedicarboxaldehyde as white crystals: mp 295–298°; ir (Nujol) 1685 cm⁻¹ (C=O); nmr (CDCl₃) τ −0.48 (s, 2 H, —CH=O), 1.28 (s, 4 H, ArH), and 1.74 (s, 4 H, ArH).

Anal. Calcd for $C_{18}H_{10}O_{2}$: mol wt, 258.063. Found (high resolution mass spectrum): mol wt, 258.067.

Reaction of 11 with Diazomethane. A mixture of 23 mg of 11 and about 420 mg of diazomethane in 25 ml of ether was allowed to stand at room temperature in the dark for 10 days. The solution was filtered and the filtrate concentrated to give a pale yellow solid. This, on chromatography over silica gel using benzene as eluent followed by recrystallization from a benzene–petroleum ether (30–60°) mixture, gave 10 mg (37%) of white crystals: mp 136–139° dec; ir (CHCl₃) no NH band; uv (absolute EtOH) 322 nm (ϵ 312); nmr (CDCl₃) τ 2.80 (s, 2 H, —CH=CH—), 2.86 (s, 2 H, —CH=CH—), 3.75 (s, 1 H, ArH), 3.78 (s, 1 H, ArH), 3.94 (d, 1 H, $J = 9.5$ Hz, >CH–), 4.05 (s, 1 H, ArH), 4.12 (s, 1 H, ArH), 4.54 (d, 1 H, $J = 4.8$ Hz, ArH), 5.03 (d, 1 H, $J = 3$ Hz, -CH₂-), 5.28 (q, 1 H, $J = 3$ Hz, $J' = 9.5$ Hz, -CH₂-), 5.42 (s, 1 H, ArH), and 6.54 (t, 1 H, $J = 9.5$ Hz, >CH–).

Anal. Calcd for $C_{19}H_{14}N_{2}$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.21; H, 5.23; N, 10.27.

4-Acetyl[2.2.2](1,3,5)cyclophane (23). To a suspension of 40 mg of anhydrous aluminum chloride in a mixture of 3 ml of carbon disulfide and 2 ml of dichloromethane was added a solution of 24 mg of acetyl chloride and 23.4 mg of [2.2.2](1,3,5)cyclophane (15) in 1 ml of carbon disulfide with stirring. After 4 min the mixture was hydrolyzed by addition of cold dilute aqueous hydrochloric acid and extracted with dichloromethane. The organic layer was separated, dried, and concentrated to give a white solid. This was chromatographed over silica gel using benzene as eluent. The crystalline solid from the main eluate fraction, when recrystallized from cyclohexane. afforded 16.3 mg (59%) of white crystals: mp 168–169°; ir (CHCL₃) 1680 cm⁻¹ (C=O); nmr (CDCl₃) τ 3.97 (t, 1 H, $J = 1.5$ Hz, ArH), 4.26 (d, 2 H, $J = 1.5$ Hz, ArH), 4.30 (s, 2 H, ArH), 6.96–7.52 (m, 12 H, ArCH₂), and 7.70 (s, 3 H, COCH₃).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.29. Found: C, 86.27; H, 7.15.

Birch Reduction of 15 to Give 22. A solution of 35 mg of [2.2.2]-(1,3,5)cyclophane (15) in 4 ml of tetrahydrofuran containing 100 mg of absolute ethanol was added slowly with stirring to a blue solution of 125 mg of sodium in 25 ml of liquid ammonia at −78°. Following this there was added an additional 100 mg of absolute ethanol in 2 ml of tetrahydrofuran. The mixture was then boiled under reflux for 3 hr and the ammonia allowed to evaporate. Water was then added and the mixture was extracted with ether. After the ether layer had been dried and concentrated, the residual solid was chromatographed over silica gel using petroleum ether (30–60°). The main eluate fraction afforded 18 mg (50%) of white crystals: mp 220–222°; uv (cyclohexane) end absorption up to 270 nm; nmr (CDCl₃) τ 4.60 (s, 2 H, —CH=C), 4.71 (s, 2 H, —CH=C), and 7.24–8.20 (complex multiplet, 18 H, >CH– and -CH₂-).

Anal. Calcd for C₁₈H₂₂: C, 90.70; H, 9.30. Found: C, 90.27; H, 9.32.

Birch Reduction of 15 to Give *anti*-5,13-Dimethyl[2.2]metacyclophane. A solution of 40 mg of [2.2.2](1,3,5)cyclophane (**15**) in 4 ml of tetrahydrofuran containing 50 mg of absolute ethanol was added slowly with stirring to a blue solution of 300 mg of sodium in 30 ml of liquid ammonia held at −78°. After 1 hr the ammonia was allowed to evaporate, water was added, and the mixture was extracted with ether. The residual solid, after concentration of the ether extracts, was chromatographed over silica gel using petroleum ether (30–60°) as eluent. The main eluate fraction afforded 20 mg (50%) of white crystals: mp 148.5–149.5; nmr (CDCl₃) τ 3.17 (s, 4 H, ArH), 5.86 (s, 2 H, ArH), 7.46 (AA'BB', 8 H, ArCH₂), and 7.65 (s, 6 H, ArCH₃). The properties of these crystals were identical in all respects with a known specimen of *anti*-5,13-dimethyl[2.2]metacyclophane[34] and a mixture melting point showed no depression of melting point.

Transformation of [2.2.2](1,3,5)Cyclophane (15) to the Novel Cage Structure 24. To a mixture of 200 mg of anhydrous aluminum chloride in 5 ml of dichloromethane saturated with anhydrous hydrogen chloride a solution of 160 mg of [2.2.2](1,3,5)cyclophane (**15**) in 5 ml of dichloromethane was slowly added (2 min). The resulting mixture was stirred an additional 10 min at 0° before adding 20 ml of cold, dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, and concentrated to give 220 mg of an oil. This oil showed a positive Beilstein halogen test, a complex nmr pattern from τ 7.6–9.0, and a mass spectral pattern with peaks corresponding to molecular ions derived from C₁₈H₁₈-H_xCl_{6−x}, where *x* is an integer less than 6. This oil was then dissolved in 10 ml of tetrahydrofuran, 100 mg of lithium and a solution of 200 mg of *tert*-butyl alcohol in 4 ml of tetrahydrofuran were added, and the resulting mixture was boiled under reflux for 3 hr. The mixture was then filtered, 20 ml of ether was added to the filtrate, and the filtrate was washed with water. After the organic layer was dried and concentrated, the residual white solid was chromatographed over silica gel using pentane as eluent. The crystalline solid from the main eluate fraction was recrystallized from a pentane–ethanol mixture to give 81 mg (49%) of white crystals: mp 178–181°; ir (CCl₄) 2920, 2880, 1460, 1440, and 1304 cm⁻¹; nmr (CDCl₃) τ 8.33 (m, 6 H, >CH–), 8.43 (t, 12 H, *J* = 1.25 Hz, –CH₂–), and 9.01 (m, 6 H, >CH); mass spectrum, *m/e* 240 (M⁺).

Anal. Calcd for C₁₈H₂₄: C, 89.94; H, 10.06. Found: C, 89.72; H, 10.18.

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Nuclear Magnetic Resonance Studies of Structure and Hindered Rotation in Tertiary Benzylic Metal Compounds

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Abstract: A variety of α-methylstyrenes have been found to undergo nearly quantitative 1:1 addition with *tert*-butyllithium in isooctane-*N,N,N',N'*-tetramethylethylenediamine, TMEDA. The ring proton shifts in several tertiary benzylic lithium and potassium compounds in ether, THF, tertiary amines, and TMEDA–isooctane, considerably shielded with respect to benzene, are independent of metal, solvent and substitution on the benzylic carbon. Also the proton–proton coupling constants differ greatly from those in covalently substituted benzyl compounds in that the J_m values are negative. These results indicate the benzylic moiety to be a planar conjugated anion within a solvent separated or loose ion pair. In the unsymmetrically substituted reagents all the ring hydrogens are magnetically nonequivalent. The shifts average at higher temperatures, 10–94°, and line-shape analysis yields rates of rotation about the ring–benzyl bond. These are first order in contained reagent but vary with both solvent and metal. In isooctane–TMEDA, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for a benzylic lithium compound are *ca.* 18.5 kcal and 5 eu. A solvent to carbon metal coordination transfer mechanism is proposed to account for the involvement of metal and solvent in the rotation process.

The molecular structure and dynamic behavior of π-conjugated carbanions have been the subject of extensive investigation. Problems which concern the structure and behavior of these species include the charge distribution, the ionic character of the carbon–metal bonds, and the various types of ion pairing involved. Further, many of these anions are not rigid, but undergo rotation about different π carbon–carbon bonds at rates conveniently within the nmr time scale.

The benzyl anion, one of the simplest conjugated carbanions, is important also for its role in the anionic polymerization of styrene.[1] Nmr studies have been reported on benzyllithium,[2] on substituted benzylpotassiums (cumyl, α-phenethyl, and benzyl),[3,4] and on adducts of styrenes with *tert*-butyllithium.[4] All these authors have commented on the considerable shielding experienced by the ring hydrogens (compared to benzene) indicative of extensive conjugation.[3,4]

In unsymmetrically substituted benzyllithiums the ring hydrogens are all magnetically nonequivalent[3,4] confirming the coplanarity of the system, and this property has been exploited to measure barriers to rotation by means of the nmr line-shape method.[5]

Of related interest to the work described above are studies of molecular structure and hindered rotation in phenylallyl metal compounds[6] and in 1- and 2-naphthylmethyl metal reagents.[7]

In much of the work quoted here the shifts in the

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