common for benzyl acetates), and other prominent peaks at *m/e* 43, 177, and 253. The uv spectrum of **8** exhibited λ_{max} 254 nm (ϵ 19,600) in ethanol.

Fraction 18 of the above chromatogram provided a higher molecular weight material (52 mg) which when further purified gave slightly yellow crystals, mp 148–152°, *m/e* 562. The ir spectrum of this material showed a carbonyl absorption at 1735 cm^{-1}. *Anal.* Found: C, 78.01; H, 7.15. The nmr spectrum and these data point to a condensation–oxidation product of 2 mol of **1**.

Run 20. A solution of 250 mg of **1** in 280 ml of absolute methanol under nitrogen gave upon chromatography, besides recovered **1**, open-chain methyl ether **6**, wt 35 mg, purified by analytical glc. Mass spectral analysis of this material gave a parent ion at *m/e* 254. *Anal.* Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.85; H, 8.51.

The nmr spectrum of **6** contained the following singlets: six protons in two overlapping broad singlets at δ 2.22 and 2.32 (aromatic methyls); four protons at δ 2.85 (methylene); three protons at δ 3.38 (methyl ether); and two protons at δ 4.43 (benzyl). The aromatic region was a distorted triplet centered at δ 7.13 (7 H).

Run 21. A solution of 500 mg of **1** in 280 ml of absolute methanol was irradiated in the presence of oxygen. Chromatography of the product gave (in order of elution) 71 mg of recovered **1**, 26 mg of open-chain ether **6** (tlc and nmr analysis), and 11 mg of 4-aldehydo[2.2]paracyclophane (**11**), mp 135–140°, undepressed by admixture with an authentic sample. This material gave the same nmr and ir spectra and tlc behavior as authentic **11**.

Attempts to detect aldehyde or acetal products formed from the bridge carbons of the original cyclophane in this and similar runs failed.

Run 22. A solution of 200 mg of **1** in 280 ml of pure 2-propanol was irradiated under nitrogen to give an oil, tlc analysis of which showed the presence of **1**, polymer, and two other components. Elution (with ether–pentane mixtures) of a chromatogram of this material gave in succession 54 mg of **1**, 16 mg of open-chain isopropyl ether **7**, and 16 mg of open-chain tertiary alcohol **9**. Ether **7** was purified by preparative glc to give a colorless oil. *Anal.* Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 84.83; H, 9.13.

The nmr spectrum of ether **7** exhibited a doublet at δ 1.21 (6 H, *gem*-dimethyl); overlapping singlets of unequal intensity at δ 2.20–2.33 (6 H, aromatic methyls); a singlet at δ 2.84 (4 H, methylene); a multiplet at δ 3.66 (1 H, methine); a broad singlet at δ 4.46 (2 H, benzyl); a multiplet at δ 6.95–7.30 (7 H, aromatic).

Attempts to purify open-chain alcohol **9** by preparative glc or flash distillation led to elimination and polymerization of the olefin produced. The substance was identified by its nmr spectrum, which gave the following poorly resolved signals: δ 1.20–1.30 (*gem*-dimethyl), δ 2.20–2.33 (aromatic methyls), δ 2.70–3.05 (benzylic methylenes), δ 6.95–7.19 (aromatic).

Macro Rings. XLV. Stereochemistry of Cyclophane Rearrangements[1,2]

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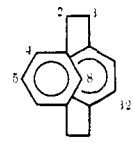
Abstract: The following transformations are reported: the acid-catalyzed rearrangement of optically pure (+)-(*S*)-4-methyl[2.2]paracyclophane ((+)-(*S*)-**3**) to optically pure (+)-(*S*)-12-methyl[2.2]metaparacyclophane ((+)-(*S*)-**4**); the photolytic conversion of [2.2]metaparacyclophane (**1**) to [2.2]metacyclophane (**5**); the photolytic racemization of (−)-(*R*)-**4** and accompanying isomerizations to a mixture of methyl[2.2]metacyclophanes; the photolytic isomerizations of (±)-**4** to give 4-methyl[2.2]metacyclophane (**6**), 5-methyl[2.2]metacyclophane (**7**), and 8-methyl[2.2]metacyclophane (**8**). The mechanisms of these reactions are discussed.

Previous papers in this series reported that [2.2]metaparacyclophane (**1**) readily is prepared by the acid-catalyzed rearrangement of [2.2]paracyclophane (**2**) and that 12-substituted [2.2]metaparacyclophanes can be prepared by the corresponding rearrangement of 4-substituted [2.2]paracyclophanes when the substituent is bromine or methyl.[3,4] Other 12-substituted [2.2]-metaparacyclophanes are available from electrophilic aromatic substitution reactions of **1**.[3] Photolyses of optically active derivatives of **2** result in racemization and ring opening, but no photolytic rearrangement of the aromatic nuclei of the paracyclophane system has been observed.[5–7]



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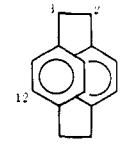


2

The present paper reports the results of studies of the acid-catalyzed rearrangement of optically pure (+)-(*S*)-4-methyl[2.2]paracyclophane ((+)-**3**) to optically pure (+)-(*S*)-12-methyl[2.2]metaparacyclophane ((+)-**4**); the photolytic rearrangement of [2.2]metaparacyclophane (**1**) to [2.2]metacyclophane (**5**); the photolytic rearrangement of (±)-**4** to a mixture of methyl[2.2]-metacyclophanes (**6–8**); and the photolytic racemization of (−)-(*R*)-**4** to (±)-**4**, which accompanies the rearrangement to **6–8**.

Results

Starting Materials. Optically pure enantiomers of 4-methyl[2.2]paracyclophane ((+)- and (−)-**3**) were pre-

(1) The authors warmly thank the National Science Foundation for a grant that supported part of this research. M. H. Delton thanks the Regents of the University of California for a First Year Fellowship, and R. E. Gilman thanks the National Science Foundation for a Science Faculty Fellowship, 1970–1971.

(2) A preliminary account of this work has appeared: M. H. Delton, R. E. Gilman, and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 2329 (1971).

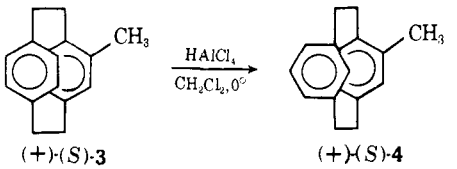
(3) D. T. Hefelfinger and D. J. Cram, *ibid.*, **93**, 4754 (1971).

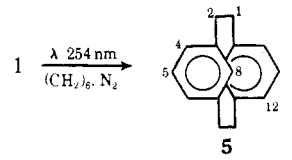
(4) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *ibid.*, **88**, 1324 (1966).

(5) M. H. Delton and D. J. Cram, *ibid.*, **94**, 2471 (1972).

(6) M. H. Delton and D. J. Cram, *ibid.*, **92**, 7623 (1970).

(7) R. C. Helgeson and D. J. Cram, *ibid.*, **88**, 509 (1966).





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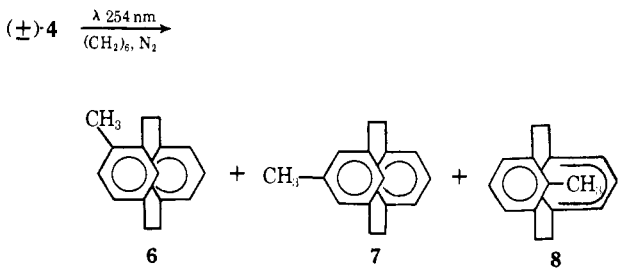
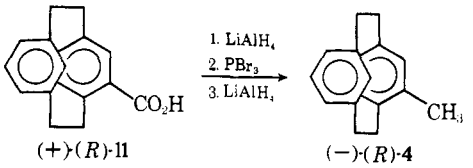


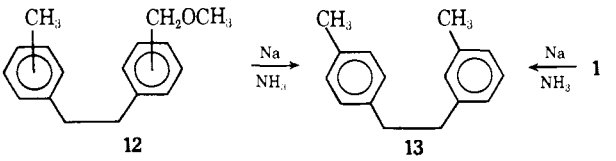
6 7 8

pared by lithium aluminum hydride reduction of the corresponding enantiomers of 4-bromomethylene[2.2]paracyclophane ((−)- and (+)-**9**)[5] which were obtained from (+)- and (−)-4-carboxy[2.2]paracyclophane ((+)- and (−)-**10**) by previously reported methods.[8] Optically pure (−)-(*R*)-12-methyl[2.2]metaparacyclophane ((−)-**4**) was prepared by an analogous series of reactions (see Experimental Section) from (+)-(*R*)-12-carboxy[2.2]metaparacyclophane ((+)-**11**), whose resolution has been reported.[9] Racemic 12-methyl[2.2]-metaparacyclophane ((±)-**4**) was prepared from 4-methyl[2.2]paracyclophane ((±)-**3**) by the acid-catalyzed rearrangement that was reported earlier.[3]

Acid-Catalyzed Rearrangement. The rearrangement of optically pure (+)-(*S*)-4-methyl[2.2]paracyclophane ((+)-**3**) in a dichloromethane solution of hydrogen chloride and aluminum chloride under conditions reported for racemic **3**[3] gave (+)-(*S*)-12-methyl[2.2]metaparacyclophane ((+)-**4**) with complete retention of configuration. The product ((+)-**4**) was purified by chromatographic and sublimation methods (48% yield) free of optical fractionation. The product was identical in all respects (ir, nmr, melting point, optical rotation magnitude, but not signs) to the optically pure reference compound, (−)-(*R*)-12-methyl[2.2]metaparacyclophane ((−)-**4**). This substance was prepared from acid (+)-**11**. Conclusive proof of the enantiomeric relationship of (+)-**4** and (−)-**4** was obtained by their combination to give racemate ((±)-**4**), identified by melting point and mixture melting point comparisons with authentic material.[5]



Photolytic Rearrangements. Irradiation of a solution of [2.2]metaparacyclophane (**1**) in cyclohexane with a quartz U-tube, low-pressure mercury arc (*ca.* 2 W, 86% at 254 nm) for 4 hr gave [2.2]metacyclophane (**5**) in 42% yield (based on consumed **1**) along with 50% recovered **1**. Irradiation of **1** under similar conditions in methanol gave a 46% yield of **5** and a 25%



12 13

yield of the open-chain ether **12**. The structure of **12** was partially elucidated by its reduction with sodium–liquid ammonia to *m,p'*-dimethylbibenzyl (**13**). The structure of **13** was established by comparison of its nmr spectrum to that of an authentic sample obtained from the analogous reduction of [2.2]metaparacyclophane.[3]

Irradiation of 12-methyl[2.2]metaparacyclophane ((±)-**4**) at 254 nm for 9 hr in cyclohexane gave a 31% yield (based on consumed **4**) of a mixture of 4-, 5-, and 8-methyl[2.2]metacyclophanes (**6**–**8**) (glc area ratio of 7.0:4.4:1.0, respectively) along with 45% recovered starting material. Only trace amounts of other chromatographable materials were produced in this photolysis. The three rearrangement products, **6**–**8**, were isolated in pure form by a combination of preparative thin layer chromatography and glc techniques. Structural assignments for **6** and **7** were based on comparisons of their nmr spectra with those of the closely related and known 4,14- and 5,13-dimethyl[2.2]metacyclophanes.[10] The structure of **8** was determined by comparison of its melting point and nmr spectrum with those reported previously for this compound.[11]

Photolytic Racemization and Rearrangement. Irradiation of 93% optically pure (−)-**4** for 8 hr under the conditions used for (±)-**4** gave a 27% yield of recovered starting material that was 13% optically pure (80% racemized), and an 18% yield (based on consumed (−)-**4**) of a mixture of **6**–**8**. This mixture was not separated but was found to be optically active, $[\alpha]^{25}_{546}$ + 2.6°, $[\alpha]^{25}_{436}$ +5.4°, $[\alpha]^{25}_{365}$ +10.2° (*c* 0.46, CCl_4).

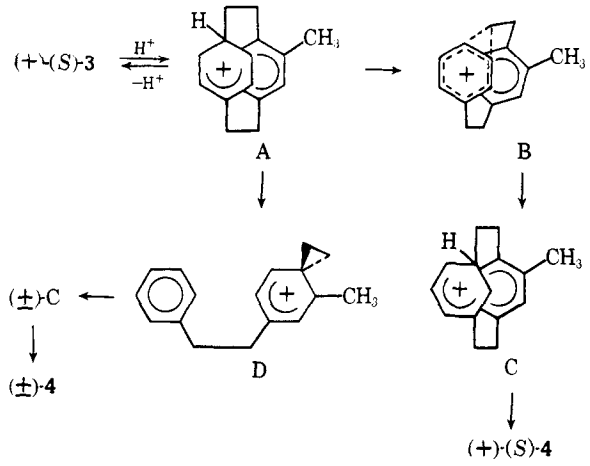
Discussion

Acid-Catalyzed Rearrangement. The two most likely general mechanisms for the acid-catalyzed rearrangement of the [2.2]paracyclophane to the [2.2]metaparacyclophane system are outlined in Chart I. The first of these involves phenonium ion (D) formation and complete scission of the benzyl–benzyl bond, followed by an intramolecular alkylation by the phenonium ion of the other benzene ring at the position meta to the bridge holding the two nuclei together. In this scheme ((+)-**3** → A → D → (±)-C → (±)-**4**), phenonium ion D possesses a mirror plane, and (+)-**3** gives (±)-**4**. The second mechanism involves migration of a methylene group from a para to a meta position through either intermediate or transition state B. In this scheme ((+)-**3** → A → B → C → (+)-(**4**)), the reaction coordinate is fully chiral, and optically pure (+)-**3** produces optically pure **4** (either (+) or (−)), provided

(8) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).
(9) D. T. Helfelfinger and D. J. Cram, *ibid.*, **93**, 4767 (1971).
(10) T. Sato, S. Akabori, S. Muto, and K. Hata, *Tetrahedron*, **24**, 5557 (1968).
(11) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3675 (1970).

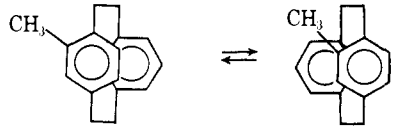
rotation of the methyl-substituted benzene ring with respect to the other benzene ring is sterically inhibited in A, B, and C. Molecular models point to such steric inhibition of rotation. Rotation of the para-substituted ring in 12-carbomethoxy[2.2]metaparacyclophane does not occur up to 200°.[9]

Chart I



The results eliminate the phenonium ion route and are consistent with the fully chiral route. The rotations of (+)-12-methyl[2.2]metaparacyclophane ((+)-**4**) produced by the rearrangement of optically pure (+)-**3** were equal in magnitude to those of (−)-**4** prepared directly from (+)-12-carboxy[2.2]metaparacyclophane ((+)-**11**). This fact indicates that (+)-**4** and (−)-**4** prepared by the two methods were essentially optically pure, and that the rearrangement of (+)-**3** to (+)-**4** proceeded stereospecifically.

The absence of alternative mechanisms with fully chiral reaction coordinates allows assignment of configuration to (+)-**4**. The meta ring of **4** rotates with



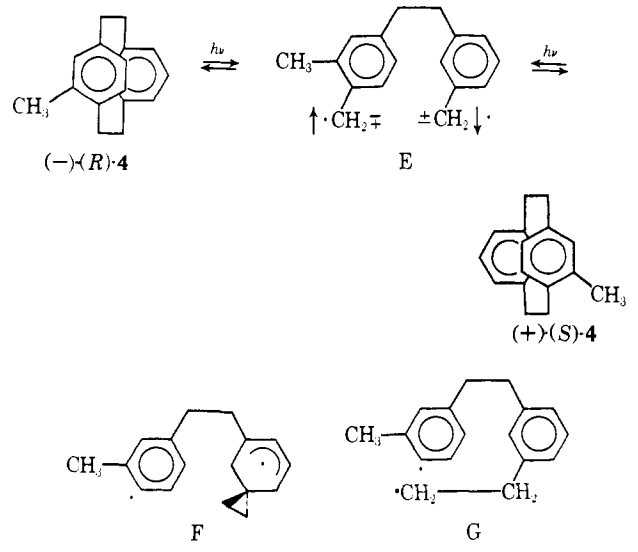
(+)-(*S*)-**4** (methyl and aryl anti) ⇌ rotamer of (+)-(*S*)-**4** (methyl and aryl syn)

respect to the para ring at 25° to provide a conformational equilibrium mixture.[3,9] This fact complicates the structure and name given to (+)-**4**. However, the form with the methyl and meta ring anti dominates the equilibrium mixture, and only this anti form crystallizes.[3,9] These facts suggest that the structure written for (+)-**4** is the more appropriate, and this structure possesses the *S* configuration.[12] This assignment fixes the configuration of (+)-**11** as *R*.

Photolytic Rearrangements. Commercially available [2.2]paracyclophane (**2**)[13] has been isomerized to [2.2]metaparacyclophane (**1**),[4] and the latter compound now has been rearranged photolytically to [2.2]metacyclophane (**5**). The simplicity of these conversions provides a convenient route to **5**, whose overall yield (18%) is comparable to the earlier multistep syntheses of this cyclophane.[14]

The photolytic racemization of (−)-(*R*)-12-methyl-[2.2]metaparacyclophane ((−)-**4**) was comparable in rate to its rearrangements to the methyl[2.2]metacyclophanes. The racemization of (−)-**4** has analogy in the photolytic racemization of [2.2]paracyclophane derivatives through open-chain zwitterion or diradical intermediates.[5,6] The fact that irradiation of [2.2]metaparacyclophane (**1**) in methanol gave an open-chain ether (**12**) as well as [2.2]metacyclophane (**5**) supports the singlet radical–zwitterion route for the racemization of (−)-**4** (Chart II).

Chart II



Although intermediates F and G (Chart II) possess the requisite mirror planes, their counterparts in the racemization of (−)-4-methyl[2.2]paracyclophane[5,6] were encountered in the acetone-sensitized or longer wavelength irradiation processes, and not with 254-nm light.

The photolytic rearrangements at λ 254 nm of [2.2]-metaparacyclophane (**1**) to [2.2]metacyclophane (**5**), and of 12-methyl[2.2]metaparacyclophane (**4**) to the mixture of 4-, 5-, and 8-methyl[2.2]metacyclophanes (**6**, **7**, and **8**), probably do not involve the intermediates of Chart II. Mechanisms that involve E, F, or G type intermediates not only involve elaborate and improbable rearrangements, but predict formation of optically inactive **6**. When (−)-**4** was irradiated at λ 254 nm, the mixture of methyl[2.2]metacyclophanes produced exhibited optical activity of (+) sign, opposite to that of the starting material. This activity must be due to isomer **6**, since isomers **7** and **8** possess mirror planes. Intermediates E, F, and G all possess mirror planes, and are therefore incapable of producing optically active **6**.

The prismane and benzvalene mechanisms[15] for rearrangement of **4** to **6**, **7**, and **8** accommodate the results. Chart III lists four prismane structures formable in principle from (−)-(*R*)-**4** and its meta ring-flipped rotamer.[3,9] Only those prismanes are drawn (H, J, K, and L) that involve the para ring, that lead to [2.2]metacyclophane ring structures, and that are formed by folding the para ring *away* from the meta

(12) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 400 (1966).
(13) W. G. Gorham, *Chem. Eng. News*, **43**, 35 (Feb 22, 1965); **43**, 41 (March 1, 1965).
(14) (a) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Amer. Chem. Soc.*, **83**, 943 (1961); (b) T. Hylton and V. Boekelheide, *ibid.*, **90**, 6887 (1968).
(15) K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965).

Chart III. Prismane Mechanisms

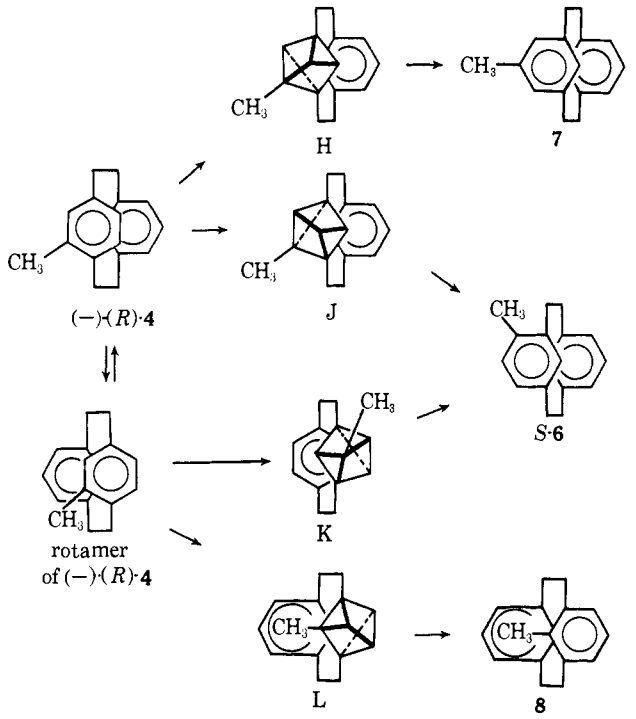
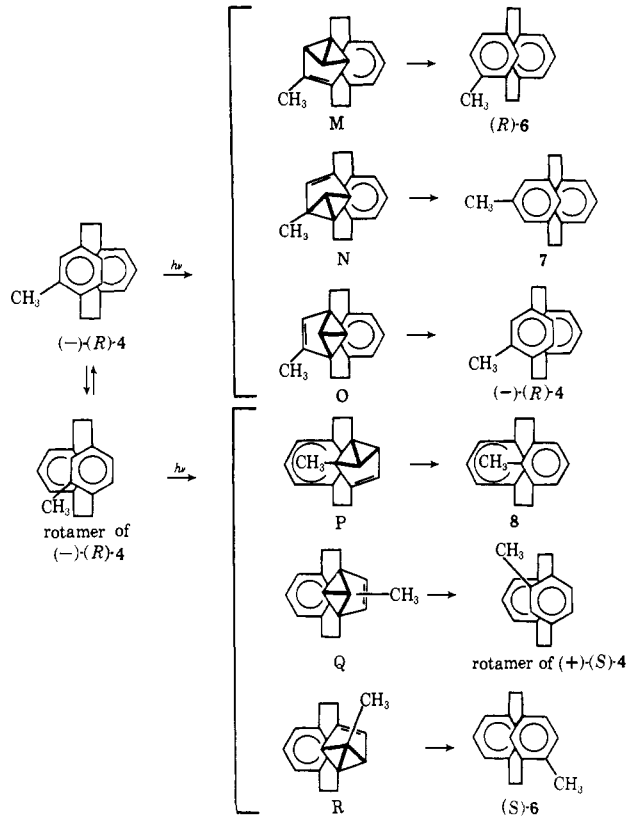


Chart IV. Benzvalene Mechanisms



ring. Alternative structures lead to [2.2]orthometacyclophanes or involve the sterically improbable reaction coordinates in which an edge of the prism butts the meta ring. The prismanes and benzene rings are presumed not to rotate with respect to one another once formed for steric reasons. The four prismanes drawn (H, J, K, and L) when *unfolded outward* lead to (*S*)-**6**, **7**, and **8**, but not to (+)-(*S*)-**4**. Unfolding the prismanes inward provides sterically less feasible reaction coordinates. Experimentally, (−)-(*R*)-**4** racemized, produced **6**, **7**, and **8** in the ratio of 7.0:4.4:1.0 (respectively) and gave **6** that was somewhat optically active. Of the four prismanes drawn, L is much more hindered than the others and is the only one that provides **8**, the isomer produced in the lowest yield. Thus the prismane mechanism accommodates the data provided that (−)-(*R*)-**4** racemizes solely by a separate mechanism, and the optically active **6** produced possesses the *S* configuration.

Chart IV lists six benzvalene structures formable in principle from (−)-(*R*)-**4** and its meta ring-flipped rotamer. Only those benzvalenes are drawn (M–R) that involve the para ring and that orient the meta benzene and the five-membered ring anti to one another. Alternative structures place the five-membered ring syn to the meta ring and provide arrangements even more sterically compromised than those drawn. Structures M–R predict only the observed products, **4**, **6**, **7**, and **8**.

Interesting structural patterns are visible in Chart IV. Routes (−)-(*R*)-**4** → M → (*R*)-**6** and [rotamer of (−)-(*R*)-**4**] → R → (*S*)-**6** if equally used would give racemic **6**, but such an event would be highly fortuitous. The dominance of (−)-(*R*)-**4** over its rotamer, coupled with the expectation that M is more stable than R (in M, the double bond is methyl substituted), point to (*R*)-**6** as the dominant enantiomer. Route (−)-(*R*)-**4** → O → (−)-(*R*)-**4** is an invisible reaction, detectable only with isotopic labels. Route [rotamer of (−)-(*R*)-**4**] → P → **8** is sterically the least probable process, and **8** is produced in the lowest yield. Route (−)-(*R*)-**4** → [rotamer of (−)-(*R*)-**4**] → Q → [rotamer of (+)-(*S*)-**4**] → (+)-(*S*)-**4** provides a means of racemizing (−)-(*R*)-**4**. Of the benzvalenes drawn only Q possesses a mirror plane.

The sterically less feasible benzvalene structures not included in Chart IV lead to either the same products as those drawn, or to [2.2]metacyclophanes with the two rings syn to one another. Similar products would be produced if M–R should undergo ring-flipping processes before decomposing to products.

Between the prismane and benzvalene mechanisms, the latter appears the more attractive, but no evidence excludes the former. However, no mechanisms other than these two fully account for the results, and one or the other probably applies.

Although [2.2]metaparacyclophane (**1**) photolytically ring contracts to [2.2]metacyclophane (**5**), [2.2]paracyclophane (**2**) fails to ring contract photolytically to [2.2]metaparacyclophane (**1**). The reduction in strain energy of about 10 kcal/mol[16] for **1** → **5** probably contributes to the occurrence of the reaction, although an 8-kcal/mol release of strain energy[16] is potentially available for the photolytically unobserved reaction, **2** → **1**. Others have noted considerable differences in the photolytic behavior of the position isomers of dialkylated benzenes, the para isomers usually being the least reactive.[17]

(16) C. Shieh, D. C. McNally, and R. H. Boyd, *Tetrahedron*, **25**, 3653 (1969).

(17) (a) U. Mende, J. L. Lasetter, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970); (b) L. Kaplan and K. E. Wilzbach, quoted in ref 17a.

Experimental Section

(+)-(*S*)- and (−)-(*R*)-Methyl[2.2]paracyclophane ((+)- and (−)-3). These compounds were available from another study[5] and the configurational assignment and synthesis of (−)-**3** have been reported by others.[18] The (+)-**3** used here gave mp 150–152°, and was of maximum rotation, $[\alpha]^{25}_{546}$ +114°, $[\alpha]^{25}_{436}$ +236° (*c* 1.00, $CHCl_3$); $[\alpha]^{25}_{546}$ +119°, $[\alpha]^{25}_{436}$ +250° (*c* 1.05, CCl_4). The (−)-**3** prepared[5] had mp 152.5–153°, $[\alpha]^{25}_{546}$ −114° (*c* 1.06, $CHCl_3$).

(−)-(*R*)-12-Methyl[2.2]metaparacyclophane ((−)-4). This substance was prepared from (+)-(*R*)-12-carboxy[2.2]metaparacyclophane[9] by the same procedure used to convert 4-carboxy[2.2]paracyclophane into **3**.[5] The starting metaparacyclophane acid gave mp 164–166°, $[\alpha]^{25}_{546}$ +33.7°, $[\alpha]^{25}_{436}$ +115° (*c* 0.99, $CHCl_3$). Its reduction (64%) gave (−)-12-hydroxymethylene[2.2]metaparacyclophane, mp 99–100°; $[\alpha]^{25}_{546}$ −7.2°, $[\alpha]^{25}_{436}$ +0.2°, $[\alpha]^{25}_{365}$ +38.2° (*c*, 0.98 $CHCl_3$); hydroxyl absorption in infrared (CH_2Cl_2), 2.78 μ; nmr ($CDCl_3$, 60 MHz) gave two superimposed spectra characteristic of racemic 12-hydroxymethylene[2.2]metaparacyclophane[9] (12 and 15 isomers) in about 2:1 ratio. Bromination of (−)-12-hydroxymethylene[2.2]metaparacyclophane with phosphorus tribromide gave (67%) (+)-bromomethylene[2.2]metaparacyclophane, mp 92–93°; $[\alpha]^{25}_{546}$ +85.7°, $[\alpha]^{25}_{436}$ +193° (*c* 0.98, $CHCl_3$). The nmr spectrum (60 MHz) of this material in $CDCl_3$ was composed of two superimposed spectra characteristic of 12- and 15-substituted isomers of [2.2]metaparacyclopane.[9] The following signals were identified: 12 isomer, δ 2.0–3.4 (m, bridge methylenes), 4.60 and 4.72 (AB quartet, J = 12 Hz, CH_2Br), 5.42 (m, *m*-ArH's), 5.78 (broad s, *p*-ArH's), 6.6–7.3 (m, ArH's, not assignable); 15 isomer, δ 2.0–3.4 (m, bridge methylenes), 3.46 and 4.30 (AX quartet, J = 11 Hz, CH_2Br), 5.85 (broad s, *p*-ArH's), 6.6–7.3 (m, ArH's, not assignable). *Anal.* Calcd for $C_{17}H_{17}Br$: C, 67.67; H, 5.69. Found: C, 68.07; H, 5.68.

Reduction of this material gave (−)-**4** (~100%), mp 65–66° (sublimation); $[\alpha]^{25}_{546}$ −26.3°, $[\alpha]^{25}_{436}$ −27.4° (*c* 1.00, $CHCl_3$); nmr ($CDCl_3$, 60 MHz) showed two superimposed spectra characteristic of the 12 and 15 isomers present in an approximate ratio of 4:1.[9] *Anal.* Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.83; H, 8.07.

Rearrangement of (+)-(*S*)-4-Methyl[2.2]paracyclophane ((+)-3) to (+)-(*S*)-12-Methyl[2.2]metaparacyclophane ((+)-4). Rearrangement of (+)-**3** (0.75 g, see above) was carried out under conditions previously reported for racemic material (**3**)[3] to give 0.74 g of crude product that was chromatographed on 120 g of silica gel. Elution of the column with pentane (25, 75-ml, then 25, 100-ml fractions) gave 0.36 g (48%) (fractions 22–37) of crystalline (+)-**4**: mp (sublimation at 50° (0.05 mm)) 61–64°; $[\alpha]^{25}_{546}$ +27.3°, $[\alpha]^{25}_{436}$ +28.2° (*c* 0.98, $CHCl_3$); $[\alpha]^{25}_{546}$ +29.5°, $[\alpha]^{25}_{436}$ +33.7° (*c* 1.02, CCl_4). Recrystallization of this material from pentane gave mp 66–67° and the identical rotation. The infrared and nmr spectra of this material were identical in all respects with those of (−)-**4**. There was no indication of the presence of 4-methyl[2.2]metaparacyclophane[3] in the purified rearrangement product. *Anal.* Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.76; H, 8.02.

A mixture of the above (+)-**4** (3.8 mg) and (−)-**4** (3.8 mg, maximum rotation) was dissolved in pentane, and the pentane was allowed to evaporate. The (±)-**4**-formed gave mp 43.5–45.5°, undepressed by admixture with authentic (±)-**4**.[3]

Photolysis of [2.2]Metaparacyclophane (1) in Cyclohexane. A solution of 0.20 g of **1** in 285 ml of cyclohexane was flushed with oxygen-free nitrogen for 30 min. The solution under nitrogen was then irradiated with a quartz U-tube, low-pressure mercury arc immersion lamp (*ca.* 2 W, 86% at λ 254 nm)[5] for 4 hr. The reaction mixture was chromatographed on 100 g of silica gel, and the column was washed with 40 50-ml fractions of pentane, then with 8 100-ml fractions of 1% ether–pentane. Fractions 34–48 gave a 50% recovery of **1** (mp 80.5–81.5°, undepressed by admixture with an authentic sample). Fractions 22–30 gave 0.042 g (42% based on consumed **1**) of [2.2]metacyclophane (**5**), mp 132–133°, undepressed on admixture with an authentic sample,[19] nmr spectrum indistinguishable from that of an authentic sample.[19]

Photolysis of [2.2]Metaparacyclophane (1) in Methanol. A solution 190 mg of **1** in 280 ml of absolute methanol was flushed with oxygen-free nitrogen for 30 min, and then under nitrogen was irradiated (same U-tube) for 6 hr. The crude product was chromatographed on 45 g of silica gel, and the column was washed with 3.5 l. of pentane, 1 l. 1% ether–pentane, and 1 l. of 50% ether–pentane. The eluate was collected in 30-ml fractions. The column eluate gave 88 mg (46%) of [2.2]metacyclophane (**5**), mp 130.5–131.5°, undepressed by admixture with an authentic sample,[19] nmr spectrum indistinguishable from that of an authentic sample.[19] Later fractions gave 57 mg (25%) of an oil: nmr spectrum ($CDCl_3$, 60 MHz), δ 2.28 (s, 3 H, $ArCH_3$), 2.90 (s, 4 H, CH_2CH_2), 3.34 (s, 3 H, CH_3O), 4.41 (s, 2 H, OCH_2), 7.06 (d, 4 H, ArH), 7.19 (s, 4 H, ArH). This ether (**12**) was identified by its nmr spectrum which was very similar to that of the open-chain methyl ether obtained by irradiation of 4-methyl[2.2]paracyclophane (**3**) in methanol.[5] An analytical sample was obtained by preparative glc.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.11; H, 8.22.

Reduction of Ether 12. The ether recovered from the photolysis of **1** in methanol was reduced with sodium in liquid ammonia by the procedure[3] used to reduce [2.2]metaparacyclophane to *m,p'*-dimethylbibenzyl (**13**). The product gave an nmr spectrum indistinguishable from **13**: ($CDCl_3$, 60 MHz) δ 2.30 (s, 6 H, CH_3), 2.83 (s, 4 H, CH_2CH_2), 7.00 (m, meta ring ArH), and 7.06 (s, para ring ArH) (total of eight aromatic protons).

Photolysis of (±)-12-Methyl[2.2]metaparacyclophane ((±)-4). A solution of 0.800 g of (±)-**4** in 855 ml of cyclohexane was divided into three equal parts. Each part was irradiated for 9 hr under conditions used for **1**. The solutions were then combined, solvent was evaporated, and the oily residue was dissolved in a minimum volume of pentane. The solution was subjected to preparative tlc on nine 20 × 20 cm plates coated with a 1-mm layer of silica gel. The plates were developed with benzene–pentane (1:10), and the bands were visualized by spraying the developed plates with water. Extraction of the silica gel with dichloromethane gave an upper band of 208 mg and a lower band of 363 mg. The lower band material crystallized, and proved to be (±)-**4** (45%, nmr indistinguishable from authentic (±)-**4**). The material from the upper band was subjected to a similar tlc separation (three 20 × 20 cm plates) to give 135 mg of an oil. Analytical glc at 177° on a 10 ft × 1/8 in. column of 5% Carbowax 20M Anakrom A indicated the presence of three components with retention times of 25 min (35%), 29 min (56%), and 33 min (8%). The maximum amount of any other volatile component was 3%. Under these conditions, (±)-**4** gave a retention time of 26 min. Preparative gas chromatography of this mixture with a 10 ft × 0.25 in. column of 10% Carbowax 20M on Chromosorb W (80–100 mesh) followed by recrystallization of each fraction from methanol gave three pure (analytical glc) compounds, **6**, 7, and **8**, characterized as follows. Compound **6**, 4-methyl[2.2]metacyclophane, gave mp 70.5–71.5°; nmr ($CDCl_3$, 60 MHz), δ 1.8–3.5 (A_2B_2 m, 8 H, CH_2CH_2), 2.36 (s, 3 H, CH_3), 4.29 (m, 2 H, C-8 and C-16 ArH), 6.85–7.33 (m, 5 H, ArH). *Anal.* Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 92.02; H, 7.96. Compound 7, 5-methyl[2.2]metacyclophane, gave mp 65–66°; nmr ($CDCl_3$, 60 MHz), δ 1.9–3.2 (A_2B_2 m, 8 H, CH_2CH_2), 2.38 (s, 3 H, CH_3), 4.16 (m, 1 H, C-8 ArH), 4.34 (m, H, C-16 ArH), 6.8–7.3 (m, 5 H, ArH). *Anal.* Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 92.02; H, 7.90. Compound **8**, 8-methyl-[2.2]metacyclophane, mp 89.0–89.5° (lit.[11] mp 91.0–91.5°); nmr[11] ($CDCl_3$, 60 MHz), δ 0.53 (s, 3 H, CH_3), 2.0–3.1 (m, 8 H, CH_2CH_2), 3.73 (s, 1 H, C-16 ArH), 6.9–7.2 (m, 6 H, ArH).

Photolysis of (−)-12-(*R*)-Methyl[2.2]metaparacyclophane ((−)-4). A solution of 200 mg of 93% optically pure (−)-**4** $[\alpha]^{25}_{436}$ −31.4° (*c* 0.85, CCl_4), mp 64–66°, prepared by rearrangement of (−)-**3**) in 280 ml of cyclohexane was irradiated for 8 hr under conditions identical with those used for **1**. The reaction mixture was chromatographed on silica gel (125 g) with pentane as developer (30-ml fractions cut). Fractions 69–119 gave 54 mg of starting material, $[\alpha]^{25}_{546}$ −3.9° (*c* 3.5, CCl_4), 13% optically pure. Thus (−)-**3** underwent 80% racemization during photolysis. Fractions 45–61 of the chromatogram gave 27 mg (18% based on (−)-**4** consumed) of a mixture of **6**, 7, and **8**, mp (after sublimation) 43–53°; $[\alpha]^{25}_{546}$ +2.6°, $[\alpha]^{25}_{436}$ +5.4°, $[\alpha]^{25}_{365}$ +10.2° (*c* 0.46, CCl_4); nmr ($CDCl_3$, 60 MHz), δ 0.52 and 2.36 (two singlet methyls), 2.1 and 3.1 (A_2B_2 m, CH_2CH_2), 3.8, 4.2, and 4.3 (m, ArH over transannular aryl), 6.8–7.3 (m, ArH). Fractions 62–68 gave 23 mg of a mixture of starting material and methyl[2.2]metacyclophanes (tlc and nmr).

(18) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4556 (1969).

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