high resonance energy. The fact that the disproportionation equilibrium $2R\cdot^- \rightleftharpoons R + R^{2-}$ is in favor of the radical anion indicates that the resonance energy in this species is closer to that of the dianion than that of the neutral annulene.

Acknowledgments. We thank Dr. P. Jung for assistance in recording the esr spectra. Our thanks are also due to Dr. L. Singer (Union Carbide Corporation, Parma Research Center) for computing the simulated esr spectra.

Macro Rings. XLVI. Solvolysis with Retention of Configuration and Cis Polar Additions in the Side-Chain Chemistry of [2.2]Paracyclophane[1]

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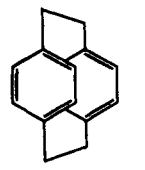
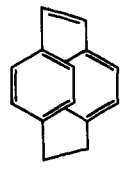
Received June 28, 1971

Abstract: Electrophilic additions to 1,2-dehydro[2.2]paracyclophane (**1**) and solvolysis of resulting products were studied. Deuterium bromide addition in nonpolar solvents and bromine addition in both aprotic and protic solvents followed a cis stereochemical course. The addition products and their diastereomers underwent silver ion catalyzed acetolysis with retention of configuration. The stereochemistries of products from both the addition and solvolysis reactions were determined by a combination of nmr and chemical techniques. Conformational factors which influence assignment of configuration to one of a pair of geometric isomers are discussed. A mechanism based on the formation of highly strained phenonium ion intermediates is used to explain the stereochemical course of both the addition and solvolysis reactions.

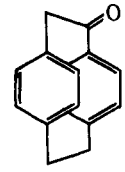
Our previous paper demonstrated the unusual solvolytic stereochemistry and reactivity in the side-chain chemistry of [2.2]paracyclophane.[2] This paper reports on the stereochemical course of electrophilic additions of 1,2-dehydro[2.2]paracyclophane (**1**), and on the reactions of the adducts. Although the methylene bridges of [2.2]paracyclophane are in a formal sense benzylic, the uv absorption spectra of the derived olefin **1**[3] and of 1-keto[2.2]paracyclophane[4] indicate that



[2.2]paracyclophane



1



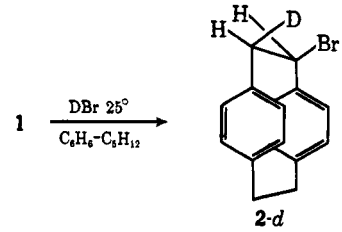
1-keto[2.2]paracyclophane

the π-electron systems of the bridge carbons and the benzene rings are essentially unconjugated with one another. The low carbonyl absorption frequency in the infrared spectrum of the ketone (1698 cm^{-1})[4] does not reflect conjugation, but rather carbonyl absorption in a large ring system.[5] Molecular models of [2.2]paracyclophane suggest a highly rigid structure which allows only slight deviation from face-to-face structures of the two benzene rings. Reviews of electrophilic additions[6] and recent investigations[7] indicate that both cis and trans products occur with hydrohalide and halogen additions to olefins. The mechanisms involve cationic intermediates, and both products and rates are highly dependent on the electrophilic agent, the solvent system, added salts, and the nature of the starting olefin.[7] The unique geometry of **1** suggested the system might exhibit unusual stereochemical behavior in directing the course of electrophilic addition reactions. The products of addition promised to be interesting starting materials for solvolytic reactions.

Results

Addition of Deuterium Bromide to 1,2-Dehydro[2.2]paracyclophane (1). Deuterium bromide in benzene–pentane at 25° was added to **1** to give within the limits of detection exclusively the product (48%) of cis addition, *cis*-1-bromo-2-deuterio[2.2]paracyclophane (**2-*d***). In the nmr spectrum of 1-bromo[2.2]paracyclophane (**2-*h***), the substituted bridge provides an ABX pattern with the highest field proton cis vicinal to the bromine on the adjacent carbon. The cis and trans coupling constants for such configurations are reported as 8.85 and 7.40 Hz, respectively.[8] In the 100-MHz nmr spectrum, the highest field proton band present for **2-*h*** was absent for **2-*d***. In the spectrum of **2-*d***, the

(1) The authors warmly thank the National Science Foundation for a grant that supported this work. Some of the results appeared in a preliminary form: R. E. Singler, R. C. Helgeson, and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 7625 (1970).
(2) R. E. Singler and D. J. Cram, *ibid.*, **93**, 4443 (1971).
(3) K. C. Dewhirst and D. J. Cram, *ibid.*, **80**, 3185 (1958).
(4) D. J. Cram and R. C. Helgeson, *ibid.*, **88**, 3515 (1966).
(5) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen and Co., London, 1968, p 123.
(6) (a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966; (b) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968); (c) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).
(7) (a) R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968); (b) J. H. Rolston and K. Yates, *ibid.*, **91**, 1469, 1477, 1483 (1969); (c) R. C. Fahey and C. A. McPherson, *ibid.*, **91**, 3865 (1969); (d) Y. Pocker, K. D. Stevens, and J. J. Champoux, *ibid.*, **91**, 4199 (1969); (e) Y. Pocker and K. D. Stevens, *ibid.*, **91**, 4205 (1969); (f) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *ibid.*, **92**, 2810 (1970); (g) R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).
(8) E. B. Whipple and Y. Chiang, *J. Chem. Phys.*, **40**, 713 (1964).

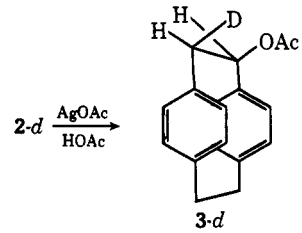


2-*d*

signals associated with the substituted bridge were reduced to an AB quartet, J_{AB} = 9 Hz. In the spectrum of 2-*d* the splittings or broadening associated with each line of the H_A doublet was attributed to geminal deuterium coupling. The nmr spectrum of 2-*d* when deuterium was decoupled supported this conclusion. The broad lines which were geminally coupled with deuterium collapsed to a sharp doublet. The outer lines, which were not highly coupled to deuterium (vicinal coupling), were not appreciably affected. Thus, both chemical shifts and coupling constants point to the product having deuterium and bromine cis to one another.

An estimate of the per cent cis addition was made using mass spectral and nmr data. The deuterium content in 2-*d* was calculated from its mass spectrum[9,10] and was found to be 5.4% d_0, 86.3% d_1, and 8.2% d_2 (1.03 atom of excess deuterium per molecule). The doubly labeled species, d_2, presumably arose through H–D exchange with the rings.[11] The nmr (100 MHz) spectrum of 2-*d* was integrated to determine the relative amounts of deuterium in the ABX portion of the spectrum. Proton H_X was set equal to unity, and its weight compared to those of H_A and H_B was determined (see Experimental Section for details). The analysis of H_A is better since it occurs in an isolated part of the spectrum, free from interference of the substituted bridge. Comparison of H_X and H_A shows 99 ± 6% cis addition. Attempts to calculate the amount of cis addition based on the H_B proton were not as successful due to the overlap with the substituted bridge. However, the integrations showed less than 0.1 atom of hydrogen in the H_B position from the addition, after subtracting the d_0 species.

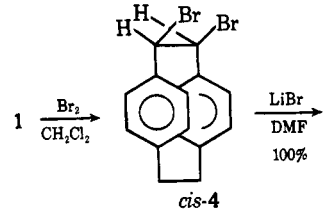
Silver Ion Assisted Solvolysis of *cis*-1-Bromo-2-deuterio[2.2]paracyclophane (2-*d*). The solvolysis of



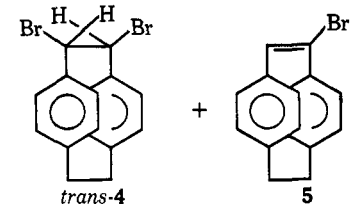
3-*d*

2-*d* provided an independent method for determining the stereochemistry of solvolysis of 1-substituted [2.2]paracyclophane derivatives.[2] The *cis*-deuterium-labeled bromide was smoothly converted to the deuterium-labeled acetate 3-*d* at 90° in 75 min. The 100-MHz nmr of 1-acetoxy[2.2]paracyclophane (3-*h*) gave 12 lines in the ABX region that resembled that of 2-*h*: for H_X, J_{AX} = 9, J_{BX} = 4 Hz; for H_A, J_{AB} = 14, J_{AX} = 9 Hz; for H_B, J_{AB} = 14, J_{BX} = 4 Hz. The deuterium-decoupled spectrum of 3-*d* gave only a pair of doublets in the same region with a coupling of 9 Hz. Clearly this large coupling indicates the two hydrogens of 3-*d* are cis to one another. Had they been trans, a vicinal coupling constant of 4 Hz would have been observed (see Table I). Mass spectral analysis of 3-*d* resembled that of 2-*d*: d_0, 5.4%; d_1, 86.3%; d_2, 8.2%; total excess atom of deuterium per molecule, 1.03. Integrations (10) of the nmr spectrum of 3-*d* coupled with mass spectral data indicated that 0.95 atom of deuterium occupied the position cis and vicinal to the acetoxy group. Clearly the acetolysis, 2-*d* → 3-*d*, proceeded with greater than 95% retention of configuration.

Addition of Bromine to 1,2-Dehydro[2.2]paracyclophane (1). Olefin 1 reacted rapidly with bromine in methylene chloride to give *cis*-1,2-dibromo[2.2]paracyclophane (*cis*-4) which contained less than 1% of the



cis-4



trans-4 5

trans isomer (*trans*-4). The configuration of the bromine adduct was shown conclusively to be cis by two chemical methods. (1) At 100° with lithium bromide in dimethylformamide, the bromine adduct isomerized to a new dibromide (58%) in which less than 1% of the initial adduct could be detected. Of the cis and trans isomers, the latter on steric grounds is expected to be the more stable. Thus, the adduct is *cis*-4, and the isomer, *trans*-4. Along with *trans*-4, vinyl bromide 5 (10%) and olefin 1 (2%) were produced. (2) Only *trans*-4 is chiral, *cis*-4 being a meso compound. Asymmetric destruction[12] of the adduct by heating in chloroform with brucine at 100° gave back adduct that exhibited no rotation, along with isomerized material that gave $[\alpha]_{546}$ +1.88° (*c* 1.13, $CHCl_3$). Isomerized material subjected to the same treatment gave recovered isomerized material, $[\alpha]_{546}$ +5.25° (*c* 1.13, $CHCl_3$). Clearly the adduct possesses the cis, and the isomerized material, the trans structure.

In acetic acid, olefin 1 with bromine gave a 35% yield of *cis*-4 and a 31% yield of *cis*-1-acetoxy-2-bromo[2.2]-

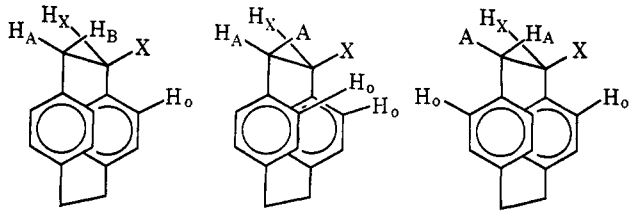
(9) K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, p 204.

(10) J. H. Beynon and A. E. Williams, "Mass Spectrometry and its Applications," Elsevier, New York, N. Y., 1960.

(11) The rate of H–D exchange (electrophilic substitution), although much slower than the rate of electrophilic addition, did bring a small amount of deuterium into the benzene ring before the addition was complete. The possibility of deuterium exchange with the vinyl protons being competitive with addition can be ruled out since work on numerous acid additions has shown that this exchange process does not occur to any appreciable extent: R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, 91, 3865 (1969), footnote 21.

(12) (a) H. J. Lucas and C. W. Gould, *ibid.*, 64, 601 (1942); (b) D. J. Cram and J. Abell, *ibid.*, 77, 1179 (1955); (c) S. J. Cristol, R. F. Stermitz, and P. S. Ramey, *ibid.*, 78, 4939 (1956); (d) P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *ibid.*, 83, 5285 (1961); (e) H. J. Reich and D. J. Cram, *ibid.*, 91, 3517 (1969).

Table I. Nmr Data for 1-Substituted and 1,2-Disubstituted [2.2]Paracyclophanes[a]

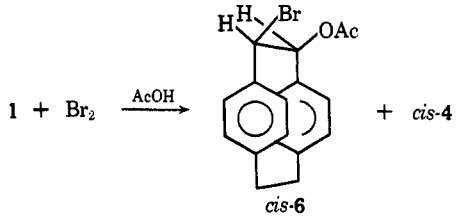


10-X *cis*-AX *trans*-AX

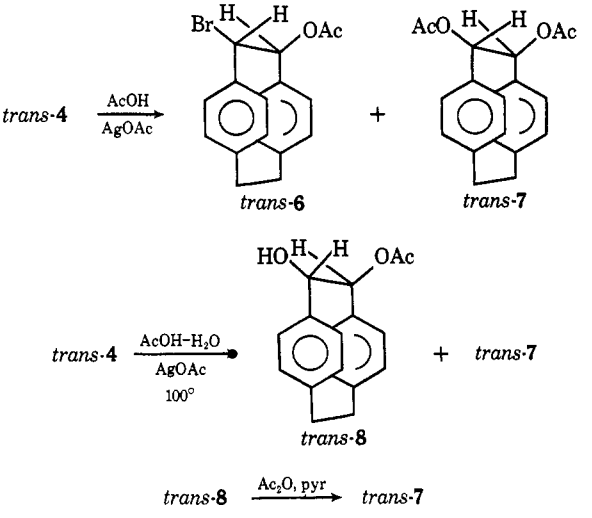
No.	Compounds: X of 10-X	*cis*-AX A	*cis*-AX X	*trans*-AX A	*trans*-AX X	Chemical shifts[b]: H_X	H_A	H_B	H_o[d]	H_o[d]	CH_3CO_2	Coupling constants[c]: J_{AX}	J_{BX}	J_{AB}[e]
	OH[f,g]					4.73	6.38	7.13	3.06			8.5	4.0	−13.5
3-*h*	OAc[g]					3.89	6.30	7.15	3.21		7.83	9.0	4.0	−14.0
	O-*tert*-Bu[h]					5.09	6.49	7.18	3.10			9.0	4.2	−13.8
2-*h*	Br[g]					4.82	6.01	6.72	3.01			9.0	7.0	−14.0
	OTs[i]					4.19	6.35	6.96	3.30			8.5	4.5	−14.0
	Cl[h]					4.84	6.10	6.89	3.05			9.0	6.0	−14.0
	OCH_3[h,i]					5.28	6.38	7.15	3.19			9.0	4.5	−14.0
	O_2CCF_3					3.70	6.24	7.01	3.16			9.0	4.0	−14.0
	O_2CH[k]					3.70	6.23	7.06	3.11			8.5	4.0	−13.5
cis-**4**		Br	Br				4.35		2.72	2.72				
trans-**4**				Br	Br		4.83		3.15	3.15				
cis-**6**		OAc	Br[l]			4.66	3.54		3.04	3.08	7.65	7.0		
trans-**6**				OAc	Br[m]	4.94	3.85		3.08	3.20	7.81	6.0		
cis-**7**		OAc	OAc				3.68		3.12	3.12	7.80			
trans-**7**				OAc	OAc		3.99		3.28	3.28	7.82			
cis-**8**		OAc	OH[n]			4.52	3.96		2.90	3.10	7.74	7.0		
trans-**8**				OAc	OH[o]	5.09	4.31		3.07	*p*	7.74	2.5		

[a] Varian A-60D analytical spectrometer with 1% TMS as internal standard and $CDCl_3$ as solvent. Concentrations 10–20% (w/v). [b] τ (±0.05 ppm). The chemical shifts of the unsubstituted bridge hydrogen (4) varied from τ 6.90 to 7.01; of the aromatic protons other than H_o (6–7) from τ 3.42 to 3.59 (centers of multiplets). [c] Hertz. [d] Doublet (1 H), $J_{ortho} \sim 8$ Hz. [e] Geminal coupling constant is assumed negative in all cases. [f] The hydroxyl proton gave τ 4.77. [g] For first preparation, see ref 4a. [h] See Experimental Section for preparation. $(CH_3)_3C$ gave τ 8.75. [i] Reference 3. [j] Reference 3, methyl group gave τ 6.54. [k] See Experimental Section. Formate hydrogen gave τ 1.69. [l] Decoupling experiment with HA-100 by irradiating H_X showed collapse of H_A to a singlet at τ 3.54. [m] Run on HA-100 machine. [n] Hydroxyl proton is τ 7.18, broad doublet. [o] Hydroxyl proton is τ 6.10, broad multiplet. [p] Only one ortho proton was observed separated from the aromatic multiplet (seven protons).

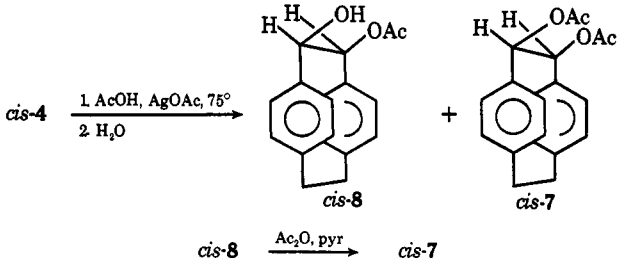
paracyclophane (*cis*-**6**). Less than 2% of *trans*-**6** (see below) could have been detected (nmr) had it been present in the reaction mixture. Under the conditions used to isomerize *cis*-**4** to *trans*-**4** (LiBr, DMF, 100°), *cis*-**6** was stable. At 135° in the same medium *cis*-**6** gave *p,p'*-dialdehydobibenzyl rather than *trans*-**6**.



Silver Ion Assisted Acetolysis of 1,2-Disubstituted [2.2]Paracyclophanes. Although inert to sodium acetate–acetic acid at 100°, and to silver acetate–acetic acid at 25°, dibromide *trans*-**4** at 75° with the latter reagent (1 mol of silver acetate/mol of dibromide) gave, besides recovered *trans*-**4** (31%), a 22% yield of *trans*-1-acetoxy-2-bromo[2.2]paracyclophane (*trans*-**6**) and a 36% yield of *trans*-1,2-diacetoxy[2.2]paracyclophane (*trans*-**7**). In "wet" acetic acid–silver acetate (excess) at 100°, *trans*-**4** gave a mixture of *trans*-**7** and *trans*-1-acetoxy-2-hydroxyl[2.2]paracyclophane (*trans*-**8**). Less than 2% of *cis*-**7** or *cis*-**8** could have been detected had they been present in this mixture (nmr). Acetylation of the mixture gave only *trans*-**7**. When optically active *trans*-**4** (from the asymmetric destruction experiment) was treated at 100° with dry acetic acid–silver acetate (excess) optically active *trans*-**7** with $[\alpha]_{546}$ +2.3° (*c* 1.03, $CHCl_3$) was the sole product. The presence of less than 2% of *cis*-**8** could have been detected (nmr). The optical activity of *trans*-**7** clearly differentiates it from *cis*-**7**, and this fact coupled with the conversion of the hydroxyacetates **8** to these diacetates **7** clearly identifies the stereostructures of *cis*-**8** (see below) and *trans*-**8**. The diastereomeric structures of the bromoacetates **6** were assigned based on nmr correlations (see next section).

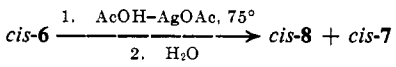


The silver ion assisted acetolysis of dibromide *cis*-**4**

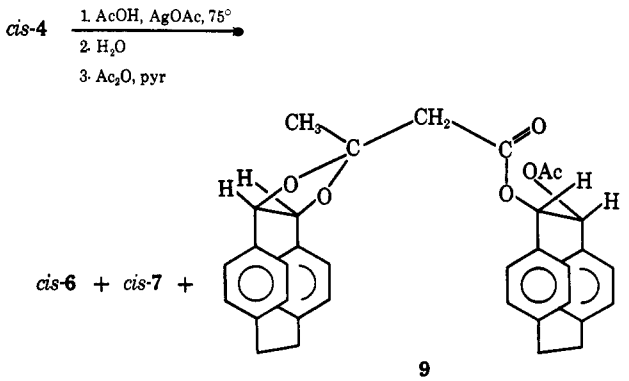


also provided highly stereospecific reactions. At high dilution in silver acetate (excess)–dry acetic acid at 70°, *cis*-**4** gave a product which when treated with water during isolation gave hydroxyacetate *cis*-**8** as the major and diacetate *cis*-**7** as the minor product (nmr). Acetylation of the total mixture gave only diacetate, *cis*-**7**. Less than 2% of *trans*-**7** could have been detected if present (nmr).

When bromoacetate *cis*-**6** was heated at 75° in dry acetic acid–silver acetate (excess), and the product isolated after a water treatment, again hydroxyacetate *cis*-**8** was the major and *cis*-**7** the minor product.



Treatment of dibromide, *cis*-**4**, with silver acetate (1.5 mol)–acetic acid at 70° at normal concentrations gave a product (after water treatment) shown by nmr to be a mixture of *cis*-bromoacetate (*cis*-**6**), *cis*-hydroxyacetate (*cis*-**8**), *cis*-diacetate (*cis*-**7**), and an unknown substance. The mixture was acetylated, and 39% *cis*-bromoacetate (*cis*-**6**) was isolated, uncontaminated with *trans*-**6** (<1.5% by nmr), as well as 20% *cis*-diacetate (*cis*-**7**), uncontaminated with *trans*-**7** (<2% by nmr). The third substance isolated was shown by elemental analysis, mass spectra, and nmr probably to possess structure **9**.

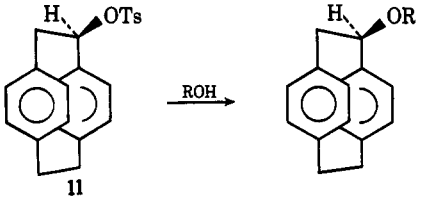


9

Nuclear Magnetic Resonance Spectra. Table I records the nmr spectra of the available bridge-substituted mono- and disubstituted [2.2]paracyclophanes. Conclusive chemical evidence for the stereostructural assignments of the dibromides **4**, the diacetates **7**, and the hydroxyacetates **8** was given in the last section. These three sets of geometric isomers of determined structure provide nmr spectra that serve as models useful in the assignment of stereostructures to the two bromoacetates, **6**. For compounds **4**, **7**, and **8**, the trans isomers gave spectra in which the chemical shift of proton H_A (and H_X for **8**) was at higher field by ~0.4 ± 0.1 ppm than the chemical shift of the analogous proton(s) of the cis isomers. In the spectra of the two bromoacetates **6**, the H_A and H_X protons of one isomer gave signals at higher fields than the corresponding protons of the other isomer, the differences being about 0.3 ppm. Accordingly, the bromoacetate with the higher field signals is assigned the trans stereostructure, and the bromoacetate with the lower field signals the cis stereostructure. The facts that compounds **4**, **6**, **7**, and **8** all possess the same nearly rigid cyclic skeleton, and that like substituents are involved (only Br, OAc, and OH), lend confidence to this assignment.

Discussion

Stereochemistry and Mechanisms for the Addition and Substitution Reactions. Within the limits of detection, the addition reactions follow a cis stereochemical course, and the solvolysis reactions occur with complete retention of configuration. Previous work[3] demonstrated that optically active tosylate **11** underwent

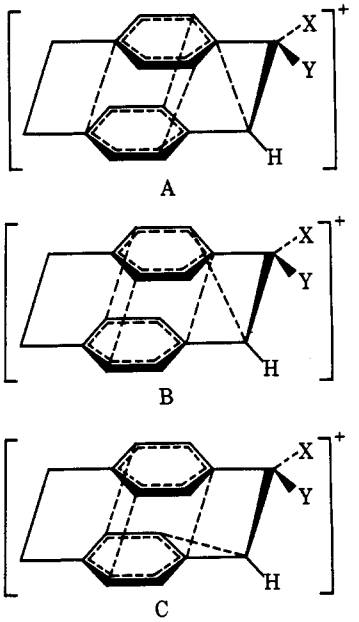


11

methanolysis, acetolysis, and trifluoroacetolysis with essentially complete retention of configuration, and that acetolysis occurred at a rate higher than expected on the basis of model compounds free of neighboring group assistance to ionization. The kinetic results suggested aryl participation in ionization, aided by the release of some π–π repulsion between the two benzene rings. The stereochemical outcome of the reaction pointed to the intervention of phenonium ions formed and decomposed with inversion at the chiral center.[3]

The present and past results correlate if one assumes that both solvolysis and electrophilic addition are dominated by aryl participation in cation formation. Several ways of delocalizing positive charge at the benzyl position into the two benzene rings (into one by relay) are envisioned in structures A, B, and C of Chart I. In

Chart I



these structures either X or Y is H, and the other is D, Br, or OAc. Structure A is a highly strained phenonium ion, whereas B and C are cations of a less usual variety. The important difference in the past and present results is the presence of bromine or acetoxyl groups on the bridge in the latter, yet the stereochemical courses of the reactions still are dominated by the aryl groups. No general correlation of the results is possible that invokes bromonium or acetoxonium ions as directing the stereochemical courses of the reactions.

Crystal-structure data[13] indicate that even at 93°K, [2.2]paracyclophane itself is equilibrating between two structures in which the methylene bridges are slightly deeclipsed. Particularly structure A would involve further deeclipsing, and redistribution of the 31 kcal of strain energy of the system,[14] which in the starting structure is concentrated somewhat in the $\pi-\pi$ repulsion between the two benzene rings.[14] Distribution of positive charge into either or both of the benzene rings should decrease this repulsion. Such distribution of positive charge acts as a driving force for several reactions of the [2.2]paracyclophane system.[15]

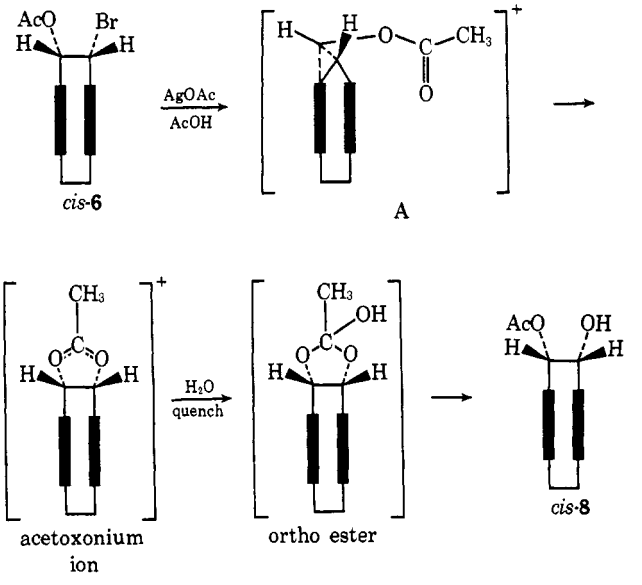
Although a clear choice between these structures is elusive, A is preferred. The points of closest approach of the two benzene rings to one another are at their bridgehead carbons, and here the $\pi-\pi$ repulsions are the greatest. Structure A more than B or C should provide the most inter-ring bonding at these positions.

Although a number of cis polar additions have been well documented in recent years[6,7] the explanation presented here is unique since it involves phenonium ion formation without rearrangement.[16] Polar additions to olefins capable of stabilization by α-phenyl have given mainly a mixture of cis and trans products, as would be expected from a benzylic carbonium ion where phenyl stabilization is competitive with halogen bridging. However, in the present case neither bromine bridging nor benzyl conjugation is observed. Likewise, silver ion assisted solvolysis reactions in vicinal systems have generally been subject to neighboring bromine or acetoxyl participation when the neighboring group has been situated trans.[17] In the present case, neighboring bromine participation is not observed, and neighboring acetoxyl involvement is observed only for the *cis*-bromoacetate (see below). In this system, a trans coplanar arrangement of leaving and neighboring bromine or acetoxyl is not possible. Thus, a phenonium ion intermediate such as A neatly explains the unusual behavior observed for these systems.

Production of *cis*-hydroxyacetate (*cis*-**8**) from *cis*-dibromide (*cis*-**4**) or *cis*-bromoacetate (*cis*-**6**), as well as formation of condensation product **9** from *cis*-**4**, indicates intervention of an acetoxonium ion intermediate when either *cis*-**4** or *cis*-**6** was treated with *dry* acetic acid–silver acetate. No *trans*-hydroxyacetate was produced in these reactions, nor in reactions of *trans*-**4** or *trans*-**6** in *dry* acetic acid–silver acetate. Since *cis*-bromoacetate (*cis*-**6**) is produced from *cis*-dibromide in dry acetic acid–silver acetate, *cis*-bromoacetate is undoubtedly the precursor of *cis*-hydroxyacetate in these dry reactions. These results indicate that neighboring acetoxyl does not displace bromide from a trans position, but only replaces bromide from a cis position. Since concerted, frontside nucleophilic displacements are unknown and improbable, the acetoxonium ion must have arisen from another intermediate ion of some kind.

Three possible ions might intervene: an open, nonsolvated secondary carbonium ion; a backside-solvated open secondary carbonium ion; or an aryl-bridged ion (A, B, or C). An open, nonsolvated secondary carbonium ion is highly unlikely, since 1-tosyloxy[2.2]paracyclophane acetolyzed 1400 times as fast[3] as 2-adamantyl tosylate,[18] and the reaction went with complete retention of configuration. A backside-solvated, open, secondary carbonium ion would have produced *trans*-hydroxyacetate (*trans*-**8**) from *cis*-bromoacetate, a process not observed. An aryl-bridged (A, B, or C) ion is a highly likely intermediate, both because reasonable alternatives are unavailable, and because the mosaic of other stereochemical results require such an intermediate for their explanation. The sequence, *cis*-**6** → A → acetoxonium ion → ortho ester → *cis*-**8**, is formulated (see Scheme I). The reason the neighboring *cis*-acetoxyl group competes successfully with solvent for opening the bridged aryl cation probably reflects the steric inhibition of solvent attack on the bridged ion by the acetoxyl group. The generation of **9** points to a ketene acetal as intermediate as well as acetoxonium ion, since its structure points to condensation of these two species. Analogies for acetoxonium ions going to ketene acetals and to ortho esters are well documented.[17]

Scheme I



Correlations of Structure with Chemical Shifts and Splitting Patterns in Proton Nuclear Magnetic Resonance Spectra. Besides providing a sound basis for assigning configurations to the *cis*- and *trans*-bromo-

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

(15) D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971).

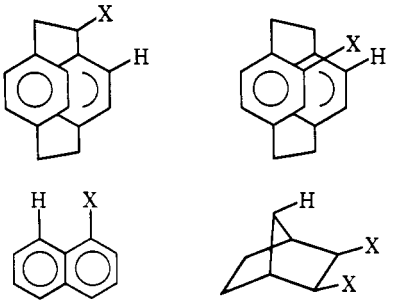
(16) Benzonorbornadiene derivatives also give cis polar additions, but rearrangements due to participating phenyl also occur: R. Caple, Fu Mei Hsu, and C. S. Ilenda, *J. Org. Chem.*, **33**, 4111 (1968).

(17) (a) S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2787 (1942); (b) R. B. Woodward and E. V. Brutcher, *ibid.*, **80**, 209 (1958); (c) B. Capon *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

(18) P. von R. Schleyer, J. L. Fry, L. K. M. Low, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970).

acetates (*cis*- and *trans*-**6**), the nmr data of Table I correlate usefully with the structures of the bridge-substituted [2.2]paracyclophanes. In all the examples listed, an electronegative atom (Cl, Br, or O) is attached directly to the nearly rigid cyclic system. Several features of the spectra are noteworthy.

The aromatic protons (H_o) ortho to the bridge and syn to the substituents are shifted downfield (15–30 Hz) from the remaining aromatic protons. This assignment is made on the basis that similar deshielding effects have been observed for the pseudogeminal proton in 4-substituted [2.2]paracyclophanes,[19] for the peri proton in 1-substituted naphthalenes,[20] and for the cis-bridge proton in exo 2,3-disubstituted norbornyl compounds.[21] What these compounds share structurally are protons whose bond axes are close to and nearly parallel with C–X bond axes where X is Cl, Br, or O.



The downfield shifts of the aromatic hydrogens ortho to the disubstituted bridge and syn to the substituents are greatest when the substituents are cis to one another. This buttressing effect indicates that *both* electronegative substituents affect both ortho-syn hydrogens in an additive and deshielding sense.

The deshielding effect of the side-chain substituent on the aromatic hydrogens is often reversed in vicinal relationships. The data in Table I show that the proton 1,2 cis to the electronegative atom (H_B) appears at a higher field than the proton which is 1,2 trans to the electronegative atom (H_A). This shielding phenomenon has been observed in a number of systems including benzocyclobutene, acenapthane, and cyclopropane derivatives.[22] This effect of increased shielding of an eclipsed β C–H by a carbon–halogen bond may be attributed to a positive magnetic anisotropy for the carbon–halogen bond.[23] A similar effect appears to be involved for the carbon–oxygen bond. Numerous examples of shielding effects and their applications to stereochemical assignments have been recently tabulated and discussed.[24]

In an attempt to correlate the chemical shifts with electronegativity, the data from Table I for the nonsubstituted compounds were used to calculate the internal chemical shifts ($\Delta\delta$). These were compared to the known electronegativity values in a manner similar to what has been done in the norbornyl system.[25] Although the internal chemical shifts do increase with increasing electronegativity, the trend is not linear. Consistent with the chemical-shift assignments is the observation that the cis vicinal coupling constant (J_{AX}) is larger than the trans vicinal coupling constant (J_{BX}) for the 1-substituted [2.2]paracyclophanes (Table I). This trend is the same for the other cyclic systems cited.[22]

Experimental Section

Reagents and Instruments. Reagent grade chemicals were used except where noted. Dry acetic acid (1% by weight acetic anhydride) was used in addition and solvolysis experiments. Technical grade pentane was distilled prior to use. Melting points were taken on a Hoover Uni-Melt Bath and are uncorrected. Mass spectra were obtained on an AEI MS9 instrument at 12 and 70 eV, using both heated inlet and direct insertion techniques. The deuterium analyses were performed using an external L & N recorder. The nmr spectra were recorded with either a Varian Associates A-60D or HA-100 spectrometer, using 10–20% w/v solutions in $CDCl_3$ with 1% TMS as an internal standard. Optical rotations were observed on a Perkin-Elmer Model 141 polarimeter, using a 1-dm cell thermostated at 25.0 ± 0.05°, employing spectrograde solvents. Infrared spectra were recorded on a Beckman IR-5 spectrophotometer; solutions were 5–10% w/v in spectograde chloroform as solvent. Baker reagent grade, Merck (30–70 mesh), or Mallinckrodt SilicAr (100–200 mesh) silica gels were used in column chromatographs. In general, the material to be chromatographed was packed on ten times its weight of silica gel prior to chromatography, and 40-ml fractions were collected.

Addition of Deuterium Bromide to 1,2-Dehydro[2.2]paracyclophane (1). Phosphorus tribromide (4 ml) and deuterium oxide (1.0 ml, 99.8% *d*) were gently warmed in a thoroughly dried flask under dry nitrogen. The deuterium bromide generated was swept into a dry cold trap. A mixture of 2 ml of the condensed deuterium bromide, 200 mg of **1** dissolved in 4 ml of benzene, and 2 ml of pentane was sealed in a tube. The solution was 0.048 *M* in **1** and 4.5 *M* in deuterium bromide. After standing at 25° for 21 hr, the tube was carefully opened, and the solvent was removed to give 301 mg of material which was mainly *cis*-1-bromo-2-deuterio[2.2]paracyclophane (**2-*d***) according to the nmr spectrum. The material was chromatographed on 30 g of SilicAr. No compounds were eluted with 200 ml of pentane. Elution with 240 ml of 1% ether–pentane gave approximately 7 mg of **1**, identified by tlc. Further elution with 240 ml of 1% ether–pentane gave 133 mg (48%) of **2-*d***, identified by tlc, nmr, and mass spectral comparisons. Elution with 250 ml of 2% and 250 ml of 10% ether–pentane gave no compounds. Further elution with 250 ml of 20% and 250 ml of 25% ether–pentane gave 52 mg of 1-hydroxy-2-deuterio[2.2]paracyclophane, identified by tlc comparisons and subsequent nmr and mass spectral analysis. Elution with 50–100% ether–pentane gave no compounds. The sample of **2-*d*** was recrystallized from ether (53 mg), mp 120–122°. The mother liquor was rechromatographed to give 37 mg of **2-*d*** and 19 mg of 1-hydroxy-2-deuterio[2.2]paracyclophane. The samples of **2-*d*** were combined and sublimed (90°, 0.030 mm)) for the analyses: mp 121–123° (lit.[4a] 121.4–122.0°); 79 mg/0.4 ml of $CDCl_3$–TMS solvent for nmr analysis.

Analysis of 1-Bromo-2-deuterio[2.2]paracyclophane (2-*d*). The product of deuterium bromide addition (**2-*d***) was submitted to 100-MHz nmr analysis by repeated (ten) integrations of **2-*d*** and **2-*h***. One standard deviation was set as a limit of error. For **2-*h***, the number of hydrogens was calculated as follows. The sum of the units for all signals was divided by 15, the number of hydrogens in the molecular formula, and the average number of units per proton obtained. This number was divided into the number of units associated with each kind of proton to give the relative number of each kind of proton: aryl protons, 8.05 ± 0.09; H_X, 0.91 ± 0.04; H_A 0.98 ± 0.02; H_B + protons of unsubstituted bridge, 5.08 ± 0.12. For **2-*d*** the same procedure was used except that the number of hydrogens in the molecular formula (mass spectra) was 13.97. Values were as follows: aryl protons, 7.94 ± 0.30; H_X, 0.96 ± 0.06; H_A, 0.95 ± 0.06; H_B + protons of unsub-

(19) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3534 (1969).
(20) (a) G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963); (b) J. Paviot and J. Hoaran, *J. Chim. Phys.*, **64**, 1415 (1967).
(21) W. C. Thorpe and W. C. Coburn, Jr., *J. Org. Chem.*, **34**, 2576 (1969).
(22) (a) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964); (b) M. J. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2704 (1963); (c) J. D. Graham and M. T. Rogers, *ibid.*, **86**, 2249 (1964).
(23) T. L. Flautt and W. F. Erman, *ibid.*, **85**, 3212 (1963).
(24) L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, Chapter 3–8.
(25) (a) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Amer. Chem. Soc.*, **86**, 762 (1964); (b) P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2709 (1963).

stituted bridge, 4.14 ± 0.16. Proton H_X was set equal to unity, and for **2-*d***, H_A/H_X = 0.99 ± 0.06. Thus, cis addition was 99 ± 6% stereospecific.

The analysis of 1-acetoxy-2-deuterio[2.2]paracyclophane (**3-*d***) obtained by acetolysis of **2-*d*** (see below) was performed the same way with very similar results.

1-Chloro[2.2]paracyclophane. Approximately 3 ml of anhydrous hydrogen chloride was condensed in a test tube at −100°, and then 66 mg of olefin **1** in 7 ml of methylene chloride was added. The tube was sealed and left at 25° for 27 hr. Isolation gave 120 mg of a mixture of two compounds, according to nmr, which was chromatographed on 12 g of SilicAr. Elution with 500 ml of pentane gave 21 mg (19%) of olefin **1** followed by, after several empty fractions, 76 mg (56%) of 1-chloro[2.2]paracylophane, which was recrystallized from pentane and sublimed (85° (0.025 mm)): mp 120–122°; nmr (Table I); mass spectrum (12 eV) *m/e* (relative intensity) 104 (100), 117 (13), 138 (45), 140 (15), 206 (16), 208 (52), 209 (12), 242 (36), 244 (12). *Anal.* Calcd for $C_{16}H_{15}Cl$: C, 79.17; H, 6.23. Found: C, 79.41; H, 6.17.

Acetolysis of 1-Bromo-2-deuterio[2.2]paracyclophane (2-*d*). A suspension containing 79 mg (0.27 mmol) of **2-*d***, 65 mg (0.39 mmol) of silver acetate, and 7 ml of acetic acid was stirred at 90° for 85 min. The suspension was added to 100 ml of water and extracted with ether. The ether solution was washed with a sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 79 mg of material which was chromatographed on 7 g of SilicAr. Elution with 5% ether–pentane gave 60 mg (81%) of 1-acetoxy-2-deuterio[2.2]paracyclophane (**3-*d***) which was sublimed: 57 mg; mp 105–106° (lit. 104–105°).[3] The nmr analysis (57 mg/0.4 ml of $CDCl_3$–TMS) and mass spectral analysis confirmed the structure. No olefin **1** (elution with pentane) nor 1-hydroxy[2.2]paracyclophane (elution with 10–100% ether–pentane) was isolated from the chromatogram.

Bromine Addition to 1,2-Dehydro[2.2]paracyclophane (1) in Methylene Chloride. A. Analytical Run. To a solution containing 100 mg (0.49 mmol) of **1** and 20 ml of methylene chloride was added 0.75 mmol of bromine in 4 ml of methylene chloride over a 15-min period. The solution was stirred for an additional 30 min and was kept in the absence of light during the total reaction time. The methylene chloride solution was then extracted with a sodium thiosulfate solution to remove the excess bromine and dried over magnesium sulfate. The solvent was evaporated leaving a light colored solid, which was characterized as *cis*-1,2-dibromo-[2.2]paracyclophane (*cis*-**4**) by tlc comparison with an authentic sample.[4a,26] A 15% w/v solution was prepared using the crude product. The nmr analysis showed no presence of *trans*-**4** up to a spectrum amplitude of 80 using the Varian A-60. With the time-averaging computer attachment (Varian C-1024) and a scan of the substituted bridge region, less than 1% of the *trans*-dibromide was observed compared to the same nmr analysis on control samples.

The crude mixture was then chromatographed on 25 g of silica gel. Elution with 1 l. of pentane and 200 ml of 1% ether–pentane gave a trace of *trans*-dibromide (<1 mg) which was identified by tlc comparison with authentic material prepared as described below. Further elution with 300 ml of 1% ether–pentane gave 174 mg (98%) of *cis*-dibromide: mp 160° dec which was recrystallized from ether–pentane; mp 161–163° dec (lit.[4a] 163–165°); nmr, see Table I; mass spectrum (70 eV) *m/e* (relative intensity) 189 (16), 191 (20), 206 (100), 364 (0.5), 366 (0.9), 368 (0.5). The *cis*- and *trans*-dibromides (*cis*- and *trans*-**4**) displayed R_f values on tlc of 0.3 and 0.4, respectively, with 6% ethyl acetate–cyclohexane as a developer. *Anal.* Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85. Found: C, 52.39; H, 3.95.

Lithium Bromide Isomerization of *cis*-1,2-Dibromo[2.2]paracyclophane (*cis*-4) to *trans*-4. A solution containing 106 mg of the *cis*-dibromide (*cis*-**4**) in 11 ml of a 1 *M* solution of lithium bromide in dimethylformamide was stirred at 25° for 7 days. Isolation followed by nmr and tlc analysis showed only the presence of starting material, indicating that no isomerization had occurred.

A solution containing 30 ml of dimethylformamide, 2.55 g of lithium bromide (predried at 100°), and 1090 mg of *cis*-dibromide was heated at 100° for 9 days in a sealed tube. A slight amount of discoloration and precipitation occurred during this time. The tube was carefully opened, the reaction was added to 200 ml of water, and the precipitate was extracted with 100 ml of ether. The ether layer was dried and evaporated partially to give 211 mg of the *trans*-bromide, mp 238–242°. The residue was chromatographed on 100 g of silica gel. Elution of the column with pentane gave 101 mg of a mixture of two compounds which according to tlc with 6% ethyl acetate–cyclohexane as a developer were olefin **1** (R_f 0.59), and 1-bromo-1,2-dehydro[2.2]paracyclophane (**5**) (R_f 0.56). The vinyl protons of the monoolefin and vinyl bromide (see below) appear as singlets at τ 2.73 and 2.50, respectively. Integration of these singlets gave a 16:84 molar ratio which corresponds to a 2% yield of the olefin and a 10% yield of the vinyl bromide, based on starting material. Although the R_f values on tlc are almost equal, the olefin spots heavier with iodine as a developer, a fact that makes it easy to distinguish the two compounds in a mixture. Elution with 1 and 2% ether–pentane gave 422 mg of the *trans*-dibromide: mp 242–244° dec; mass spectrum (70 eV) (relative intensity) 182 (18), 184 (17), 206 (100), 285 (1.4), 287 (1.4), 364 (1.9), 366 (3.6), 368 (1.9). A sample was sublimed (120° (0.015 mm)); mp 244–246° dec). The total amount of *trans*-**4** obtained was 633 mg (58%). *Anal.* Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85. Found: C, 52.62; H, 3.93.

None of the cis isomer was obtained from the chromatogram. Materials of longer retention time on tlc were eluted from the chromatogram with 10–50% ether–pentane. These were not positively characterized, but they appeared to be solvolysis products (~5% yield).

Attempted Isomerization of *trans*-1,2-Dibromo[2.2]paracyclophane (*trans*-4). A solution containing 122 mg of *trans*-**4**, 125 mg of lithium bromide, and 10 ml of dimethylformamide was heated in a sealed tube for 8 days. Work-up gave 124 mg of material, which was chromatographed on 15 g of silica gel to give only 100 mg (82%) of *trans*-**4**, and trace amounts of olefin **1** and the vinyl bromide **5**, identified by tlc. No *cis*-1,2-dibromo[2.2]paracyclophane was detected in eluate from the chromatogram.

Treatment of *cis*-1,2-Dibromo[2.2]paracyclophane (*cis*-4) with Brucine. A solution containing 200 mg (0.55 mmol) of *cis*-**4**, mp 160–163°, 433 mg (1.1 mmol) of brucine, and 10 ml of chloroform was heated at 100° in a sealed tube for 15 days. Isolation gave 218 mg of crude material which showed the presence (tlc) of both dibromides. According to nmr, the composition was 54% cis and 46% trans, obtained by integration of the respective two-proton singlets for the substituted bridge. Chromatography of the mixture on 25 g of silica gel gave a trace amount (<5 mg) of a mixture of olefin **1** and vinyl bromide **5** identified by tlc. Further elution with pentane gave 58 mg (29%) of *trans*-**4** which was sublimed to give a sample for rotations with 40.5 mg in 2 ml of chloroform (Table II). The *trans*-**4** was not contaminated with *cis*-**4** or any other material according to tlc. Rotations were as shown in Table II. The polarimeter was zeroed with solvent before and after rotations of dibromides at 546 nm and corrected at other wavelengths. Immediately after *trans*-**4** was removed from the chromatogram, the *cis*-**4** started to appear. It was eluted with pentane giving 68 mg (34%), mp 162–163.5°. Rotations were taken on sublimed material (100° (0.010 mm)) with a concentration of 39.5 mg in 2 ml of chloroform. The slight positive observed rotations for two of the wavelengths are within the limits of measurement for the polarimeter (±0.002°) and are considered to be zero. Further elution with up to 100% ether gave no discernible products such as alcohols or open-chain materials.

Table II

λ, nm	Isomerized dibromide (*trans*-4) α_{obsd}, deg	Starting dibromide (*cis*-4) α_{obsd}, deg
589	+0.029	+0.002
578	+0.033	+0.000
546	+0.038	+0.000
436	+0.082	+0.000
365	+0.214	+0.001

Treatment of *trans*-1,2-Dibromo[2.2]paracyclophane (*trans*-4) with Brucine. A solution containing 200 mg of *trans*-**4** (0.55 mmol, mp 245–247°, crystallized from ether–pentane), 433 mg of brucine (1.1 mmol), and 10 ml of chloroform was heated at 100° for 12 days in a sealed tube. Isolation gave 238 mg which showed the presence of starting material and a trace of vinyl bromide **5** according to tlc. Chromatography of the material on 25 g of silica gel and elution with pentane gave a small amount (less than 5

(26) In the original preparation (ref 4a), this compound was mistakenly assigned the trans configuration.

mg) of **5** identified by tlc. Further elution with pentane gave 143 mg (72%) of *trans*-**4** which was sublimed (110° (0.015 mm)), mp 241.5–244°. A solution containing 40.4 mg in 2 ml of chloroform was used for rotations (see Table III). The machine was zeroed

Table III

λ, nm	α_{obsd}, deg	$[\alpha]_\lambda$, deg
589	+0.090	+4.45
578	+0.090	+4.45
546	+0.106	+5.25
436	+0.234	+11.6
365	+0.608	+30.1

with solvent at 546 nm before and after taking rotations. The values obtained at the other wavelengths were corrected. Further elution of the chromatogram with pentane produced no *cis*-**4**.

Thermal Isomerization of *cis*-1,2-Dibromo[2.2]paracyclophane (*cis*-4). Upon treatment with brucine in chloroform at 100°, *cis*-**4** underwent partial isomerization to *trans*-**4** (see above). Without brucine, *cis*-**4** also underwent partial isomerization when a solution containing 125 mg of the dibromide and 12 ml of chloroform was heated for 28 days at 100°. Chromatography of recovered material gave 2 mg (2%) of vinyl bromide **5**, 60 mg (48%) of *trans*-**4**, 9 mg (7%) of *cis*-**4**, and 6 mg (7%) of open-chain material (aromatic nmr spectrum). The exact mechanism of this thermal isomerization is not clear, but it probably involved a diradical form as was observed for [2.2]paracyclophane itself.[12e]

1-Bromo-1,2-dehydro[2.2]paracyclophane (5). A solution containing 105 mg (0.29 mmol) of *trans*-**4**, 208 mg (1.7 mmol) of 1,5-diazabicyclo[4.3.0]non-5-ene, and 5 ml of dimethyl sulfoxide was heated in a sealed tube at 75° for 15 hr. The solution was then added to a dilute hydrochloric acid solution and extracted with ether. Isolation gave 81 mg of material which contained *trans*-**4** and -**5** according to nmr and tlc analysis. Chromatography of the mixture on 10 g of silica gel and elution with pentane gave 40 mg (49%) of vinyl bromide **5**. The sample was recrystallized from ether–pentane: mp 112–113°; nmr ($CDCl_3$) 2.50 (s, 1, vinyl), 3.49 (s, 4, aromatic), 6.99 (s, 4, benzyl); mass spectrum (70 eV) *m/e* (relative intensity) 102 (17), 205 (100), 284 (56), 286 (56). *Anal.* Calcd for $C_{16}H_{13}Br$: C, 67.39; H, 4.59. Found: C, 67.55; H, 4.63.

Further elution of the column with pentane gave 16 mg (15%) of starting material (*trans*-**4**). No further material was obtained upon elution with up to 100% ether.

Bromine Addition to 1,2-Dehydro[2.2]paracyclophane (1) in Acetic Acid. To a solution containing 727 mg (3.5 mmol) of olefin **1**, 35 ml of acetic acid, and 4 g of anhydrous sodium acetate was added 4.2 mmol of bromine in 3 ml of acetic acid over a 15-min period. The reaction was stirred for an additional 45 min, then added to 200 ml of water, and the excess bromine was reduced with a sodium thiosulfate solution. The solution was extracted with 100 ml of ether, which was washed with a sodium bicarbonate solution to remove acetic acid, and then dried over magnesium sulfate. The dried ether solution gave 1295 mg of material which showed two major components according to tlc analysis. The mixture was chromatographed on 112 g of Merck silica gel. Elution of the column with 1 l. of pentane gave no compounds. Elution with 500 ml of 1% ether–pentane gave 25 mg (3%) of starting material **1**. Elution with 800 ml of 2% ether–pentane gave 429 mg (35%) of *cis*-dibromide (*cis*-**4**), mp 160–164°. Analysis of this product did not reveal the presence of any *trans*-**4** (less than 1% trans addition as described above). Elution of the column chromatogram with 250 ml of 4% ether–pentane and 250 ml of 5% ether–pentane gave no compounds. Further elution with 400 ml of 5% ether–pentane gave 372 mg (31%) of *cis*-1-acetoxy-2-bromo-[2.2]paracyclophane (*cis*-**6**): mp 169–171°; nmr, see Table I; mass spectrum (70 eV) *m/e* (relative intensity) 105 (11), 120 (100), 183 (9), 185 (8), 206 (53), 223 (50), 344 (7), 346 (7); tlc (R_f 0.63, 15% EtOAc–C_6H_{12}). A sample was recrystallized from ether–pentane: mp 170–171°. *Anal.* Calcd for $C_{18}H_{17}O_2Br$: C, 62.61; H, 4.97. Found: C, 62.72; H, 5.05.

None of the *trans*-bromoacetate (*trans*-**6**) was detected from the chromatogram. Less than 1.5% of this isomer could be easily observed by nmr analysis of the acetate protons (τ 7.5–8.0) and comparison with control samples. Further elution of the chromatogram with 10–100% ether–pentane mixtures gave no discernible compounds.

Attempted Isomerization of *cis*-1-Acetoxy-2-bromo[2.2]paracyclophane (*cis*-6). A 1 *M* solution of lithium bromide in 10 ml of dimethylformamide containing 100 mg of *cis*-**6** was heated at 135° for 7 days. The reaction mixture was added to 100 ml of water and extracted with 100 ml of ether. The extract was dried with magnesium sulfate, and the ether was evaporated to give 136 mg which was chromatographed on 13 g of silica gel. Elution of the column with 5% ether–pentane gave 60 mg of material identified as diphenylethane-4,4′-dialdehyde: ir ($CHCl_3$) 1690 cm^{-1} (C=O); nmr ($CDCl_3$) τ 0.07 (s, 2, CHO), 2.72, 2.22 (A_2B_2 quartet, 8, J = 7 Hz, C_6H_4), 6.96 (s, 4, CH_2CH_2). Sublimation gave material which melted at 123–128° (lit.[27] mp 126°). Further elution of the column with up to 10% ether–pentane mixtures gave no discernible compounds such as starting material (*cis*-**6**) or isomerized bromoacetate (*trans*-**6**).

Dry Acetolysis of *trans*-1,2-Dibromo[2.2]paracyclophane (*trans*-4). A mixture containing 189 mg (0.052 mmol) of *trans*-**4**, 86 mg (0.052 mmol) of silver acetate, and 10 ml of dry acetic acid was heated at 75° for 6.5 hr. The mixture was added to 100 ml of water and extracted with 100 ml of ether, and the ether solution was washed with sodium carbonate solution and dried to give 178 mg of material. This recovered material showed only the presence of *trans*-**4**, *trans*-**6**, and *trans*-**7** according to nmr and tlc analysis. This material was chromatographed on 18 g of Merck silica gel. Elution of the column with 500 ml of pentane and 200 ml of 1% ether–pentane gave no compounds. Further elution with 1 and 2% ether–pentane (400 ml total) gave 59 mg (31%) of starting material (*trans*-**4**). Elution with an additional 200 ml of 2% ether–pentane gave no compounds. Elution with 200 ml of 5% ether–pentane gave 39 mg (22%) of *trans*-1-acetoxy-2-bromo[2.2]paracyclophane (*trans*-**6**): mp 148–153°. The nmr spectrum of this chromatographed material showed that no *cis*-**6** was present, based on inspection of the acetate methyl region (τ 7.5–8.0). Comparison with control samples showed that less than 1.5% of *cis*-**6** could have been detected in the presence of *trans*-**6**. The product was crystallized from ether–pentane and sublimed (100° (0.015 mm)): mp 148–150.5°; mass spectrum (70 eV) *m/e* (relative intensity) 105 (16), 120 (100), 183 (5), 185 (5), 206 (45), 223 (33), 344 (4), 346 (4). *Anal.* Calcd for $C_{18}H_{17}BrO_2$: C, 62.62; H, 4.96. Found: C, 63.01; H, 5.20.

Repeated recrystallizations did not improve the analysis, and so a high-resolution mass measurement was obtained. Using perfluorotri-*n*-butylamine as a standard, a resultant mass of 344.04113 was obtained (reference peak, 325.98390). Subtraction of ^{79}Br gives a mass of 265.12274. The calculated mass for $C_{18}H_{17}O_2$ is 265.12285; this is the most reasonable empirical formula for the experimentally determined value.[28]

Elution of the chromatogram with an additional 300 ml of 5% ether–pentane and 100 ml of 10% ether–pentane produced no compounds. Elution with 500 ml of 10% ether–pentane gave 61 mg (36%) of *trans*-1,2-diacetoxy[2.2]paracyclophane (*trans*-**7**), mp 148–150.5°. The nmr spectrum of this chromatographed material showed that no *cis*-**7** was present, based on observation of the substituted bridge region (τ 3.6–4.0). Comparison with control samples showed that less than 2% of *cis*-**7** could have been detected in the presence of *trans*-**7**. The chromatographed material was recrystallized from ether–pentane and sublimed (105° (0.015 mm)): mp 149–151°; mass spectrum (70 eV) *m/e* (relative intensity) 105 (11), 120 (65), 206 (39), 239 (100), 281 (26), 324 (5). *Anal.* Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.17; H, 6.22.

Further elution of the column with 10% ether–pentane gave no compounds. Total yield from the chromatogram was 89%. A mixed melting point determination on a sample of *trans*-**7**, mp 148–150.5°, and *trans*-**6**, mp 149–151°, melted at 132–142°.

In a separate experiment, 100 mg of *trans*-**7** and 97 mg of silver acetate were heated at 100° in 20 ml of dry acetic acid for 38 hr. Isolation by chromatography as above gave 66 mg (75%) of *trans*-**7**, mp 148–150.0°. The nmr analysis showed that none of *cis*-**7** was present before and after chromatography, within the limits of detection (2%). Only *trans*-**7** was obtained from the chromatogram.

"Wet" Acetolysis of *trans*-1,2-Dibromo[2.2]paracyclophane (*trans*-4). A mixture containing 100 mg (0.27 mmol) of *trans*-**4**, 101 mg (0.6 mmol) of silver acetate, 50 μl (2.8 mmol) of water, and 5 ml of

(27) T. Reichstein and R. Oppenauer, *Helv. Chim. Acta*, **16**, 1373 (1933).

(28) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectroscopy," Elsevier, New York, N. Y., 1963.

glacial acetic acid was stirred at 85° for 11 hr. The acetic acid contained a few per cent of water. Isolation in the usual manner gave 103 mg of material which showed two methyl groups in the nmr in a mole ratio of approximately 15:85 for *trans*-hydroxyacetate (*trans*-**8**) and *trans*-diacetate (*trans*-**7**), respectively. The mixture was acetylated with acetic anhydride–pyridine to give 86 mg (77%) of *trans*-**7** according to nmr. No *cis*-**7** could be detected in the nmr.

Dry Acetolysis of Optically Active *trans*-1,2-Dibromo[2.2]paracyclophane ((+)-*trans*-4). A mixture containing 79 mg (0.22 mmol) of (+)-*trans*-**4**, $[\alpha]_{546}$ +5.25° (*c* 2.0, $CHCl_3$), 72 mg (0.43 mmol) of silver acetate, and 4.5 ml of dry acetic acid was heated at 85° for 10 hr. Isolation gave 84 mg of material which was pure *trans*-**7** according to tlc: $[\alpha]_{546}$ +1.6° (*c* 3.0, $CHCl_3$). This material was chromatographed on 9 g of Merck silica gel. Elution with 100 ml of pentane, 250 ml of 1%, 500 ml of 2%, 100 ml of 3%, and 500 ml of 5% ether–pentane gave no compounds. Further elution with 480 ml of 5% ether–pentane gave 54 mg (71%) of (+)-*trans*-**7**: mp 147–150°; $[\alpha]_{546}$ +2.1°. Further elution of the chromatogram with up to 100% ether gave no compounds. The chromatographed material was then sublimed: mp 148–151.5° (racemic *trans*-**7**, mp 149–151°); $[\alpha]_{546}$ +2.3°, $[\alpha]_{436}$ +4.6° (*c* 3.92, $CHCl_3$).

***trans*-1-Hydroxy-2-acetoxy[2.2]paracyclophane (*trans*-8).** An asymmetric transesterification was attempted on *trans*-**7**. To a solution containing 100 mg (0.64 mmol) of *l*-menthol and 5 ml of benzene (distilled from lithium aluminum hydride) was added 0.27 ml (0.44 mmol) of an *n*-butyllithium solution in hexane. A solution containing 70 mg (0.22 mmol) of *trans*-**7** in 5 ml of benzene was added over a 15-min period. The solution was stirred at 25° for 2 hr. The reaction was quenched by adding wet ether. The organic layer was washed with dilute hydrochloric acid and with a sodium bicarbonate solution, and was dried. The ether solution was evaporated to give 142 mg of material that contained *trans*-**7** and *trans*-**8** according to nmr analysis. The crude material was chromatographed on 14 g of Merck silica gel. Elution of the column with up to 5% ether–pentane yielded only traces of compounds containing the odor of menthol or its derivatives. Once the odor of menthol was not detectable in the column eluates, the column was eluted with 10% ether–pentane, giving 16 mg (23%) of *trans*-**7** which was sublimed: mp 148–150°; $[\alpha]_{546}$ −8.0° (*c* 1.1, $CHCl_3$). Elution of the column with 15% ether–pentane yielded 26 mg (43%) of *trans*-**8** which was sublimed (110° (0.015 mm)): mp 145–149°; nmr, see Table I; mass spectrum (70 eV) *m/e* (relative intensity) 105 (27), 120 (100), 239 (65), 282 (5). *Anal.* Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.50; H, 4.23.

This material (*trans*-**8**) was acetylated in the usual manner to give 28 mg of *trans*-diacetate (*trans*-**7**) which was sublimed: mp 148–150°; $[\alpha]_{546}$ −0.5° (*c* 1.9, $CHCl_3$). Further elution of the chromatogram gave materials that were not identified.

Acetolysis of *cis*-1,2-Dibromo[2.2]paracyclophane (*cis*-4). A. High Dilution. A suspension containing 52 mg (0.14 mmol) of *cis*-**4**, 59 mg (0.35 mmol) of silver acetate, and 10 ml of dry acetic acid was stirred at 75° for 2.5 hr. The suspension was added to 100 ml of water and extracted with ether, and the ether layer was neutralized with a sodium carbonate solution and dried. Evaporation of the ether gave 45 mg of a mixture of *cis*-hydroxyacetate (*cis*-**8**) and *cis*-diacetate (*cis*-**7**) in a greater than 7:1 ratio according to nmr. The mixture was dissolved in 0.5 ml of acetic anhydride and 0.5 ml of pyridine. After standing at 25° for 20 hr, the solution was added to 100 ml of water, neutralized with dilute hydrochloric acid, and extracted with ether. The ether layer was washed with a sodium carbonate solution, dried, and evaporated to give 44 mg (96%) of *cis*-1,2-diacetoxy[2.2]paracyclophane (*cis*-**7**): mp 182–185°; nmr, see Table I; mass spectrum (70 eV) *m/e* (relative intensity) 105 (19), 120 (74), 239 (100), 281 (38), 324 (2). The nmr spectrum of recovered material showed that none of the *trans*-diacetate (<2%) was present by comparison of the substituted bridge region of the product with that of standard samples. The product was recrystallized from an ether–pentane–methylene chloride solution: mp 187–189°. *Anal.* Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.99; H, 6.28.

B. High Concentration. A suspension containing 250 mg (0.68 mmol) of *cis*-**4**, 171 mg (1 mmol) of silver acetate, and 10 ml of dry acetic acid was stirred at 70° for 5 hr. The reaction mixture was quenched and the product isolated as described above to give 232 mg of material which preliminary nmr analysis revealed to be a mixture of *cis*-bromoacetate (*cis*-**6**), *cis*-diacetate (*cis*-**7**), *cis*-hydroxyacetate (*cis*-**8**), and an unknown compound. The mixture was acetylated to give 205 mg of material which was chromatographed on 15 g of SilicAr. Elution of the column with up to 2% ether–pentane gave no compounds. Elution with 250 ml of 3% ether–pentane gave 91 mg (39%) of *cis*-bromoacetate (*cis*-**6**), mp 169–171°, undepressed by admixture with an authentic sample of *cis*-**6**. The nmr spectral analysis of the acetate methyl region did not reveal the presence of any of the *trans*-bromoacetate (<1.5%). Elution of the chromatogram with 250 ml of 5% and 200 ml of 10% ether–pentane gave no compounds. Further elution with 360 ml of 10% ether–pentane gave 45 mg (20%) of *cis*-diacetate (*cis*-**7**), mp 184–188°, undepressed by admixture with an authentic sample. The nmr spectral analysis did not reveal any of the *trans*-diacetate (<2%). Elution of the column with 500 ml of 20% ether–pentane gave 16 mg (8%) of condensation product **9**, which was recrystallized from pentane–acetone and characterized as follows: mp 155–158° dec; ir ($CHCl_3$) 1735 cm^{-1} (C=O); nmr ($CDCl_3$) τ 3.5 (m, Ar), 4.4 (d, J = 7 Hz, substituted bridge), 6.95 (m, unsubstituted bridge), 7.8 (CH_3COO); mass spectrum (70 eV) *m/e* (relative intensity) 120 (100), 265 (100), 307 (10), 308 (10), 350 (13), 528 (2), 546 (1), 573 (1), 588 (2). *Anal.* Calcd for $C_{38}H_{36}O_6$: C, 77.53; H, 6.16. Found: C, 77.85; H, 6.29.

Dry Acetolysis of *cis*-1-Acetoxy-2-bromo[2.2]paracyclophane (*cis*-6). A mixture containing 207 mg (0.57 mmol) of *cis*-**6**, 150 mg (0.90 mmol) of silver acetate, and 60 ml of dry acetic acid was stirred at 75° for 4 hr. The reaction was quenched in 200 ml of water and worked up in the usual manner to give 206 mg of material which was chromatographed on 19 g of Merck silica gel. Elution of the column with 250 ml of 0, 1, 2, and 5% ether–pentane did not give any compounds. Further elution with 250 ml of 5% ether–pentane gave 5 mg (2%) of starting material (*cis*-**6**). Elution with 500 ml of 10% ether–pentane gave 9 mg (5%) of *cis*-**7**, mp 180–184° undepressed by admixture with an authentic sample. Elution with 450 ml of 15% ether–pentane gave no compounds. Elution with 450 ml of 20% and 560 ml of 25% ether–pentane gave 93 mg (55%) of *cis*-hydroxyacetate (*cis*-**8**), mp 120–126°. The sample was sublimed (105° (0.05 mm)): mp 124–126.5°; nmr, see Table I; mass spectrum (70 eV) *m/e* (relative intensity) 120 (100), 163 (6), 206 (7), 222 (6), 239 (44), 264 (4), 282 (3). *Anal.* Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.54.

Further elution of the column gave small amounts of material which were not positively identified, but were probably condensation products similar to **9**.

1-Formoxy[2.2]paracyclophane (Table I). A solution containing 50 mg of 1-tosyloxy[2.2]paracyclophane[4a] and 2 ml of dimethylformamide was heated at 70° for 72 hr. The solution was added to 100 ml of water and extracted with ether. The ether solution was extracted with dilute hydrochloric acid, dried, and evaporated to give 22 mg (65%) of 1-formoxy[2.2]paracyclophane which was sublimed (85° (0.015 mm)): mp 122–125°; nmr, see Table I. *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.90; H, 6.35.

1-*tert*-Butoxy[2.2]paracyclophane. In a separate preparation of olefin **1**, 6 g of 1-tosyloxy[2.2]paracyclophane was refluxed for 4 hr in a 1 *M* potassium *tert*-butoxide solution in 100 ml of *tert*-butyl alcohol. After cooling, the suspension was poured into 300 ml of water, the aqueous layer was extracted with ether, and the ether layer was dried. The residue from the ether solution was chromatographed on 200 g of silica gel. Elution with 2 l. of pentane gave 1.52 g (44%) of olefin **1** which possessed a vpc retention time, tlc R_f, and an nmr spectrum ($CHCl_3$) τ 2.72 (s, 2, vinyl), 3.53 (s, 8, aromatic), 6.98 (s, 4, benzyl)) identical with those of samples previously prepared. Elution with 5% ether–pentane provided 0.97 g (22%) of 1-*tert*-butoxy[2.2]paracyclophane: mp 73–74°; nmr see Table I. *Anal.* Calcd for $C_{20}H_{24}O$: C, 85.66; H, 8.67. Found: C, 85.63; H, 8.81.[29]

(29) The authors thank R. Helgeson for this preparation.