Studies in Stereochemistry. XLII. A Highly Strained Phenonium Ion Incorporated in the [2.2]Paracyclophane System[1]

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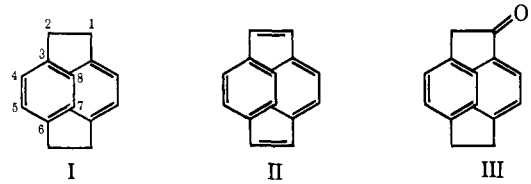
Abstract: The stereochemical course and rates of solvolyses of optically active 1-tosyloxy[2.2]paracyclophane have been studied. Acetolysis of this tosylate at 50°, methanolysis at 47°, and trifluoroacetolysis at 3° all proceeded with complete retention of configuration. Relative configurations of the compounds involved and stereospecificities of the reactions were determined by completing three-reaction stereochemical cycles of the classical variety. Titrimetric acetolysis rate constants in unbuffered acetic acid were determined at 25 and 50° to be $8.49 \pm 0.06 \times 10^{-6}$ sec^{-1} and $2.28 \pm 0.07 \times 10^{-4}$ sec^{-1}, respectively, which provided $\Delta H^{\ddagger} = 24.6 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.7 \pm 0.9$ eu. These acetolysis rates are about 10^2 times faster than those of aliphatic secondary tosylates. These results are interpreted tentatively in terms of either α- or β-aryl participation in the ionization of 1-tosyloxy-[2.2]paracyclophane to produce a highly strained bridged ion in which positive charge is distributed in both benzene rings, in one by direct benzene to α-carbon bonding, in the other by benzene to benzene bonding (relayed conjugation). The bridged ion is formed with inversion at C-1, and opened by solvent with a second inversion at C-1 to produce retention in the overall solvolytic process.

The methylene bridges of [2.2]paracyclophane (I) are in a formal sense benzylic. However, the ultraviolet absorption spectra of derived olefin II[2] and ketone III[3] indicate the π-electron systems of the bridge carbons and the benzene rings are unconjugated with one another. The low carbonyl absorption frequency in the infrared spectrum of III (1698 cm^{-1})[3] does not reflect conjugation but probably expanded OCC bond angles. Molecular models of I–III suggest highly



I II III

rigid structures which allow only slight if any deviation from *face-to-face* structures for the two benzene rings. The plane of C-1, C-2, and C-3 intersects the plane of C-3, C-4, and C-8 at 90° in such models, and conjugation of the classical type would require an angle that approached 0°.

The unique geometry of these systems suggested that the stereochemical course and kinetics of solvolysis of 1-tosyloxy[2.2]paracyclophane (IV) might be interesting for a number of reasons. The 31 kcal[4] of strain energy of I reflects the strong π–π repulsions between the two benzene rings. This repulsion should be somewhat relieved by any distribution of positive charge, generated in the bridge, into either the α- or β-benzene rings. Yet any delocalization involves generation of new strain energy to bring the orbitals involved within overlap distance of one another. Comparisons of the rates of solvolysis of IV with those of open-chain systems might provide clues as to whether the aryl group's π systems participate in ionization. Determination of the stereochemical course of the solvolysis reactions of IV provides criteria for solvent *vs.* aryl participation in ionization, as well as for the possible intervention of bridged carbonium ion intermediates in the reaction sequence.

Results

Starting Materials and Products. Resolution of 1-hydroxy[2.2]paracyclophane[2] (V) was accomplished through the brucine salt of its acid phthalate. Both enantiomers of the acid phthalate were brought close to maximum rotation. Reduction of each enantiomer with lithium aluminum hydride gave the corresponding alcohols V. Recrystallization of (+)-V gave material of maximum rotation. Isomer (−)-V was of 93% maximum rotation. From (−)-V of 93% maximum rotation was prepared tosylate (−)-IV, acetate (−)-VI, and trifluoroacetate (−)-VII. Care was taken not to change the optical purity of these derivatives by fractional sublimination, crystallization, or dissolution of racemate and enantiomer (all were demonstrated possible). From (+)-V of maximum rotation was prepared tosylate (+)-IV and ether (+)-VIII of maximum rotation. Conventional sulfonation, acylation, and alkylation procedures were used in these transformations in which the oxygen of alcohol V served as a nucleophile, and the C–O bond of V was not broken.

Acetolysis at 50° in potassium acetate buffered glacial acetic acid of the total sample of unpurified tosylate prepared from (−)-V alcohol of 93% maximum rotation gave acetate (−)-VI (69% overall yield based on (−)-V) of 92–93% optical purity. Analytical procedures demonstrated that less than 0.6 mol % of 1,2-dehydro[2.2]paracyclophane[2] was present in the solvolysis product mixture. Acetolysis at 75° in unbuffered glacial acetic acid of the total sample of unpurified tosylate prepared from (−)-V of 65% maximum rotation gave acetate (−)-VI (52%) of 65% maximum rotation.

(1) The authors warmly thank the National Science Foundation for a grant that supported this research. Some of these results appeared in preliminary form (R. E. Singler, R. C. Helgeson, and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 7625 (1970)).
(2) K. C. Dewhirst and D. J. Cram, *ibid.*, **80**, 3185 (1958).
(3) D. J. Cram and R. C. Helgeson, *ibid.*, **88**, 3515 (1966).
(4) (a) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); (b) C. Shieh, D. C. McNally, and R. H. Boyd, *ibid.*, **25**, 3653 (1969).

Table I. Kinetic Data for Solvolyses of 1-Tosyloxy[2.2]paracyclophane (IV)

Run no.	Solvent	Tosylate Nature	Tosylate Concn, M	Buffer Nature	Buffer Concn, M	T, °C	Method	$k \times 10^6$, sec^{-1}	Activation parameters[a] $\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
1	AcOH	(+)-IV	0.035	AcONa	0.036	25.00 ± 0.05	Polarimetric[b]	9.92 ± 0.12			
									24.3 ± 0.7	24.3 ± 0.5	0.2 ± 1.4
2	AcOH	(+)-IV	0.035	AcONa	0.036	47.4 ± 0.2	Polarimetric[b]	188 + 1			
3	AcOH	(±)-IV	0.010	None		25.00 ± 0.02	Titrimetric	8.49 ± 0.06			
									24.4 ± 0.4	24.6 ± 0.3	0.7 ± 0.9
4	AcOH	(±)-IV	0.010	None		50.00 ± 0.02	Titrimetric	228 ± 7			
5	CH_3OH–$CHCl_3$[c]	(−)-IV	0.084	None		25.00 ± 0.05	Polarimetric[d]	23.8 ± 0.2			

[a] Calculated for 25°. [b] Rotations followed at λ 436 nm. Other runs demonstrated identical rate constants were obtained with λ 436 and 546 nm (see Experimental Section). [c] 15% by volume of chloroform. [d] At λ 546 nm, $k = 2.36 \times 10^{-5}$ sec^{-1}; at 436 nm, $k = 2.40 \times 10^{-5}$ sec^{-1}.

Trifluoroacetolysis was conducted at 3° in sodium trifluoroacetate buffered trifluoroacetic acid–methylene dichloride (3:1, v/v). The total sample of unpurified tosylate prepared from (−)-V alcohol of 93% maximum rotation was used. Trifluoroacetate (−)-VII (49% overall yield based on (−)-V) of 96% maximum rotation was obtained. No olefin could be detected in the reaction product.

Methanolysis at 47° (in potassium acetate buffered methanol) of tosylate (+)-IV prepared from the (+)-alcohol of maximum rotation gave ether (+)-VIII (82% based on tosylate) of maximum rotation. Less than 0.6% olefin was produced in the reaction.

Kinetics. Acetolysis kinetics at 25 and 47° in sodium acetate buffered solutions were carried out polarimetrically on tosylate (+)-IV prepared from alcohol (+)-V of 83% maximum rotation. The reactions were followed in a polarimeter at either or both of two wavelengths, λ 546 and 437 nm. Data points (23–40) that followed at least 75% reaction were determined, and the infinity point was taken when the rotation of the solution no longer changed. Observed rotational changes ranged from 1.1 to 2.1°, and could be measured to ±0.002°. The data points were analyzed by a least-squares computer program for determination of first-order rate constants. The limits of error were set with two standard deviations. In determination of activation parameters, the limits of error include both deviations in rate constants and temperature. Table I records the rate constants and activation parameters. Each rate constant is the average of two runs made under identical conditions.

Table I also includes titrimetric rate constants and activation parameters for acetolyses of racemic tosylate IV in unbuffered acetic acid at 25 and 50°.[2,5] Standard procedures were used.[6] The reactions were followed through about 60% appearance of *p*-toluenesulfonic acid with nine data points. The small difference in rate constants obtained by the two methods probably reflects ordinary salt effects due to the presence of sodium acetate in the polarimetric but absent in the titrimetric runs. The activation parameters determined by the two methods are identical within error.

Methanolysis kinetics at 25° were followed polarimetrically on tosylate (−)-IV prepared from alcohol (−)-V of 68% maximum rotation. The solution was unbuffered, and was 15% by volume chloroform (ethanol free) in methanol. Chloroform was required to provide solubility. Eighteen data points that covered 90% reaction were taken at each of two wavelengths, λ 546 and 436 nm. Observed rotational changes were about 0.5° at the former and 1.1° at the latter wavelength. Least-squares rate constants were calculated from the data at each wavelength, and were identical within probable error (two standard deviations). Table I records the average rate constant.

(5) The authors warmly thank Dr. R. C. Helgeson for these results.

(6) S. Winstein. B. K. Morse, E. Grunwald, K. C. Schrieber, and J. Corse, *J. Amer. Chem. Soc.*, 74, 1113 (1952).

Discussion

Stereochemical Course of Nucleophilic Substitution. The three stereochemical cycles of this investigation were all completed with three reactions and three chiromers,[7] and are of the ordinary triligostatic[7] variety. Thus, either all reactions occurred with retention, or two with inversion and one with retention. Two of the reactions of each cycle did not involve bond making or breaking at the chiral center and therefore must have gone with retention.[8] Therefore, the remaining solvolytic reaction in each cycle must also have gone with retention. The ratio of rate constants for solvolysis with retention (k_r) to solvolysis with inversion (k_i) is about equal to or greater than two orders of magnitude ($k_r/k_i \gtrsim 100$). Although this ratio may have varied widely in value with variation in nucleophilicity of solvent, such changes were not detectable by the analytical methods used. Chart I indicates the stereochemical relationships involved.[9]

Interpretation of the high retention of configurations observed for these three solvolysis reactions requires comparison with the stereochemical outcome of solvolyses of sulfonate esters or halides of other secondary systems. These roughly fall into three categories: (1) cases where $k_r/k_i \lesssim 10^{-2}$; (2) cases where $k_r/k_i \gtrsim 10^2$; (3) cases where $k_r/k_i \sim 1 \pm 3$.

The first class of secondary systems solvolyzes with high inversion.[10] For example, 2-octyl tosylate acetolyzes with $k_r/k_i \lesssim 10^{-2}$,[10a] the high inversion being as-

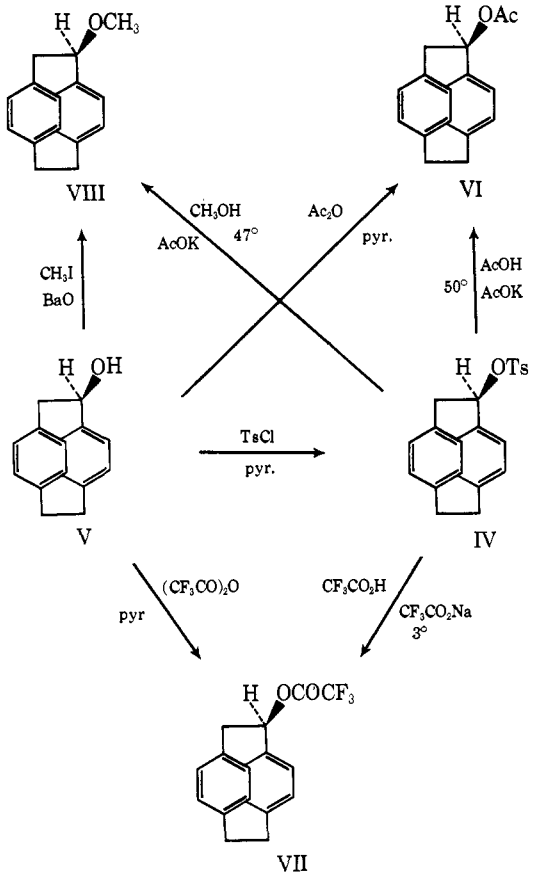
(7) D. J. Cram and D. C. Garwood, *ibid.*, 92, 4575 (1970).

(8) The classical stereochemical reaction cycle of Phillips and Kenyon [see J. Kenyon, H. Phillips, and H. G. Turley, *J. Chem. Soc.*, 127, 399 (1925)] involved three reactions and four chiromers, since one of their three reactions went with inversion.

(9) No absolute configurations were determined, so the configurations pictured are only illustrative. The same enantiomers of IV and V were not used in all experiments, but to save space the same one is formulated.

(10) (a) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Amer. Chem. Soc.*, 87, 3682 (1965); (b) A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, 87, 3686 (1965); (c) H. Weiner and R. A. Sneen, *ibid.*, 87 287, 289 (1965), and subsequent papers; (d) M. C. Whiting, *Chem. Brit.*, 2, 482 (1966), and subsequent papers.

Chart I



sociated with acetic acid participation in ionization. These systems are characterized as offering poor neighboring carbon or hydrogen participation in ionization, little steric inhibition of nucleophilic solvation, and no α-substituent (*e.g.*, aryl or vinyl) that provides high delocalization of charge.

The second class of secondary systems solvolyzes with high retention of configuration due to neighboring group participation in ionization to form a bridged ion (inversion at secondary carbon). In a second stage this ion is opened by nucleophilic attack by solvent (inversion) to give a product with overall high retention of configuration.[11] For example, in acetolysis of 3-phenyl-2-butyl tosylate,[12a] $k_r/k_i \sim 105$ for threo and $k_r/k_i \sim 101$ for erythro material.[12b] These values reflect the balance of stereochemical control exerted by phenyl *vs.* acetic acid in directing the reaction toward product (acetate plus racemized or scrambled tosylate) of retained (phenyl controlled) or inverted (acetic acid controlled) configuration. In formolysis, *threo*-3-phenyl-2-butyl tosylate gave formate with $k_r/k_i \sim 10^4$. This class of system is characterized by the presence of a β group with nucleophilic character, and the absence of α substituents such as phenyl or vinyl that delocalize charge.

The third class of secondary systems solvolyzes with low inversion or retention. Secondary benzyl systems provide several examples.[13] Thus methanolysis of α-phenylethyl chloride gave $k_r/k_i \sim 0.5$,[13a,b] and acetolysis of α-phenylethyl tosylate gave $k_r/k_i \sim 0.8$.[13c] Acetolysis of the two diastereomers of 1,2-diphenyl-1-propyl brosylate[13d] gave $k_r/k_i = 2.3$ for the threo isomer and 0.6 for the erythro isomer. Similarly acetolysis of 1,2,2-triphenylethyl tosylate[10e,f] gave $k_r/k_i \sim 1.3$. In these systems, charge delocalization into the α-phenyl group diminishes neighboring group or solvent participation in ionization to the point where conformational or intrinsic asymmetry of the open ions contributes to the stereochemical results.

A different type of secondary system provided little stereochemical control by either nucleophilic neighboring group or solvent participation in ionization. Thus acetolysis of *trans*-5-methyl-2-adamantyl tosylate gave $k_r/k_i = 4.00$ whereas the cis isomer gave $k_r/k_i = 0.85$.[14] The small tendency to give retention in this system is probably associated with steric inhibition of nucleophilic solvation on the one hand, and a very minor participation in ionization of the β-methylene group on the other.[14]

Of course, secondary systems are known where proper manipulation of solvent and neighboring group nucleophilicity provides k_r/k_i values that can be made to vary continuously from $>10^2$ to $<10^{-2}$. Examples are the 1-phenyl-2-propyl tosylate[15] and para-substituted 3-phenyl-2-butyl tosylate systems.[12b,c,16] These cases provide blends of our first and second classes, and lend validity to the concept that these two classes exist. Blends of the first and third or second and third classes undoubtedly exist, but have not been systematically demonstrated.

The fact that $k_r/k_i \geqq 100$ over a range of solvents of very widely differing nucleophilicity places the 1-tosyloxy[2.2]paracyclophane (IV) in the second of the above classes. Clearly the stereochemical results provide strong evidence that the course of the solvolysis reactions of this system is controlled by some sort of nucleophilic neighboring group participation in ionization to produce a bridged ion with inversion at the chiral center. In a second stage this bridged ion is opened by nucleophilic attack by solvent with inversion of the chiral center to give solvolysis product with retention of configuration. The question that arises is what structure to attribute to the intermediate bridged ion.[17]

(11) Examples are too numerous to list. A few are reviewed by D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed. Wiley, New York, N. Y., 1956, Chapter 5.

(12) (a) D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 2129 (1952); (b) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967); (c) J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969).

(13) (a) E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937); (b) H. M. R. Hoffman and E. D. Hughes, *ibid.*, 1244 (1964); (c) J. Kenyon, H. Phillips, and F. M. H. Taylor, *ibid.*, 173 (1933); (d) F. A. Abd Elhafez and D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 339 (1953); (e) W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956); (f) C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

(14) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

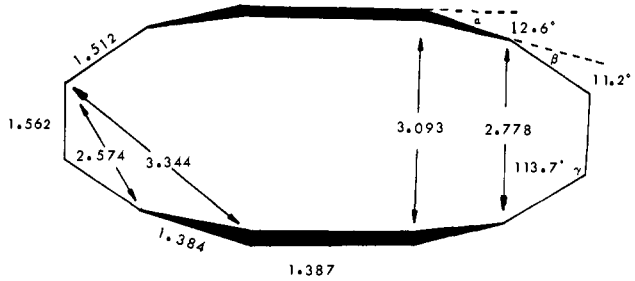
(15) (a) S. Winstein, K. C. Schreiber, M. Brown, and A. H. Schlesinger, *J. Amer. Chem. Soc.*, **74**, 1140 (1952); (b) P. von R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969).

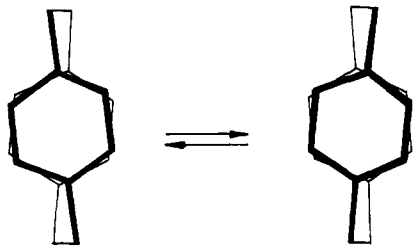
(16) (a) S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964); (b) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(17) Schleyer, *et al.* (H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5244 (1970)), have equated k_Δ (neighboring group assisted ionization rate constant) with k_r, and have *empirically correlated* with a Hammett plot, k_s's (solvent assisted ionization rate constants), by assuming that $k_s \sim k_i + k_{olefin}$, where k_{olefin} is the rate constant for olefin production. The mechanistic significance of their correlation is obscured by the fact that total olefin arises by several different mechanisms in many systems (*e.g.*, see D. J. Cram, *ibid.*, **74**, 2137 (1952)), some of which involve hydrogen migration, others of which might be pure E_2 reactions with solvent acting as base. Our use of k_r/k_i values as mechanistic criteria depend only on the balance of nucleophilically substituted products in a particular system. Use of k_Δ and k_s values depends on kinetic comparisons involving many systems and many structural parameters. We do not imply that $k_i \sim k_s$, since a *fraction* of k_{olefin} *might* contribute to k_s. In the absence of knowledge of what this fraction might be, we prefer the use of k_r/k_i

The original crystal structure of [2.2]paracyclophane (I)[18a] indicated a symmetrical face-to-face rigid arrangement of the two benzene rings with respect to one another, with the benzyl hydrogens completely eclipsed. Later work provided the skewed structure of Chart II.[18a] Highly refined recent work[18b] provides the distances and angles of Chart II in which even at

Chart II. Crystal Structure of [2.2]Paracyclophane





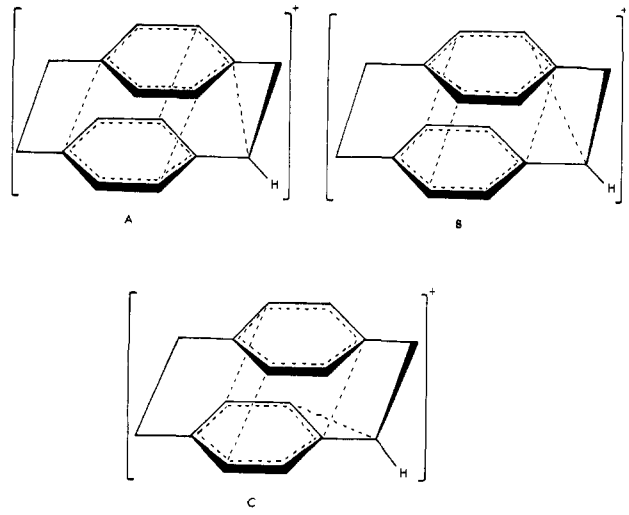
93°K the compound is equilibrating between two structures in which the methylene bridges are slightly deeclipsed. In this molecular motion, the benzene rings rotate about an axis perpendicular to and passing through the center of each face. The angle swept by this rotation is about 7°.

The slightly skewed structure provides poor overlap opportunities for the derived benzyl cation with the π systems of either ring. However, much of the 31-kcal strain energy of the system is concentrated in the $\pi-\pi$ repulsions between the two benzene rings,[4] and distribution of positive charge into either or both of the benzene rings would decrease this repulsion. Several ways of delocalizing charge that preserve molecular asymmetry are envisioned in structures A, B, and C (Chart III). All three structures allow distribution of charge in both rings. In A, a distorted ethylene phenonium ion is drawn in which the β ring carries charge by direct overlap and the α ring by relayed overlap. In B, a distorted propylene phenonium ion is formulated whose β ring also carries charge by direct, and the α ring by relayed overlap. In C, a partial bond is formed between the benzyl and ortho positions of the α ring; charge is delocalized directly into the α ring, and by relayed overlap into the β ring. All of these structures involve further molecular distortion of an already highly strained system, but involve exchange of bond angle strain for $\pi-\pi$ repulsion strain.

values as a more delicate, simple, and secure criterion of mechanism than k_Δ/k_s values, particularly since we do not *really know* how to determine k_s.

(18) (a) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (b) D. K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.*, **255**, 82 (1960); (c) K. N. Trueblood, J. Bernstein, and H. Hope, private communication. We warmly thank these authors for this information in advance of publication. (d) The observed skewing of [2.2]paracyclophane was anticipated by J. T. S. Andrews and E. F. Westrum, Jr., *J. Phys. Chem.*, **74**, 2170 (1970).

Chart III



Although a clear choice between these three structures is elusive, A is preferred. The points of closest approach of the two benzene rings to one another are 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. In this connection, [2.2]paracyclophane was found to protonate in strong acids at the point of attachment of the benzene ring to the bridge.[19] An interesting feature about the structure of [2.2]paracyclophane is the elongated benzyl–benzyl bond. Probably in the bridged ion the two electron pairs of these σ bonds are also somewhat delocalized, although the bonds have not been dotted in structures A, B, and C for visual reasons.

Other explanations for the observed high retention in the solvolysis reactions of tosylate IV are possible but highly improbable. The low flexibility of the ring system makes rationalizations involving conformational asymmetry of an open benzyl ion untenable. Another interesting possibility is that an open carbonium ion is formed which instead of being flat is pyramidal, and retains its configuration during its short lifetime. Calculations of various sp^2- and sp^3-hybridized carbonium ions suggest the planar ions are 8–10 kcal more stable than nonplanar ions.[20] The longer than usual benzyl–benzyl bond in [2.2]paracyclophane (I) is probably enriched somewhat in p character. Thus a pure p orbital would be less available than usual for the benzyl cation derived from I. However, such an effect is hardly expected to become important enough to overcome the larger energy difference between an sp^2 and sp^3 carbonium ion. An sp^3-hybridized open carbonium ion derived from I would do little to relieve the strain inherent in the starting material, and should produce exceedingly slow solvolysis rates, which is not observed.

Rates of Solvolyses. Because of the unusual geometry of the [2.2]paracyclophanyl system, solvolytic rate comparisons are of limited value for diagnosis of the mechanism. However, a few comparisons are instructive. Unfortunately rate data on ordinary secondary benzyl tosylates are scarce.

(19) D. T. Hefelfinger and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, in press.

(20) R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969).

At 25° in acetic acid, if the rate constant for acetolysis of 2-adamantyl tosylate[21] is set equal to unity, the relative rate constants for acetolysis at the same temperature are as follows: isopropyl tosylate,[21] 13.2; 1-tosyloxy[2.2]paracyclophane (IV), 1430; α-phenylneopentyl tosylate,[22] 4500. The 2-adamantyl system was used as a standard since it provides the best measure of k_c (rate constant for nonnucleophilic solvent or nonanchimerically assisted ionization) in a secondary system.[21] The last system provided a 42% yield of unrearranged acetate with $k_r/k_i = 0.67$. The rates of the two benzyl systems differ by about a factor of three. The neopentyl system offers more steric hindrance to nucleophilic solvation than IV, but less steric inhibition of delocalization of charge in its carbonium ion. The differences in redistribution of strain energies upon ionization in the two systems make analysis of various contributions to the rates difficult. Release of B strain in ionization probably accelerated the rate of the neopentyl system, but ionization of IV *in the absence of neighboring group participation* would have changed the CCC bond angle very little (from 114 to 119°, if diolefin II is used as a model[23] for the open carbonium ion).

Both the neopentyl and cyclophanyl systems gave rate factors about 10^2 greater than isopropyl tosylate and over 10^3 greater than the adamantyl system. The adamantyl and neopentyl systems acetolyze with about the same stereochemical course ($k_r/k_i \sim 1 \pm 3$), but in striking contrast to the 2-octyl ($k_r/k_i \leqq 10^{-2}$) or cyclophanyl system ($k_r/k_i \geqq 10^2$). The difference of $>10^4$ in k_r/k_i values between the nonbenzyl open-chain and cyclophanyl systems was interpreted in the last section as strong evidence for neighboring group participation in ionization in the cyclophanyl systems. The 10^2 faster rate for the cyclophanyl system supports this interpretation. The greater steric inhibition of solvation and rate-reducing inductive effects of two nonconjugating phenyl groups of the cyclophanyl system should make k_s (nucleophilic solvent assisted rate component) for the isopropyl system considerably greater than k_s for the cyclophanyl system. Thus the source of the 10^2 rate factor must lie in k_Δ (neighboring group assisted rate component) for the cyclophanyl system. More than in open-chain systems, k_Δ for the paracyclophanyl system must reflect a redistribution of strain energies which are intimately tied to charge delocalization.

Another fact that points to little contribution of k_s to the rate constant for solvolysis of the cyclophanyl system is the almost total absence of olefin in the products, and the high yields of products of methanolysis and acetolysis. The near absence of olefin in the product from acetolysis of *threo*-3-anisyl-2-butyl tosylate where k_Δ dominated the rate and phenonium ion the configuration of the product provides an analogy.[16]

Experimental Section

General. Reagent grade chemicals and solvents were used except where noted. Dry acetic acid (1% by weight acetic anhydride) and trifluoroacetic acid (1% by weight trifluoroacetic anhydride) were used in the solvolysis experiments.[12c] The methanol used was refluxed with calcium hydride for 6 hr and distilled to give a center cut, bp 65°. Reagent grade pyridine was distilled from barium oxide and stored over barium oxide. Melting points were taken in a Hoover Uni-Melt bath and are uncorrected. Mass spectra were determined on an AEI MS9 instrument at 12 and 70 eV, using both heated inlet and direct insertion techniques. Optical rotations were taken in spectrograde solvents and changes followed on a Perkin-Elmer Model 141 polarimeter in a 1-dm cell thermostated at 25.00 ± 0.05°. Silica gel layers 0.25 mm thick on glass plates were used in tlc. Baker reagent grade or Merck silica gel (30–70 mesh) or Mallinckrodt SilicAr (100–200 mesh) were used in column chromatographs. In general, the material to be chromatographed was packed on ten times its weight in silica gel prior to chromatography and 40-ml fractions were collected. Gas–liquid chromatography (glc) was carried out on an F and M Model 720 instrument with 3 ft × ¼ in. columns packed with 20% SE30 on 60–80 firebrick at a flow rate of 60 ml/min, unless specified otherwise.

1-Hydroxy[2.2]paracyclophane (V). A suspension containing 17.5 g (0.84 mol) of [2.2]paracyclophane (I), 24 g (0.135 mol) of *N*-bromosuccinimide, 100 mg of benzoyl peroxide, and 1400 ml of carbon tetrachloride (dried over molecular sieves) was refluxed with ultraviolet irradiation (Hanovia Model 30620) for 10 hr. The reaction could be followed by examining aliquots on glc, and observing the ratio of starting material to 1-bromo[2.2]paracyclophane. The ratio was constant after 8 hr. The approximate glc retention times were 1 min for I and 2.5 min for the monobromide. When the mixture was cooled to room temperature, all of the undissolved material floated to the surface, which fact indicated that all of the *N*-bromosuccinimide had been consumed. This suspension was filtered, and the solution was evaporated to give 28.5 g of solid. This material was dissolved in 250 ml of glacial acetic acid and heated at 100–110° for 8 hr with 22 g (0.132 mol) of silver acetate. Then 100 ml of water was added, and the suspension was heated at 100° for an additional 3 hr. After cooling to room temperature, 250 ml of water was added, and the mixture was extracted three times with ether. The ether layers were combined, washed with a sodium bicarbonate solution to remove the acetic acid, and dried over magnesium sulfate. Evaporation of the solution gave 15 g of an orange syrup which partially solidified upon standing.

This mixture of unreacted I, monoketone III, and acetates (15 g) was reduced with 4 g of lithium aluminum hydride in refluxing ether for 6 hr employing a Soxhlet apparatus. The excess hydride and lithium salts were removed with wet ether, water, and dilute hydrochloric acid solution, and the ether solution was dried and evaporated to give 11.8 g of a crude solid which was chromatographed on 400 g of silica gel. The column was eluted with 16 l. of pentane to give 1.1 g (6.3%) of unreacted I. Elution with 1–10% ether–pentane mixtures gave no compounds. Elution with 3 l. of 15% ether–pentane gave a mixture of two compounds according to tlc and glc analysis. The major component was alcohol V (tlc $R_f = 0.4$, 1:1, v:v ethyl acetate–cyclohexane; glc retention time, 2 min). The minor component was a ring-brominated derivative of V (tlc $R_f = 0.43$; glc retention time, 4 min). The minor component was identified by a positive Beilstein test and the presence of a parent peak in the mass spectrum at *m/e* 302, 304. Since the ring-brominated derivative was more soluble than V, V was separated from the mixture by crystallization from ether–pentane. The ring-brominated compound was not obtained in a pure state suitable for analysis. Further elution of the column with 5 l. of 15% ether–pentane gave only V. The total recovered yield of V was 34%. Elution with up to 50% ether–pentane gave 1.2 g (6.1%) of a mixture of diols.

Alcohol V gave mp 228–231°, was identical in all respects with authentic material,[2] and gave a mass spectrum (70 eV) *m/e* (relative intensity) 103 (6), 104 (7), 105 (100), 106 (9), 120 (50), 121 (5), 222 (1), 224 (11), 225 (2).

Acid Phthalate of 1-Hydroxy[2.2]paracyclophane (V). A solution of 3.1 g (0.014 mol) of 1-hydroxy[2.2]paracyclophane, 2.3 g (0.016 mol) of phthalic anhydride (sublimed at 100° (0.03 mm)), and 20 ml of pyridine was stirred at 100° for 12 hr. The solution was added to 400 ml of ice water, and sodium carbonate was added to adjust the pH to 8. The suspension was then extracted several times with ether to remove unreacted alcohol (600 mg, 19% recovery after removal of pyridine). The aqueous layer was first extracted with 200 ml of chloroform to remove most of the color, and then the pH was adjusted to 3 with dilute hydrochloric acid, precipitating the acids. The suspension was extracted with 200 ml of chloro-

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form, and the chloroform solution was decolorized by a charcoal treatment, evaporated to about 10 ml, and diluted with acetone. The product crystallized: wt 3.6 g (62%); mp 194–195.5°; mass spectrum (70 eV) *m/e* (relative intensity) 91 (31), 92 (9), 103 (5), 104 (26), 105 (100), 106 (9), 120 (57), 121 (5), 149 (7), 224 (7), 372 (<1). The peak at 372 is the parent ion. A sample was recrystallized from acetone–chloroform to a melting point of 196–198° for analysis. *Anal.* Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.19; H, 5.59.

Resolution of 1-Hydroxy[2.2]paracyclophane Acid Phthalate Ester. A mixture containing 10.112 g of the acid phthalate ester (mp 195–197°) and 10.710 g of anhydrous brucine (mp 177–179°, from acetone) was dissolved in a solution containing 1100 ml of acetone and 500 ml of methylene chloride. This solution was evaporated to 850 ml total volume. No salt formation was observed after 24 hr at 0°. The solution was evaporated to 250 ml and when cooled slowly 10.8 g of a white flocculent precipitate was obtained. Attempts to recrystallize this salt using very little acetone gave 3.8 g of uncharacterized material. The remaining salt (7.0 g) was recrystallized three times from acetone–methylene chloride to give 6.6 g of salt, mp 223–224.5° dec. This material was stirred for 40 min in a mixture of 20 ml of 4 *N* sulfuric acid, 100 ml of water, and 10 ml of acetone. Ether (200 ml) was added to the mixture to give a clean two-phase system. The ether layer was washed, dried, and evaporated to give 2.8 g of acid phthalate ester: mp 175.5–176°; $[\alpha]^{25}_{546}$ −49.8°; $[\alpha]^{25}_{436}$ −78.2° (*c* 1.06, CH_3OH). *Anal.* Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.33; H, 5.50.

The mother liquors from the initial crystallization of the brucine salt were evaporated, and the residual salt converted to acid phthalate ester. This material was crystallized fractionally from ether to give six crops, the third, fourth, and fifth of which gave: mp 174.5–176°; $[\alpha]^{25}_{546}$ +47.8°; $[\alpha]^{25}_{436}$ +75.1° (*c* 1.02, CH_3OH); wt 1.18 g. *Anal.* Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.39; H, 5.58.

(+)- and (−)-1-Hydroxy[2.2]paracyclophane ((+)- and (−)-V). To a chilled suspension of 0.700 g of lithium aluminum hydride in dry ether was added 1.49 g of (+)-phthalic acid ester of V, $[\alpha]^{25}_{546}$ +47° (*c* 1.05, CH_3OH). The suspension was warmed to reflux temperature for 7 hr. After standing overnight, the suspension was quenched by adding wet ether and finally dilute hydrochloric acid until the pH of the water layer was approximately 7. After stirring for several hours, the inorganic salts dissolved, leaving a clear two-phase system. The ether layer was separated and dried over sodium sulfate–potassium carbonate. Two crops of (−)-alcohol were obtained from the ether layer: 0.431 g, $[\alpha]^{25}_{546}$ −72.0°, $[\alpha]^{25}_{436}$ −166°; 0.315 g, $[\alpha]^{25}_{546}$ −71.7°, $[\alpha]^{25}_{436}$ −166° (*c* 0.9, $CHCl_3$). The (−)-V was pure by tlc. The total yield was 83%. A small sample was recrystallized from acetone–ether, mp 228–232°. *Anal.* Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.82; H, 7.27.

The same procedure was applied to 1.232 g of the (−)-phthalic acid ester of V, $[\alpha]^{25}_{546}$ −49.8° (*c* 1.1, CH_3OH). Two crops of alcohol were obtained pure to tlc. The first crop of (+)-V, 0.320 g, gave: mp 228–231°; $[\alpha]^{25}_{546}$ +76.9°; $[\alpha]^{25}_{436}$ +177° (*c* 0.98, $CHCl_3$). *Anal.* Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.66; H, 7.36. Recrystallization of this material did not change its rotation, and it is regarded as optically pure. The second crop was 0.350 g (total yield 91%): mp 228–230.5°; $[\alpha]^{25}_{546}$ +71.5°; $[\alpha]^{25}_{436}$ +166° (*c* 0.93, $CHCl_3$). Recrystallization of this material from ether–pentane gave: 0.190 g; $[\alpha]^{25}_{546}$ +77.0°; $[\alpha]^{25}_{436}$ +178° (*c* 0.98, $CHCl_3$), whose rotation did not change on further recrystallization.

(−)-1-Tosyloxy[2.2]paracyclophane ((−)-IV). To a solution of 0.200 g of alcohol (−)-V, $[\alpha]^{25}_{546}$ −72.0° (*c* 0.91, $CHCl_3$), dissolved in 0.6 ml of pyridine was added 0.200 g of tosyl chloride. After standing 36 hr at 25°, the reaction mixture was shaken with ether–water; the ether layer was washed with water, dilute acid, and dilute base, and dried and evaporated to a small volume. Addition of pentane to the solution produced 0.321 (96%) of tosylate (−)-IV as long needles: mp 85–87° dec; $[\alpha]^{25}_{546}$ −92.0°; $[\alpha]^{25}_{436}$ −204° (*c* 0.25, CS_2). *Anal.* Calcd for $C_{23}H_{22}O_3S$: C, 72.97; H, 5.87. Found: C, 72.94; H, 6.02.

Optically impure tosylate fractionated upon crystallization, and solvolyzed to alcohol on silica gel tlc or chromatography, but could be stored at 5°.

(−)-1-Acetoxy[2.2]paracyclophane ((−)-VI). In a typical experiment, 0.086 g of alcohol (−)-V, $[\alpha]^{25}_{546}$ −71.7° (*c* 0.96, $CHCl_3$), was dissolved in 0.5 ml of acetic anhydride and 0.5 ml of pyridine, and left at 25° for 24 hr. The mixture was shaken with ether and dilute hydrochloric acid. The ether solution was washed with water and dilute sodium bicarbonate solution, dried, and evaporated to give 0.098 g of crude (−)-VI. After sublimation at 80° (0.015 mm) 0.090 g (88%) of acetate was obtained: mp 104–110°; $[\alpha]^{25}_{546}$ −66.9°; $[\alpha]^{25}_{436}$ −157° (*c* 0.931, $CHCl_3$). This material was pure to tlc with 15% ethyl acetate-cyclohexane as developer, and identical in nmr spectra with racemic acetate.[2] Recrystallization of this material resulted in optical fractionation, and gave material with: mp 110–111°; $[\alpha]^{25}_{546}$ −69.1°; $[\alpha]^{25}_{436}$ −163° (*c* 0.369, $CHCl_3$); about 96% optically pure. *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.35; H, 6.92.

Acetolyses of (−)-Tosyloxy[2.2]paracyclophane ((−)-IV). Since optically pure alcohol (−)-V was scarce, alcohol of 65–93% optical purity was used to complete the stereochemical cycles. No techniques were employed that fractionated racemate from enantiomer (*e.g.*, crystallization). In the first run, 0.036 g of 65% optically pure alcohol (−)-V was converted to tosylate, the total sample of which was solvolyzed in 2 ml of unbuffered acetic acid at 75° for 4 hr. Crude acetate isolated in the usual way was exhaustively sublimed to give (−)-IV (free of alcohol V or 1,2-dehydro[2.2]-paracyclophane[2] by tlc): 0.022 g; $[\alpha]^{25}_{546}$ −50.2°; $[\alpha]^{25}_{436}$ −117° (*c* 1.9, $CHCl_3$). Acetate prepared by direct acetylation of the same sample of alcohol (−)-V gave after sublimation $[\alpha]^{25}_{546}$ −50.0°, $[\alpha]^{25}_{436}$ −118° (*c* 1.9, $CHCl_3$). The acetate thus appears to be optically stable to the small amount of *p*-toluenesulfonic acid liberated in the solvolysis under the reaction conditions used.

In a second run, 0.200 g of (−)-V, $[\alpha]^{25}_{546}$ −71.7° (*c* 0.90, $CHCl_3$), was converted to tosylate. The total sample contained trace amounts of unreacted (−)-V according to tlc on Kiesselguhr, but was used without separation. It was dissolved in 8 ml of acetic acid containing 0.090 g of freshly fused potassium acetate. The solution was heated at 50° for 66 hr, quenched in 300 ml of water, and isolated in the usual way. The crude reaction mixture, 0.206 g, upon tlc analysis showed the presence of traces of alcohol V, but no 1,2-dehydro[2.2]paracyclophane. Control experiments with synthetic mixtures of racemic acetate and olefin on tlc with 15% ethyl acetate-cyclohexane as developer demonstrated that as little as 0.64 mol % of olefin in acetate could be detected. Control experiments were performed with glc on a Wilkens Aerograph Model 200 gas chromatograph with an 8 ft × $\frac{1}{8}$ in. column packed with 5% SE-30 or 0.5% Atpet 80 on 80–100 Chromosorb W at a helium flow rate of 60 ml/min. The injection port was 235°, the column was 205°, and the detector was 225°. Under these conditions, the synthetic mixture of acetate VI, 0.64 mol % in olefin, gave 3.5 min retention time for the olefin and 8.5 min retention time for the acetate. Less than 0.64 mol % olefin was detected in the crude reaction mixture from the acetolysis reaction. The crude solvolysis reaction mixture was chromatographed on 20 g of Merck silica gel. Elution of the column with 400 ml of pentane and 320 ml of 1% ether-pentane gave less than 1 mg of olefin, identified by tlc comparison with authentic material.[2] Elution of the column with 600 ml of 2% and 240 ml of 3% ether–pentane gave (−)-VI, which after sublimation came to 0.164 g (69% overall yield from alcohol): mp 104–111°; $[\alpha]^{25}_{546}$ −65.8°; $[\alpha]^{25}_{436}$ −157° (*c* 0.91, $CHCl_3$).

An 0.086-g sample of the same (−)-V alcohol used in the second run was acetylated to give 0.090 g of sublimed acetate: $[\alpha]^{25}_{546}$ −66.9°; $[\alpha]^{25}_{436}$ −157° (*c* 0.93, $CHCl_3$); mp 104–111°. Within the limits of detection, the acetolysis reaction proceeded with complete retention of configuration, and with production of only a trace of olefin.

A control experiment with partially optically active acetate (−)-VI demonstrated that incomplete sublimation resulted in slight fractionation of racemate and enantiomer (the racemate was slightly more volatile). Therefore, in all experiments care was taken to sublime total samples, and to homogenize acetate samples on which rotations were taken.

(−)-1-Trifluoroacetoxy[2.2]paracyclophane ((−)-VII). To a chilled solution containing 0.116 g (0.52 mmol) of alcohol (−)-V, $[\alpha]^{25}_{546}$ −72.0°, $[\alpha]^{25}_{436}$ −166° (*c* 0.91, $CHCl_3$), in 1 ml of pyridine was cautiously added 1 ml of trifluoroacetic anhydride. The solution was stirred at room temperature for 22 hr after which it was quenched by addition to 100 ml of water. The mixture was extracted with 100 ml of ether and the ether solution was washed with a dilute hydrochloric acid solution, a sodium bicarbonate solution, and water. After drying over sodium sulfate–potassium carbonate, the ether solution was evaporated to give 0.135 g of crude material which was sublimed twice (85° (0.030 mm)) to give 0.104 g (63% yield) of 1-trifluoroacetoxy[2.2]paracyclophane:

$[\alpha]^{25}_{546}$ −105°; $[\alpha]^{25}_{436}$ −224° (*c* 0.99, $CHCl_3$); mp 94–97° dec. The material was pure to tlc on Kiesselguhr-G with 15% ethyl acetate–cyclohexane as a developer. Tlc on silica gel resulted in partial hydrolysis to the alcohol. A small sample of material was crystallized from ether–pentane for analysis. *Anal.* Calcd for $C_{18}H_{15}O_2F_3$: C, 67.50; H, 4.72. Found: C, 67.33; H, 4.86.

Trifluoroacetolysis of (−)-1-Tosyloxy[2.2]paracyclophane ((−)-IV). Optically impure samples of alcohol (−)-V were used, so total samples were always submitted to reaction and analyzed to avoid optical fractionation. In the first run, 0.100 g of alcohol (−)-V, $[\alpha]^{25}_{546}$ −40.0° (*c* 0.90, $CHCl_3$), was converted to tosylate (−)-IV, and the total sample (0.160 g) was dissolved in 100 ml of methylene dichloride. This solution was cooled to 3° and under dry nitrogen was added to 10 ml of trifluoroacetic acid at 3° in which had been dissolved 0.028 g of sodium carbonate and 0.1 ml of trifluoroacetic anhydride. The solution immediately turned dark purple. After 4 min, the reaction mixture was quenched in water (color was discharged) and shaken with ether, and the ether solution was washed with sodium bicarbonate solution and water, and dried and evaporated. Sublimation of the total volatile material gave 0.015 g of trifluoroacetate, pure to tlc: $[\alpha]^{25}_{546}$ −61.6°; $[\alpha]^{25}_{436}$ −132° (*c* 1.24, $CHCl_3$). Direct trifluoroacetylation of the same sample of alcohol (−)-V gave trifluoroacetate: $[\alpha]^{25}_{546}$ −62.0°; $[\alpha]^{25}_{436}$ −133° (*c* 1.21, $CHCl_3$).

In the second run, 0.200 g of (−)-V, $[\alpha]^{25}_{546}$ −72.0° (*c* 0.90, $CHCl_3$). was converted to tosylate (0.321 g), and the total sample was dissolved in 10 ml of methylene dichloride and cooled to 3°. This solution under nitrogen with stirring was added all at once to a solution of 30 ml of trifluoroacetic acid (3°) containing 0.056 g of sodium carbonate and 0.13 ml of trifluoroacetic anhydride. By the end of the addition period the solution was turning color, and it was deep purple after 2 min. The solution was stirred for 5.5 min and quenched in 150 ml of water. Isolation provided 0.249 g of crude material. Analysis with controls by tlc with 15% ethyl acetate–cyclohexane on silica gel demonstrated that none of the monoolefin and less than 2.6 mol % of tosylate IV could be detected. The limits of detection of IV were established by comparisons with control samples containing known amounts of tosylate and trifluoroacetate. The 2.6 mol % of tosylate corresponds to greater than 5 half-lives of a reaction, and an estimate of the minimum rate constant for solvolysis was made, $k > 10^{-2}$ sec^{-1}. Tlc analysis using Kiesselguhr-G showed that no alcohol V was present (less than 1%).

The reaction product was sublimed exhaustively at 90° (0.02 mm) (2.5 hr) to give 0.140 g (51%) of 1-trifluoroacetoxy[2.2]paracyclophane: mp 94–96° dec, $[\alpha]^{25}_{546}$ −108°; $[\alpha]^{25}_{436}$ −230° (*c* 0.96, $CHCl_3$). The material contained a trace of impurity according to tlc. A second sublimation (80° (0.015 mm)) gave pure material according to tlc, but the rotations were not changed: $[\alpha]^{25}_{546}$ −108°; $[\alpha]^{25}_{436}$ −231° (*c* 0.96, $CHCl_3$); mp 92–96° dec. A sample of the same starting alcohol was directly trifluoroacetylated. After isolation and two sublimations the material was pure by tlc: $[\alpha]^{25}_{546}$ −105°; $[\alpha]^{25}_{436}$ −224° (*c* 0.99, $CHCl_3$); mp 92–96° dec.

1-Methoxy[2.2]paracyclophane (VIII). A suspension containing 0.132 g of silver tetrafluoroborate, 0.120 g of 1-bromo[2.2]paracyclophane, and 8 ml of methanol was refluxed for 6 hr. The suspension was added to 100 ml of water, extracted with ether, and dried over magnesium sulfate. Removal of the ether gave 0.087 g of material which was chromatographed on 10 g of Mallinckrodt SilicAr. Elution with 1% ether–pentane gave 0.046 g (46%) of ether VIII, mp 93–97°. The material gave a mass spectrum (70 eV) *m/e* (relative intensity) 91 (18), 103 (8), 104 (13), 105 (13), 119 (23), 133 (0.1), 134 (100), 135 (10), 237 (0.1), 238 (8), 239 (2), 240 (0.1). Ether VIII had an R_f value of 0.5 with 15% ethyl acetate–cyclohexane as a developer, and an R_f value of 0.36 with 7% ethyl acetate–cyclohexane as a developer. The sample was recrystallized from pentane for analysis, mp 97–99.5°. *Anal.* Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.33; H, 7.63.

(+)-1-Methoxy[2.2]paracyclophane ((+)-VIII). To a suspension containing 0.208 g (1.36 mmol) of barium oxide, 0.3 ml of water, 2 ml of dimethylformamide, and 0.076 g of (+)-1-hydroxy[2.2]paracyclophane, $[\alpha]^{25}_{546}$ +76.9° (*c* 0.98, $CHCl_3$), was slowly added 0.193 ml of methyl iodide. The suspension was stirred for 24 hr, quenched in water, extracted into ether, and dried to give 0.065 g of crude material. This was chromatographed on 7 g of Merck silica gel. Elution with 1% ether–pentane, followed by sublimation (85° (0.015 mm)), gave 0.026 g (32%) of ether (+)-VIII: mp 114–117°; $[\alpha]^{25}_{546}$ +168° (*c* 0.602, $CHCl_3$). Tlc analysis both before and after sublimation showed that only one compound was present. This material, without further purification, was the control sample for methanolysis of optically pure tosylate described in the next experiment. *Anal.* Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.75; H, 7.46.

Methanolysis of Optically Pure (+)-1-Tosyloxy[2.2]paracyclophane ((+)-IV). A sample of (+)-IV was prepared from 0.11 g of optically pure (+)-1-hydroxy[2.2]paracyclophane, $[\alpha]^{25}_{546}$ +76.9° (*c* 0.98, $CHCl_3$). A solution containing 0.172 g of the tosylate, 0.045 g of fused potassium acetate, and 20 ml of methyl alcohol was heated in a sealed tube at 47° for 45 hr. The tosylate completely dissolved after 10 hr, and the solution remained clear throughout the heating period. The solution was then added to 250 ml of water and extracted with ether, and was dried over sodium sulfate and potassium carbonate. Evaporation of the solvent gave 0.240 g of a mixture of product and salts. The nmr spectrum indicated only the presence of 1-methoxy[2.2]paracyclophane. Preliminary tlc showed the presence of a trace of 1-hydroxy[2.2]paracyclophane but no elimination product, the monoolefin. Comparison of the reaction residue with control samples showed that less than 0.6 mol % of olefin could have been detected with glc analysis with the F and M, using a column temperature of 220°. The crude material was chromatographed on 17 g of Merck silica gel. Elution with 500 ml of pentane and 280 ml of 1% ether–pentane gave no compounds. As little as 1 mg of olefin could have been isolated from the chromatogram. Further elution with 320 ml of 1% ether–pentane gave 90 mg (82%) of (+)-1-methoxy[2.2]paracyclophane, identified by tlc and optical rotation after sublimation: wt 0.086 g; mp 113.5–117°; $[\alpha]^{25}_{546}$ +168° (*c* 0.608, $CHCl_3$).

Polarimetric Kinetics. For a rate determination, the sample was dissolved in a 1-ml volumetric flask and transferred to a polarimeter cell. All rotations for a given run were obtained on this solution. The acetolysis runs were carried out on (+)-1-tosyloxy[2.2]paracyclophane, prepared from the (+)-alcohol $[\alpha]^{25}_{546}$ +63.8° (*c* 0.98 $CHCl_3$), in buffered acetic acid (Table I). The first-order least-squares rate constant, measured on the same solution at two different wavelengths, was the same within experimental error. Preliminary experiments using potassium acetate as a buffer gave rates slightly higher than values expected from the titrimetric data (Table I). Furthermore, the values increased with increasing salt concentrations, reflecting a normal salt effect. For determination of activation parameters, buffered solutions containing sodium

Table II. Determination of First-Order Polarimetric Rate Constant for Acetolysis of a 0.061 *M* Solution of (+)-1-Tosyloxy[2.2]paracyclophane at 25.00 ± 0.05° in Acetic Acid 0.10 *M* in Potassium Acetate and 1% in Acetic Anhydride

Reaction followed at λ 546 nm		Reaction followed at λ 436 nm	
t, min	α_t	*t*, min	α_t
0.0	2.560	0.0	5.475
15.0	2.589	15.0	5.450
30.0	2.577	30.0	5.423
62.0	2.550	60.0	5.374
90.0	2.530	90.0	5.325
120.0	2.502	120.0	5.276
180.0	2.458	180.0	5.187
245.0	2.411	250.0	5.084
305.0	2.369	305.0	5.005
365.0	2.328	365.0	4.922
425.0	2.287	425.0	4.841
485.0	2.250	485.0	4.765
625.0	2.170	625.0	4.602
785.0	2.088	775.0	4.446
1173.0	1.955	1171.0	4.173
1445.0	1.820	1447.0	3.898
1561.0	1.784	1559.0	3.830
1760.0	1.729	1764.0	3.717
1913.0	1.693	1911.0	3.643
2188.0	1.633	2191.0	3.524
3026.0	1.507	3030.0	3.273
3215.0	1.488	3212.0	3.233
3510.0	1.461	3510.0	3.179
3700.0	1.450	3697.0	3.154
∞	1.346	∞	2.943
$k = 1.13 \pm 0.01 \times 10^{-5}$ sec^{-1}		$k = 1.12 \pm 0.01 \times 10^{-5}$ sec^{-1}	

acetate were used (Table I), and each run was done in duplicate. The rate constants were identical within probable error, and were averaged. Table II provides data for a typical run.

The methanolysis rates were measured on tosylate (−)-IV prepared from alcohol (−)-V with $[\alpha]^{25}_{546}$ −52.3° (*c* 0.98, $CHCl_3$). The solution was unbuffered, and was 15% (by volume) chloroform that had been freed of ethanol. The two first-order least-squares rate constants obtained by following the reaction at two wavelengths were the same within experimental error (see Table I).

Titrimetric Kinetics. The procedure described previously[6,24] was applied to racemic 1-tosyloxy[2.2]paracyclophane, mp 88° dec. *Anal.* Calcd for $C_{23}H_{22}O_3S$: C, 72.97; H, 5.87. Found: C, 73.02; H, 6.04.[5] The conditions and results are reported in Table I.

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Hydrocarbon Thermal Degenerate Rearrangements. IV. The Stereochemistry of the Methylenecyclopropane Self-Interconversion. Chiral and Achiral Intermediates[1]

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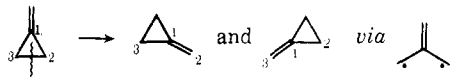
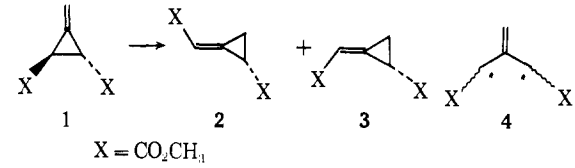
Abstract: Under conditions of kinetic control, *trans*- and *cis*-2,3-dimethylmethylenecyclopropanes, **5** and **6**, respectively, were interconverted thermally with rates comparable to those for rearrangement to the same 7:1 mixture of *anti*- and *syn*-2-methylethylidenecyclopropanes, **9** and **10**, respectively. Pyrolysis of optically active **5** gave inverted **9** as well as optically active **10** of the same sign and magnitude of rotation as that of **9**. Racemization of optically active **5** was twice as fast initially as calculated for reversible formation of **5** from **6**. Orthogonal trimethylenemethane diradical intermediates are proposed to account for the interconversion of **5** and **6** as well as formation of inverted **9** and **10**, and excess racemization is attributed to intervention of achiral, either planar or bisorthogonal, trimethylenemethane diradicals. The energetics and stereochemical features of the rearrangement and of the intermediates are discussed, and the suggestion is made that the orthogonal diradicals are at least 12 kcal/mol more stable than the planar or bisorthogonal diradicals.

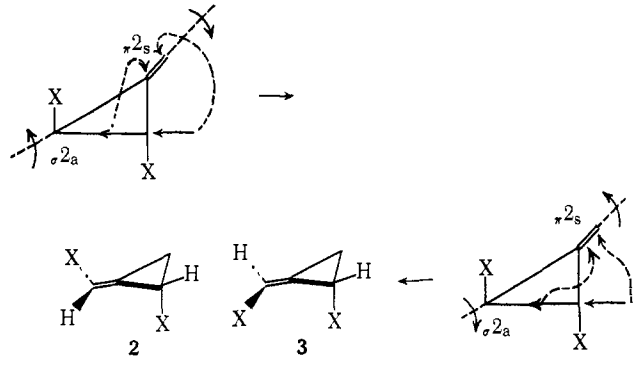
Methylenecyclopropanes are known to undergo thermal self-interconversions by cleavage of the allylic bond and bond formation between an original ring carbon and the original exocyclic methylene carbon.[2] The transition state or intermediate in the reaction is most likely a trimethylenemethane diradical.[3] However, it is the geometry of this species involved in this degenerate rearrangement that is of con-



cern. Feist's ester, **1**, has long been known to undergo this rearrangement. Ullman demonstrated that optically active products, **2** and **3**, were formed when the starting ester was optically active.[2a] This observation precludes the sole intervention of an achiral intermediate such as planar **4**. More recently Doering and Roth have determined the absolute configurations of **1**, **2**, and **3** involved in the thermolysis and found inversion of configuration at the remaining chiral center in **2** and **3** when produced from **1** as depicted above.[2g] Significantly, there was little *trans*-**1** to *cis*-**1** isomerization and even *cis*-**1** gave **2** and **3** with formation of only small amounts of *trans*-**1** kinetically.



These facts have been cited by Woodward and Hoffmann[4] as being consistent with an orbital symmetry allowed $_{\pi}2_s + {}_{\sigma}2_a$ sigmatropic shift in the methylenecyclopropane degenerate rearrangement. There are



(1) (a) For part III, see J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **91**, 5900 (1969). (b) For a preliminary report of this work, see J. J. Gajewski, *ibid.*, **90**, 7178 (1968).

(2) (a) E. F. Ullman, *ibid.*, **81**, 5316 (1959); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (c) J. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *ibid.*, **87**, 3026 (1965); (d) J. K. Crandall and D. R. Paulson, *ibid.*, **88**, 4302 (1966); (e) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 2168 (1970); (f) D. R. Paulson, J. K. Crandall, and C. A. Bunnell, *J. Org. Chem.*, **35**, 3708 (1970); (g) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

(3) For alternative sources of this diradical, see: (a) P. Dowd, A. Gold, and K. Sachder, *J. Amer. Chem. Soc.*, **90**, 2715 (1968); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966); (c) P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967); (d) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).