Cleavage of Alcohols 2 and 3. Excess potassium (0.1 g) was added to a dry dimethoxyethane solution of 0.170 g (0.64 mmol) of alcohol at −78°. After 1 hr the reaction mixture was allowed to come to room temperature where it was maintained for 12 hr. Absolute ethanol (3 ml) and then water (30 ml) were added. After 0.5 hr, the reaction mixture was extracted twice with ether. The combined ethereal extracts were washed with water and then dried over sodium sulfate. Preparative tlc on 2-mm thick plates of silica gel GF were developed three times with 2:8 ether–petroleum ether (bp 30–60°). Single alcohol products were obtained in 30% yields. After recrystallization from ether–pentane, or distillation onto a cold finger, these alcohols melted at 64–65°. The cleavage product from alcohol **3** had $[\alpha]^{24}_{546}$ −38.4°; the product derived from alcohol **2** has a circular dichroism spectrum which is superimposable with that of alcohol **7** derived from alkylation of 4,4′-dimethylbibenzyl with (+)-*R*-propylene oxide.

Alkylation of Bibenzyl with (+)-*R*-Propylene Oxide. A solution of 4,4′-dimethylbibenzyl (1.0 g, 4.86 mmol) in 10 ml of methylene chloride was cooled to −30°. Aluminum chloride (1.5 g, 11.3 mmol) was added followed by addition of 0.415 g (7.17 mmol) of (+)-*R*-propylene oxide ($[\alpha]^{24}_{546}$ +26.8° (*c* 5.2, carbon tetrachloride)[20] in 5 ml of methylene chloride. The reaction mixture was stirred at −20 to −30° for 30 min. The reaction mixture was then poured into an ice slush of 5% hydrochloric acid. The organic layer was separated, washed with saturated sodium bicarbonate solution, and then with water until it was neutral. The organic layer was dried (sodium sulfate) and evaporated. The residue was applied to 2-mm thick silica gel GF plates which were repeatedly developed in 2:8 ether–petroleum ether until two closely spaced bands separated in the alcohol portion of the plate. Both alcohols were eluted from the silica gel with ether and recrystallized from ether–pentane. The upper band was identified as (+)-2-(1-*R*-methyl-2-hydroxyethyl)-4,4′-dimethylbibenzyl (**9**),[15] mp 73–74°; $[\alpha]^{21}_{546}$ +66° (*c* 0.11, chloroform). *Anal.* Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01. Found: C, 84.56; H, 9.18. The lower band was identified as (+)-3-(1-*R*-methyl-2-hydroxyethyl)-4,4′-dimethylbibenzyl (**7**), mp 64–65°; $[\alpha]^{21}_{546}$ +37.5° (*c* 0.008, chloroform). *Anal.* Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01. Found: C, 85.37; H, 8.91.

(+)-1-(4-*S*-[2.2]Paracyclophanyl)-2-*R*-propanol (4). To a solution of 0.8 ml of 2.1 *M n*-butyllithium in hexane was added 0.10 g (0.35 mmol, $[\alpha]^{29}_{546}$ +186°) of (+)-4-*S*-bromo[2.2]paracyclophane in 5 ml of ether at 0°. After 1 hr at 0° and 2 hr at room temperature, 0.102 g (1.75 mmol) of (+)-*R*-propylene oxide ($[\alpha]^{21}_{546}$ +26.8°) was added. After 1 hr at 0° the reaction mixture was stirred at room temperature overnight. Water was then added and the ethereal layer was separated. The organic layer was washed with water until it was neutral and then dried (magnesium sulfate). The solvent was removed and the residue was dried *in vacuo* (25 μ). Preparative layer chromatography on silica gel GF (35:65 ether–petroleum ether) produced 0.07 g (75%) of the desired alcohol; recrystallization from ether–pentane produced material with mp 74–76°, $[\alpha]^{24}_{546}$ +123° (*c* 0.34, chloroform). The alcohol had a nmr spectrum which was identical with the racemic material.[3,4] Treatment of this alcohol with acetyl chloride in pyridine produced the acetate,[3] mp 96–99°; $[\alpha]^{24}_{546}$ +218° (*c* 0.24, chloroform).

(−)-1(4-*R*-[2.2]Paracyclophanyl)-2-*R*-propanol was prepared in the manner described above from (−)-*R*-bromide, $[\alpha]^{24}_{546}$ −186°. The alcohol melted at 94–96°, $[\alpha]^{24}_{546}$ −120° (*c* 0.24, chloroform). Both the alcohol and its acetate derivative had nmr spectra which were identical with authentic samples.[3,4]

Acknowledgment. The authors thank Janice Sommers for help in resolving starting materials. This work was supported by NSF Grant GP-16356; [2.2]paracyclophane was generously supplied by Union Carbide Corp.

(20) Direct comparison of this rotation with literature values ($[\alpha]_D$ +7.23°)[14] is not possible since this rotation was taken at 589 nm. This compound is probably optically pure because it gave optically active bibenzyl **7** of the same unsigned rotation (±0.5°) as the bibenzyl produced by cleavage of pure diastereomers **2** and **3**.

Competing Pathways of Phenonium Ion Formation and Neutralization in the Formolysis of Isomeric 2-(4-[2.2]Paracyclophanyl)propyl Tosylates[1]

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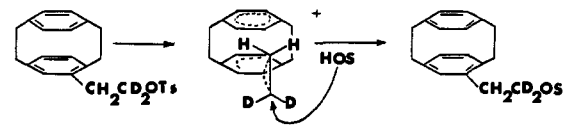
Abstract: The formolysis rates of the threo (**1**) and erythro (**2**) isomers of 2-(4-[2.2]paracyclophanyl)-1-propyl tosylate have been measured. Tosylate **1** solvolyzes 68 times faster than tosylate **2**. Tosylate **1** formolyzes to give a mixture of rearranged and unrearranged threo formates, whereas, tosylate **2** gives only rearranged erythro formate. These results show that **1** ionizes to an exo-bridged ion, and that both endo and exo solvent neutralizations of this ion occur. Tosylate **2** undergoes ionization to an endo-bridged ion, and only exo solvent neutralization of this ion occurs.

A previous investigation of the solvolysis of fused-ring [2.2]paracyclophane derivatives showed that exo phenonium ion formation is preferred by a factor of seven, and that neutralization always occurs in these systems from the exo direction.[2] By analogy, the solvolysis of deuterated 2-(4-[2.2]paracyclophanyl)ethyl tosylate[3] can be formulated as



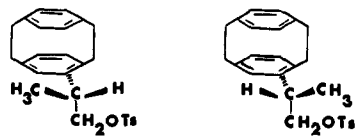
The analogy appears to be qualitatively compatible with the experimental evidence that no deuterium scrambling occurs during this solvolysis.[3] However, the rate difference between exo and endo phenonium ion formation must be larger than 7; otherwise *ca.* 14% deu-

(1) Taken in part from the Ph.D. Thesis of A. Guest, Tulane University, 1970. Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 13, 1970.

(2) M. J. Nugent and T. L. Vigo, *J. Amer. Chem. Soc.*, **91**, 5483 (1969).

(3) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).

terium scrambling would have been observed. For this reason, and because of conformational effects in fused-ring paracyclophanes, it was estimated[2] that exo phenonium ion formation was preferred by a factor of 100. Kinetic measurements of the formolysis rates of the threo (**1**) and erythro (**2**) diastereomers[4] of 2-(4-



1 **2**

[2.2]paracyclophanyl)-1-propyl tosylates have given a closer approximation to this rate factor in open chain systems. In addition, product studies together with kinetic evidence have shown that both endo- and exo-bridged ion formation and neutralization can occur in these open chain systems, whereas, only exo phenonium ion formation and neutralization had been reported previously for closely related systems.[5] In contrast to the corresponding phenyl derivatives,[6] solvolytic rate acceleration accompanied by bridging between primary and secondary electron-deficient centers in these paracyclophane systems does not necessarily lead to skeletal rearrangement of a primary sulfonate to a secondary ester.[7]

Results

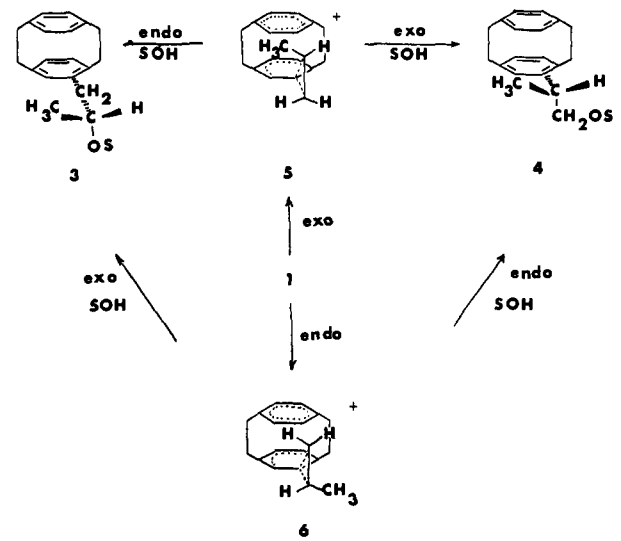
Solvolysis rates were measured conductometrically in formic acid containing 2.5 vol % methylene chloride according to previously published procedures.[2] The kinetic data and activation parameters[8] are shown in Table I.

Table I. Formolysis Data for *threo*- (**1**) and *erythro*- (**2**) 2-(4-[2.2]Paracyclophanyl)-1-propyl Tosylates

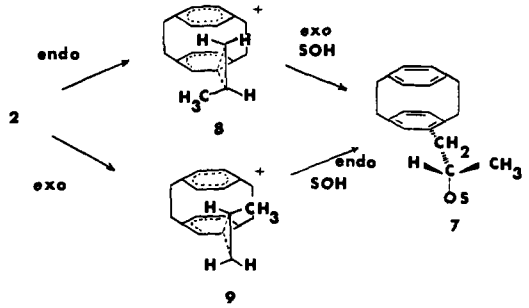
Compd	Temp, °C	$k \times 10^5$ sec^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
1	19.45	22.6 ± 0.2		
	31.02	96.1 ± 3.4	20.4 ± 1.0	−5.3 ± 0.3
	41.98	299 ± 1		
2	41.98	4.40 ± 0.18		
	53.08	15.9 ± 1.0	24.3 ± 1.7	−1.4 ± 1.0
	62.07	48.3 ± 0.3		

Solvolysis products were isolated from sodium formate buffered formic acid solutions after ten solvolytic half-lives. Formate esters were the sole products observed by tlc. The formates were obtained as oils in 90–99% yields after chromatography on silica gel. These oils were characterized spectroscopically and then saponified with dilute sodium hydroxide[2] to the corresponding alcohols[4,5] and for further identification converted to their acetates.[5] Both the alcohols and the acetates had physical and spectroscopic properties which were in good agreement with the literature values.[4,5]

Nmr analysis of the formolysis products of threo tosylate **1** showed two formyl resonances, one at τ 2.00, and the other at τ 2.09 in a ratio of 1.7:1, respectively. This mixture was saponified to give an oil whose nmr spectrum is superimposable, except for the OH resonance, with that of a synthetic mixture of unrearranged threo alcohol **4** (S = H)[4] and rearranged *threo*-1-(4-[2.2]paracyclophanyl)-2-propanol (**3**, S = H). Exhaustive chromatographic and crystallization attempts to separate the formates, these corresponding alcohols, or the tosylate derivatives proved to be unsuccessful. In order to show that these solvolytic results were not due to equilibrium control, and in order to obtain a large sample of rearranged formate **3** (S = CHO), the formolysis products were saponified, reconverted to a mixture of tosylates, and subjected again to buffered formolysis. A total of three formolysis–saponification–tosylation cycles were carried out after which time the mixture consisted of 70% of rearranged threo formate **3** (S = CHO). Saponification of this mixture led to a 58% yield of alcohols from which threo alcohol **3** (S = H) was isolated by crystallization. Thus, the formolysis of **1** proceeds stereospecifically under kinetically controlled conditions to give 63% unrearranged threo formate **4** (S = CHO) and 37% rearranged threo formate **3** (S = CHO).



Nmr analysis of the formolysis product of the erythro isomer **2** showed only one formate which was saponified to *erythro*-1-(4-[2.2]paracyclophanyl)-2-propanol (**7**, S = H)[4,5] and converted to the corresponding acetate **7** (S = Ac)[5] for positive identification. Thus



(4) A. Guest, P. H. Hoffman, and M. J. Nugent, *J. Amer. Chem. Soc.*, **94**, 4241 (1972).
(5) D. J. Cram and F. L. Harris, Jr., *ibid.*, **89**, 4642 (1967).
(6) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).
(7) This result has been previously reported for some [2.2]paracyclophane derivatives (ref 2) as well as for some ferrocene derivatives, *cf.* M. J. Nugent, R. Kummer, and J. H. Richards, *ibid.*, **91**, 6141 (1969).
(8) The uncertainties in the rate constants are standard deviations based on at least three kinetic runs. The uncertainties in the activation parameters are maximum uncertainties calculated from these standard deviations.

the formolysis of erythro tosylate **2** results in complete and stereospecific rearrangement.

Discussion

The threo tosylate **1** undergoes formolysis 68 times faster than the erythro tosylate **2**. Examination of the pathways by which **1** and **2** become exo-bridged ions **5** and **9**, respectively, shows that this exo ionization pathway is very unfavorable for erythro tosylate **2**. As tosylate **2** becomes bridged ion **9**, steric repulsions between the methyl group and the hydrogens of the ethylene link between the two rings in the paracyclophane system increase. This interaction makes exo ionization of **2** sterically unfavorable, whereas, similar steric repulsions do not occur along the exo pathway from threo tosylate **1** to exo-bridged ion **5**. Therefore the exo pathway is more favorable for **1** than it is for **2**, and is reflected in a rate enhancement of 68. The lower energy of the exo ionization pathway to bridged ion formation is in accord with previous investigations.[2,3,5]

Formolysis of **1** gives a mixture of rearranged (**3**) and unrearranged (**4**) threo products. Rearrangement to **3** accounts for 37% of the products under kinetically controlled conditions. Formation of **3** *via* exo-bridged ion **5** must occur by endo solvent attack; however, all previous investigations of [2.2]paracyclophanylphenonium ions have reported exclusive exo solvent neutralization.[2,3,5] The kinetic results preclude the occurrence of rearrangement by exo solvent attack on endo-bridged ion **6**. From previous data and this investigation, the endo ionization pathway from **1** to bridged ion **6** is only $^1/_7$th to $^1/_{68}$th as fast as the exo ionization of **1** to bridged ion **5**. Therefore only a maximum of 14% of rearranged product **3** could occur *via* exo solvent attack on **6**. Thus the major portion of rearranged threo product **2**, if not all of it, must occur by endo solvent attack on exo-bridged ion **5**. That some rearrangement and therefore some endo solvent attack does occur probably reflects the driving force for neutralization at the secondary electron-deficient carbon atom in an ion where an aryl group is bridged between a primary and secondary carbon atom.[6,9,10] That complete rearrangement does not occur reflects the importance of exo solvent attack in these systems.

The erythro tosylate **2** undergoes formolysis with complete and stereospecific rearrangement. If **2** undergoes exo ionization to bridged ion **9**, predominant exo neutralization would be expected to occur just as it does for threo tosylate **1**. Solvent neutralization *via* an exo pathway on **9** would lead to the formation of unrearranged product. Since this product was not observed, **2** probably undergoes formolysis to endo-bridged ion **8** because of the previously mentioned steric interactions in the exo pathway for tosylate **2**. This endo-bridged ion **8** then undergoes exo solvent attack, which is necessarily at the secondary carbon, to give complete rearrangement. Ion **8** is identical with the [2.2]paracyclophanylphenonium ion derived from the formolysis of *erythro*-1-(4-[2.2]paracyclophanyl)-2-propyl tosylate (**7**, S = Ts) and the observed products are the same.[5,11]

(9) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969), and references cited therein; A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

(10) Even the driving force for neutralization at the secondary rather than a primary carbon atom in a bridged ion is not large enough to cause rearrangement in some systems; *cf.* ref 2 and 7.

Experimental Section[12]

Kinetics. Rates were followed conductometrically and analyzed according to previously published procedures[2] on 0.01 *M* solutions of tosylate in purified formic acid[13] (97–100% Matheson Coleman and Bell) which contained 2.5 vol % methylene chloride to improve the solubility of these tosylates.[2] A minimum of 28 kinetic points were taken for each run and rates were followed to four half-lives.

Formolysis of *threo*-2-(4-[2.2]Paracyclophanyl)-1-propyl Tosylate (1). To 7 ml of purified formic acid[13] containing 0.027 g (0.404 mmol) of sodium formate was added 0.170 g (0.404 mmol) of tosylate **1**. The mixture was allowed to react at 42° for 40 min (ten half-lives). The reaction was quenched with ice water and extracted with methylene chloride. The methylene chloride solution was washed with water until it was neutral, dried over sodium sulfate, and evaporated to yield an oil (0.114 g). The nmr spectrum of this material showed two formyl resonances (see text). All the attempts to separate these formates failed. The formate mixture was dissolved in 10 ml of ether and added to 20 ml of 50% aqueous ethanol which contained 2% sodium hydroxide.[14] After 16 hr at room temperature, the reaction mixture was extracted with 100 ml of ether. The ethereal extract was washed with water until it was neutral and then dried over sodium sulfate. The crude products were chromatographed on silica gel and eluted as a mixture in 65% yield with 3:7 ether–hexane. The nmr spectrum of this alcohol mixture was superimposable with the nmr spectrum of a synthetic mixture of 63% alcohol **1** and 37% **3**.[3,4] The alcohol mixture was reconverted to a tosylate mixture, formolyzed, and saponified two times. The final alcohol mixture contained 70% rearranged material (nmr). The mixture was chromatographed on silica gel and eluted with 3:7 ether–hexane in 58% yield. When this mixture was dissolved in ether–pentane and cooled to −78°, a yellow oil separated which was dissolved in ether–pentane. After 2 days at −20°, 23 mg of pure *threo*-1-(4-[2.2]paracyclophanyl)-2-propanol (**3**, S = H) was collected, mp 87–89° (lit.[5] 88.7–89.3°). This alcohol was converted to the acetate,[5] mp 87–89° (lit.[5] 89–89.8°). The nmr and ir spectra of both the alcohol and the acetate were in good agreement with the literature[5] values.

Formolysis of *erythro*-2-(4-[2.2]Paracyclophanyl)-1-propyl Tosylate (2).[4] To a solution of sodium formate (0.034 g, 0.51 mmol) in 10 ml of purified[13] formic acid was added 0.209 g (0.495 mmol) of tosylate **2**. After 4 hr at 63° (ten half-lives), the reaction mixture was quenched and purified as described above for tosylate **1**. The formate was obtained in 90% yield (0.128 g) after chromatography of silica gel. This formate was saponified as described above and the alcohol obtained in 71% yield was crystallized from ether to give a white solid, mp 118–120° (lit.[5] for *erythro*-1-(4-[2.2]paracyclophanyl)-2-propanol (**7**, S = H) 120–121°). The acetate[5] was prepared and crystallized from pentane, mp 55–60° (lit.[5] 58.7–60°).

Acknowledgment. The authors are grateful to the National Science Foundation for Grant GP-16356 for support of this research; [2.2]paracyclophane was generously supplied by Union Carbide Corp.

(11) D. J. Cram, private communication, wishes to correct a mislabeling of formulas in D. J. Cram and F. C. Harris, Jr., *J. Amer. Chem. Soc.*, **89**, 4642 (1967). At the top of page 4644, right column, the left hand formula should read A-β (not A-α), and the right hand formula should read A-α (not A-β).

(12) All melting points are uncorrected. Nmr spectra were taken in deuteriochloroform on a Varian A-60 spectrometer with TMS as an internal standard.

(13) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, 74, 1120 (1952).

(14) Saponification has been used rather than reduction with lithium aluminum hydride because of side reactions caused by the latter method in similar systems, *cf.* T. L. Vigo, Ph.D. Thesis, Tulane University, 1969.