Absolute Configurations of Isomeric [2.2]Paracyclophanylpropanols

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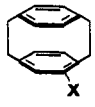
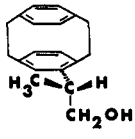
Abstract: Absolute configurations have been assigned to 2-(4-[2.2]paracyclophanyl)-1-propanol diastereomers (**2**, **3**). These alcohols were synthesized from precursors which have an *S* configuration at the aryl ring. The optically active diastereomeric alcohols were cleaved to the corresponding enantiomeric 4,4′-dimethylbibenzyl derivatives. One of these bibenzyls was synthesized from optically active precursors in such a way that the configuration in the alcohol side chain is *R*. Comparison of this enantiomer with the cleavage products shows that (+)-2-(4-[2.2]paracyclophanyl)-1-propanol whose methyl doublet is at τ 8.70 has an *S* configuration at the aryl ring and an *R* configuration at the side chain. Accordingly, (+)-2-(4-[2.2]paracyclophanyl)-1-propanol whose methyl doublet appears at τ 9.02 has an *S* configuration at the aryl ring and an *S* configuration in the side chain. Absolute configurations have also been assigned to the diastereomeric 1-(4-[2.2]paracyclophanyl)-2-propanols by synthesis from optically active precursors of known configuration in such a way that no change of configuration at the chiral centers occurred during these syntheses. The absolute configurations of these dextrorotatory alcohols are shown by **4** and **5**.

Because of restricted internal rotation, all monosubstituted [2.2]paracyclophanes represented by **1** are



1a X = $COCH_3$

chiral.[2] Introduction of a second asymmetric site in the X moiety results in the formation of diastereomeric compounds, each of which consists of enantiomeric pairs. The diastereomeric 2-(4-[2.2]paracyclophanyl)-1-propanols (**2**, **3**) and the diastereomeric 1-(4-[2.2]-paracyclophanyl)-2-propanols (**4**, **5**) are examples of



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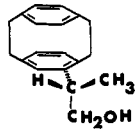

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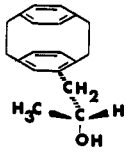

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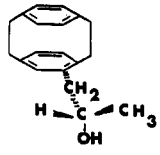

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compounds useful for mechanistic studies.[3,4]

Relative configurations of racemic **3** and **4** have been provisionally assigned on the basis of their nmr spectra and kinetic behavior.[3] The assignments to these racemic compounds are in agreement with the results reported herein.

Nomenclature. All of the diastereomers formulated above have the *S* configuration at the paracyclophane ring.[5,6] Alcohol **2** is *S,R* and **3** is *S,S*. Thus, alcohol **2** and its mirror image correspond to threose which also has opposite configurations at each chiral center. Alcohol **3** and its mirror image have the same configurations at each center and therefore correspond to erythrose. Accordingly, we designate **2** and its mirror image as *threo*-2-(4-[2.2]paracyclophanyl)-2-propanol. Application of this nomenclature to the other pair of diastereomers designates **4** (*S,R*) and its mirror image as *threo*-1-(4-[2.2]paracyclophanyl)-2-propanol, whereas **5** (*S,S*) and its mirror image are *erythro*-1-(4-[2.2]paracyclophanyl)-2-propanols. According to previously used nomenclature, alcohol **4** and its mirror image have been designated as β isomers, and **5** and its mirror image as α isomers.[3]

Results

Synthesis of Optically Active *threo*- and *erythro*-2-(4-[2.2]Paracyclophanyl)-1-propanols (2 and 3).[7] Reaction of (+)-*S*-4-acetyl[2.2]paracyclophane (**1a**)[8] with methylenetriphenylphosphorane followed by hydroboration with diborane[9] gave a mixture of **2** and **3** from which (+)-**3** was obtained by fractional crystallization from ether. Alcohols **2** and **3** can be experimentally differentiated by the chemical shifts of the methyl protons. The methyl doublet for alcohol **3** occurs at τ 9.02, whereas the resonance for these protons in alcohol **2** occurs at τ 8.70.

All attempts to isolate pure threo alcohol **2** from the mother liquors failed. An alternate route to alcohol **2**

(1) (a) Taken in part from the Ph.D. Thesis of A. Guest, Tulane University, 1970; (b) National Science Foundation Undergraduate Research Participant, 1971.

(2) D. J. Cram and N. C. Allinger, *J. Amer. Chem. Soc.*, 77, 6289 (1955).

(3) (a) D. J. Cram and F. C. Harris, Jr., *ibid.*, **89**, 4642 (1967); (b) D. J. Cram, private communication, wishes to correct a mislabeling of formulas in this paper. 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).

(4) M. J. Nugent and A. Guest, *ibid.*, **94**, 4244 (1972).

(5) H. Falk and K. Schloegel, *Agnew. Chem., Int. Ed. Engl.*, **7**, 383 (1968).

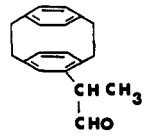
(6) O. E. Weigang and M. J. Nugent, *J. Amer. Chem. Soc.*, **91**, 4555, 4556 (1969).

(7) These procedures are similar to those reported for the syntheses of the exo and endo isomers of 17-hydroxymethyl-4,5-tetramethylene-[2.2]paracyclophane; *cf.* M. J. Nugent and T. L. Vigo, *J. Org. Chem.*, **34**, 2203 (1969).

(8) H. Falk, P. Reich-Rohrwig, and K. Schloegl, *Tetrahedron*, **26**, 511 (1969).

(9) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

employed the Wittig reaction of methoxymethylenetriphenylphosphorane with ketone **1a**. Acidic hydrolysis of the vinyl ether mixture led to a mixture of threo and erythro aldehydes **6** which could not be separated



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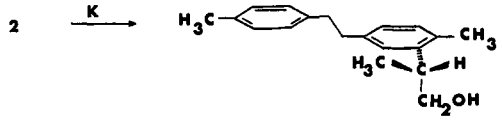
by preparative tlc or fractional crystallization. Careful column chromatography on silica gel of the aldehyde mixture gave material enriched in the threo isomer. Reduction of this aldehyde mixture with sodium borohydride, and tosylation with tosyl chloride followed by fractional crystallization produced (+)-threo tosylate. Conversion of this tosylate to (+)-threo alcohol **2** was accomplished with sodium naphthalenide in tetrahydrofuran.[10]

Identical procedures beginning with racemic ketone **1a** produced the corresponding racemic diastereomers **2** and **3** which were separated in a similar manner.

Cleavage of (+)-*threo*- and (+)-*erythro*-2-(4-[2.2]-Paracyclophanyl)-1-propanols. Metal cleavage of [2.2]-paracyclophane occurs under certain conditions to give 4,4′-dimethylbibenzyl.[11] Reaction of (+)-alcohol **2** with potassium in dimethoxyethane gave (+)-3-(1-methyl-2-hydroxyethyl)-4,4′-dimethylbibenzyl (**7**), while reduction of (+)-alcohol **3** gave the enantiomer, (−)-3-(1-methyl-2-hydroxyethyl)-4,4′-dimethylbibenzyl (**8**).



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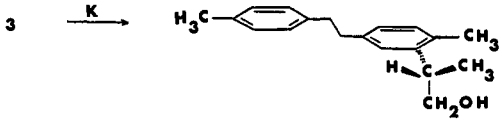

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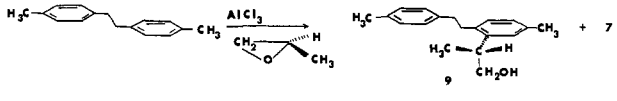
Alkylation of 4,4′-dimethylbibenzyl with (+)-*R*-propylene oxide[12] produced two dextrorotatory alcohols which were separated by multiple development, preparative tlc. Spectral and analytical data show that these alcohols are isomeric. The less mobile alcohol of this isomeric pair has a circular dichroism spectrum which is superimposable with the spectrum of alcohol **7** derived from potassium reduction of (+)-threo alcohol **2**. This less mobile alcohol is enantiomeric to alcohol **8** derived from potassium reduction of (+)-erythro alcohol **3**.



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Synthesis of Optically Active *threo*- and *erythro*-1-(4-[2.2]Paracyclophanyl)-2-propanols. Reaction of *n*-butyllithium with (+)-*S*-4-bromo[2.2]paracyclophane[13] (**10**) produced optically active 4-*S*-lithio[2.2]paracyclophane. Alkylation of this optically active organolithium derivative with (+)-*R*-propylene oxide[12] produced (+)-alcohol whose nmr and ir spectra are superimposable with those of authentic racemic *threo*-1-(4-[2.2]paracyclophanyl)-2-propanol (**4**) which is obtained from other reactions.[3,4] The same reaction between (+)-*R*-propylene oxide[12] and 4-*R*-lithio[2.2]paracyclophane produced (−)-alcohol whose nmr and ir spectra are superimposable with racemic *erythro*-1-(4-[2.2]-paracyclophanyl)-2-propanol (**5**) obtained from other reactions.[3,4] As a further check, these optically active alcohols were converted to the corresponding acetates. The nmr spectra of these derivatives were also superimposable with the spectra of the corresponding racemic compounds.[3,4]

Discussion

Assignment of Absolute Configurations to (+)-*threo*- and (+)-*erythro*-2-(4-[2.2]Paracyclophanyl)-1-propanols (2, 3). Since the synthesis of these diastereomeric alcohols began with (+)-4-*S*-acetyl[2.2]paracyclophane,[8] the absolute configurations at the aryl ring in both alcohols are also *S*. Therefore these two diastereomeric, dextrorotatory alcohols differ only in configuration at the asymmetric carbon in the side chain. Cleavage of the ethylene bridge in these alcohols destroys the configurational integrity at the aryl ring and results in the formation of enantiomeric substituted bibenzyls **7** and **8**. An authentic sample of one of these bibenzyls, (+)-3-(1-*R*-methyl-2-hydroxyethyl)-4,4′-dimethylbibenzyl (**7**), was obtained by the stereospecific reaction[14] of (+)-*R*-propylene oxide with 4,4′-dimethylbibenzyl. Of the two isomeric *R* alcohols produced in this latter reaction, the less mobile isomer[15] is identical with the cleavage product from alcohol **2** and enantiomeric to the cleavage product from alcohol **3**. Thus (+)-2-(4-[2.2]paracyclophanyl)-1-propanol whose methyl doublet appears at τ 8.70 has an *S* configuration at the aryl ring and an *R* configuration in the side chain as shown by structure **2**, and (+)-2-(4-[2.2]paracyclophanyl)-1-propanol whose methyl doublet appears at τ 9.02 has an *S* configuration at the aryl ring and an *S* configuration in the side chain as shown by structure **3**.

Assignment of absolute configurations to (+)-*threo*- and (+)-*erythro*-1-(4-[2.2]paracyclophanyl)-2-propanols (4, 5) follows directly from their synthesis *via* bromides **10**. Since the absolute configuration at each chiral center is preserved in these reactions, the (+)-1-(4-[2.2]-paracyclophanyl)-2-propanol has configurations at each center shown by **4**. Likewise, the (−)-1-(4-[2.2]paracyclophanyl)-2-propanol product from (−)-*R*-4-bromo-[2.2]paracyclophane has configurations at each center which are mirror images of **5**. Alcohol **4** is spectro-

(10) W. D. Closson, P. Wriede, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 1581 (1966).

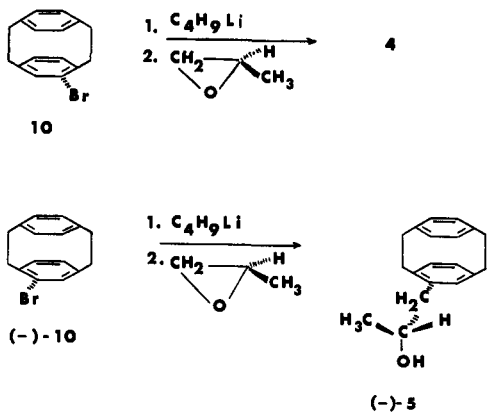
(11) J. L. Marshall and T. K. Folsom, *Tetrahedron Lett.*, 757 (1971).

(12) P. A. Levene and A. Walter, *J. Biol. Chem.*, **68**, 418 (1926); C. C. Price and M. Osgan, *J. Amer. Chem. Soc.*, **78**, 4787 (1956).

(13) P. H. Hoffman, Undergraduate Honors Thesis, Tulane University, 1971. The absolute configurations of the bromides are assigned on the basis of their synthesis from acids of known configuration[5,6] by reactions similar to those already reported for the corresponding racemic compounds; *cf.* D. J. Cram and N. C. Allinger, *J. Amer. Chem. Soc.*, 77, 6289 (1955).

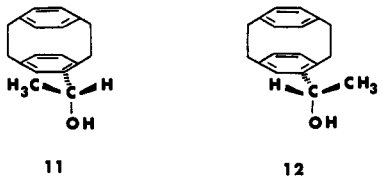
(14) T. Nakajima, S. Suga, T. Sugita, and K. Ichikawa, *Bull. Chem. Soc. Jap.*, **40**, 2980 (1967).

(15) Alcohols **7** and **9** are the possible products in this reaction. Models show that the OH group in alcohol **9** is more hindered than the OH group in alcohol **7**. For this reason we provisionally assign structure **7** to the less mobile isomer. The absolute configurations of the [2.2]paracyclophanylpropanols are in no way affected by any error in this isomer assignment.



scopically identical with Cram and Harris' racemic β alcohol, and the acetate derivatives also are spectroscopically identical.[3] Alcohol (−)-**5** and its acetate derivative are also spectroscopically identical with the corresponding racemic α isomers.[3,4,16]

Relative Configurational Assignments from Nmr Spectra. Nmr spectroscopy has been shown to be a reliable method for the assignment of relative configurations in the case of the diastereomeric 1-(4-[2.2]paracyclophanyl)-1-ethanols (**11**, **12**).[3] The chemical shift of the methyl



11 **12**

protons of the threo isomer **11** is at τ 8.46, whereas, the chemical shift for the methyl protons in the erythro isomer **12** is upfield at τ 8.76. The corresponding phenyl compound, 1,4-dimethyl-2-(α-hydroxyethyl)-benzene has the corresponding methyl resonance at τ 8.68, which is between the resonances of the diastereomers. For the isomeric alcohols **2** and **3** and their derivatives, the methyl doublet in the threo isomers is downfield (**2**, τ 8.70; **2**-OTs, τ 8.62; **6**, τ 8.58) from the corresponding signal in the erythro isomer (**3**, τ 9.02; **3**-OTs, τ 9.00; **6**, τ 8.85). The resonance for the methyl protons in the corresponding phenyl compounds ($C_6H_5CH(CH_3)X$; X = CH_2OH, τ 8.77; X = CH_2OTs, τ 8.72; X = CHO, τ 8.68) is in between these values.

These absolute configurations, and the relative configurations they demand, are in complete accord with previous assignments based on mechanistic studies[3] and with the results presented in the following paper.[4]

Experimental Section

All melting points are uncorrected. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Nmr spectra were recorded on a Varian A-60 as 10% solutions in deuteriochloroform. Polarimetric data were obtained from a Bendix TBL-NPL automatic polarimeter.

(+)-4-*S*-Acetyl[2.2]paracyclophane (1a) was prepared from optically pure acid;[8] $[\alpha]^{24}_{546}$ +230° (*c* 5.2, chloroform), lit.[17] $[\alpha]^{25}_{546}$ +198°. Ketone **1a** melts at 130–131° and has $[\alpha]^{29}_{546}$ +191° (*c* 0.94, chloroform).

(+)-2-(4-*S*-[2.2]Paracyclophanyl)propene. The Wittig reagent was generated from 2.14 g (6.0 mmol) of triphenylmethylphosphonium bromide in dimethyl sulfoxide.[18] A solution of ketone **1a** in dimethyl sulfoxide was then added and the reaction was carried out according to the previously published procedure.[7] The olefin was isolated in 91% yield, mp 89–90.5° (ether); $[\alpha]^{29}_{546}$ +330° (*c* 6.6, chloroform). The racemic compound, prepared in the same manner, has mp 73–74°. *Anal.* Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.83; H, 8.13.

(+)-2-*S*-(4-*S*-[2.2]Paracyclophanyl)-1-propanol (3). To a solution of 0.06 g (1.6 mmol) of sodium borohydride and 0.4 g (1.6 mmol) of (+)-*S*-2-(4-[2.2]paracyclophanyl)propene in 10 ml of diglyme was added 0.26 g of boron trifluoride etherate dropwise under nitrogen. After 2 hr at room temperature, 2 ml of water, 1 ml of 3 *N* sodium hydroxide, and 1 ml of 30% hydrogen peroxide were added. After 16 hr the reaction mixture was worked up in the usual way to give 0.39 g (91%) of alcohol **3** which was recrystallized from ether, mp 99–100.5°, $[\alpha]^{28}_{546}$ +61° (*c* 1.64, chloroform). The racemic erythro alcohol prepared in the same manner had mp 147–148°. *Anal.* Calcd for $C_{19}H_{22}O$: C, 85.66; H, 8.33. Found: C, 85.75; H, 8.42. The racemic alcohol was converted to the tosylate in the usual manner and recrystallized from ether, mp 93–94°. *Anal.* Calcd for $C_{26}H_{28}O_3S$: C, 74.26; H, 6.70; S, 7.69. Found: C, 74.40; H, 6.84; S, 7.64.

(+)-*cis*- and *trans*-1-Methoxy-2-(4-[2.2]paracyclophanyl)propene. To a solution of 6 g (17.6 mmol) of triphenylmethoxymethylphosphonium chloride in 40 ml of ether was added 14.6 ml of a 2.1 *M* hexane solution of *n*-butyllithium under nitrogen. After 30 min at room temperature, the reaction mixture was cooled to −70° and 1.5 g (5.86 mmol) of (+)-*S*-4-acetyl[2.2]paracyclophane (**1a**) was added. The reaction mixture was stirred at −70° for 1 hr and then allowed to come to room temperature. The reaction mixture was then poured into water. The ethereal layer was separated and the aqueous solution was washed with ether. The combined ethereal solutions were washed with water and dried over sodium sulfate. The reaction mixture, after evaporation of solvent, was chromatographed on silica gel. The vinyl ethers were eluted with hexane (77% yield). The racemic vinyl ether melts at 104–110°. *Anal.* Calcd for $C_{20}H_{22}O$: C, 86.27; H, 7.97. Found: C, 86.05; H, 8.03.

(+)-2-*R*-(4-*S*-[2.2]Paracyclophanyl)-1-propyl Tosylate. The mixture of (+)-*cis*- and *trans*-1-methoxy-2-(4-[2.2]paracyclophanyl)-propene was hydrolyzed with perchloric acid saturated ether according to previously published procedures.[7,19] The resulting dextrorotatory aldehyde mixture was chromatographed on silica gel. Careful elution with 1:9 ether–hexane led to fractions which were enriched in the threo isomer, which was eluted last. Fractions which consisted of 80% threo (**2**) and 20% erythro (**3**) isomers were obtained after successive chromatographies. These fractions were then reduced with excess sodium borohydride in ethanol. The crude alcohol mixture 0.280 g (1.05 mmol) was converted to the tosylate as described above. After one crystallization from ether, pure (+)-threo tosylate was isolated in 61% yield, mp 112–114° $[\alpha]^{24}_{546}$ +14.7° (*c* 0.38, chloroform). The racemic tosylate prepared in the same manner melted at 97–98°. *Anal.* Calcd for $C_{26}H_{28}O_3S$: C, 74.26; H, 6.70; S, 7.69. Found: C, 74.24; H, 6.80; S, 7.66.

(+)-2-*R*-(4-*S*-[2.2]Paracyclophanyl)-1-propanol (2). Sodium naphthalenide was prepared from a dry tetrahydrofuran solution of 0.238 g (1.94 mmol) of naphthalene and 0.04 g of sodium under nitrogen. After formation of the radical anion was complete, the reaction mixture was cooled to −70° and 0.247 g (0.35 mmol) of (+)-threo tosylate in tetrahydrofuran was added dropwise. After 30 min at −70°, ethanol was added to destroy excess sodium. Water was then added and the reaction mixture was extracted twice with ether. The ethereal extracts were washed with water until they were neutral and then dried over sodium sulfate. After evaporation of the solvent, the product alcohol was isolated in 95% yield by preparative layer chromatography, 1:1 ether–hexane on silica gel GF. Recrystallization from ether–pentane produced material melting at 121–123°; $[\alpha]^{24}_{546}$ +73.2° (*c* 0.65, chloroform). The racemic threo alcohol, prepared from racemic threo tosylate, had mp 90–91°. *Anal.* Calcd for $C_{19}H_{22}O$: C, 85.66; H, 8.33. Found: C, 85.45; H, 8.26.

(16) Cram and Harris report data in ref 3 for α and β isomers which have deuterium at the 2-carbon atom in the side chain; therefore they report singlets where we observe doublets.

(17) D. J. Cram and L. A. Singer, *J. Amer. Chem. Soc.*, **85**, 1075 (1963).

(18) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 2063 (1963).

(19) G. Wittig, W. Boell, and K. H. Kruek, *Chem. Ber.*, **95**, 2514 (1962); A. G. Levine, *J. Amer. Chem. Soc.*, **80**, 6150 (1958).

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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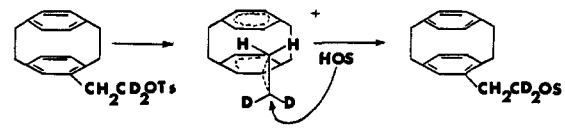
Abstract: The formolysis rates of the threo (**1**) and erythro (**2**) isomers of 2-(4-[2.2]paracyclophanyl)-1-propyl tosylate have been measured. Tosylate **1** solvolyzes 68 times faster than tosylate **2**. Tosylate **1** formolyzes to give a mixture of rearranged and unrearranged threo formates, 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).