# Macro Rings. XLIV. Photolytic Racemization Mechanisms of Chiral Compounds[1,2]

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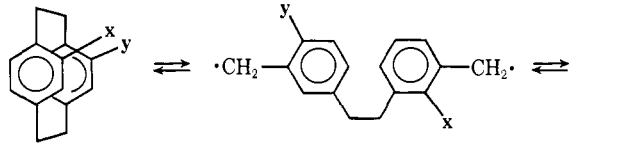
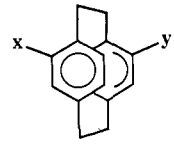
**Abstract:** Four optically active compounds have been found to undergo photolytic racemization: (−)-4-methyl[2.2]paracyclophane ((−)-**1**), (−)-4,7-dimethyl[2.2]paracyclophane ((−)-**2**), (−)-1-carbomethoxy[2.2]paracyclophane ((−)-**3**), and (+)-1-hydroxymethylene[2.2]paracyclophane ((+)-**4**). With light λ 254 nm, (−)-**1** racemized in acetic acid, methanol, isopropyl alcohol, and benzene, and (−)-**2** and (−)-**3** racemized in methanol. With light λ >270 nm, (−)-**1** and (+)-**4** racemized in acetone. With light λ 350 nm, (−)-**1** racemized in acetophenone. Recovered paracyclophane yields varied from 42 to 97% and per cent racemization from >99 to 46%. Naphthalene and oxygen inhibited the racemization of (−)-**1** in methanol and acetone at λ >270 nm, and oxygen inhibited racemization of (−)-**1** in acetone at λ >300 nm. Although racemization rates exceeded those of other reactions, long reaction times produced open-chain solvolysis products of benzyl–benzyl bond cleavage, as well as homolysis products from benzyl–benzyl and methylene–phenyl bond cleavages. Excited state aryl rotation, benzvalene, Dewar benzene, and double Diels–Alder mechanisms for racemization are eliminated, but *p*-xylylene, diradical, and zwitterionic routes are accommodated by the evidence.

Previous studies[3] established that [2.2]paracyclophane underwent photolytic ring opening[3a] at both the benzyl–benzyl and methylene–phenyl positions to give open-chain products. Optically active 4-carbomethoxy[2.2]paracyclophane underwent thermal racemization through a diradical intermediate at about 200°.[3b,c] Similarly disubstituted [2.2]paracyclophanes atropisomerically equilibrated (*e.g.*, A ⇄ B) at about the same temperature.[3b,c] Others observed that *syn*-[2.2]paracyclonaphthane isomerized both thermally and photolytically to the more stable anti isomer.[4]

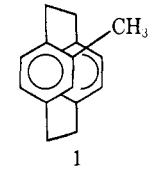



ψ-gem
A




ψ-meta
B

The present investigation was undertaken to see if the thermal isomerizations in the [2.2]paracyclophane systems had photolytic counterparts and, if so, to characterize them mechanistically. The structures of the photolytic cleavage products of [2.2]paracyclophane itself suggested the existence of intermediate diradicals or zwitterions that might, after conformational reorganization, return to starting material. Use of optically active, substituted [2.2]paracyclophanes such as **1**–**4** as starting materials allows symmetrical intermediates to be detected in reactions whose intermediates partition between racemized starting material and open-chain products.

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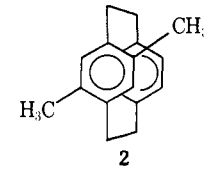


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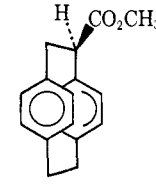


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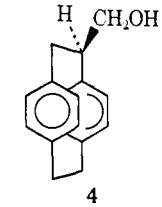


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## Methods and Results

**Starting Materials.** Racemic[5a] and optically active[5b] 4-methyl[2.2]paracyclophane ((±)-**1** and (−)-**1**) have been reported previously, although not before the outset of this work. Optically active (−)-4-carboxy[2.2]paracyclophane[6a] was reduced to (−)-4-hydroxymethylene[2.2]paracyclophane, whose corresponding (−)-bromide[6b] was easily recrystallized to optical purity and reduced to (−)-**1**. Identical rotations for (−)-**1** were obtained from starting acid of maximum or less than maximum rotation. Monobromination of (±)-**1** followed by lithiation and methylation of the product gave (±)-**2**. Similarly, (−)-**1** was converted to (−)-**2**. A better route to (−)-**2** involved the sequence formulated. Both enantiomers of **2** were prepared, and the magnitude of their rotations and that of (−)-**2** prepared from (−)-**1** were the same within experimental error, a fact that points to optical purity. Optically pure 4-acetyl[2.2]paracyclophane was pre-

(1) The authors warmly thank the National Science Foundation for a grant used in support of this research.

(2) Parts of this work appeared as a communication: M. H. Delton and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 7623 (1970).

(3) (a) R. C. Helgeson and D. J. Cram, *ibid.*, **88**, 509 (1966); (b) H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967); (c) *ibid.*, **91**, 3517 (1969).

(4) H. H. Wasserman and P. M. Keehn, *ibid.*, **91**, 2374 (1969).

(5) (a) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3505 (1969); (b) M. J. Nugent and O. E. Weigang Jr., *ibid.*, **91**, 4556 (1969).

(6) (a) D. J. Cram and N. L. Allinger, *ibid.*, 77, 6289 (1955); (b) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).

Table I. Photolytic Racemization Experiments at 25° of Optically Pure Compounds under Nitrogen[a]

| Run no. | Substrate: Nature | Substrate: Concn, $M \times 10^3$ | Medium | λ, nm | Time, hr | Recovered paracyclophane: % | Recovered paracyclophane: % racemiz |
|---|---|---|---|---|---|---|---|
| 1 | (−)-**1** | 0.69 | AcOH | 254[b] | 0.5 | 42 | >99 |
| 2 | (−)-**1** | 0.66 | $CH_3OH$ | 254[b] | 0.5 | 78 | >99 |
| 3 | (−)-**1** | 0.55 | $CH_3OH$ | 254[b] | 0.17 | 97 | 95 |
| 4 | (−)-**1** | 0.67 | $(CH_3)_2CHOH$ | 254[b] | 0.5 | 43 | >99 |
| 5 | (−)-**1** | 0.78 | $C_6H_6$ | 254[b] | 0.5 | 75 | 72 |
| 6 | (−)-**1** | 45 | $CH_3COCH_3$ | >270[c] | 4.0 | 92 | 96 |
| 7 | (−)-**1** | 43 | $C_6H_5COCH_3$ | 350[d] | 5.75 | 55 | 46 |
| 8 | (−)-**1** | 43 | $n$-$C_6H_{14}$ | 350[d] | 5.75 | 65 | 11 |
| 9 | (−)-**2** | 0.50 | $CH_3OH$ | 254[b] | 0.5 | 68 | >99 |
| 10 | (−)-**3** | 0.42 | $CH_3OH$ | 254[b] | 0.5 | 87 | >99 |
| 11 | (+)-**4** | 42 | $CH_3COCH_3$ | >270[c] | 4.0 | 76 | 57 |

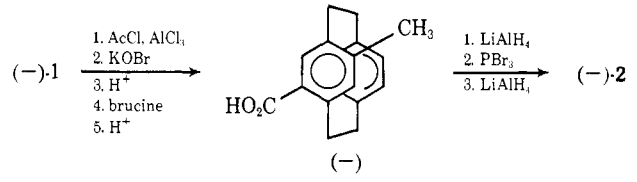
[a] Solvent was flushed with and irradiated under a blanket of pure nitrogen. [b] Radiation source was a quartz U-tube, low-pressure mercury arc of *ca.* 2 W at 254 nm. Emission characteristics (as per cent of output) were 86% at 254 nm; 8.5% at 578 nm; 2.5% at 185 nm; and less than 1% each at 313, 365, and 436 nm. Irradiated solution was in direct contact with lamp. [c] Medium-pressure, 450-W Hanovia lamp with Corex filter in a quartz tube in a merry-go-round apparatus. [d] Rayonet RPR-100 reactor equipped with lamps of 350-nm emission.

Table II. Quenching Experiments at 25° of Optically Pure (−)-**1**[a]

| Run no. | Medium | (−)-**1** concn, $M$ | Inhibitor: Nature | Inhibitor: Concn | λ, nm | Time, hr | Recovered paracyclophane: % | Recovered paracyclophane: % racemiz |
|---|---|---|---|---|---|---|---|---|
| 12 | $CH_3OH$[b] | 0.004 | None | | >270[c] | 3 | 85 | 99 |
| 13 | $CH_3OH$[b] | 0.004 | Naphthalene | 0.01 $M$ | >270[c] | 3 | 100 | 4 |
| 14 | $CH_3OH$ | 0.004 | Oxygen | satd | >270[c] | 3 | 70 | 42 |
| 15 | $(CH_3)_2CO$ | 0.004 | Oxygen | satd | >270[c] | 3 | 70 | 52 |
| 16 | $(CH_3)_2CO$[b] | 0.0035 | None | | >300[d] | 2 | 95 | 44 |
| 17 | $(CH_3)_2CO$ | 0.0035 | Air | satd | >300[d] | 2 | 90 | 0–10 |

[a] Merry-go-round reactor, 4-mm i.d. tubes. [b] Degassed thoroughly. [c] Run simultaneously with medium-pressure, 450-W Hanovia lamp (L679A) with Corex filter in an immersion apparatus. [d] Run simultaneously in same apparatus used for runs 12–15 except with Pyrex filter.

pared by treatment of optically pure 4-carboxy[2.2]-paracyclophane with methyllithium.[7]




Racemic 1-carboxy[2.2]paracyclophane[8] was resolved through its salts of optically active α-phenylethylamine, and the enantiomers obtained exhibited rotations of opposite sign but of equal magnitude. Their methyl esters ((+)-**3** and (−)-**3**) also possessed rotations of equal magnitude. These facts suggested that optical purity was reached with these compounds. Reduction of (−)-1-carboxy[2.2]paracyclophane with lithium aluminum hydride gave (+)-1-hydroxymethylene[2.2]paracyclophane ((+)-**4**). The ultraviolet absorption spectra of **1**, **2**, and **4** were almost identical with those of the parent [2,2]paracyclophane system.[9]

**Photolytic Reactions.** Table I reports the results of the photolytic racemization experiments of optically active compounds **1**–**4**. In each run the products were separated by column chromatography or preparative glc (internal standard) and the rotations of the recovered paracyclophanes taken. In all runs conducted in acetic acid, methanol, or isopropyl alcohol with λ 254 nm radiation, racemization was complete in 30 min, and the amount of recovered paracyclophane (42–87%) indicated that racemization had occurred much faster than any other reactions (runs 1, 2, 4, 9, and 10). Compounds (−)-**1**, (−)-**2**, and (−)-**3** were all involved in these reactions, and no difference in their racemization efficiency was detected. Run 5 with (−)-**1** was conducted in benzene with λ 254 nm, and the 75% of **1** recovered was 72% racemized. In run 6, acetone served as medium, λ >270 nm. The 92% recovered **1** was 96% racemized. With acetophenone as medium and λ 350 nm (run 7), (−)-**1** went to **1** (55%) that was 46% racemized. A control run (8) made in $n$-hexane under the same conditions gave **1** (65%) only 11% racemized. In run 11, (+)-**4** in acetone with λ >270 nm, the 76% recovered **4** was 57% racemized. Attempts to racemize (−)-4-carbomethoxy[2.2]paracyclophane and (−)-4-acetyl[2.2]paracyclophane in acetone with λ >300 nm failed, although the former compound racemized inefficiently with λ >210 nm.

Table II records the results of quenching experiments with (−)-**1** as substrate in a merry-go-round apparatus.[10] Runs 12–15 were made simultaneously under identical conditions[10] with λ >270 nm. Run 12 in methanol (99% racemization) served as a control for runs 13 (methanol, 0.01 $M$ in naphthalene, 34% racemization), 14 (methanol, oxygen saturated, 42% racemization), and 15 (acetone, oxygen saturated, 52% racemization). Run 16 in degassed acetone was conducted with (−)-**1** at λ >300 nm in a merry-go-round apparatus[10] to give 44% racemization. Run 17 made simultaneously but not degassed gave only 0–10% racemization.

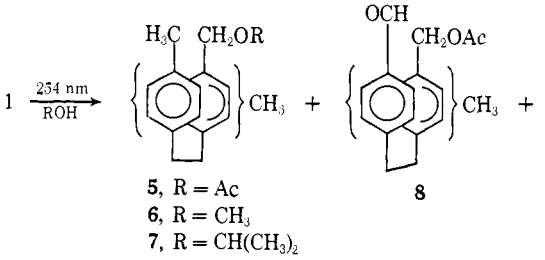
(7) H. Falk, P. Reich-Rohrwig, and K. Schlögl, *Tetrahedron*, **26**, 511 (1970).
(8) E. Hedaya and L. M. Kyle, *J. Org. Chem.*, **32**, 197 (1967).
(9) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).
(10) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Table III. Products of 254-nm Irradiation of ~4 × $10^{-3}$ *M* Solutions of (±)-**1**[a]

| Run no. | Solvent | Atm[b] | Time, hr | Products[c] Type | % yield | Type | % yield | Type | % yield |
|---|---|---|---|---|---|---|---|---|---|
| 18 | AcOH | $N_2$ | 4 | **5** | 9 | | | | |
| 19 | AcOH | $O_2$ | 5 | **8** | 4 | Dimer[d] | 3 | | |
| 20 | $CH_3OH$ | $N_2$ | 10 | 6 | 6 | | | | |
| 21 | $CH_3OH$ | $O_2$ | 10 | 6 | 6 | **11** | 2 | | |
| 22 | $(CH_3)_2CHOH$ | $N_2$ | 14 | **7** | 4 | **9** | ~3 | **10** | 3 |

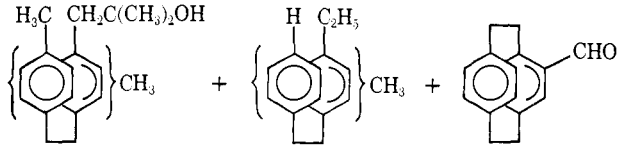
[a] See footnote *b*, Table I. [b] Solution saturated and blanketed. [c] See text for structural identification. Trace amounts (glc) of xylene-type cleavage products were also produced and much polymer. Yields varied with reaction time, but are near optimal. [d] Polar, nonvolatile, open-chain compound with C=O, *m/e* 562.

Five runs (Table III) with (±)-**1** were designed to investigate processes other than that of racemization with λ 254 nm. The reaction times were adjusted to maximize open-chain products. In all runs polymer was the major product, particularly in the presence of oxygen. Small amounts of open-chain products were also isolated, and their structures (except for the position in the products of the original arylmethyl group) were determined by spectroscopic methods. Table III records the results.




**5**, R = Ac
**6**, R = $CH_3$
**7**, R = $CH(CH_3)_2$

**8**

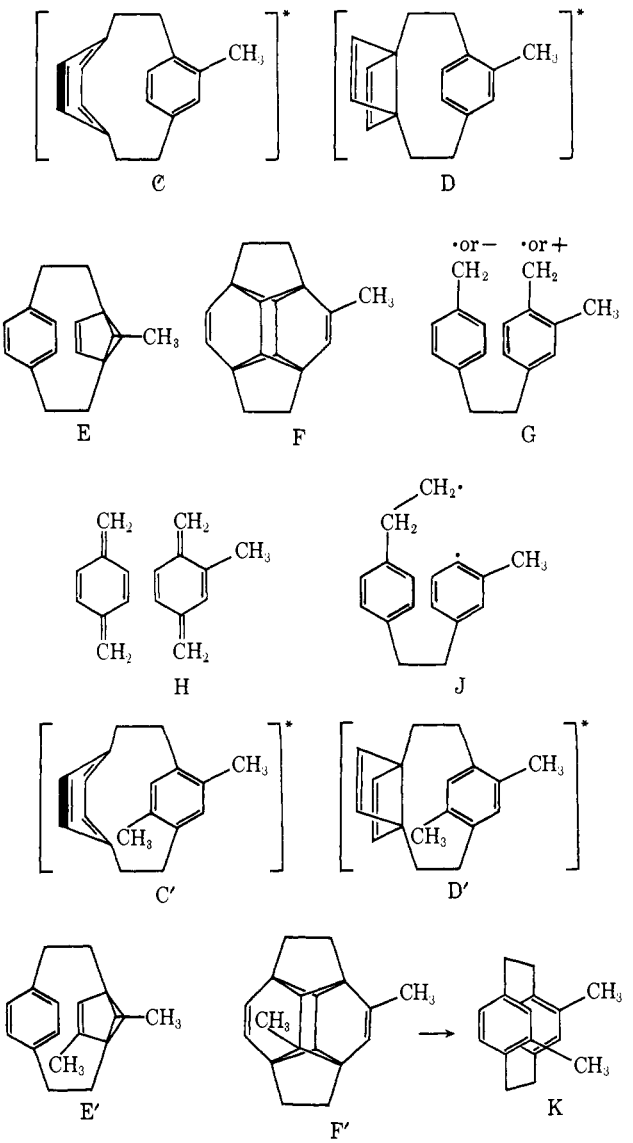



**9** **10** **11**

In acetic acid, methyl alcohol, or isopropyl alcohol, solvolysis products **5**, **6**, or **7** were produced, respectively (runs 18, 20–22). In the presence of oxygen in acetic acid (run 19), only aldehyde acetate **8** and a higher molecular weight compound were isolated. Under the same conditions, **5** did not give **8**. In a similar run (21) in methanol, no corresponding aldehyde ether was detected, although a trace of oxidation product of the methyl group of **1** (4-aldehydo[2.2]paracyclophane, **11**) was isolated. Only under nitrogen in isopropyl alcohol (run 22), the best hydrogen atom donor, were the direct products of radical reaction with solvent detected. Alcohol **9** was isolated as well as hydrocarbon **10**.

## Discussion

**Mechanisms for Reactions Caused by 254-nm Light.** The results of runs 1–8 (Table I) demonstrate that (−)-4-methyl[2.2]paracyclophane ((−)-**1**) underwent photolytic racemization at λ 254 nm. The reaction coordinate for these reactions must involve a nonchiral structure. Structures C–J all possess mirror planes, and might be either transition states (*e.g.*, C) or intermediates that could produce racemic **1** from (−)-**1**. Although photoracemization of (−)-**1** *via* C finds some analogy in other studies,[11] this alternative as well as structures D, E, and F are eliminated by the fact that (−)-4,7-dimethyl[2.2]paracyclophane ((−)-**2**) racemizes (run 9) under the same conditions as (−)-**1**. Structures C′ and D′ for racemization of (−)-**2** are ruled out on steric grounds. Benzvalene[12] (E′) and Diels–Alder (F′) intermediates for racemization of (−)-**2** are eliminated by virtue of their chirality. Benzvalene E′ might racemize by equilibrating with rearranged benzvalenes, but such a process would surely generate [2.2]metaparacyclophane[13] or dimethyl[2.2]paracyclo-



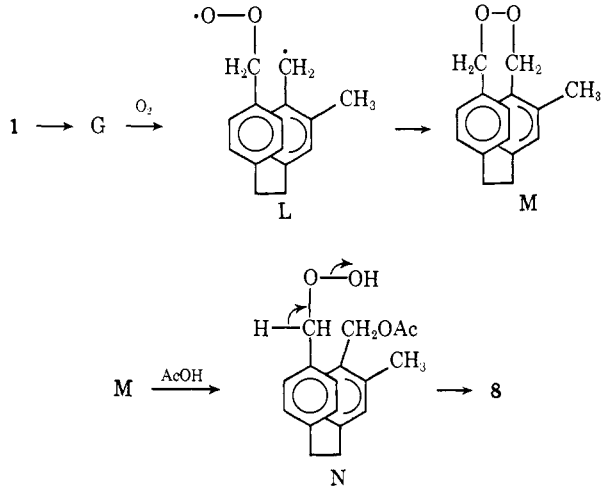

(11) K. Mislow and A. J. Gordon, *J. Amer. Chem. Soc.*, **85**, 3521 (1963).

(12) K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968), and previous papers and references.

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

phanes in which two methyl groups were ortho or meta to one another. No such products were observed. Although a double Diels–Alder intermediate actually was observed in the [2.2]paracyclonaphthane system,[14] if formed from (−)-**2**, E′ should decompose either back to (−)-**2** or to optically active pseudo-*o*-dimethyl[2.2]paracyclophane (K), but not to (±)-**2**. The products from run 9 gave a mass spectrum that demonstrated that both methyl groups were still in the same benzene ring. Had K been produced, some of the product would have had one methyl in one ring and the other methyl in the other.[15]

The racemization of (−)-1-carbomethoxy[2.2]paracyclophane ((−)-**3**) in run 10 under the same conditions as (−)-**1** and (−)-**2** clearly rules out all reaction mechanisms that do not involve bond breaking to the chiral center. Intermediates G, H, and J all fulfill this condition. The open-chain solvolysis product (**6**) was observed with extended reaction times in run 20, which was conducted with **1** in methanol under the same conditions used for the above racemization runs (λ 254 nm). This fact suggests that zwitterion or singlet diradical G was the main intermediate in both the racemization and solvolysis reactions at this wavelength. That G can behave either like a diradical or a zwitterion is suggested by the structures of the other open-chain products in runs 18, 19, and 22 (λ 254 nm). In acetic acid under nitrogen (run 18), acetate **5** was produced (solvolysis), but under oxygen (run 19), aldehyde acetate **8** was obtained. Probably **8** was produced as an acetolysis product of the process, **1** → G → L → M → N → **8**.




In run 22 made in isopropyl alcohol, solvolysis product **7** was observed along with radical reaction products, alcohol **9** and hydrocarbon **10**. Previous work[3a] established that [2.2]paracyclophane in methanol or ethanol with broad spectrum light gave alcohols analogous to **9** along with *p,p′*-dimethylbibenzyl. The fact that isopropyl alcohol is a better source of hydrogen atoms and hydroxycarbinyl radicals than methanol correlates with the production of radical product **9** in isopropyl alcohol, and the absence of an analogous product in methanol. As in the presence of oxygen in acetic acid, intermediate G appears able to act as a diradical, provided appropriate reactants are available.

Hydrocarbon **10** as a product clearly points to cleavage between the aryl group and the bridge of the [2.2]paracyclophane system. The analogous *p*-ethylbibenzyl was produced as the exclusive product from [2.2]paracyclophane itself with λ >270 nm, or with acetone as a photosensitizer.[3a] Naphthalene served as an efficient quenching reagent under either condition. These facts suggested that production of *p*-ethylbibenzyl occurred through the lowest energy triplet of [2.2]paracyclophane. Production of **10** at λ 254 nm in isopropyl alcohol suggests either that the small amount of light of longer wavelengths present is responsible, or that acetone is produced from the isopropyl alcohol by two hydrogen atom abstractions, and once produced serves as photosensitizer[3a] for the production of **10**. In any case, it seems likely that at λ 254 nm, the racemizations involve benzyl–benzyl rather than aryl–bridge cleavage processes, and that the same zwitterion–diradical singlet that gives rise to racemic product also produces the open-chain products.

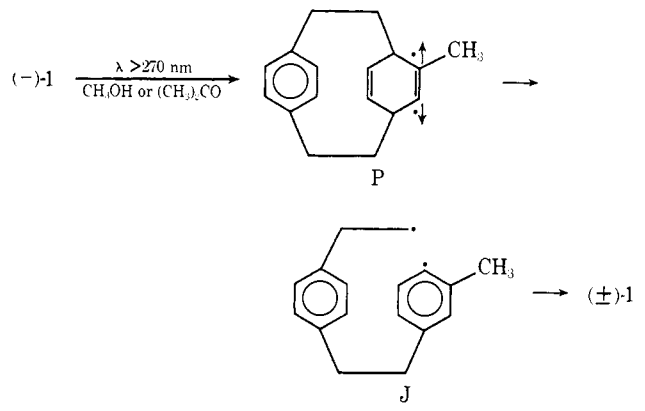
**Mechanisms for Reactions Caused by Light >270 nm.** Racemization of (−)-4-methyl[2.2]paracyclophane ((−)-**1**) with light >270 nm was observed in methanol (run 12) and acetone (run 6). Likewise (+)-1-hydroxymethylene[2.2]paracyclophane ((+)-**4**) racemized in acetone with λ >270 nm (run 11). This fact demonstrates the absence of C, D, E, or F as intermediate structures. Racemization of (−)-**1** was inhibited in methanol by the presence of either naphthalene or oxygen (runs 13 and 14). Racemization of (−)-**1** in acetone was inhibited by the presence of air with light of λ >300 nm (runs 16 and 17).

Earlier experiments with [2.2]paracyclophane demonstrated that in ethanol with light >270 nm, or with broad spectrum light in acetone, only *p*-ethylbibenzyl was produced.[3a] With broad spectrum light in ethanol, naphthalene inhibited only the formation of *p*-ethylbibenzyl, not that of solvolysis product. Air also inhibited formation of the hydrocarbon. Likewise, naphthalene prevented the formation of the same hydrocarbon in acetone. Production of *p*-ethylbibenzyl by either the photosensitized (acetone) or nonphotosensitized process (ethanol) was interpreted as involving as the first intermediate the lowest triplet state of [2.2]paracyclophane, formed by a process inhibited by air and quenchable by naphthalene.[3a]

Racemization of (−)-**1** and *p*-ethylbibenzyl formation occurred under the same two sets of conditions (alcohol or acetone, λ >270 nm), and both processes were inhibited by oxygen and quenched by naphthalene. If *p*-ethylbibenzyl formation involves as the first intermediate the lowest triplet of [2.2]paracyclophane, it seems likely that racemization of (−)-**1** involves as the intermediate the lowest triplet of 4-methyl[2.2]paracyclophane (P). Thus (−)-**1** → P → J → (±)-**1** is a plausible route for the λ >270 nm photolytic racemization of (−)-**1**.

No experimental evidence exists that eliminates the pair of *p*-xylene molecules (H) as intermediates for racemization. The facts that [2.2]paracyclophane produces *p*-xylylene at 550° and that *p*-xylylene produces [2.2]paracyclophane at low temperatures are well documented.[16] Absence of disproportionation prod-

(14) H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **89**, 2770 (1967).
(15) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3534 (1969).
(16) (a) W. F. Gorham, *J. Polym. Sci.*, 4, 3027 (1966); (b) Y. L. Yeh and W. F. Gorham, *J. Org. Chem.*, 34, 2366 (1969).




ucts (*e.g.*, [2.2]paracyclophane and dimethyl[2.2]paracyclophane) of 4-methyl[2.2]paracyclophane in these experiments does not eliminate H as intermediates. An efficient recombination reaction of the two reorganized tetraenes within the solvent cage would produce racemized product, and any tetraene that escaped the cage would probably go to other products.

**Survey Experiments.** The results of a number of survey experiments point additionally to the diversity of conditions available for racemizing substituted [2.2]paracyclophane. Run 5 conducted in benzene with λ 254 nm efficiently racemized (−)-**1**. At λ 350 nm, (−)-**1** racemized more efficiently in acetophenone than *n*-hexane as solvent (runs 8 and 9). With λ >210 nm, (−)-4-carbomethoxy[2.2]paracyclophane was 19% racemized in methanol. Both (−)-4-carbomethoxy[2.2]paracyclophane and (−)-4-acetyl[2.2]paracyclophane failed to racemize in acetone with λ >300 nm. Thus benzene, acetone, and acetophenone act as photosensitizers for (−)-**1** racemization, whereas an acetyl or carbomethoxy group on the system inhibits photoracemization in the acetone-sensitized process. Clearly the [2.2]paracyclophane nucleus is highly vulnerable to light under a variety of conditions. Only a few of the gross mechanistic features of the reactions have been delineated here.

## Experimental Section

**General.** Commercial [2.2]paracyclophane, recrystallized from chloroform, was used. All solvents were reagent grade unless specified otherwise. Fractionally distilled pentane was used. Anhydrous benzene was distilled from calcium hydride; anhydrous methanol was distilled from magnesium turnings. Melting points were taken on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Nuclear magnetic resonance (nmr) measurements were made with either a Varian A-60D or HA-100 spectrometer, using 5–20% (w/v) solutions in deuteriochloroform with tetramethylsilane as internal standard. Infrared spectra (ir) were run in spectrograde chloroform or as a Nujol mull on a Beckman IR-5 spectrophotometer. Mass spectra were run at 12 eV on an AEI Model MS-9 instrument. Ultraviolet spectra (uv) were recorded on a Cary Model 14M spectrophotometer in 1-cm quartz cells using 95% ethanol. Weighings of less than 10 mg were done on a Cahn gram electrobalance and are accurate to ±0.001 mg. Silica gel for column chromatography was either Baker or Merck chromatographic grade. For thin layer chromatography (tlc), Brinkmann silica gel G was used on Pyrex plates with appropriate cyclohexane–ethyl acetate mixtures as developer and iodine vapor for visualization. Eluents for column chromatography were uniformly ether–pentane mixtures. Gas–liquid chromatography (glc) was carried out on an F and M Model 720 instrument with 1 to 2 ft × 0.25 in. columns packed with 20% SE 30 on 60–80 Firebrick at a flow rate of 60 ml/min. Analytical glc was done on an Aerograph Model 200 instrument at 155° using 7 ft × 0.12 in. columns packed with 7% SE 30 on 80–90 Anakrom ABS. Optical rotations were taken in spectrograde chloroform or carbon tetrachloride on a Perkin-Elmer Model 141 polarimeter with 1-dm, water-jacketed cells thermostated at 25.0 ± 0.5°

**Irradiation Apparatus.** For small-scale irradiation experiments at wavelengths other than 254 nm when high uniformity of irradiative conditions was desired, a merry-go-round apparatus was used.[10] The quartz tubes containing the solutions were placed in slots in a turntable which was rotated about a 450-W immersion lamp (Hanovia Co., L679A) contained in a water-cooled quartz immersion well. Each tube also was periodically rotated about its axis. Cylindrical filter sleeves were placed around the light source for the irradiations in Corex and Pyrex.

For preparative runs, solutions to be irradiated were placed in the outer well of an immersion apparatus with a 450-W lamp (Hanovia, L679A) as light source. The solutions were stirred magnetically, and nitrogen or oxygen gas was bubbled through the solution before and during reaction.

For irradiations at 254 nm, a U-tube, low-pressure mercury arc (Ultraviolet Products Co., *ca.* 2 W; see footnote *b*, Table I for characteristics) was used in direct contact with the solution which was stirred magnetically. Either pure nitrogen or oxygen was bubbled through the solution both before and during irradiation.

For monochromatic radiation experiments at 350 nm, a Rayonet RPR-100 reactor (Southern New England Ultraviolet Co.) equipped with a set of 350-nm light sources was used. Solutions to be irradiated were suspended in quartz tubes inside the reactor.

**(−)-4-Methyl[2.2]paracyclophane ((−)-1).** The precursors to optically pure (−)-**1** were prepared as reported previously and exhibited the following rotations: 4-carbomethoxy[2.2]paracyclophane,[15] $[\alpha]^{25}_{436}$ −570.5° (*c* 0.185, $CHCl_3$); 4-carboxy[2.2]paracyclophane,[6a] $[\alpha]^{25}D$ −157° (*c* 1.0 $CHCl_3$); 4-hydroxymethylene[2.2]paracyclophane,[6b] $[\alpha]^{25}_{546}$ −79.3° (*c* 1.0, $CHCl_3$); 4-bromomethylene[2.2]paracyclophane,[2d] $[\alpha]^{25}_{546}$ +37.6° (*c* 1.02, $CHCl_3$). Typically, from 4 g of optically pure starting acid was obtained 4.15 g (61%) of optically pure (−)-**1**, mp 152.5–153°, $[\alpha]_{546}$ −114° (*c* 1.0, $CHCl_3$), $[\alpha]_{436}$ −236° (*c* 1.0, $CHCl_3$), $[\alpha]_{546}$ −119° (*c* 1.0, $CCl_4$), $[\alpha]_{436}$ −250° (*c* 1.0, $CCl_4$). *Anal.* Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.92; H, 8.10.

**(−)-4-Bromo-7-methyl[2.2]paracyclophane.** Racemic material was prepared as before[5a] in 30% yield, mp 160–161°, lit.[5a] mp 159–160°. When optically pure (−)-**1** served as starting material, the bromomethyl product gave mp 164.5–166°, $[\alpha]_{546}$ −214° (*c* 0.8, $CCl_4$), $[\alpha]_{436}$ −465° (*c* 0.8, $CCl_4$). *Anal.* Calcd for $C_{17}H_{17}Br$: C, 67.78; H, 5.69. Found: C, 67.75; H, 5.77.

**(−)-4,7-Dimethyl[2.2]paracyclophane ((−)-2).** Racemic **2** and (−)-**2** were both prepared by the following procedure, detailed for **2** as follows. To a stirred refluxing solution prepared from 15 ml of anhydrous ether and 30 ml of 1.6 *N* *n*-butyllithium in hexane was added, under dry nitrogen, 814 mg of 4-bromo-7-methyl[2.2]paracyclophane. The reaction mixture was stirred at 25° for 1 hr and cooled to 0°; 9.0 ml of dimethyl sulfate was added slowly. After the solution had stood at 25° for 2 hr, a concentrated aqueous ammonia solution was added to destroy the excess dimethyl sulfate. The mixture was shaken with an ether–water mixture; the ether layer was washed, dried, and evaporated. Glc analysis of the residue demonstrated the presence of 15% **1** and 85% **2**, which proved impossible to separate by fractional crystallization. Preparative glc on a small sample provided pure **2** (trace), mp 151–151.5°. From optically pure (−)-4-bromo-7-methyl[2.2]paracyclophane was obtained (−)-**2**, mp 137–137.5°, $[\alpha]_{546}$ −189°, $[\alpha]_{436}$ −390° (*c* 0.15, $CCl_4$). *Anal.* Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.34; H, 8.48. A better preparation of (−)-**2** is detailed below.

**4-Acetyl-7-methyl[2.2]paracyclophane.** To 2 g of **1**[5a] in 75 ml of dichloromethane at −60° was added, all at once, a dichloromethane solution of 1.32 g of acetyl chloride and 1.7 g of anhydrous aluminum chloride. An immediate dark red color appeared. The mixture was stirred for 0.5 hr at −60 to −40° and then poured into 125 ml of 3 *N* hydrochloric acid at 0°. Ether was added until the organic portion was lighter than water. The organic layer was washed with water, bicarbonate solution, and brine and dried. Solvent was removed under vacuum, and the residual solid was recrystallized twice from dichloromethane–ether to afford 0.7 g of 4-acetyl-7-methyl[2.2]paracyclophane, mp 116–117°. A second crop yielded another 1.1 g (total of 75% yield). The samples were combined and sublimed at 85° (0.5 mm) to give an analytical sample. *Anal.* Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.48; H, 7.52.

The nmr spectrum of this material was consistent with the assigned (title) structure. The spectrum consisted of a sharp singlet at δ 6.80 (1 H, ortho to acetyl), a doublet of doublets centered at δ

6.61 with $J$ = 8, 2 Hz (1 H, pseudo geminal to methyl), a singlet at $\delta$ 6.44 (1 H, aromatic), an AB quartet at $\delta$ 6.37 (2 H, aromatics), and a broad singlet at $\delta$ 6.11 (1 H, ortho to methyl). The bridge protons fell in a range of $\delta$ 4.2–2.5; the acetyl methyl was a sharp singlet at $\delta$ 2.41, the aromatic methyl, a singlet at $\delta$ 2.09.

**4-Carboxy-7-methyl[2.2]paracyclophane.** The bromoform reaction was done by a standard procedure.[6a] With 15 g of potassium hydroxide in 40 ml of water and 8.65 g of bromine, 3.6 g of 4-acetyl-7-methyl[2.2]paracyclophane was converted to 2.95 g of the title compound (82%) which was recrystallized from glacial acetic acid, mp 258–259°. *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.19; H, 6.84.

**Resolution of 4-Carboxy-7-methyl[2.2]paracyclophane.** The brucine salt of racemic acid was prepared by dissolving 5.0 g (18 mmol) of the acid and 7.4 g (18 mmol) of recrystallized (from acetone) brucine in 550 ml of acetone. The volume of solvent was reduced to 500 ml and the resulting solution allowed to stand at 25° for 1 hr and at 0° for 48 hr. The first crop of 4.5 g was recrystallized three times, the third recrystallization not improving the rotation. A total of 3.66 g of this (−) salt was obtained and converted to acid by shaking the salt with 50 ml of ether and 50 ml of 6 *N* hydrochloric acid. The 1.5 g of (−) acid obtained gave mp 213.5–214°, and $[\alpha]_{436}$ −752°, $[\alpha]_{546}$ −284° (*c* 0.76, $CHCl_3$). The second diastereomeric salt was obtained from the original mother liquors. Three recrystallizations of the first mother liquor crop afforded constantly rotating (+) salt. From 1.2 g of this salt was obtained 0.55 g of (+) acid of mp 213.5–214° and $[\alpha]_{436}$ +763°, $[\alpha]_{546}$ +280° (*c* 0.78, $CHCl_3$). Recrystallization of this material from dichloromethane afforded an analytical sample of the same melting point. *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.07; H, 6.90.

**(−)-4,7-Dimethyl[2.2]paracyclophane ((−)-2).** Optically pure (−)-4-carboxy-7-methyl[2.2]paracyclophane (see above) was converted to (−)-**2** by the same reaction sequence used to convert 4-carboxy[2.2]paracyclophane to 4-methyl[2.2]paracyclophane. From 1.5 g of (−) acid was obtained 1.0 g (75%) of (−)-**2**, mp 138–139°, $[\alpha]_{436}$ −412°, $[\alpha]_{546}$ −198° (*c* 0.58, $CCl_4$). By the same sequence, optically pure (+) acid gave (+)-**2**, mp 140–141°, $[\alpha]_{436}$ +412°, $[\alpha]_{546}$ +199° (*c* 1.4, $CCl_4$). Both enantiomers of the intermediate compounds in the above preparations were also characterized. The data for the (−) isomers are as follows. The (−)-4-hydroxymethylene-7-methyl[2.2]paracyclophane gave mp 101–102°, $[\alpha]_{436}$ −351°, $[\alpha]_{546}$ −163° (*c* 1.2, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.61; H, 8.12. The (−)-4-bromomethylene-7-methyl[2.2]paracyclophane gave mp 143–145°, $[\alpha]_{436}$ −107°, $[\alpha]_{546}$ −32.4° (*c* 0.33, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{19}Br$: C, 68.80; H, 5.77. Found: C, 68.92; H, 5.96.

**(+)- and (−)-1-Carboxy[2.2]paracyclophane.** A mixture of 10 g of racemic 1-carbomethoxy[2.2]paracyclophane[8,17] (**3**) was hydrolyzed in the usual way to give acid, wt 8.6 g, mp 186–186.5° (from ethyl acetate). *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.13; H, 6.42. A mixture of 14.0 g of this acid and 6.72 g of optically pure (−)-α-phenylethylamine in 600 ml of acetone (or methanol) deposited needles after 21 hr: 6.2 g first crop; 2.6 g second crop. Four recrystallizations of the combined crops gave 3.55 g of diastereomerically homogeneous salt, which when converted to the acid gave 2.24 g of acid, mp 187–188° (hygroscopic), $[\alpha]_{546}$ −42.9 ± 1° (*c* 0.5, $CHCl_3$), whose rotation was not changed by recrystallization. *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.97; H, 6.41.

The other diastereomeric salt crystallized as large prisms that were manually separated from the fine needles in the original crystallization. These prisms were used to seed mother liquors from the crystallizations of the needles, and in this way 2.4 g of prisms was collected. Recrystallization of this salt from methanol gave 1.1 g of plates, which were converted to the free acid, wt 0.7 g, mp 186–188°, $[\alpha]_{546}$ +42.0° (*c* 0.56, $CHCl_3$).

**(+)- and (−)-1-Carbomethoxy[2.2]paracyclophane ((+)- and (−)-1).** Treatment of optically pure (+)-1-carboxy[2.2]paracyclophane with diazomethane in ether gave the methyl ester, mp 115.5–116.5°, $[\alpha]_{546}$ +49.2° (*c* 0.6, $CHCl_3$). Partially optically pure (−)-1-carboxy[2.2]paracyclophane, $[\alpha]_{546}$ −39° (*c* 0.5, $CHCl_3$), was similarly converted to (−)-**1**, $[\alpha]_{546}$ −45.1° (*c* 0.5, $CHCl_3$), one recrystallization of which gave material, mp 115.5–116.5°, $[\alpha]_{546}$ −51.2° (*c* 0.5, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.35; H, 6.97.

(17) M. H. Delton and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 1669 (1972).

**4-Aldehydo[2.2]paracyclophane.**[18] The same procedure was used here as was applied to oxidation of 12-hydroxymethylene[2.2]-metaparacyclophane to 12-aldehydo[2.2]metaparacyclophane.[19] From 390 mg of 4-hydroxymethylene[2.2]paracyclophane (see above) was obtained 287 mg (73%) of 4-aldehydo[2.2]paracyclophane, mp 156–160°, mp 166–166.5° (evacuated capillary). *Anal.* Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.43; H, 6.95.

**(−)-4-Acetyl[2.2]paracyclophane.** From 253 mg of (−)-4-carboxy[2.2]paracyclophane of $[\alpha]_D$ −157.4° (*c* 1.0, $CHCl_3$) was prepared[7] 135 mg of (−)-4-acetyl[2.2]paracyclophane, mp 127–128° (lit.[7] mp 120–124°), $[\alpha]_{436}$ −336°, $[\alpha]_{546}$ −97.2° (*c* 0.195, $CHCl_3$), $[\alpha]_D$ −65.0° (*c* 1.0, $CHCl_3$) (lit.[7] $[\alpha]_D$ +65°, *c* 0.5, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.28; H, 7.08.

**(+)-1-Hydroxymethylene[2.2]paracyclophane ((+)-4).** From 1.87 g of (−)-1-carboxy[2.2]paracyclophane, $[\alpha]_{546}$ −42° (*c* 0.5, $CHCl_3$), was produced 1.61 g of (+)-**4** by the same procedure used for the corresponding racemates.[17] The (+)-**4** produced gave mp 122.5–123° (ether–pentane), $[\alpha]_{436}$ +136°, $[\alpha]_{546}$ +51.5° (*c* 0.56, $CHCl_3$). *Anal.* Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.63; H, 7.59.

**Photolytic Racemization Experiments of Table I.** The general procedures used are illustrated by descriptions of particular runs. Runs 1–5, 9, and 10 were all carried out with the U-tube light source (see footnote *b* of Table I for characteristics) immersed in a reaction vessel containing a magnetically stirred solution of the compound to be photolyzed. Before and during the reaction, purified nitrogen was bubbled through the solution, and nitrogen blanketed the vessel.

Run 1 was typical. In 280 ml of glacial acetic acid was dissolved 43.5 mg of optically pure (−)-**1**, $[\alpha]_{546}$ −110° (*c* 1.0, $CHCl_3$). After 0.5 hr of irradiation the solvent was evaporated and the product was examined by tlc. Polymer, **1**, and a slower moving component were present. The material was chromatographed on 3 g of silica gel, and **1** was eluted with 1% ether in pentane. The **1** collected was sublimed to give 18 mg (42%) of material pure to tlc and glc analysis, $[\alpha]_{436}$ 0 ± 1°, $[\alpha]_{546}$ 0 ± 1° (*c* 0.8, $CHCl_3$).

In run 9, 33 mg of optically pure (−)-**2**, $[\alpha]_{436}$ −412° (*c* 0.6, $CCl_4$), in 280 ml of anhydrous methanol was irradiated for 0.5 hr. After chromatography of the product and sublimation, **2** pure to glc and tlc was recovered, wt 22.5 mg, $[\alpha]_{546}$ 0 ± 1°, $[\alpha]_{436}$ 0 ± 1° (*c* 0.9, $CCl_4$). A mass spectrum of this material showed no significant *m/e* 118 peak.

In run 10, a solution of 31 mg of optically pure (−)-**3**, $[\alpha]_{546}$ −51.2 (*c* 0.5, $CHCl_3$), in 280 ml of methanol was irradiated for 0.5 hr. The solvent was evaporated and the residue sublimed to give 26.8 mg of **3**, pure to glc, $[\alpha]_{546}$ 0.0 ± 0.5°, $[\alpha]_{436}$ 0.0 ± 0.5° (*c* 1.0, $CHCl_3$).

Run 6 was carried out in the merry-go-round apparatus with a Corex filter sleeve on the lamp. A solution of 40 mg of opitcally pure (−)-**1**, $[\alpha]_{546}$ −110°, $[\alpha]_{436}$ −252° (*c* 0.8, $CCl_4$), in 4 ml of spectrograde acetone in a quartz tube was flushed with pure nitrogen, and was irradiated under a blanket of nitrogen for 4 hr. The acetone was evaporated and the white crystalline residue sublimed to give 36.7 mg of **1**, pure to glc, $[\alpha]_{546}$ −4.63°, $[\alpha]_{436}$ −10.1° (*c* 0.95, $CCl_4$).

Run 11 was carried out similarly to run 6 except that optically pure (+)-**4** was employed, $[\alpha]_{546}$ +51.5°, $[\alpha]_{436}$ +136° (*c* 0.56, $CHCl_3$). After 4 hr of irradiation, recovered, sublimed **4**, pure to tlc, gave $[\alpha]_{546}$ +21°, $[\alpha]_{436}$ +57.6° (*c* 2.1, $CHCl_3$).

Runs 7 and 8 were made simultaneously in two identical quartz tubes in the Rayonet reactor (footnote *d*, Table I) for 5.75 hr. Each tube contained 38 mg of optically pure (−)-**1**, $[\alpha]_{546}$ −110° (*c* 1.0, $CHCl_3$). In run 7, 5 ml of *n*-hexane and in run 8, 5 ml of reagent grade acetophenone served as solvent, and in both runs the solvents were flushed and blanketed with pure nitrogen. In run 8 after irradiation, the solution was placed on a short column of neutral alumina, and **1** was eluted with pentane. The amounts of **1** and its optical purity were determined by a standardized glc and polarimetric technique (see future section and Table I). In run 7 after irradiation, the contents of the tubes were added to an excess of lithium aluminum hydride in refluxing tetrahydrofuran. The syrup obtained after the usual isolation procedure was chromatographed on 200 g of neutral alumina, eluted with pentane, and

(18) The authors warmly thank Dr. D. T. Hefelfinger for this preparation.

(19) D. T. Hefelfinger and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 4767 (1971).

collected in 100-ml fractions. Fractions 40–44 contained **1** (glc). They were combined, and the amounts of **1** and its optical purity were determined by the standardized glc and polarimetric method (see future section and Table I).

**Determination of Amount and Optical Purity of 4-Methyl[2.2]paracyclophane (1) Obtained in Runs 7, 8, and 12–17.** Triphenylmethane gave a good retention time and peak shape relative to that of **1** on glc. A standard solution of 25.5 mg of triphenylmethane in 5.0 ml of carbon tetrachloride was prepared, and 1.0-ml aliquots were withdrawn (always the same pipette) and transferred to the sample for which the amount of **1** present was to be determined. After thorough mixing, the solutions were analyzed by analytical glc on a Aerograph 200 flame ionization instrument with a 5-ft × 0.12 in. column of 7% SE 30 on 90–100 Anakrom ABS at 150° and a flow rate of 20 ml/min. The injector temperature was 225° and the detector temperature was 335°. The retention time of **1** under these conditions was 5 min, and that of the triphenylmethane was 8.5 min. Areas were determined with a Disc integrator or by cut-and-weigh procedures. The results of two calibration runs are given in Table IV. From the data for sample

Table IV

| Sample no. | Known wt of **1**, mg | Area for **1** | Area for $(C_6H_5)_3CH$ |
|---|---|---|---|
| 1 | 8.75 | 200 | 106.5 |
| 2 | 0.56 | 153.5 | 1288 |
| 3 | 4.26 | 201 | 225.1 |
| 4 | 4.01 | 225 | 268 |

1, the weight of **1** in sample 2 was calculated to be 0.56 mg (known weight, 0.56 mg). From the data for sample 3, the weight of **1** in sample 4 was calculated to be 4.04 mg (known weight, 4.01).

The per cent recovery and optical purity of **1** produced in the photolysis experiments were determined as follows. A 1-ml aliquot of the above standard solution of triphenylmethane was pipetted directly into the photolysis solution, except in runs 7 and 8, where the chromatograph eluate was used instead. The resulting solution was passed through a short column of silica gel to remove polymer (this step was omitted in runs 7 and 8). The solvent was then removed under vacuum at 25° and the residue was quantitatively transferred to a 2.00-ml volumetric flask with carbon tetrachloride, and diluted to the mark. Rotations were taken on this solution, and a sample also was submitted to glc analysis. From the ratio of peak areas of **1** and triphenylmethane from the glc and the known concentration of triphenylmethane in the sample, the concentration of **1** in the sample was calculated. The yield and optical purity of **1** were then calculated.

**Photolytic Racemization and Quenching Experiments of Table II.** Runs 12–15 were conducted simultaneously in four quartz test tubes of 4-mm i.d. fitted with Corex filters in the merry-go-round apparatus. Each tube contained 10–12 mg of optically pure (−)-4-methyl[2.2]paracyclophane, $[\alpha]_{546}$ −110° (*c* 1.0, $CHCl_3$). All tubes contained 1.2 ml of solvent. Run 12 involved methanol flushed with nitrogen; run 13, methanol flushed with nitrogen but 0.01 *M* in naphthalene; run 14, methanol flushed with oxygen; run 15, acetone flushed with oxygen. All tubes were then sealed with serum caps and irradiated for 3 hr. The results were analyzed as described in the last section and are found in Table II.

Runs 16 and 17 were conducted simultaneously in the same apparatus, but with only a Pyrex filter. Two tubes were each filled with a solution of 8.0 mg of optically pure (−)-**1** in 1 ml of acetone. In run 16, the solution was degassed thoroughly by five freeze–pump–thaw cycles at 0.04 mm. In run 17, the solution was not degassed. The tubes were sealed with serum caps and irradiated for 2 hr and the solutions analyzed by the polarimetric glc technique. Table II records the results.

**Photolyses of 4,7-Dimethyl[2.2]paracyclophane (2) at λ >270 nm.** A 3-hr irradiation run was made with 11 mg of **2** in 1 ml of methanol in Pyrex tubes fitted with the Corex filter sleeve on the lamp in the merry-go-round apparatus. The **2** recovered was purified by preparative glc and submitted to mass spectral analysis. No *m/e* 118 peak was detected.

Two runs were made simultaneously for 3 hr in the merry-go-round apparatus fitted with the Corex filter sleeve. One tube contained 46 mg of optically pure (−)-**2** of $[\alpha]_{436}$ −412° (*c* 0.58, $CCl_4$) in 5 ml of acetone, and the other contained 46 mg of optically pure (−)-**1** of $[\alpha]_{436}$ −372° (*c* 0.8, $CCl_4$) in 5 ml of acetone. After evaporation of the solvent, the residues from each tube were dissolved in pentane and passed through columns of silica gel to removed polymer. The column eluates were evaporated, the residues sublimed, and their rotations taken. The rotation of recovered **2** was $[\alpha]_{436}$ −145° (*c* 0.5, $CCl_4$) and, by analytical glc, contaminated with about 8% (total) of two open-chain hydrocarbons. When the rotation of the sample was corrected for the impurity, the **2** present was calculated to be 65 ± 8% racemized. The rotation of **1** recovered from the second tube was $[\alpha]_{436}$ −51.9° (*c* 0.41, $CCl_4$), and analytical glc indicated the presence of about 0.5% impurity. Thus (−)-**1** was 86 ± 2% racemized in this experiment. The above sample of recovered **2** was purified by preparative glc, and the **2** obtained was submitted to mass spectral analysis and shown to have no *m/e* 118 peak.

**Photolysis of (−)-4-Carbomethoxy[2.2]paracyclophane.** A solution of 19 mg of optically pure (−)-4-carbomethoxy[2.2]paracyclophane[15] of $[\alpha]_{436}$ −577° (*c* 0.20, $CHCl_3$) in 2 ml of anhydrous methanol was irradiated for 0.5 hr in quartz tubes without filter (λ >210 nm) in the merry-go-round apparatus. The solution was chromatographed on 3 g of silica gel and the recovered ester sublimed to give 11.8 mg of material, $[\alpha]_{436}$ −464° (*c* 0.59, $CHCl_3$), 19% racemized. A similar experiment in tridecane as solvent produced 15% racemized ester.

A similar 1-hr irradiation experiment performed with the optically pure (−) ester in acetone with a Pyrex filter on the lamp of the merry-go-round apparatus (λ >300 nm) gave recovered, optically pure ester. A similar experiment performed with optically pure (−)-4-acetyl[2.2]paracyclophane gave back optically pure (−)-4-acetyl[2.2]paracyclophane.

**Photolysis of Products of Irradiation of 4-Methyl[2.2]paracyclophane (1) at λ 254 nm (Table III).** Runs 18–22 were made with the U-tube lamp and racemic **1** for periods of time much longer than those needed for racemization of (−)-**1**. Table III records the times, conditions, kinds, and yields of products. In each run, either pure nitrogen or oxygen was flushed through the stirred solution of **1** before and during photolyses. Isolation procedures are outlined below.

**Run 18.** After irradiation of 200 mg of **1** in 200 ml of glacial acetic acid under nitrogen, the acetic acid was evaporated under vacuum and the residue chromatographed on 35 g of Merck silica gel. The column was washed successively with 1% ether–pentane (500 ml), 5% (500 ml), and 10% (500 ml), and 30-ml fractions were collected. Appearance of products was monitored with tlc. Fractions 9–11 gave 90 mg of recovered **1**, and fractions 18–23 gave 13 mg of open-chain acetate **5** and no other materials (polymer remained on the column). Acetate **5** was a sweet-smelling colorless oil purified by preparative glc.

The nmr of **5** exhibited a distorted triplet at δ 6.85–7.23 (7 H, aromatic), a broad singlet at δ 5.07 (2 H, benzyl), a broad singlet at δ 2.85 (4 H, methylene), at least two overlapping singlets of unequal intensities at δ 2.1–2.31 (6 H, aromatic methyls), and a singlet at δ 2.07 (3 H, acetate methyl). The mass spectrum was consistent with an isomeric (methyl groups on ring) mixture. The ir of **5** exhibited a carbonyl absorption at 1735 $cm^{-1}$ characteristic of acyclic esters. *Anal.* Calcd for $C_{19}H_{22}O_2$: C, 80.92; H, 7.85. Found: C, 80.88; H, 7.72.

**Run 19.** In 280 ml of glacial acetic acid was dissolved 1.0 g of **1.** The product, a yellow oil, by tlc showed at least four components besides the polymer. This oil was chromatographed on 150 g of Merck silica gel and eluted with 1 l. portions of ether in pentane in the following percentages, 2, 4, 6, 8, 12, 20, 30, 40, and 75. The column was then washed with 0.5 l. of 50% ether–methanol and finally with 0.5 l. of methanol. Fractions collected were 450 ml. Fraction 3 gave 350 mg of **1**. Fraction 14 gave 34 mg of open-chain aldehyde acetate **8** as needles, mp 59–60° (ethanol). *Anal.* Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.01; H, 6.84.

The ir of **8** was characteristic of an aldehyde ester and exhibited an aldehydic carbon–hydrogen stretch at 2732 $cm^{-1}$, an aldehyde carbonyl stretch at 1695 $cm^{-1}$, and an ester carbonyl stretch at 1724 $cm^{-1}$. The nmr spectrum of **8** gave the following signals: an aldehydic proton at δ 9.95 (not exchangeable by adding $D_2O$ to the sample), a singlet at δ 5.09 (2 H, benzyl), a broad singlet at δ 2.94 (4 H, methylene), a broad singlet at δ 2.30 (3 H, aromatic methyl). The aromatic region (7 H) was an AA′BB′ pattern superimposed on a more complex splitting pattern of another phenyl nucleus. The mass spectrum gave a parent peak at *m/e* 296 (1.5% of base peak), a base peak at *m/e* 236 (loss of acetic acid,

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

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

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

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

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

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

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

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

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

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

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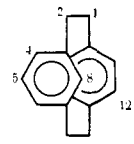
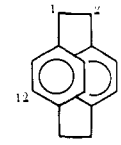
**Abstract:** The following transformations are reported: the acid-catalyzed rearrangement of optically pure (+)-(*S*)-4-methyl[2.2]paracyclophane ((+)-(*S*)-**3**) to optically pure (+)-(*S*)-12-methyl[2.2]metaparacyclophane ((+)-(*S*)-**4**); the photolytic conversion of [2.2]metaparacyclophane (**1**)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

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



**1**



**2**

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

## Results

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

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