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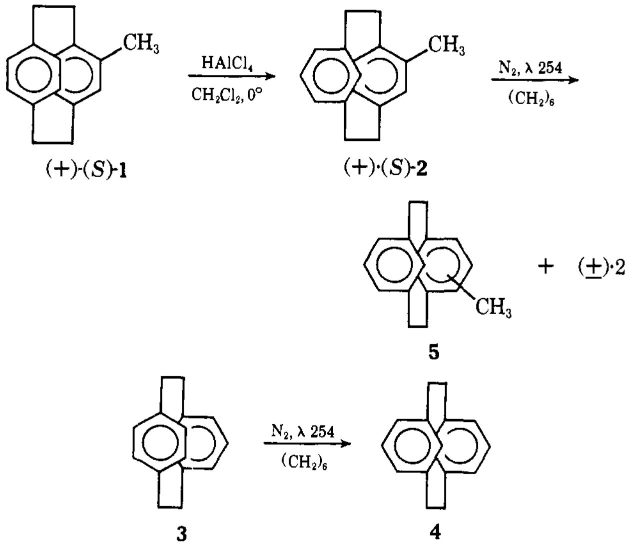
Stereochemistry of [2.2]Cyclophane Rearrangements[1]

Sir:

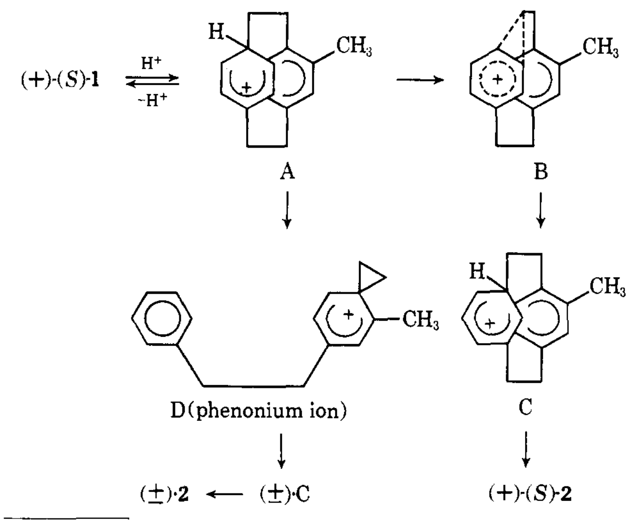
We report the acid-catalyzed rearrangement of optically pure (+)-(*S*)-4-methyl[2.2]paracyclophane ((+)-**1**) to optically pure (+)-(*S*)-12-methyl[2.2]metaparacyclophane ((+)-**2**), the photolytic conversion of [2.2]metaparacyclophane (**3**) to [2.2]metacyclophane (**4**), and the photolytic racemization and rearrangement of (−)-**2** to a mixture of methyl[2.2]metacyclophanes (**5**).



Optically pure (+)-(*S*)-**1**[2] [mp 150–152°, $[\alpha]^{25}_{546}$ +114° (*c* 1.0 $CHCl_3$)] (the configuration of (−)-(*R*)-**1** is established)[3a] was prepared[3b] and submitted to the acid conditions used to rearrange [2.2]paracyclophane to [2.2]metaparacyclophane.[4] The product, (+)-**2**, was isolated (52%) by chromatographic and sublimation procedures free of optical fractionation, mp 61–64.5°, $[\alpha]^{25}_{546}$ +27.0°, $[\alpha]^{25}_{436}$ +28.0° (*c* 1.02 $CHCl_3$). Recrystallization gave material, mp 66–67°, rotation unchanged. The enantiomer, (−)-**2**, was prepared from (+)-12-carboxy[2.2]metaparacyclophane ((+)-**6**),[5a] mp 164–168°, $[\alpha]^{25}_{546}$ +33.7°, $[\alpha]^{25}_{436}$ +115° (*c* 1.0 $CHCl_3$). Reduction of this acid with lithium aluminum hydride (in THF) gave (64%) (−)-12-hydroxymethylene[2.2]metaparacyclophane[2] ((−)-**7**), mp 99–100°, $[\alpha]^{25}_{546}$ −7.3°, $[\alpha]^{25}_{436}$ +0.2°, $[\alpha]^{25}_{365}$ +38.2° (*c* 1.0 $CHCl_3$), which with phosphorus tribromide in methylene dichloride gave (67%) (+)-12-bromomethylene[2.2]metaparacyclophane[2] ((+)-**8**), mp 92–93°, $[\alpha]^{25}_{546}$ ±85.7°, $[\alpha]^{25}_{436}$ +193° (*c* 1.0 $CHCl_3$). Reduction of this bromide with lithium aluminum hydride (THF) gave (60%) (−)-**2**,[2] mp 65–66°, $[\alpha]^{25}_{546}$ −26.3°, $[\alpha]^{25}_{436}$ −27.4° (*c* 1.0 $CHCl_3$). At each stage, the above compounds were recrystallized to maximum melting points and rotations. Admixture of equal amounts of the above samples of (−)- and (+)-**2** gave mp 43–45°, undepressed by admixture with authentic (±)-**2**.[5b] The fact that the rotations of **2** prepared by rearrangement of (+)-**1** and from (+)-**6** are of equal magnitude indicates that (+)-**1**, (+)-**2**, and (−)-**2** were essentially optically pure, and that (+)-**1** → (+)-**2** proceeded stereospecifically.

Of the two most likely general mechanisms formulated, these results eliminate the phenonium ion route ((+)-**1** → A → D → (±)-C → (±)-**2**), since D possesses a mirror plane, and only (±)-**2** would be produced. The route (+)-(*S*)-**1** → A → B → C → (+)-**2** provides the required fully chiral reaction coordinate if rotation of the methyl-substituted benzene ring with respect to the other benzene ring is sterically inhibited in A, B, and C. Molecular models point to such steric inhibition of rotation, and such rotation in (+)-12-carbomethoxy[2.2]metaparacyclophane does not occur up to 200°.[5a] Structure B might be an intermediate or a transition state in this mechanism.

The absence of alternate mechanisms with fully chiral reaction coordinates allows assignment of configuration to (+)-**2**. The fact that the meta ring of **2** rotates with respect to the para ring at 25° to provide a conformational equilibrium mixture[5a,6] complicates the structure and name given to compound (+)-**2**. However, the facts that the equilibrium mixture is dominated by the form with the methyl anti to the meta ring and crystallizes only in that form[5a,6] suggest that the structure written for (+)-**2** is the more appropriate and this structure possesses the *S* configuration.[7] This assignment fixes the configurations of (+)-**6**, (−)-**7**, and (+)-**8** as *R*.



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(2) All new compounds gave carbon and hydrogen analyses within 0.3% of theory and nmr spectra expected for the assigned structures.

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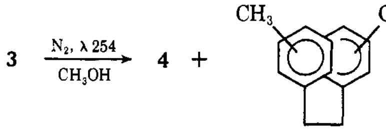
Irradiation (quartz U tube, low-pressure mercury arc of *ca.* 2 W, 86% at 254 nm) of a cyclohexane solution (10^{-4} *M*) of [2.2]metaparacyclophane (**3**) under nitrogen for 4 hr gave a mixture of starting material (50% recovery) and [2.2]metacyclophane (**4**): yield 42% (based on consumed **3**); mp 132–133°, undepressed by admixture with an authentic sample;[8] nmr spectrum indistinguishable from that of the authentic sample.[8] This conversion, coupled with the isomerization (44% yield)[4] of commercially available[9] [2.2]paracyclophane to [2.2]metaparacyclophane, provides a simple route to [2.2]metacyclophane.

When submitted to the above irradiation conditions for 8 hr, (−)-**2** (maximum rotation) gave 27% recovered (−)-**2** that was 86% racemized and a mixture of isomeric methyl[2.2]metacyclophanes[2] (**5**). When **3** was submitted to the same radiative conditions in methanol for 4 hr, a 46% yield of **4** was produced as well as a 25% yield of an open-chain ether,[2] **9**. These facts suggest that like the [2.2]paracyclophane, the [2.2]metaparacyclophane system[3b] undergoes a photolytic benzyl–benzyl bond cleavage reaction to give a zwitterion-like intermediate which, after conformational adjustments, either ring closes back to **3** or gives methanolysis product. However, unlike [2.2]paracyclophane, [2.2]-metaparacyclophane (**3**) photolytically ring contracts to a less strained cyclophane (**4**) probably by a benzvalene or prismane route.[10a] Others have noted considerable differences in the photolytic behavior of the position isomers of dialkylated benzenes, the para isomers usually being the least reactive.[10b,c] The reduction in strain energy of 10 kcal/mol in passing from **3** to **4**[11] probably contributes to the occurrence of this reaction, although an 8-kcal/mol release of strain energy[11] is potentially available for the photolytically unobserved conversion of [2.2]paracyclophane to [2.2]metaparacyclophane.[3b]



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Bond Index Interpretation of Valence Isomerization

Sir:

In most cases it has been assumed that photochemical reactions start from the first excited state as a consequence of its longer lifetime. Recently, however, van der Lugt and Oosterhoff have emphasized the possibility that after excitation of a molecule into a higher excited state the reaction originates from this state before radiationless conversion to the first excited state occurs.[1]

Although extensive studies of photochemical reactions using monochromatic light are required to determine which of the excited states is involved, we can approach this problem by a simple method, at least in the case of valence isomerization reactions. In this report we describe an interpretation of Wiberg's bond index[2,3] which partitions the charge into various valence-bond (VB) structures for excited states.

The bond index in an excited state is defined as the square of the bond order in that state

$$W_{ab}^* = (P_{ab}^*)^2 \qquad (1)$$

where the asterisk labels the excited state and a and b label atomic orbitals in LCAO expansion. Let us suppose that a molecule is in the excited state corresponding to the one-electron excitation $\psi_j \rightarrow \psi_k$. If we sum W_{ab}^* over all atomic orbitals b, we obtain

$$\begin{aligned}\sum_b W_{ab}^* &= 2q_a - 3C_{ja}^2 + C_{ka}^2 \\ &= 2q_a^* - (C_{ja}^2 + C_{ka}^2) \qquad (2)\end{aligned}$$

where q_a is the charge density of the ground state and q_a^* is that of the excited state. Equation 2 may be modified as follows

$$q_a^* - {}^1\!/_2(C_{ja}^2 + C_{ka}^2) - {}^1\!/_2 W_{aa}^* = {}^1\!/_2 \sum(K) \sum(\text{b in } B_K) W_{ab}^* \qquad (3)$$

We define the term $[q_a^* - {}^1\!/_2(C_{ja}^2 + C_{ka}^2) - {}^1\!/_2 W_{aa}^*]$ as the active charge in the excited state, A_a^*.

From the partitioning of active charge into VB structures we observe that the relative weight of a certain VB structure changes greatly depending on the electronic state. Consider the π system in butadiene. The active charges in the ground state are $(A_1, A_2, A_3, A_4) = (0.5, 0.5, 0.5, 0.5)$, in the configuration $(\psi_2 \rightarrow \psi_3)$, $(A_1^*, A_2^*, A_3^*, A_4^*) = (0.138, 0.362, 0.362, 0.138)$. The active charges of *cis*- and *trans*-butadiene are partitioned in various VB structures (Chart I,[4] where the superscript $(j \rightarrow k)$ labels the one-electron excitation $\psi_j \rightarrow \psi_k$). The bond index, W_{ab}, is considered as the charge in orbital a which participates in an a–b bond. If a certain electronic state of a molecule has little charge in a region where a new bond is formed during valence isomerization, the state is considered energetically unfavorable for the isomerization to occur, since the nuclear configuration of the molecule must be changed much to acquire charge in that region. Therefore, we can assume that photochemical valence isomerization occurs from the excited state which most resembles the structure of the product in the VB structure.

The eigenvalues corresponding to the first and second excited states for singly excited singlet configurations of *trans*-butadiene are −71.283 and −70.381 eV, re-

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