

usually favored over square-planar ones: G. Wilkinson and F. A. Colton, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1966, Chapter 29-H.

- (12) Molecular models indicate that C-C bond breaking will occur if attempts are made to change III and IV.  
 (13) For a discussion of the role of "extrinsic" effects in the determination of redox potentials of  $[\text{Fe}_4\text{S}_4(\text{SR})_4^{x-}]$  systems, see C. L. Hill, J. Renaud, R. H. Holm, and L. E. Mortenson, *J. Am. Chem. Soc.*, **99**, 2549 (1977).

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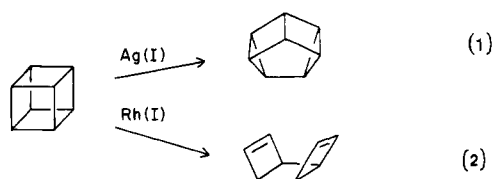
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## Octahydro- and Perhydro[0.0]paracyclophane

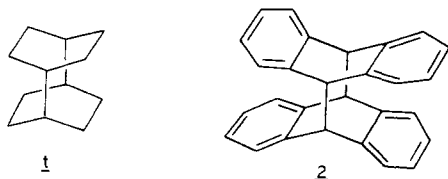
Sir:

Transition metal catalyzed reactions of strained polycyclic compounds offer special opportunities for the synthesis of new ring systems. Rearrangements of the cubane  $\rightarrow$  cuneane type (eq 1) induced by silver(I) are most familiar and have certainly been used profitably.<sup>1</sup> We have also been considering the



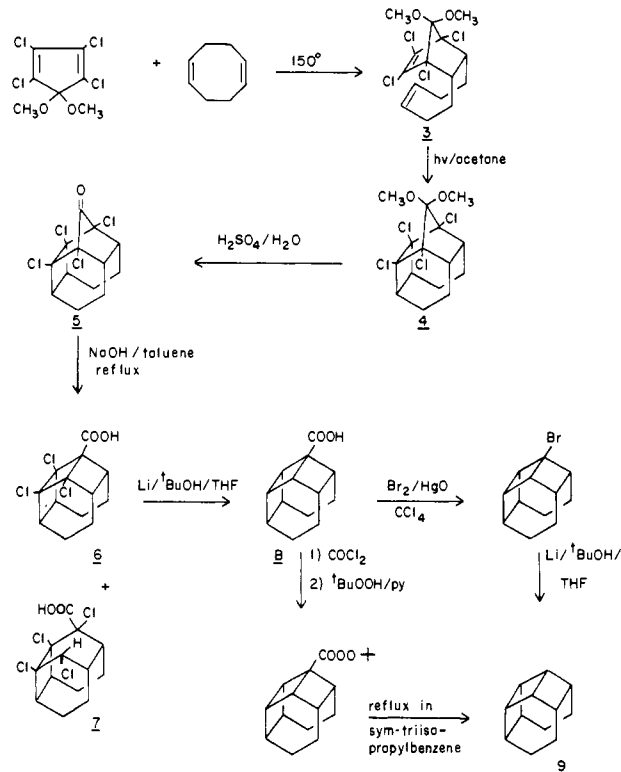
mechanistically important, but synthetically less appreciated, conversion of the type cubane  $\rightarrow$  *syn*-tricyclooctadiene (eq 2) brought about by rhodium(I).<sup>2</sup> In this communication we describe the critical use of just this kind of metal-induced reaction for the tactical synthesis of octahydro- and perhydro[0.0]paracyclophanes.

The frame of the title system, **1**, tricyclo[4.2.2.2<sup>2,5</sup>]dodecane, is constructed of two cyclohexane rings joined by single bonds at their 1 and 4 positions. This seems simple enough; yet the system is hardly known at all. Although at the core of the common anthracene photodimers (e.g., **2**), its properties there



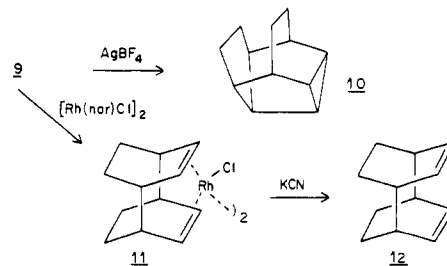
are totally obscured by the four fused benzene rings. More open examples have been obtained by Yang at Chicago by photoadditions of *cis*-1,2-dihydrophthalic anhydride to anthracene, naphthalene, and even benzene.<sup>3</sup> Until now, however, no other approach has been used successfully,<sup>4</sup> and there has been no report of any synthesis of the unsubstituted system.

Reaction of 5,5-dimethoxytetrachlorocyclopentadiene<sup>5</sup> with an eightfold excess of 1,5-cyclooctadiene at reflux gave a single 1:1 Diels-Alder adduct (**3**, 80%), mp 71–72 °C (lit.<sup>6</sup> mp 71–72 °C). It is assigned endo stereochemistry, for on ultraviolet irradiation in dilute (~0.1 M) solution in acetone it was closed to the cage isomer (**4**, 70%), mp >230 °C dec.<sup>7</sup> Deketalization in strong acid freed the corresponding ketone (**5**, 95%), mp >250 °C dec. Boiling **5** with dry, powdered sodium hydroxide suspended in toluene gave, after acidification, the carboxylic acids **6**, mp >270 °C (methyl ester mp 161.5–162 °C),<sup>8</sup> and **7** (methyl ester mp 170.5–171 °C)<sup>9</sup> in 55 and 42% yield, respectively. Dechlorination of **6** with lithium and *tert*-butyl alcohol in THF gave **8** (66%), mp 142–143 °C. Decarboxylation was achieved, as illustrated, by way of the Hunsdiecker



reaction and subsequent reduction or by thermolysis of the *tert*-butyl perester. The hydrocarbon **9**, pentacyclo[6.4.0.0<sup>2,7</sup>.0<sup>3,12</sup>.0<sup>6,9</sup>]dodecane, was obtained pure in 25–30% yield by preparative gas chromatography on OV-17: mp >210 °C dec; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  2.87 (8 H, br s,  $W_{1/2H} \sim 5$  Hz), 1.92 (4 H br d,  $J \sim 9$  Hz), 1.53 ppm (4 H, br d,  $J = 9$  Hz); <sup>13</sup>C NMR (22.63 MHz, CDCl<sub>3</sub>)  $\delta$  33.6 (4 C, d,  $J = 143$  Hz), 31.3 (4 C, d,  $J = 136$  Hz), 17.3 ppm (4 C, t,  $J = 128$  Hz).

Reaction of **9** with a catalytic amount of silver tetrafluoroborate in benzene at 70 °C resulted in slow, quantitative rearrangement to cyclopropane **10**: IR (CDCl<sub>3</sub>)  $\nu$  3030 cm<sup>-1</sup>; <sup>13</sup>C NMR  $\delta$  56.5 (1 C), 54.2 (2 C), 34.8 (2 C), 28.7 (2 C), 25.8 (2 C), 23.3 (1 C), 19.3 ppm (2 C). The assignment of structure is based on precedents established for simpler systems<sup>1</sup> and is consistent with the NMR data. As expected, the reaction with rhodium(I) complexes took a different course. Treatment of **9** (0.56 M in CDCl<sub>3</sub>) with an equivalent of [Rh(norbornadiene)Cl]<sub>2</sub> at room temperature gave free norbornadiene and rhodium complex **11** quantitatively in <30 min.<sup>10</sup> Diene **12** was

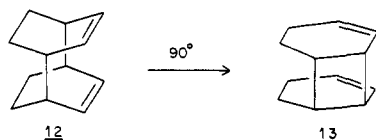


liberated by destruction of the complex with potassium cyanide in aqueous Me<sub>2</sub>SO. It ligates rhodium(I) very strongly; it was not displaced significantly from complex **11** even by a high concentration of norbornadiene.

Diene **12**, octahydro[0.0]paracyclophane, is a colorless solid: mp 149.5–150 °C; IR  $\nu$  3040 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  5.93 (4 H, m), 2.72 (4 H, m), 2.15 (4 H, br d,  $J = 9$  Hz), 1.38 ppm (4 H, br d,  $J = 9$  Hz); <sup>13</sup>C NMR  $\delta$  134.3 (4 C, d,  $J = 160$  Hz), 37.4 (4 C, d,  $J = 132$  Hz), 22.6 ppm (4 C, t,  $J = 128$  Hz). Ultraviolet irradiation in the presence of a sensitizer resulted in fairly ef-

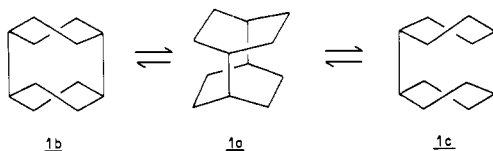
ficient regeneration of **9**. The ultraviolet spectrum of **12**, no maximum  $>190$  nm, gives no clear evidence for an interaction between the neighboring, but nonconjugated,  $\pi$  systems. Photoelectron spectroscopy will provide a better probe of this important possibility.

Diene **12** is not thermally stable. At  $90^\circ\text{C}$ , Cope rearrangement to **13** occurred quantitatively over a 2-day period.<sup>11,12</sup> Apparently, the trans-skeletal interactions in **12**, probably of simple steric origin, are of sufficient magnitude (and therein remarkable) to destabilize **12** relative to the all-cis tetrasubstituted cyclobutane **13**.



Catalytic hydrogenation of **12** gave **1**, perhydro[0.0]paracyclophane: IR  $\nu$  2920, 1480, 1460  $\text{cm}^{-1}$ . The high symmetry of **1** on the NMR time scale is apparent from its two line proton-decoupled  $^{13}\text{C}$  NMR spectrum:  $\delta$  30.2 (4 C, d,  $J = 130$  Hz) and 24.6 ppm (8 C, t,  $J = 126$  Hz). The  $^1\text{H}$  NMR spectrum shows a significant downfield shift for the endo protons, presumably a result of steric compression:<sup>13</sup>  $\delta$  2.03 (8 H, br d,  $J = 9$  Hz), 1.95 (4 H, br s), 1.48 ppm (8 H, br d,  $J = 9$  Hz).

Although more conveniently drawn in the symmetric, double boat conformation **1a**, **1** is better represented as the lower energy, double twist boat **1b** and its mirror image **1c**. It is interesting to speculate whether passage from **1b** to **1c** is by way of the high energy  $D_{2h}$  conformer **1a**.



Application of our synthetic scheme to somewhat modified intermediates should permit us access to hexaprismane (**14**) and, via rhodium(I) induced opening of **14**, to tetrahydro[0.0]paracyclophane (**15**), *p*-dibenzene. We shall report our progress with these systems in due course.



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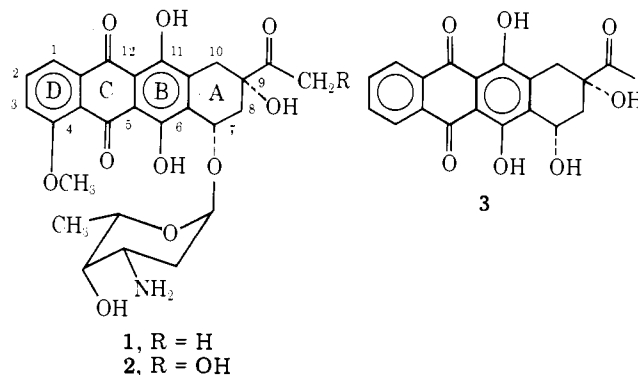
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## A Novel Synthesis of ( $\pm$ )-4-Demethoxydaunomycinone

Sir:

The anthracyclines daunorubicin (**1**) and adriamycin (**2**) are of current interest in view of their activity against various experimental tumors as well as some types of human cancer.<sup>1</sup>



The activity of these compounds can be improved by structural modification, as shown by the recent report that 4-demethoxydaunorubicin is four to eight times more active than daunorubicin itself.<sup>2</sup> We now wish to report a basically new, simple, and efficient synthesis of the dimethyl ether of the corresponding aglycone 4-demethoxydaunomycinone (**3**).

Our synthetic strategy centers on the construction of ring

