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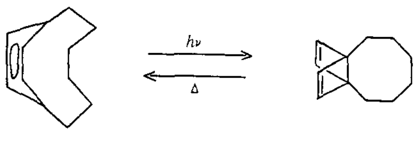
Interconversion of [6]Paracyclophane and 1,4-Hexamethylene(Dewar benzene)[1]

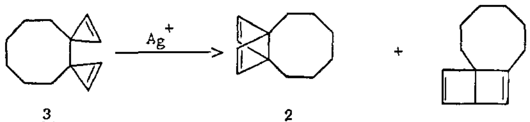
Sir:

Although many valence isomerizations of substituted benzenes are known,[2] photochemical isomerizations to a single Dewar form are rare, and there seems to be no example of a quantitative isomerization to a Dewar form followed by an equally clean thermal rearomatization. Hexafluorobenzene is photochemically isomerized in modest yield to a Dewar form which is reconverted to the aromatic form on heating.[3] Similarly, photolysis of *peri*-di-*tert*-butylnaphthalenes produces a photostationary state in which the Dewar form greatly predominates. Here too, thermal rearomatization has been achieved.[4] We present here our results on the light-induced closure of [6]paracyclophane (**1**) to 1,4-hexamethylene(Dewar benzene) (**2**) and the subsequent thermal rearomatization.



1 2

Irradiation of a solution of [6]paracyclophane[5] in cyclohexane-d_{12} with an unfiltered 450-W Hanovia medium-pressure mercury arc led to slow and apparently quantitative conversion to a single new product (33% in 90 min) which was identified as 1,4-hexamethylene(Dewar benzene) by a comparison of spectra with those of a sample prepared by the silver-catalyzed[6] rearrangement of the bicyclopropenyl **3**.[7] Treatment of **3** [NMR ($CDCl_3$): δ 7.10 (s, 4 H), 1.60 (m, 12 H)] with silver perchlorate in acetonitrile at 0 °C gives **2** and its 1,2 isomer **4** in the ratio 1:9. Separation by gas chromatography on a 3% S.E. 30 column at 55 °C gave **2** [NMR ($CDCl_3$): δ 6.53 (s, 4 H), 1.80 (m, 4 H), 1.50 (m, 8 H)] contaminated only by a few percent benzocyclooctene.[7]



3 2 4

Heating **2** between 50 and 90 °C results in a rapid and clean reversion to **1**. The activation parameters for the formation of **1** from **2** were determined both by integration of the signals for the aromatic protons in the NMR spectrum of **1** ($E_a = 20.9 \pm 1.5$ kcal/mol; $\log A = 9.8 \pm 0.9$) and by monitoring the band at 253 nm in the ultraviolet spectrum ($E_a = 19.9 \pm 0.9$ kcal/mol; $\log A = 9.3 \pm 0.6$). Thus only 1-chloro- and 1-fluoro-(Dewar benzene) exceed **1** in their measured rates of rearomatization.[8]

This work establishes the "breakpoint" in the series of [*m*]paracyclophanes and their Dewar isomers. In the hexamethylene case (**1**) and doubtless all higher homologues, it is the aromatic partner that is the more stable. For the pentamethylene case it has already been shown that the Dewar form is favored thermodynamically.[6] Here the Dewar form does not rearrange to the open compound on heating in solution, but instead undergoes a remarkable rearrangement to benzocycloheptene. At higher temperatures [5]paracyclophane may be formed as an intermediate on the way to other compounds.[6] It is not yet known if [5]paracyclophane is protected by a sufficiently high kinetic barrier to be isolable at lower temperatures.

Under conditions sufficient to completely rearrange **1** to **2**, the higher congener, [7]paracyclophane, undergoes only a slow photochemical polymerization. We are now testing to see if a Dewar benzene is formed, only to revert rapidly at room temperature to the aromatic compound.

References and Notes

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