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[2.2](1,4)Naphthaleno(2,5)furanophane[1]

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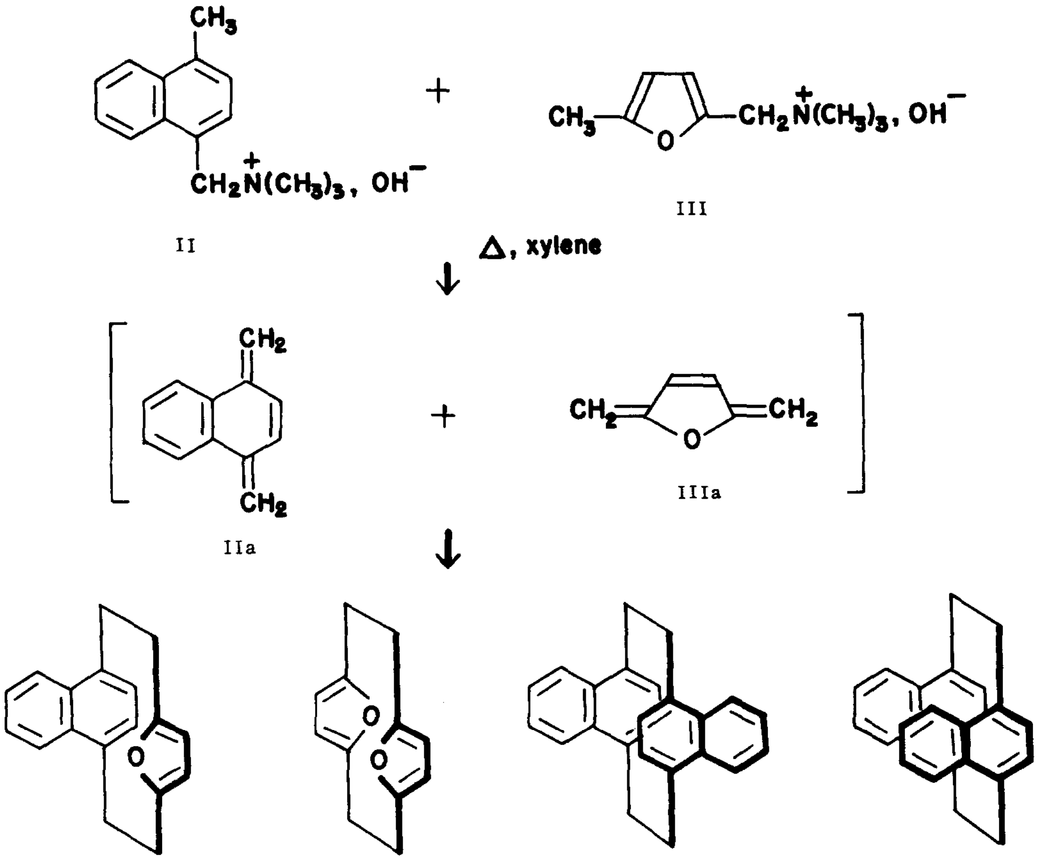
During studies on the reactions of singlet oxygen with strained aromatic systems[2,3,4], we have prepared the [2.2]naphthalenofuranophane (I). Our nmr studies on this system, outlined below, show that it exists predominantly in the anti-form.



II

III

IIa

IIIa

I

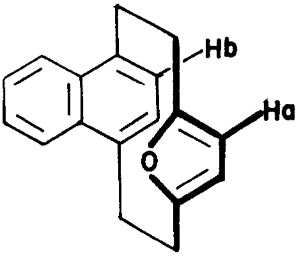
IV

V

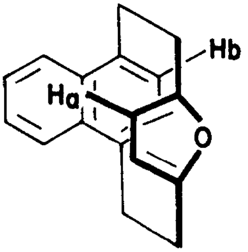
VI

Pyrolysis of an equimolar mixture of quaternary hydroxides II and III yielded the cyclophane I (11%) along with the [2.2]furanophane[5] (IV) (10%), anti-[2.2](1,4)naphthalenophane[6] (V) (14%) and syn-[2.2](1,4)naphthalenophane[7] (VI) (3%). Crystallization of I from benzene afforded white colorless plates, mp 164-165°. *Anal.* Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.21; H, 6.25. The mass spectrum of I exhibits a molecular ion peak at m/e 248. In addition, two peaks appear at m/e 154 and 94. The latter peaks correspond to the molecular weights of the two units IIa and IIIa[8] which would result from the cleavage of the ethylene bridges in the parent molecule (I). This type of cleavage appears to be characteristic of all [2.2] cyclophanes which we have recently studied[9].

The nmr spectrum of I shows peaks at τ 2.22 (A_2B_2, 4H), 3.45 (s, 2H), 4.38 (s, 2H), 6.20 (m, 2H) and 7.35 (m, 6H). Since β-furanoid protons absorb at higher fields (*ca.* 1 ppm) than benzenoid protons[10], the 4.38 singlet is assigned to the furan protons (Ha), while the singlet at τ 3.45 is assigned to the Hb protons of the naphthalene ring.



Ia

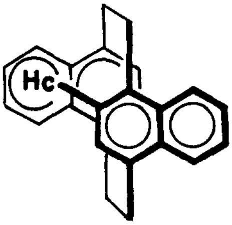


Ib

Of the two possible structures (Ia or Ib) for the cyclophane I, the anti-form (Ia) is clearly favored over the syn-structure (Ib) by the nmr data. Specifically, the absorption (singlet at τ 4.38) associated with the β-furanoid protons in I is very close (Table I) to the absorption of the corresponding Hg protons in VIII, a compound containing no fused outer aromatic ring. In cyclophanes where there can be transannular shielding effects on protons by aromatic nuclei, one observes a characteristic upfield shift as shown, for example, by the Hc and Hf protons in V and VII (Table I). Both the Hc and Hf protons, held in the fields of the outer rings of the naphthalene nuclei, absorb at about 1 ppm higher than their less-shielded counterparts, Hd and He. Thus, if the naphthalenofuranophane were to have the syn-structure (Ib), one would expect the β-furanoid protons (Ha) to show shielding effects similar to those experienced by protons Hc and Hf, and to be shifted upward to *ca.* τ 5.55.

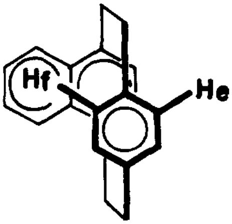
Table I

Chemical Shifts of Ring Protons, τ Values



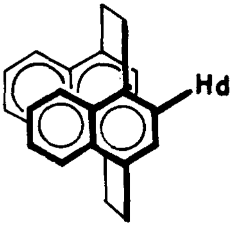
V

Hc, 4.22



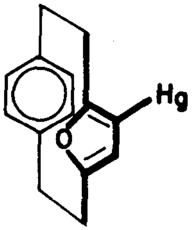
VII

He, 3.50
Hf, 4.36



VI

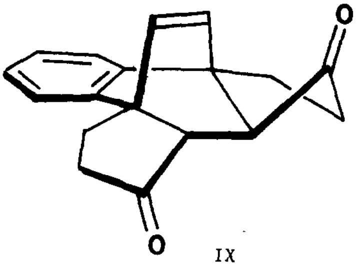
Hd, 3.29



VIII

Hg, 4.55

The naphthalenofuranophane Ia undergoes rapid oxidation with bromine in methanol at 0° yielding, among other products, a crystalline diketone mp 220-222°. This oxidation product is identical to the polycyclic product (IX) recently isolated from the reaction of singlet oxygen with Ia, as described in a separate communication.[11]



IX

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