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SYNTHESIS AND THERMAL REARRANGEMENT OF A POTENTIAL BUTALENE-ANTHRACENE ADDUCT

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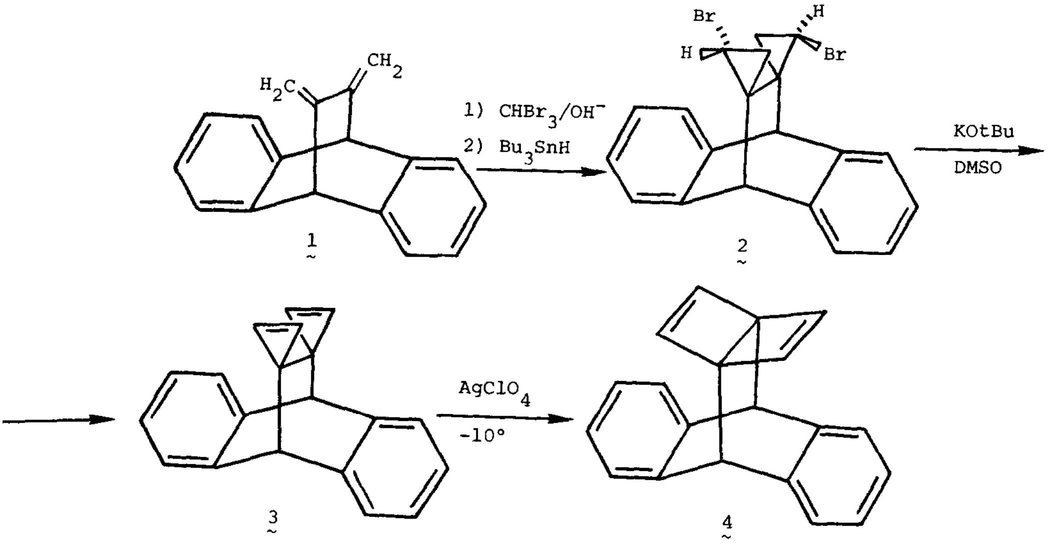
Summary: The synthesis of propellane 4, a formal Diels-Alder adduct of 1,4-dehydrobenzene and anthracene, is reported. This material does not undergo a retro-Diels Alder reaction on pyrolysis, but instead rearranges to benzofluoranthene 5.

Recent studies have provided evidence that 1,4-dehydrobenzene may be trapped in both ring-opened and ring-closed forms.[1,2] Because of the uncertainties raised by these experiments regarding the relationship of the two isomers, it has been of interest to seek potential precursors for 1,4-dehydrobenzene capable of undergoing minimal structural change during generation of the reactive species. In connection with this goal, we have prepared compound 4, which is formally a Diels-Alder adduct of ring-closed 1,4-dehydrobenzene ("butalene")[2] and anthracene. Although neither pyrolysis nor photolysis of this compound leads to 1,4-dehydrobenzene, its interesting thermal chemistry, as well as its relationship to other important propellanes which have recently been prepared[3], prompts us to report our results here.

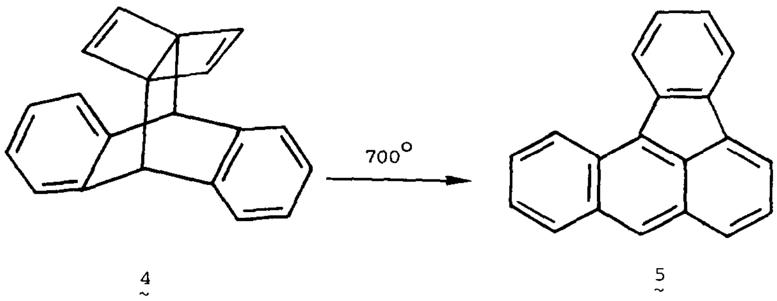
The synthesis of 4 is outlined in Scheme 1. The starting diene 1 was prepared[4] by base-catalyzed elimination of HCl from the Diels-Alder adduct of anthracene and 1,4-dichloro-2-butene. This was treated with bromoform and base under phase-transfer conditions, and the tetrabromo-bis-cyclopropane derivative so produced (89%) was reduced with tri-n-butyltin hydride. This gave a crystalline dibromide (2) in 70% yield which we believe to be the syn, syn-dibromide[5] illustrated in Scheme 1. Treatment of 2 with potassium t-butoxide in DMSO gave bis-cyclopropenyl derivative 3 (m.p. 180°-184° (dec.)) in 75% yield after chromatography and crystallization from ethanol-water.

Conversion to the Dewar benzene 4, normally a relatively straightforward process[6], gave substantial amounts of triptycene as well as decomposition products when attempted at room temperature. In addition, active catalyst was apparently consumed in a side reaction. However, Scheme 1



treatment of 3 with silver perchlorate in benzene-toluene solvent at -10° for two hours, followed by rapid workup with cold 10% aqueous sodium thiosulfate, gave a mixture of 3 and 4. Recrystallization from ethanol gave recovered starting material; pure 4 (51%) was obtained by precipitation from the mother liquor by addition of water, followed by recrystallization from absolute ethanol.

Compound 4 was obtained as white crystals, m.p.157-8°. It was characterized by precise mass spectrometry (calculated for $C_{20}H_{14}$: 254.1096; found: 254.1088), IR spectroscopy (KBr, cm^{-1}: 1450, 1270, 1028, 1015, 970, 797, 782, 768, 740, 726, 628, 615 cm^{-1}) and proton NMR (δ, CCl_4):



4.41 (s, 2H), 6.08 (s, 4H), 6.8-7.2 (m, 8H). On catalytic hydrogenation the material took up two moles of H_2, leading to the corresponding bicyclohexane derivative. Most surprisingly, compound **4** is exceedingly stable to heat. It undergoes only slight change on sublimation through a tube heated to 500°C. At 700°, it undergoes approximately 30% conversion to a trace of anthracene and a yellow solid that exhibits green fluorescence and has only aromatic absorption in the NMR. This material was identified as the known 2,3-benzofluoranthene (**5**) by comparison with published data.[7] This is obviously a deep-seated reaction and we have little information as yet concerning its mechanism. It is possible, however, that the first step is a Cope rearrangement involving interaction of one of the cyclobutene double bonds and a proximate aromatic ring.[8,9]

In summary, propellane **4** may be prepared in an efficient manner using the recently developed[6] metal-catalyzed bis-cyclopropene rearrangement. Considering its strain, it is a surprisingly stable molecule. Rather than releasing 1,4-dehydrobenzene on thermolysis, temperatures near 700° are required to force conversion to **5**.

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5. One recrystallization of this material from $CHCl_3$ gave material, m. p. 201-4°, pure by NMR and suitable for use in the dehydrohalogenation. A second recrystallization yielded materials which melted sharply at 205° (Anal: Calc'd for $C_{20}H_{16}Br_2$: C 57.72, H, 3.88; Found: C, 57.88; H 3.92%), and had the following NMR: 0.7 (d of d, J_1 = 15 Hz, J_2 = 8 Hz), 0.98 (d of d, J_1 = 8 Hz, J_2 = 5 Hz), overlapping, total 4H; 2.43 (d of d, 2H, J_1 = 8 Hz, J_2 = 5 Hz); 4.08 (s, 2H); 7.0 - 7.5 (m, 8H).

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9. We have also been unsuccessful in our attempts to induce fragmentation of **4** under a variety of photolytic conditions. Upon irradiation of **4** at 10°K in an argon matrix, Professor G. Maier and his coworkers have observed new IR bands attributable to the formation of a prismane derivative resulting from [2 + 2] cyclization of the cyclobutene double bonds in **4**.

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