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1,2-DIPHENYLPHENANTHRO[<u>l</u>]CYCLOBUTADIENE: A HIGHLY UNSTABLE CONDENSED AROMATIC CYCLOBUTADIENE

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Recently we described the synthesis of 1,2-diphenylnaphtho[<u>b</u>]cyclobutadiene (I), the first example of an isolable compound containing a cyclobutadiene nucleus which has only one pair of neighboring carbons fused to an aromatic system.[1] The unique stability of hydrocarbon I may be attributed not only to the two phenyl substituents, but also to the fact that the cyclobutadiene ring in I is fused to the β,β-bond of naphthalene, a position of low π-bond order.[1,2] It may be predicted, consequently, that fusion of a 1,2-diphenylcyclobutadiene moiety to a position of high π-bond order in an aromatic system (<u>e.g.</u> the 9,10-bond of phenanthrene) would lead to a molecule of much lower stability than that of I. This prediction has been confirmed by the generation of the very unstable molecule 1,2-diphenylphenanthro[<u>l</u>]cyclobutadiene (II) as reported here.

The photolysis of dihydrophencyclone (III)[3] in benzene solution, using a Hanovia medium pressure ultraviolet lamp (quartz probe), afforded <u>trans</u>-1,2-diphenylphenanthro[<u>l</u>]cyclobutene (IV), m.p. 195-197°, in good yield (82%, based on unrecovered ketone III);[4,5] derivatives of phenanthro[<u>l</u>]cyclobutene have not been synthesized previously.[6,7] The trans configuration was assigned to hydrocarbon IV on the basis of a comparison of NMR data with related compounds in the benzocyclobutene and the naphtho[<u>b</u>]cyclobutene series.[4,8,9] Thus, the phenyl protons (7.42 δ) showed no evidence of shielding, whereas the benzylic protons (3.78 δ) were highly shielded by the phenyl groups. The presence of a thermally labile four-membered ring in IV is in accord with its quantitative rearrangement at 150° to an isomeric hydrocarbon, m.p. 196-198°, assigned the structure of 9-phenyl-9,14-dihydrodibenz[*a*,*c*]anthracene (V); similarly, reaction of IV with sulfur dioxide at 150° afforded, in 49% yield, a sulfone, m.p. > 320°, assigned the structure of 1,3-diphenyl-1,3-dihydrophenanthro[9,10-*c*]thiophene-2,2-dioxide (VI).[10]

Bromination of IV with *N*-bromosuccinimide (2 equivalents) gave, in 64% yield, 1,2-dibromo-1,2-diphenylphenanthro[*l*]cyclobutene (VII), m.p. 253-255°; the bromine atoms in VII were shown to be benzylic and reactive, since they were lost by solvolysis of VII in methanol with the formation of the corresponding dimethoxy compound (VIII), m.p. 192°, in 61% yield.[11]

Attempts to prepare 1,2-diphenylphenanthro[*l*]cyclobutadiene (II) from only an amorphous high-melting polymer; the assumed intermediate II could not be trapped in a Diels-Alder reaction by conducting the debromination in the presence of diphenylisobenzofuran. The debromination of VII was effected also in benzene by nickel tetracarbonyl, but the product again was a polymeric hydrocarbon rather than a nickel bromide-cyclobutadiene complex. Strong evidence for the intermediary formation of II in these reactions was obtained by conducting the zinc debromination of VII in benzene in an oxygen atmosphere, when 9,10-dibenzoylphenanthrene (IX),[12] m.p. 198°, was formed in 85% yield. The oxidation of an unstable cyclobutadiene to a diketone by molecular oxygen, probably by way of a cyclic peroxide, has been observed previously in the case of tetraphenylcyclobutadiene.[13]

The failure of the unstable 1,2-diphenylphenanthro[*l*]cyclobutadiene (II) to yield a definite dimer or to behave as an active dienophile, as well as its rapid reaction with oxygen, suggests that this molecule may exist as a triplet in the ground state. Molecular orbital calculations concerning II will be of considerable interest in this regard.

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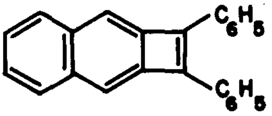
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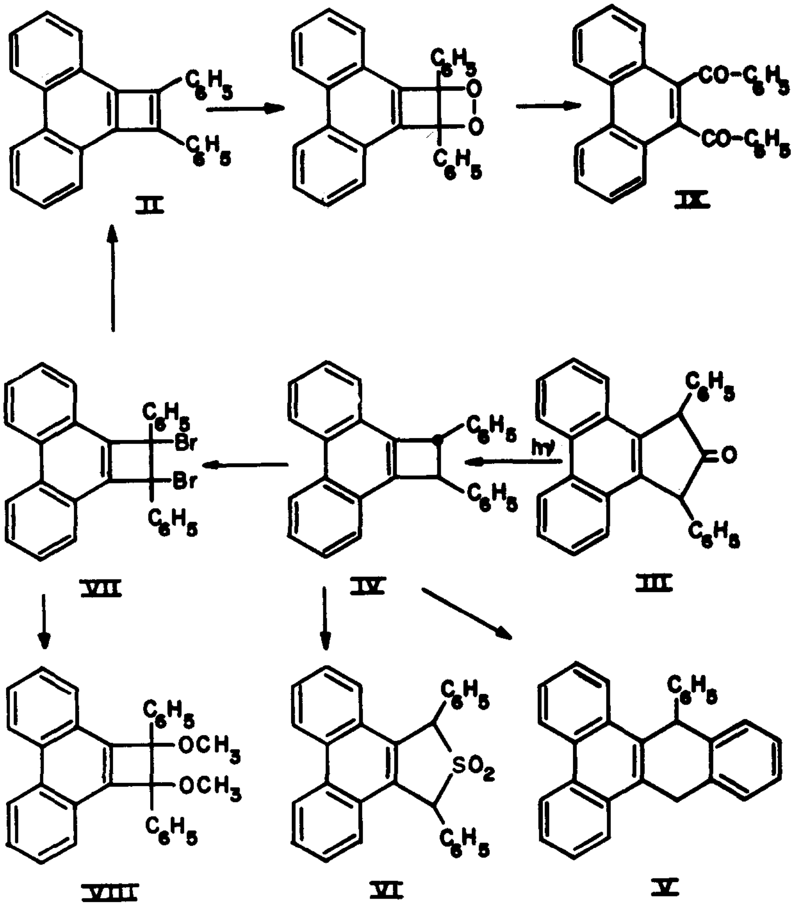
I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IX
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Br
Br
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III
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OCH_3
OCH_3
C_6H_5
VIII
C_6H_5
SO_2
C_6H_5
VI
C_6H_5
V

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2. This qualitative explanation is in accord with molecular orbital calculations carried out by Dr. A. G. Anastassiou and quoted in *Chem. and Eng. News*, **42**, No. 3, 37 (1964).

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4. For related photolyses of benzylic ketones in solution, see G. Quinkert, K. Opitz, W. W. Wiersdorff and J. Weinlich, *Tetrahedron Letters*, No. **27**, 1863 (1963).

5. Elemental analyses and spectral properties of all new compounds are in accord with the assigned structures.

6. Some reactions which might have been expected to give phenanthro[*l*]cyclobutenes have been described. See (a) L. Horner, K. Muth and H. G. Schmelzer, *Ber.*, **92**, 2953 (1959); (b) P. D. Gardner and H. Sarrafizadeh R., *J. Amer. Chem. Soc.*, **82**, 4287 (1960); (c) J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2708 (1963).

7. The synthesis of several phenanthro[*l*]cyclobutenes, by a route different from that employed by us, has been achieved recently by H. Schechter and W. Sullivan (private communication). We thank Prof. Schechter for kindly informing us of this work prior to publication.

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10. For analogies to these reactions, see ref. 8 and also F. R. Jensen and W. E. Coleman, *J. Amer. Chem. Soc.*, **80**, 6149 (1958).

11. The analogous solvolysis of the closely related 1,2-dibromo-1,2-diphenylnaphtho[*b*]cyclobutene has been observed (B. Hwang, unpublished observations).

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