

THE SYNTHETIC POTENTIAL OF THE 1,2-PHOTOAROMATIZATION (1) REACTION

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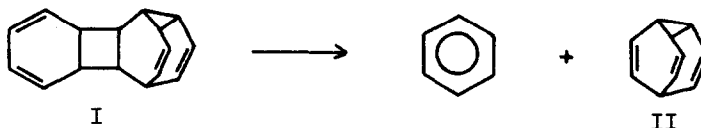
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The facile conversion of the cyclooctatetraene dimer (I) into benzene and bullvalene (II) by ultraviolet irradiation (2) is an excellent example of the 1,2-photoaromatization reaction.



For this type of reaction to be of synthetic value one must have: a) a simple route to the ring-fused cyclohexadienes; and b) a knowledge of the generality of the photoaromatization step. In this report we discuss these topics as they relate to the formation and fragmentation of the cyclobutane ring in derivatives of the bicyclo[4.2.0]octa-2,4-diene system, and illustrate its synthetic potential by the two step conversion of cyclobutene (III) (3) to olefin (IV).



Step 1: Derivatization of the Cyclobutene

In practice bridged carbonyl derivatives, which are readily available in

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high yield, by the thermal $(4 + 2) \pi$ cycloaddition reaction of cyclobutenes* and cyclopentadienones (VI) are utilized as starting materials. The bicyclo-[4.2.0]octa-2,4-dienes are subsequently generated in situ by photodecarbonylation** under the irradiation conditions used in the second step. Table I lists several adducts with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (V).

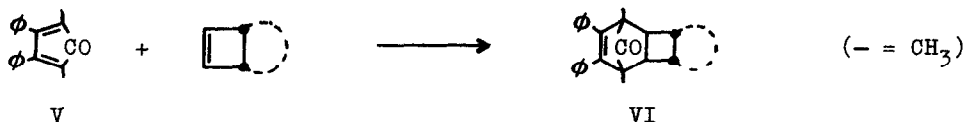


TABLE I

No.	Cycloadduct ^a	m.p.	Yield(%)	No.	Cycloadduct ^a	m.p.	Yield(%)
VII		288°C	68	X		214°C	73
VIII		265°C	80	XI		173°C	74
IX		297°C	95				

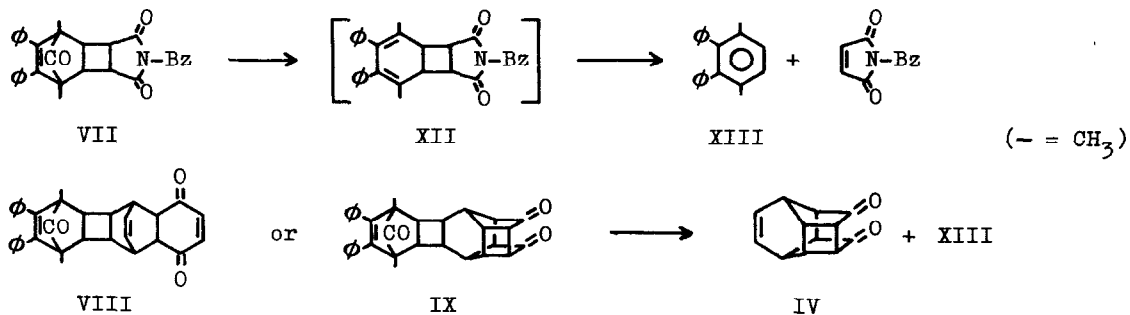
^aPrepared in benzene solution by heating the appropriate olefin with the dimer of the dienone (V) for periods varying (in order) from 6 to 96 hours.

Step 2. Photoaromatization

In favorable systems this reaction is extremely efficient. The irradiation of adduct VII in acetone gave a high yield of the aromatic hydrocarbon XIII together with N-benzylmaleimide. The cyclohexadiene (XII) is the presumed intermediate, but its presence has not been detected.

* Cyclobutenes, like many other ring-strained olefins, are reactive dienophiles (4). Their reactivity, however, is quite dependent on steric factors, which presumably can greatly increase the activation energy for cycloaddition. For example, 1,2-dimethyl-cyclobut-3-ene-1,2-dicarboxylic anhydride forms no Diels-Alder adduct with V, while the cyclobutene lacking these two methyl groups reacts normally.

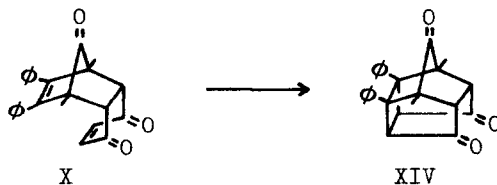
** Secondary electrocyclic ring opening of the bicyclo[4.2.0]octadiene to a 1,3,5-cyclooctatriene, an allowed reaction, makes thermal decarboxylation procedures unfavorable in the present case. Huisgen has recently shown that this equilibrium is markedly affected by substituents in the cyclobutane ring (5).



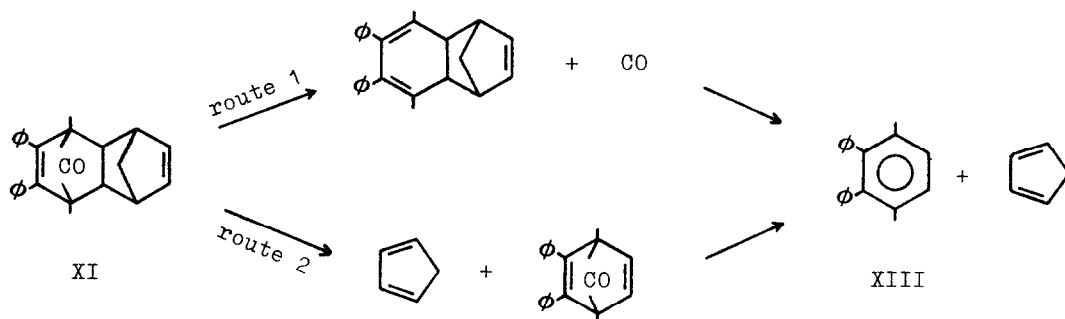
Irradiation of trione adducts (VIII or IX) for 2½ hours in acetone solution gave an excellent yield of the hydrocarbon (XIII) and pentacyclo[6.4.0.0^{3,6}.0^{4,12}.0^{5,9}] 10-dodecen-2,7-dione (IV). These were separated by chromatography on silicic acid (benzene/ethylacetate 5:1). The enedione (IV) was recrystallised from hexane, m.p. 179-81°. (Mass spectral molecular weight: found 186.067; calc. 186.068; nmr (CDCl₃) τ = 3.4 (2H, doublet of doublets), 6.75, 7.13, 7.5 (4H, 2H, 2H, broad singlets).

The feature of this interconversion is that cage structures derived from photolysis of adducts originating from (4 + 2) π cycloaddition to cyclooctatetraene can readily be converted into adducts formally derived from 1,4-addition to benzene, a reaction not readily attained under standard laboratory conditions. Indeed vpc analysis showed no trace of diketone (IV) upon sensitised irradiation of *p*-benzoquinone in benzene solution.

Two main features have been observed which restrict the present photoaromatization reaction, intramolecular photocycloaddition and intramolecular triplet energy transfer. The former can be illustrated by irradiation of the *p*-benzoquinone endo-adduct X, which gives the cage trione XIV. As the cis-stilbene chromophore is removed in this step subsequent photoaromatization does not occur. In cases where the cis-stilbene is not involved in the cycloaddition, fragmentation can still occur and only the leaving group is modified (e.g. VIII to IX \rightarrow IV).



A more restricting reaction involves intramolecular triplet energy quenching by an olefinic center other than the one initiating photoaromatization. Photolysis of the bicyclo[2.2.1]heptadiene adduct XI gives the aromatic hydrocarbon XIII as well as cyclopentadiene. It is not clear at this stage if these products result from photoaromatization (route 1) or via the reverse Diels-Alder reaction (route 2). Indeed a number of adducts containing an olefinic group elsewhere in the molecule undergo abnormal fragmentation (6).



REFERENCES

1. By 1,2-photoaromatization we mean the ultra-violet irradiation induced fragmentation where a portion (containing the energy absorbing chromophore) is converted to an aromatic hydrocarbon and the other fragment remains structurally intact. The prefix numbers represent the relative positions of the two σ -bonds involved in the fragmentation. A similar result can often be achieved thermally (7).
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