

CRYSTAL AND MOLECULAR STRUCTURE OF INTRAMOLECULAR CYCLOADDUCT OF
DICYCLOHEPTATRIENYL KETONE BY PHOTOCHEMICAL REACTION

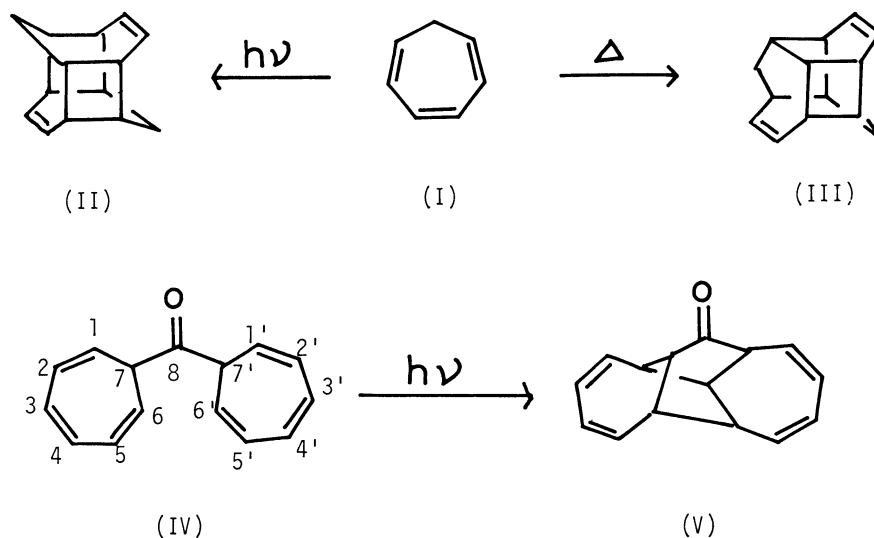
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A Photochemical reaction of dicycloheptatrienyl ketone affords a crystalline intramolecular ($\pi 2s + \pi 6s$) cycloadduct, the structure of which has been determined by X-ray analysis.

It is known that cycloheptatriene (I) gives dimer (II) by photochemical¹⁾ and (III) by thermal²⁾ reaction.

In connection with these facts, we have examined photochemical reaction of dicycloheptatrienyl ketone (IV) not only from a general mechanistic viewpoint³⁾ but also from our expectation of leading to some novel polycyclic cage molecules by possible intramolecular cycloaddition reaction.



Irradiation of (IV) in acetone with a high pressure mercury lamp through a pyrex filter under nitrogen atmosphere for 15 hours, followed by silica-gel chromatography gave a crystalline compound as a main product (V), mp 97-98°C, in 44% yield, IR; 3020, 1737, 1613, 1592, 700 cm^{-1} , UV; 251 nm

(log ϵ 3.97), 259 (3.99), 243 (3.97), MP; $m/e = 210$ (M^+). The NMR spectrum (100 MHz, $CDCl_3$, δ) shows the asymmetric complex olefinic multiplet 6.25-5.25 (8H) and 3.31, 3.11, 2.81, 2.65, 2.19, 2.13 (each 1H, methylene protons).

The structural determination of the adduct (V) from the physical data mentioned above has not established the unambiguous structure and so X-ray crystal analysis was carried out as follows. Suitable crystals were obtained from n-hexane and methylene chloride solution. *Crystal data*: $C_{15}H_{14}O$, $M = 312$, monoclinic, space group $P2_1/C$, $a=11.162$, $b=8.129$, $c=11.896$ Å, $\beta=91.53^\circ$, $D_m=1.15$, $D_c=1.16$ g/cm³, $Z=4$. The intensity data of 2389 ($2\theta \leq 55^\circ$ for Mo- $K\alpha$ radiation) were measured by a $2\theta-\omega$ technique using a Rigaku automatically controlled four circle diffractometer. The structure was solved by symbolic addition method and the first E-map has shown the complete structure of (V). Refinements by block-diagonal least-squares method gave $R=0.08$ with all nonhydrogen atoms. The addition of the hydrogen atoms which were located by difference Fourier synthesis and the successive refinements reduced to $R=0.072$ for 1723 non-zero reflections. Standard deviations are 0.08 Å and 0.06° for bond lengths and angles.

The atomic numbering and the molecular shape is shown in Figure 1. Hydrogens on C(1) and C(6) are cis and also hydrogens on C(5') and C(6') are cis, which indicate apparently suprafacial combinations between 2π and 6π systems. All bond lengths are normal. The sp^2 and sp^2 bond lengths of 1.34-1.35 Å and the sp^2-sp^2 bond lengths are in somewhat wide range (1.49-1.52 Å for sp^2-sp^3 and 1.55-1.58 Å for sp^3-sp^3).

On the other hand, C(7)C(1)C(6') angle of 94° is characteristically small but it should be expected for this bicyclo [2,2,1] heptyl moiety, as has been found for norbornane (93.2°)⁵⁾ and other related compounds ($92-96^\circ$).⁶⁾

The only interesting observation may be a conformation of cycloheptadiene skeletons in this molecule. As shown in Table 1, these conjugated diene systems are forced into a planer conformation (maximum deviation is only 0.045 Å) and therefore it can be concluded that the increment of energy from maximum π -overlap is large enough to offset increase in repulsion and strain energy induced by planer conformation. Moreover this result may provide a powerful information about the preferred-conformation of cyclohepta-1,3-diene being recently a subject of interest.^{7,8)}

The reaction has been investigated with expectation of $(6+6)\pi$ and/or, $(2+2)\pi$ and/or, $(6+2)\pi$ -type intramolecular adducts but main product (V) was proved to be a $(6+2)\pi$ -type adduct. It is noted that C_5-C_6 , double bond in one ring and triene system in another ring are easy of parallel approach, in such a conformation of (IV) that two rings with a boat form are twisted round into a propeller like shape by a steric requirement. This reaction seems to be a typical and indisputable example of a concerted symmetry allowed in excited state [$\pi 2s + \pi 6s$] combination although the $(6+2)\pi$ -type adducts between benzene ring and double bond in the same molecule have been reported,⁹⁻¹¹⁾

FIGURE 1

A perspective drawing of molecule (V). The numbering of atoms is based on that of (IV).

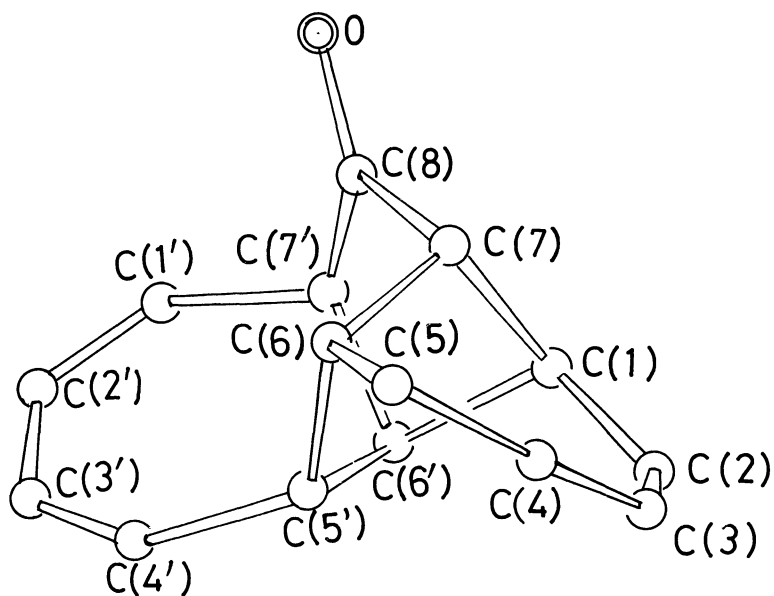


Table 1

Least-squares planarity analysis of conjugated diene system. Deviations are in Å and asterisks indicates atoms used to form best least-squares plane.

C(2) [*]	-0.017	C(1') [*]	-0.004
C(3) [*]	0.038	C(2') [*]	0.009
C(4) [*]	-0.045	C(3') [*]	-0.009
C(5) [*]	0.026	C(4') [*]	0.004
C(1)	-0.258	C(5')	0.006
C(6)	0.017	C(7')	-0.088
C(7)	-0.959	C(6')	-0.717

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