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PHOTOCHEMICAL INTRAMOLECULAR CYCLOADDITION OF 2,4-CYCLOHEXADIENONE DIELS-ALDER DIMERS

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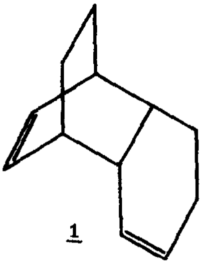
The photochemical intramolecular cycloaddition of numerous non-conjugated dienes has been reported[1]. However, attempts to convert the endo-Diels-Alder dimer of 1,3-cyclohexadiene (1) into a cage compound by irradiation in the presence of a variety of sensitizers have not been successful[2,3]. It has been assumed[3] that this lack of photochemical reactivity may be attributed to a sterically unfavorable arrangement of the diene system in 1 since the Diels-Alder adduct 2 does give the expected photo-cage product.[2]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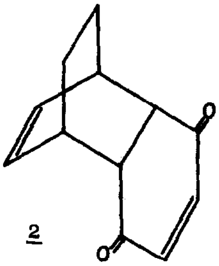
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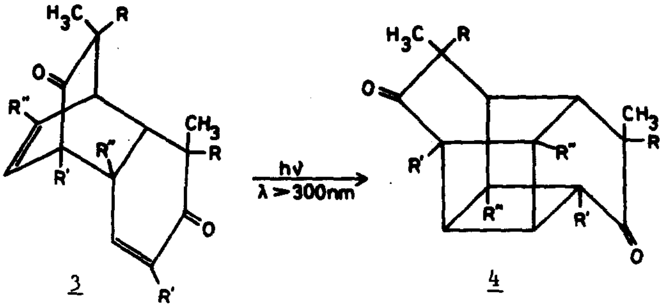
In order to establish whether or not cage formation is generally precluded in compounds containing a diene system as in structure 1, we investigated the photochemical isomerization of some substituted 2,4-cyclohexadienone Diels-Alder dimers of structure 3. Inspection of Dreiding molecular models reveals that the distance between the carbon-carbon double bonds in 3 is about the same as it is in 1.

Dimers 3a-e exhibit a longest-wavelength UV absorption maximum around 310 nm (ε 250) which is attributed to the n-π* transition of the α,β-unsaturated carbonyl group and the homoconjugated carbonyl group.[4] Irradiations were thus carried out in the absence of added sensitizer in an immersion well apparatus at room temperature under nitrogen, using a high-pressure mercury lamp (PHILIPS HPK 125 W) with a Pyrex filter sleeve.

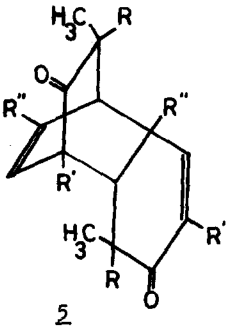


3 4

	R	R'	R''
a:	OH	CH_3	H
b:	OH	CH_3	CH_3
c:	OH	H	CH_3
d:	OAc	CH_3	CH_3
e:	OAc	CH_3	H
f:	$CH_2C_6H_5$	CH_3	H

Irradiation of 3a (2.76 g; 10 mmol) in methanol (100 ml) for two hours results in the precipitation of a colorless crystalline product (m.p. about 340°; 91 % yield) for which elemental analysis and spectroscopic data (UV; IR; NMR; MS) are in agreement with the cage product 4a.[5] Likewise, diene 3b (3,04 g; 10 mmol/65 ml methanol) was smoothly converted into the cage product 4b (m.p. 275°) which was isolated in 96 % yield after three hours of irradiation. Similar irradiation of the o-quinol dimer 3c and of the diacetates 3d and 3e gave the cage compound 4c (m.p. 244-247°; 82 % yield) and the cage diacetates 4d (m.p. 211-212°; 63 % yield) and 4e (m.p. 239-241°; 81 % yield), respectively. The photo-cycloaddition thus provides the evidence for the endo-configuration of the Diels-Alder dimers 3.[6]

The photo-products 4a-e exhibit a UV absorption maximum around 310 nm (ε∼100). The NMR spectra of 4a-e indicate that all substituents are pair-equivalent, as the cycloaddition gives rise to a cage structure with a twofold axis of symmetry. This finding is of significance because it confirms the structural orientation of the Diels-Alder dimers 3 to be as shown above.[7] The photo-cycloaddition of the conceivable dimer structure 5[7] would give rise to the asymmetrical cage structure 6.



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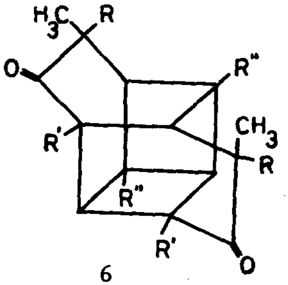

6

In analogy with the photochemical isomerization of compounds 3a-e, irradiation of the benzyl-substituted Diels-Alder dimer 3f^8 (0.5 g in a mixture of 50 ml of ethanol and 15 ml of methylene chloride) for 1 hour gave the cage compound 4f (m.p. 276-278°) in 91 % yield. Spectroscopic monitoring of this photochemical conversion in dioxane solution revealed some remarkable features of the isomerization reaction (see Fig. 1): The disappearance of the enone π-π* absorption results in the exhibition around 260 nm of the previously hidden π-π* transition of the phenyl substituent. The longest-wavelength absorption around 340 nm decreases and may, therefore, be attributed to the n-π* transition of the enone system and the homoconjugated carbonyl group.

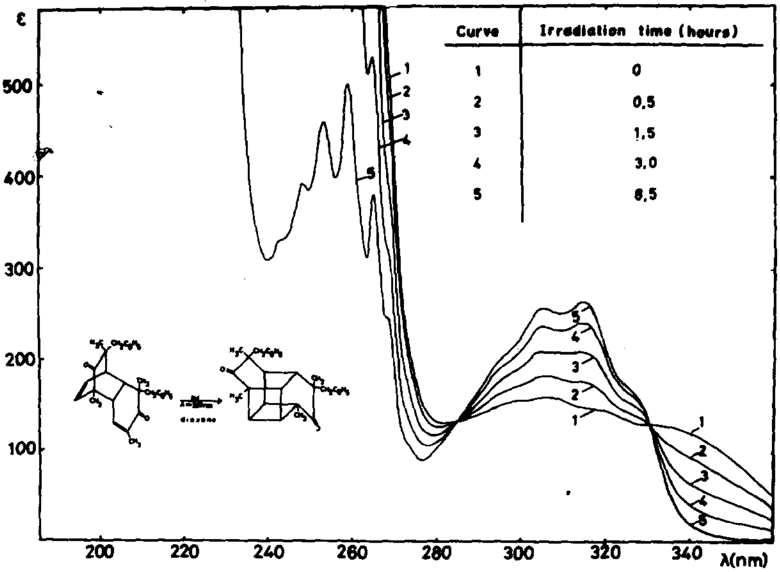

Fig. 1. Irradiation of dimer 3f above 340 nm. (1.75x10^{-3} molar in dioxane; 1 cm cell; conversion ca. 100 %; Corning cut-off filter 0-52)

An unexpected increase of the absorption around 310-320 nm is indicative of π-orbital overlap of the carbonyl group and the β-phenyl substituent, which appears to be more favorable in the rigid cage structure than in the enone precursor. Significantly, isosbestic points were observed only when 3f was irradiated above 340 nm, suggesting that the cage compound is photochemically labile and the intramolecular cycloaddition to give 4f is brought about cleanly only by n-π* excitation.

The photochemical intramolecular cycloaddition reaction should prove useful for confirming or establishing the structural orientation of other 2,4-cyclohexadienone Diels-Alder dimers. Furthermore, the results presented above suggest that the failure to obtain a photo-cage product from the *endo*-diene 1 may be attributable to ineffecient sensitization rather than to a sterically unfavorable arrangement of the diene system.

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