# Intramolecular [2 + 2] Photocycloadditions of *E* and *Z* Olefins to Cyclohex-2-enone

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The [2 + 2] intramolecular photocycloaddition of *E* and *Z* olefins to a cyclohexenone has been investigated; it is concluded that the bond to C(3) in the cyclohexenone is formed first to give the diradical intermediates (**7a**) and (**7b**).

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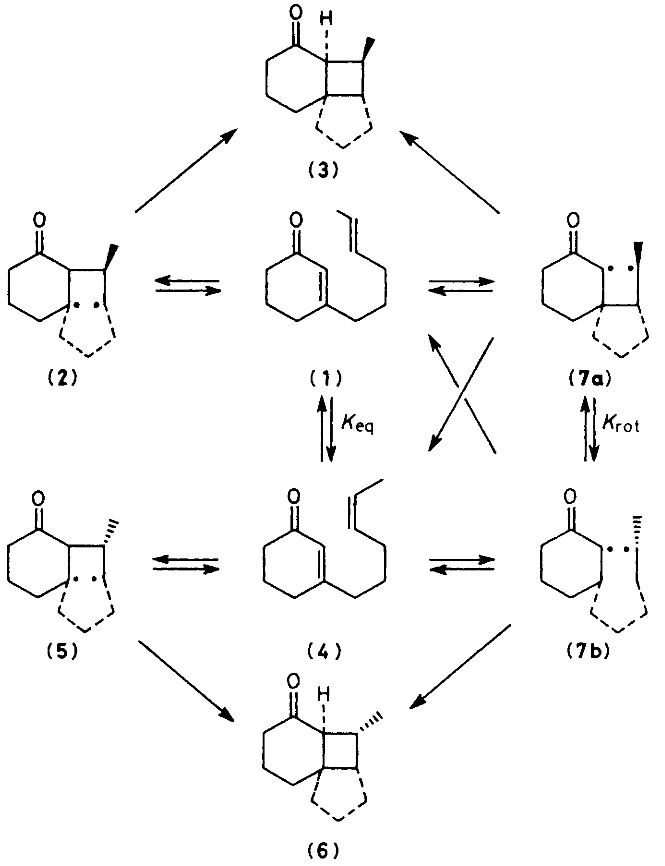
Inter- and intra- [2 + 2] photocycloaddition of unsaturated bonds to enones is an efficient reaction well established in organic synthesis[1] despite the fact that the mechanism is not yet fully known. It is assumed that 1,4-diradicals are intermediates, but to date it has not been determined whether the bond to C(2) or C(3) of the enone system is formed first.[2] The assumption that the first bond is formed to C(3) was made recently in order to explain some experimental results.[3] We now describe results of an intramolecular [2 + 2] photocycloaddition of *E* and *Z* olefins to a cyclohexenone which are consistent with a mechanism where the first bond is formed to C(3).

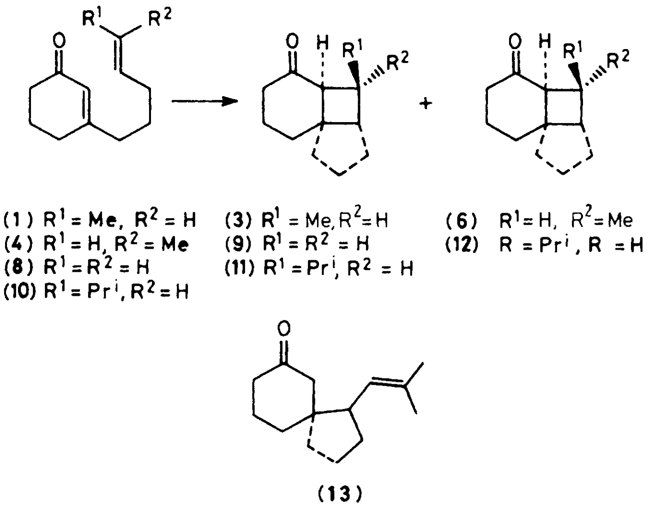
Our approach was based on product analysis. If the photocycloaddition of the *E* isomer (**1**) occurs either *via* a concerted



Scheme 1

mechanism or by formation of the first bond to C(2) leading to diradical **(2)**, product **(3)** is to be expected. On the other hand, the *Z* isomer **(4)** will form, *via* a concerted mechanism or diradical **(5)**, the product **(6)**. However if the first bond is formed to C(3), both **(1)** and **(4)** will form the equilibrating diradicals **(7a)** and **(7b)** which will lead to a mixture of two stereoisomers **(3)** and **(6)**.

Compounds **(1)**, **(4)**, **(8)**, and **(10)** were synthesised by Grignard reaction of the corresponding alkenylmagnesium bromide with 3-ethoxycyclohex-2-en-1-one.† On irradiation‡ **(8)** was transformed into **(9)** in high yield. [While we were investigating the structure of **(9)**, Cargill[4] published results on the photocyclisation of **(8)**, and determined the structure of **(9)** unambiguously.] Irradiation of **(1)** produced, in high yield, a mixture of **(3)** and **(6)** in 1 : 1 ratio, and precisely the same mixture was formed when **(4)** was irradiated. Four conditions must be fulfilled in order to deduce the mechanism, as follows. (i) Compounds **(3)** and **(6)** must be inactive photochemically. (ii) $k[(7a)\rightarrow(3)]$ and $k[(7b)\rightarrow(6)] >> k[(7a)\rightarrow(1) + (4)]$ and $k[(7b)\rightarrow(1) + (4)]$ (in intermolecular photocycloaddition it is believed that the reversion process from 1,4-diradical to starting materials is faster than the closure[2a]). (iii) If there is an equilibrium between **(1)** and **(4)** it must be much slower than the cycloaddition. (iv) The equilibrium $(7a)\rightarrow(7b)$ must be accomplished much more quickly than the closure process.



Scheme 2

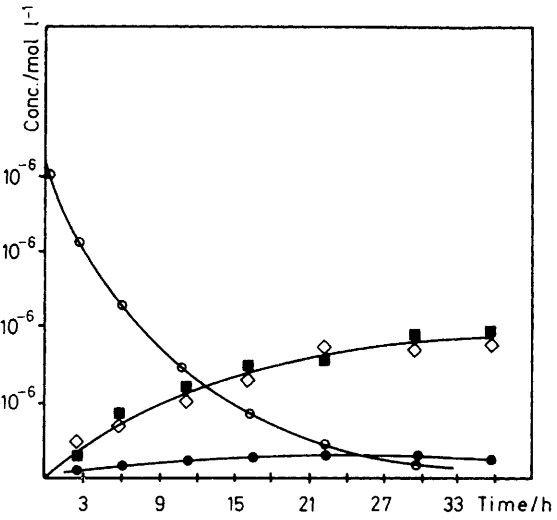


**Figure 1.** Irradiation (λ 366 nm) of **(1)** in cyclohexane followed by u.v. spectroscopy and gas chromatography. Symbols: ○ **(1)**, ● **(4)**, ■ **(3)**, ◇ **(6)**.

Compounds **(3)** and **(6)** were separated by preparative gas chromatography and their structures were determined by comparison with known compounds.[5] Each isomer was irradiated for periods three times longer than needed for cyclisation, and found to be photochemically inactive. The progress of the reaction could be followed by gas chromatography and u.v. spectroscopy simultaneously when **(1)** was irradiated in a u.v. cell (using u.v. filter λ 366 nm). The results are described in Figure 1. Similar curves were obtained for **(4)** and **(10)**. The quantum yields for the cyclisation of **(1)**, **(4)**, **(8)**, and **(10)** were found to be 0.43, 0.55, 0.5, and 0.42, respectively, which are 10 times larger than those reported[2a] for the intermolecular process. From the high quantum yields and the fact that **(1)** and **(4)** do not equilibrate during the irradiation one can conclude that the intramolecular photocycloaddition closure is much faster than the reversion process.

The possibility that **(3)** and **(6)** are formed from different excited states[6] was ruled out since upon irradiation in the

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† All new compounds reported in this paper gave i.r., $^1$H n.m.r., and high-resolution mass spectra in accordance with the structures shown.

‡ Irradiations were carried out using a 450 W Hanovia lamp with Pyrex or uranium glass filters. Conc. < 0.05 mol in cyclohexane.

presence of $Bu^t_2NO$ they are formed simultaneously in a 1 : 1 ratio; a triplet excited state is probably an intermediate because the Stern–Volmer plot gave a straight line.

It is widely accepted[7] that spin inversion in triplet 1,4-diradicals is the rate-determining step and $k_{rot}$ (rotation) is larger than $k_{inv}$ (inversion) by a factor of $10^2$. In order to examine whether the ratio of the two stereoisomers is dependent on the nature of R, compound **(10)** was synthesised and irradiated through a uranium glass filter ($\lambda > 330$ nm) to give **(11)** and **(12)** in a 1 : 1 ratio. Irradiation of **(10)** through Pyrex ($\lambda > 285$ nm) leads to **(13)** in high yield, a well documented reaction.[8]

From a synthetic point of view it should be obvious that any attempt to form one stereoisomer *via E* or *Z* olefins will fail since the first bond is formed to C(3) and the equilibration of the triplet 1,4-diradicals **(7a)**→**(7b)** is much faster than the closure to products.

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