Tetrahedron Letters,Vol.30,No.20,pp 2661-2664,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

TRAPPING OF 1,4-DIRADICAL INTERMEDIATE IN INTRAMOLECULAR [2+2] PHOTOCYCLOADDITION

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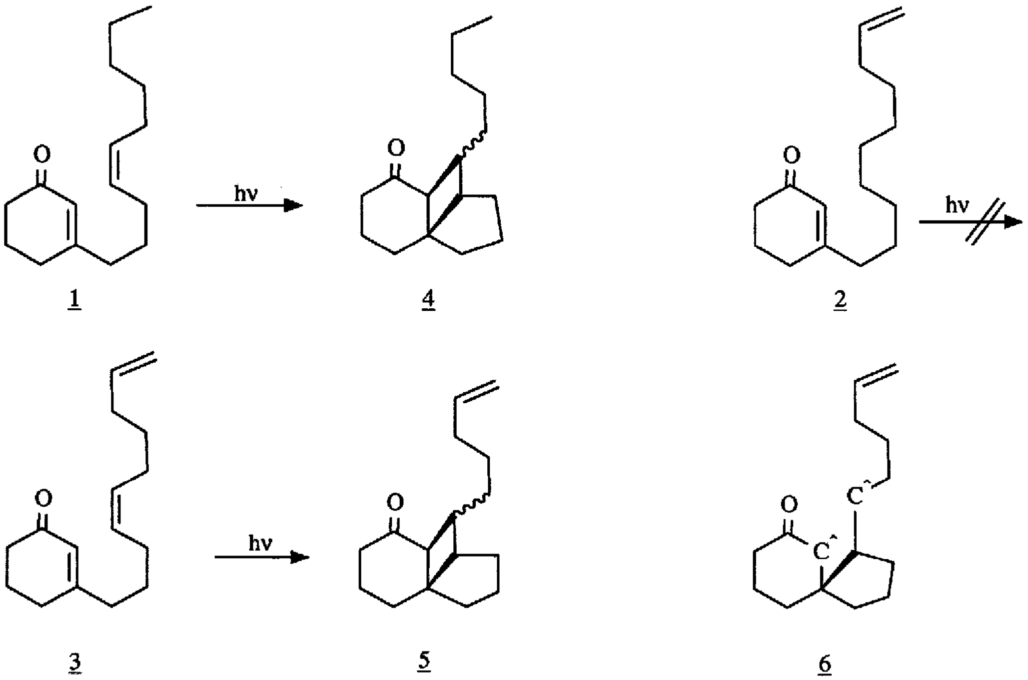
Abstract: For the first time a 1,4-diradical intermediate <u>10</u> was trapped in 43% yield in an intramolecular [2+2] photocycloaddition of olefins to cyclohexenone. The results support the assumption that the first bond is formed to carbon-β of the enone system.

A 1,4-diradical has been proposed by Corey[1] in 1964 to be an intermediate in the mechanism for the [2+2] photocycloaddition of olefins to cyclohexenones. His proposal was mainly based on product analysis. To our knowledge, this report is the only support for the existence of a 1,4-diradical. All attempts to trap the diradical in intermolecular [2+2] photoadditions so far failed. It is worth noting at this point, that a 1,4-diradical intermediate, in the formation of oxetane by [2+2] Paterno-Büchi reaction, has been trapped by molecular oxygen[2,3](~10 atm.). Irradiation of system I[4] in oxygen atmosphere led to the normal [2+2] photoadducts, no trapped product could be detected. Although the 1,4-diradical has not been trapped, it's existence has been inferred and often used in interpretation of experimental results of [2+2] photocycloaddition reactions.

It is known[5] that cyclopropylcarbinyl radicals rearrange to but-3-enyl radicals, the rate constant was lately determined[6] to be $1\text{x}10^{8}$ s^{-1}. It has been shown by Wagner[7] that 1,4-diradicals formed by Norrish Type II reactions can be trapped intramolecularly in low yields; Olefins and cyclopropyl rings were used as trapping functions. In recent publications it was shown that cyclopropyl rings can be used for detection of radical-like intermediates in penicillin biosynthesis[8] and as a "free radical clock" [9] in kinetic studies. We have used cyclopropyl rings for trapping the elusive 1,4-diradical which is formed in the [2+2] photocycloaddition. It is the first direct support that a diradical is an intermediate and that the first bond is formed between the olefin and carbon-β of the excited cyclohexenone[10].

Our first approach was based on intramolecular trapping of the 1,4-diradical by an olefin. Three compounds were prepared[11] and irradiated in cyclohexane *via* Uranium glass. The results are described in scheme I. It was found that when <u>1</u> was irradiated it formed <u>4</u> in high yield (the epimer ratio was found to be 1:1). On the other hand when <u>2</u> was irradiated for a period three times longer than required for complete reaction of <u>1</u>, no photoadduct was detectable. It can be concluded that when the olefin is separated from the enone by eight methylenes the intramolecular addition process is suppressed to negligible levels in the time scale of this

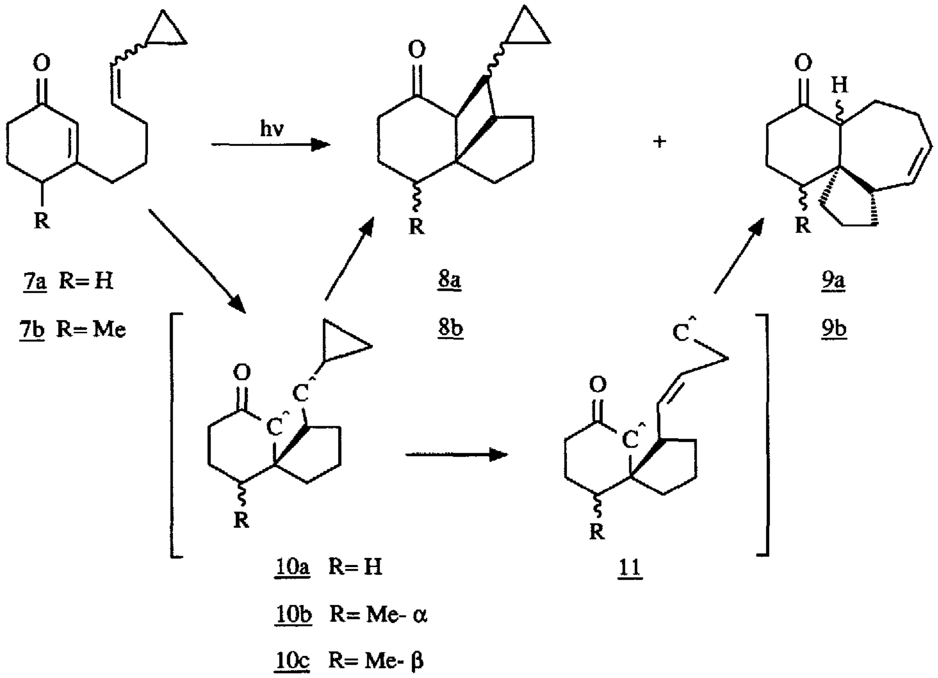


Scheme I

experiment. At this stage system 3 was irradiated. To our disappointment, the two epimers 5 were formed in high yield and 1:1 ratio. Two additional photoadducts were also detected by GC, in yields less than 2%. According to NMR, the compounds did not contain vinylic protons, and by HRMS appeared to be structural isomers of the starting material. They may be the trapped products which were formed *via* 6, but experimentally we could not isolate enough material for complete structure determination. At that point we decided to improve the efficiency of the trapping, hexenyl radicals have rate constants of 10^5 s^{-1}, by replacing the olefin with a cyclopropyl ring.

System 7[11] was prepared by Wittig reaction between cyclopropylmethantriphenylphsphonium iodide and the corresponding aldehyde to give in 60% yield, a mixture of Z and E in a 3:1 ratio. Irradiation of 7a (0.01xmMol) in cyclohexane *via* Uranium glass led to a mixture of four photoadducts A-D in a 2.7: 1.7: 2.5: 1 ratio respectively. GC/MS verified that all were structural isomers of 7a. The mixture was irradiated *via* Pyrex and it was found that A and B decompose slowly, but did not form C and/or D, while C and D were unaffected. This rules out the possibility that C and D are secondary photoproducts. Photorearrangement of compounds having structures similar to 8 is well documented in the literature[10], leading through 1,5 hydrogen abstraction to the cleavage of the four membered ring. A+B and C+D were separated by preparative GC and the mixtures were analyzed by NMR. It was found that A and B were two epimers having the structure 8a, namely that of the expected [2+2] photoadducts and were formed in 47% yield. Careful analysis of the NMR spectrum of C+D enabled us to conclude that those compounds have: 1) no cyclopropyl hydrogens and 2) a Z vinylic system $-CH-CH=CH-CH_2-$. The mixture A-D was hydrogenated using Pd/C as catalyst, it was found that A and B (8a) were unaffected, whereas C and D formed new products by absorbing one molar eq. of hydrogen. Based on the spectroscopic and chemical evidence[12] we propose the structure 9a for C and D.

Based on the assumption that 10a is an intermediate in the photocycloaddition of 7a, we constructed the following experiment to test our hypothesis. Having a substituent on C-4 of the six membered ring, should lead to formation of two epimeric intermediates 10b and 10c. The ratio of the two intermediates 10b to 10c will determine the ratio of the epimers at C-4 in the products 8b and 9b. Compound 7b was irradiated and the ratios of the epimers were found by GC/MS to be 2:1 in both, the [2+2] photoadduct 8b and the trapped product 9b. This experiment well supports the assumption that 10 represents the structure of the 1,4-diradical intermediate.



Scheme II

Our results provide the first direct support to the commonly accepted assumption that a 1,4-diradical is an intermediate in [2+2] photocycloaddition processes. The structure of the trapped product can be explained by cleavage of the cyclopropyl ring to form a second intermediate 11. Since the rate constant for the cleavage of cyclopropyl ring is known to be $1\mathrm{x}10^{8}\ \mathrm{s}^{-1}$, the rate at which 10 cyclizes to form 8 should be on same order. On the other hand, the formation of 10 is in full agreement with our finding[10] that in those systems the first bond is formed to carbon-β of the enone.

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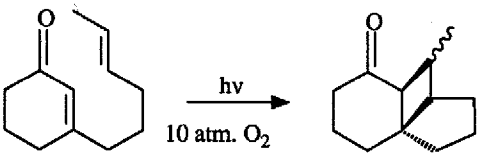
4. System I was irradiated under oxygen pressure of 10 atm. to give in quantitative yield the [2+2] photoadduct II, no detectable amount of trapped 1,4-diradical was found. We thank Prof. W. Adam for preforming the irradiation of I in his laboratory.



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11. The spectroscopic properties of all new compounds reported herein are in full agreement with the structures assigned.

12. Treating C+D with base led to a rearrangement which is under investigation in our lab.

(Received in UK 21 March 1989)