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THE REACTIVE INTERMEDIATE IN THE PHOTOINDUCED ALCOHOL ADDITION OF cis-2-CYCLOOCTENONE

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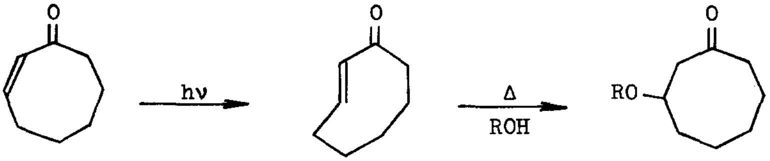
Recently various examples of photochemical polar addition of protic solvents to cyclic α,β-unsaturated ketones have been recorded. Irradiation of 2-cycloheptenone (1) or 2-cyclohexenones (2) in water or alcohol gives rise to the corresponding β-hydroxy- or β-alkoxycycloalkanones. The product-forming states have been postulated to be the π,π* triplet states (2c, 3) or the strained ground molecules derived therefrom (1, 3). Intervention of the polar state, hypothetical species, has also been proposed (2b). We have examined the behavior of cis-2-cyclooctenone (I) in view of the moderate stability of the photoisomerized trans enone II (4), and found that the latter is the reactive intermediate in the photoinduced alcohol addition.

Irradiation (5) of the enone I (6) in methanol at room temperature for 30 min gave 3-methoxycyclooctanone (III) in a 72% yield (based on consumed I), which was identified by comparison with the authentic sample (7). Photolysis in isopropanol for 2.5 hr yielded 3-isopropoxycyclooctanone (IV), b.p. 70-74° (3 mm), in a 43% yield. The structure was confirmed on the basis of spectroscopic data (ir, nmr, ms) as well as elemental analyses.

In order to specify the reactive species of the polar addition, exposure was effected at lower temperature. Irradiation of I in 2-methyltetrahydrofuran at -78° caused cis-trans isomerization giving a mixture of I and II as recorded previously (4). After 15 min irradiation, the photolysate was poured into cold methanol or isopropanol, and allowed to warm up to room temperature in the dark producing the corresponding alcohol adducts III (75% yield) and IV (60%), respectively. Irradiation of I in isopropanol at -78° for 15 min followed by treatment with a large excess of methanol in the dark provided almost exclusively III (97%)



I II III R = Me
IV R = Me$_2$CH

together with a small amount of IV (<1%), suggesting that the polar addition to the photoexcited states, if any, should not be significant.

Finally, attempts to quench the triplet state of I with 0.1-3.0 M piperylene, an efficient quencher with a triplet energy of ~50 kcal/mole (8), resulted in failure. If the lifetime were long enough to enter into intermolecular reactions, the energy transfer to piperylene would probably be diffusion controlled.

These findings imply that the photoinduced alcohol addition of cis-2-cyclooctenone (I) involves prior photochemical isomerization to the trans isomer II and subsequent thermal nucleophilic attack of alcohol. Although further investigations will be required, this may suggest that the polar addition of 2-cycloheptenone (1) also intervenes the strained trans isomer (9).

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