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PHOTOCHEMICAL SYNTHESIS OF A CYCLOPROPANONE PRECURSOR[1]

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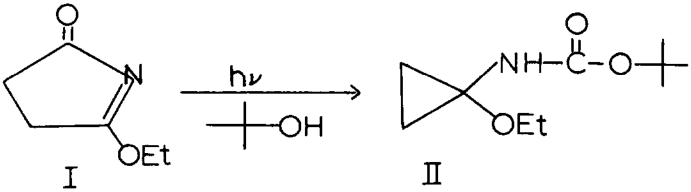
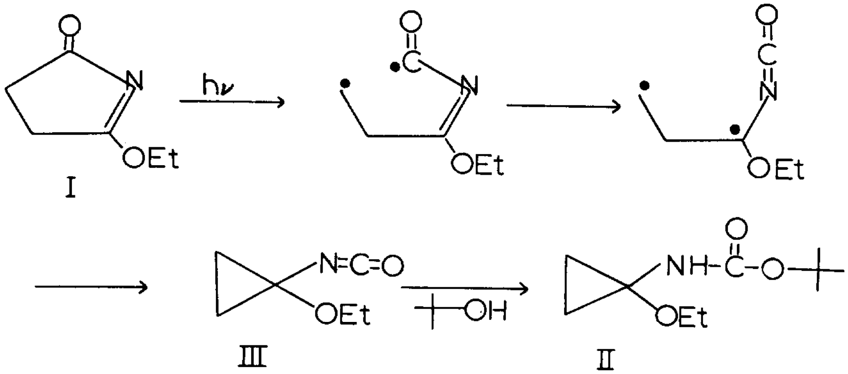
Photodimerization[2,3] and photocycloaddition to olefins[4] are the predominant photochemical reactions of 2-cyclopentenone. An alternate mode of photoreactivity, α-cleavage and subsequent rearrangement to a cyclopropane derivative, has recently been reported for 5,5-diphenyl and 5,5-dimethyl-2-cyclopentenone.[5]

We have observed a preferential α-cleavage reaction in the photochemistry of a molecule which formally resembles a 2-cyclopentenone, 2-ethoxypyrrolin-5-one (I).[6] Irradiation of the pyrrolinone (I) in t-butyl alcohol at 2537A° results in a rearrangement to a cyclopropanone precursor, t-butyl N-(1-ethoxycyclopropyl)carbamate (II) (70% yield, m.p. 44-45°).



The product structure is clearly established from spectroscopic evidence. The photoproduct (II) exhibits infrared absorption at 3310 and 1720 cm^{-1}, consistent with the carbamate functional group. The n.m.r. spectrum shows an A_2B_2 pattern extending from 0.80 to 1.15 δ (4H), a triplet at 1.13 δ (3H, J=7Hz), a strong singlet at 1.47 δ (9H), a quartet at 3.68 δ (2H, J=7Hz), and a broad absorption at 5.98 δ (1H).[7] In the mass spectrum at 70 ev the carbamate (II) does not give a parent ion; however a strong peak at m/e 145 (62% of base; base peak at m/e 57) can be assigned to loss of isobutylene from the parent ion by a McLafferty rearrangement. Loss of isobutylene is characteristic for the mass spectra of *t*-butyl esters.[8]

The photoproduct structure suggests a reaction mechanism involving initial α-cleavage followed by rearrangement to a 1,2-diradical and ring closure to ethoxycyclopropylisocyanate (III). The isolated product II then results from solvent addition to the intermediate isocyanate.



Using the technique of low temperature photochemistry with infrared analysis,[9] a strong isocyanate, infrared absorption was observed at 2280 cm^{-1} after a 10 min. irradiation of a neat sample of pyrrolinone (I) at -190° with unfiltered light from a 200 watt high pressure mercury lamp.

In contrast to many cyclopentenones, photodimerization is not an important photoreaction of 2-ethoxypyrrolin-5-one. Likewise, photocycloaddition to olefins does not seem to compete favorably with α-cleavage. Irradiation of pyrrolinone (I) in *t*-butyl alcohol with a 450 watt mercury lamp and a Corex filter in the presence of 1,1-dimethoxyethylene, a very good olefin in the photocycloaddition reaction,[10] yields only the product of α-cleavage (II). An explanation for the photoreactivity of pyrrolinone (I) may be apparent from the ultraviolet absorption spectrum. In contrast to α,β-unsaturated ketones, pyrrolinone (I) does not exhibit a maximum for the π-π^* band in the near ultraviolet but only strong end absorption. 2-Cyclopentenone and 3-ethoxycyclohexenone exhibit π-π^* bands at 217 and 238 nm, respectively.[11] In cyclohexane the n-π^* band of I occurs at 273 nm (ϵ=55) and is shifted to 265 nm (ϵ=45) in purified absolute ethanol. The ultraviolet absorption of pyrrolinone (I) suggests that there is little delocalization between the functional groups which are formally conjugated. The infrared carbonyl stretching frequency of I, 1750 cm^{-1}, is also consistent with this conclusion. The photoreactivity of I should then be compared with photoreactivity of saturated ketones. It is well established that electronically excited cyclopentanones readily undergo α-cleavage in the vapor phase[12] and in solution.[13]

The photoreactivity and π-electronic structure of other conjugated imines and imino ethers are presently under investigation.

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