

THE PHOTOLYSIS OF TRANS-4-HEXEN-2-ONE: A NOVEL TRANS-CIS ISOMERIZATION

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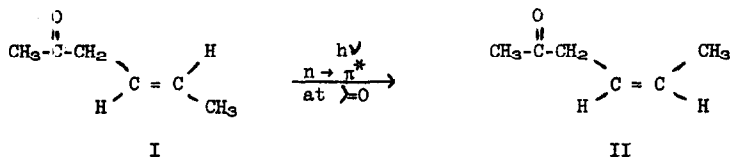
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Although the photochemistry of α,β -unsaturated ketones has been extensively explored, (1) few data are available on the photolytic reactions of aliphatic non-conjugated olefinic ketones. (2) We became particularly interested in β,δ -unsaturated ketones, in which electronic interaction of the two chromophores is evidenced by an exaltation of the extinction coefficient observed for the $n \rightarrow \pi^*$ band of the carbonyl group. (3) It was our feeling that this class of compounds might provide a chemical demonstration of intramolecular energy transfer with initial excitation of the carbonyl function resulting in isomerization of the double bond. (4)

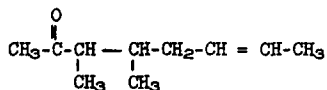
The title compound (I) was prepared by the rapid steam distillation of an aqueous acidic solution of 3-hexene-2,5-diol, followed by redistillation and preparative vapor chromatography: b.p. $45^\circ/29$ mm.; λ_{max} 5.84, 10.36 μ ; $\lambda_{\text{max}}^{\text{MeOH}}$ 280 m μ (ϵ 79); n.m.r. 1.70, 2.04, 3.02, 5.50 δ . (5) Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.26; H, 10.33. Photolyses were conducted in pentane solution using a Hanovia 450 watt high pressure mercury arc contained in a water cooled quartz immersion well. A Corex filter was employed so as to limit the incident light to that which would effect only the carbonyl $n \rightarrow \pi^*$ transition. The reaction was followed by periodic withdrawal of aliquots and examination of these by v.p.c.. A rapid initial formation of a shoulder on the starting material peak was observed followed by the gradual disappearance of both peaks and the

formation of an exceedingly complex reaction mixture. Reaction of one gram of I was complete within two hours.

The initial photoproduct (II) was isolated by removal of solvent followed by preparative vapor chromatography. The mass spectrum (parent peak 98 m/e) and n.m.r. spectrum of II were essentially identical with those of the starting material; λ_{max} , 5.84, 14.8 μ . Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{O}$: C, 73.43; H, 10.27. Found: C, 73.40; H, 10.27. These data require that this photoproduct be cis-4-hexen-2-one thus establishing that the desired transformation had indeed taken place.



Longer reaction times allowed the isolation, by preparative vapor chromatography, of two new photoproducts, III and IV. On the basis of spectral and chemical data⁺, these compounds were identified as the trans and cis isomers of 3,4-dimethyl-6-octen-2-one, products which may formally be derived by addition of the acetyl and 2-butenyl radicals to a molecule of 2-butene. Formation of 2-butenyl and acetyl radicals in this photolysis



III (trans), IV (cis)

⁺ Elemental analyses showed III and IV to be isomers, with the molecular formula $\text{C}_{10}\text{H}_{18}\text{O}$. Mass spectra were essentially identical: parent peak 154, base peak 43 (CH_3CO), strong peaks 82 and 72 m/e ($\text{CH}_3\text{COCH}(\text{CH}_3)-$). N.m.r. were also very similar: multiplet, 0.9, 6H, (CH_3CH); doublet, 1.66, 3H, ($\text{CH}_3\text{CH}=\text{C}$); singlet, 2.01, 3H (CH_3CO); multiplet, 5.33, 2H, ($\text{CH}=\text{CH}$); broad absorption in the region 1.88-2.32 δ , 4H. Infrared spectra: III- λ_{max} , 5.84, 10.4 μ ; IV- λ_{max} , 5.84, 14.4 μ . Hydrogenation of III and IV afforded a single dihydro compound identical in all respects to 3,4-dimethyl-2-octanone synthesized independently by the addition of butylmagnesium bromide to 3-methyl-3-penten-2-one. (6)

is further indicated by the isolation of 3-methyl-1,5-heptadiene and a mixture of the stereoisomers of octa-2,6-diene. Finally, photolysis in the presence of added 2-butene afforded 3-methyl-2-pentanone. (7)

As discussed above, energy transfer from the carbonyl's n, π^* triplet excited state to the double bond, with concomitant formation of the olefinic π, π^* triplet, would satisfactorily explain the observed trans-cis isomerization of the 4-hexen-2-one. However, several other mechanisms must also be considered -- (a) Internal conversion of the n, π^* excited state to a high vibrational level of the ground state followed by "thermal" isomerization. (b) Dissociation of the ketone into the acetyl and 2-butenyl radicals, stereoisomerization of the 2-butenyl radical and recombination. The nature of the secondary photoproducts strongly suggests homolytic cleavage is occurring. However, the required loss of configuration of the 2-butenyl radical would be the first such observation for an allylic radical. (8) (c) Initial conversion of the trans-4-hexen-2-one to the conjugated ketone (perhaps via abstraction of a hydrogen atom at the 3 position by radicals in the reaction mixture), followed by photolytic isomerization to a mixture of β, γ isomers. (1)

Experiments, designed to indicate which mechanism is operative, are now in progress; we are also investigating other unsaturated ketones to determine the generality of our observation.

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References

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