

AN UNUSUAL PHOTOCHEMICAL BEHAVIOR OF SPIROCYCLOPROPYLKETONE. PHOTO-CHEMISTRY OF SPIRO[2,4]HEPTAN-4-ONE, 5-ONE, SPIRO[2,5]OCTAN-4-ONE AND 5-ONE

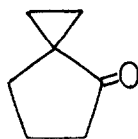
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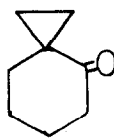
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There have been reported that a principal course of the photochemical conversion of cyclopropylketones is a cleavage of the cyclopropane ring.⁽¹⁾ A primary process of the reaction is an $n \rightarrow \pi^*$ excitation of the carbonyl group; its energy is transferred to a highly strained cyclopropane ring through a conjugative interaction between them.⁽²⁾ The cleavage of the cyclopropane by the carbonyl excitation is thus a characteristic of the photoreaction of cyclopropylketones.

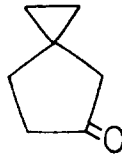
In a course of the photochemical studies of spiroketones, we observed an unusual behavior in the photoreaction of cyclopropylketones. That is, in spirocyclopropylketones, the cyclopropane ring is not cleaved but the principal course of the reaction is an alpha-cleavage of the carbonyl compound. The compounds investigated in the present letter are following four spiroketones in which I and II are conjugated and III and IV are not. The spiroketones I—IV were prepared through known synthetic routes⁽³⁾ and each of them was characterized carefully by the elemental analysis and spectrometries.



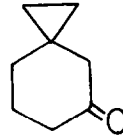
I



II



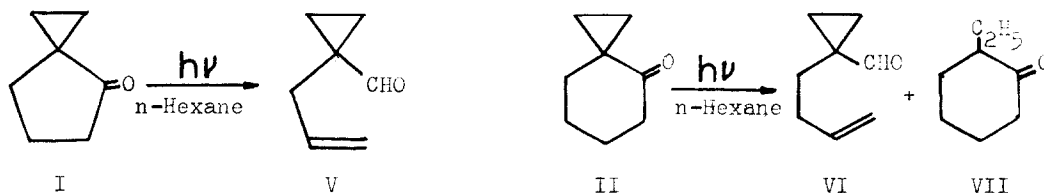
III



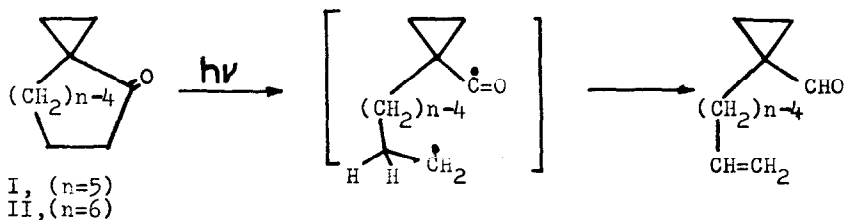
IV

An irradiation of the spiroketone I in n-hexane at 10-15° by a high pressure mercury lamp under a nitrogen atmosphere resulted in the formation of an unsaturated aldehyde in 34% yield. The remainder was a polymeric material which was not characterized further. A prolonged irradiation of the solution caused a marked increase in the amounts of polymeric material; therefore, the reaction was followed by vpc. and the irradiation was discontinued when the maximum amount of product was produced. The aldehyde V, mp of 2,4-dinitrophenylhydrazone was 139-139.5°, had a terminal double bond and a cyclopropane ring. The nmr, IR, and elemental analysis of this compound were all consistent with 1-formyl-1-(2'-propenyl)cyclopropane V.

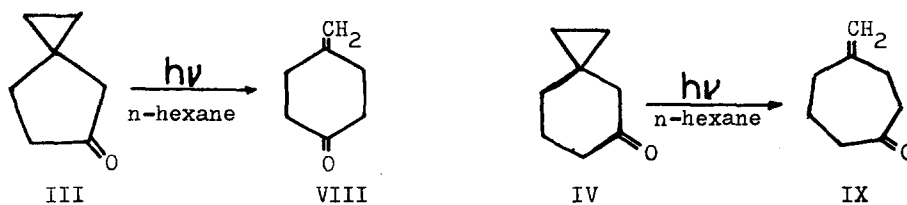
An irradiation of II in the same way as above also resulted in the formation of the aldehyde VI in 37% yield besides a ring opened product VII in 10%. The compound VII was confirmed by a comparison with an authentic specimen. Again, the compound holding the cyclopropane was a principal reaction product; the cyclopropane was only partly cleaved in the present irradiation. In the photoreaction of I, a product corresponding to VII was checked carefully by vpc., but it was concluded that it could be less than 1% at best if it was produced.



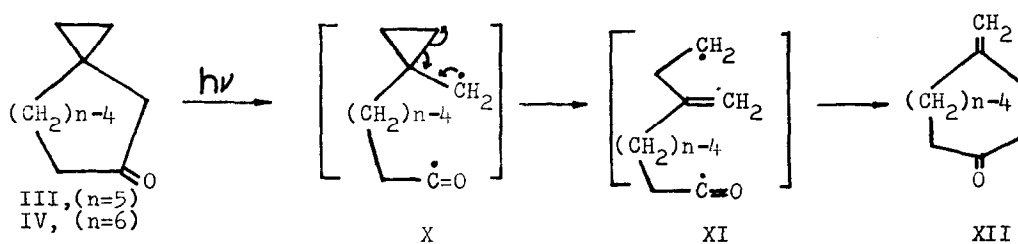
When a Pyrex filter was used for the reaction of I, the same reaction proceeded at the same rate; hence the reaction is clearly proceeded by the excitation of the carbonyl group as those observed in the numbers of the photoreactions of various ketones. The reaction was markedly quenched by the addition of naphthalene or in the presence of molecular oxygen, which suggested that the conversion underwent through $n \rightarrow \pi^*$ triplet state of the carbonyl compounds. The formations of V and VI should be understood by an alpha-cleavage which is followed by a hydrogen abstraction as those known for a typical photoreaction of cyclic ketones.⁽⁴⁾



The photochemical conversion of the ketone III and IV proceeded to somewhat different way. The cyclopropane ring in these ketones was cleaved in the irradiation and only isolated products from III and IV were 4-methylenecycloalkanones, VIII and IX, in 33% and 22% yield respectively.



These reactions could be explained in a following way. The first step of the reaction might be the alpha-cleavage, which gives a diradical X. The resulted cyclopropyl radical could induce the opening of the ring as shown below and gives the second diradical XI, which might cyclize intramolecularly to afford 4-methylenecycloalkanone XII. There have been several cases in which the cyclopropyl radical results in the formation of a ring cleaved product. (5)



After these experiments and discussions, it can be concluded that the cyclopropane ring in these spiroketones is not primarily cleaved by the photo-excitation. This is quite a contrast when we consider the photochemical behavior of various cyclopropylketones. Dauben and his coworkers have reported that bicyclo[4.1.0]-heptan-2-one undergo exclusive ring cleavage by $n \rightarrow \pi^*$ photoexcitation. (1h)

This marked difference between spiro system and bicyclic system cannot apparently be due to the difference in relative stabilities of the intermediate biradicals. The ring cleavage of the bicyclic ketone will result in the formation of primary-secondary biradical while the spiro ketone will produce primary-tertiary biradical. Consequently, if this is an important factor for the photoreaction of cyclopropylketone, the more of the ring cleaved product must be observed in the spiro system; this is a direct opposition to the results obtained in the present experiments. Further, the degree of the conjugation between the cyclopropane and the carbonyl group also indicates that the energy transfer must be more effective in the spiro ketone than in the bicyclic ketone.⁽⁶⁾

Apparently, existing explanations cannot account for the present contradiction and it seems to us that a conformational factor will operate in the photoreaction of these cyclopropylketones. A biggest difference between these two systems is that in both systems the relative conformational arrangements of the cyclopropane and carbonyl are fixed but in different directions. This problem is a subject of the further investigations.

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