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THE PHOTOCHEMICAL ISOMERIZATION OF 1-ACETYLBICYCLO[4.1.0] HEPTANE AN INTRAMOLECULAR REARRANGEMENT

Rudolph Ernst K. Winter and Richard F. Lindauer*
Department of Chemistry
Polytechnic Institute of Brooklyn
Brooklyn, New York 11201

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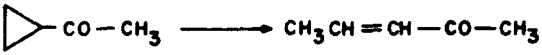
The photosensitivity of cyclopropyl-conjugated ketones was first investigated in 1954 by Pitts and Norman.(1) These workers noted that photolysis of acetylcyclopropane led to 2-pentene-4-one and that the normal α-cleavage of ketones (Norrish Type I) was almost entirely suppressed in favor of this isomerization.



Additional examples of such photochemical isomerizations(2) as well as closely related photochemical cis - trans interconversions(3) of cyclopropyl-conjugated ketones have been reported in recent years. This communication describes experiments pertaining to the mechanism of the cyclopropyl ketone to enone isomerization.

The photolysis of 1-acetylbicyclo [4.1.0] heptane (I)(4) in either acetic acid or methanol led to the disappearance of (I) with formation of several products. 1-Acetyl-cycloheptene (II)(5) was the major volatile reaction product. In a typical experiment, irradiation of a solution of 1 gm of cyclopropyl ketone (I) in 15 cc acetic acid for two hours gave distillable volatiles comprising 70% of the reaction mixture.(6) Vapor phase chromatographic analysis of these volatiles indicated 71% (I) and 23% (II), the remainder consisting of four as yet unidentified products (see, however, below). Similar results were obtained when methanol was used as the solvent.

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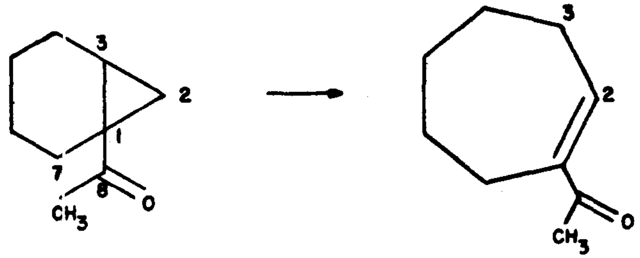
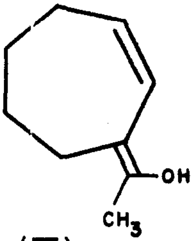
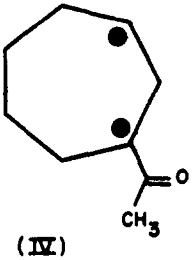


(I) (II)

Two plausible mechanisms have been suggested(1, 2, 3) to account for the cyclopropyl ketone to enone isomerization. In the case of (I) these can be formulated as: (*a*) formation of enol (III), either by an intramolecular pathway or by hydrogen transfer to and from the solvent; and (*b*) rearrangement of (I) accompanied by intramolecular hydrogen migration. In either pathway biradical (IV) could be an intermediate.



(III)

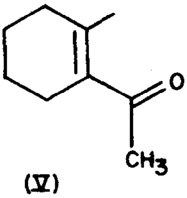


(IV)

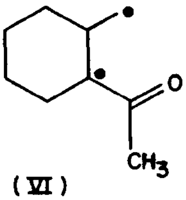
Our experiments with deuterated solvents distinguish these possibilities. A reaction pathway involving the enol intermediate (III) would result in deuterium incorporation at C_3 of the 1-acetyl-cycloheptene produced thereby. In that case the H-2 triplet in the n. m. r. spectrum of (II) (τ 3.02, $J \sim 6.5$ cps) would reduce to a doublet. However, photolysis of (I) in acetic acid-d_4 furnished 1-acetylcycloheptene which still displayed the olefinic proton as a triplet. In fact, the n. m. r. and infrared spectra of this material were identical in all respects with the spectra of authentic 1-acetylcycloheptene, indicating that no deuterium had been incorporated at all.(8) Similar results were obtained in photoreactions carried out in methanol-d_1. These observations rule out the intervention of enolic intermediates in the formation of 1-acetylcycloheptene and are consistent only with a mechanism involving an intramolecular hydrogen migration. It seems most reasonable that a 1, 2-migration of hydrogen from C_2 to C_3 has occurred, perhaps concurrent with C_1-C_3 bond cleavage.(9) This mechanism could thus represent a general formulation for the photoisomerization of cyclopropyl-conjugated ketones and is similar to the mechanism recently proposed by

Griffin and co-workers(10) for the photoisomerization of 1, 2-arylcyclopropanes.

The almost exclusive formation of 1-acetylcycloheptene in the photolysis of (I) deserves some comment. Although one of the minor products formed has gas chromatographic character identical with that of the other "expected product", 1-acetyl-2-methylcyclo-hexene (V)(11), it comprises less than 2% of the distillable volatiles.



(V)



(VI)

Predominant formation of only one of the possible cyclopropane cleavage products in the photolysis of cyclopropyl-conjugated ketones has been observed previously.(2) In conformationally rigid ketones the specificity may well reflect, as has recently been suggested(12), a required geometry for carbonyl-cyclopropane interaction, similar to that proposed for the reductive cleavage of cyclopropyl-conjugated ketones.(13) Examination of models of 1-acetylbicyclo [4. 1. 0] heptane, however, suggests essentially free rotation about the C_1-C_8 bond and does not reveal any obviously preferred conformation. Thus, the predominant formation of (II) rather than (V) is probably a consequence of electronic effects, i.e. the stability of radical type intermediates [(IV) vs. (VI)], rather than of stereochemical factors such as optimum geometry.

This point, as well as other aspects of cyclopropyl ketone photochemistry, deserves further investigation.

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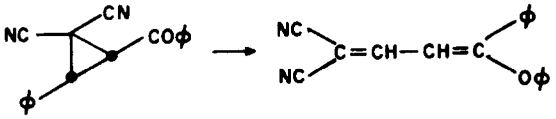
6) A Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with RPR-3000 A^{o} lamps was employed as a light source. Prolonged irradiation resulted in decreased amounts of distillable volatile reaction product.

7) Homolytic C_1-C_3 bond cleavage is considered most likely, by analogy to the photochemical reactions of other cyclopropyl systems, (10) and has been demonstrated in the case of isomerization:



H.E. Zimmerman, results presented at the Symposium on Photochemistry: Recent Developments and Applications, Houston, February, 1967.

8) The appropriate control experiments have indicated that the work-up method does not involve hydrogen-deuterium exchange.

9) A 1,4 hydrogen migration from C_7 to C_3 cannot be ruled out, but is probably less likely.

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