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THE INTRAMOLECULAR PHOTOREARRANGEMENT OF CYCLOPENTENONES

William C. Agosta[1, 2] and Amos B. Smith, III
Laboratories of The Rockefeller University
New York, New York 10021
and
Andrew S. Kende,[1] Robert G. Eilerman, and Judith Benham
Department of Chemistry
University of Rochester
Rochester, New York 14627

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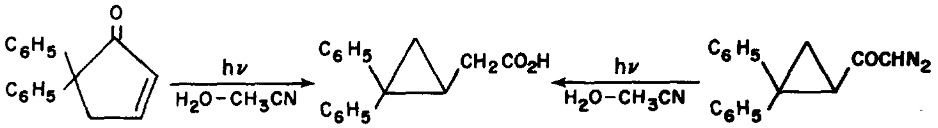
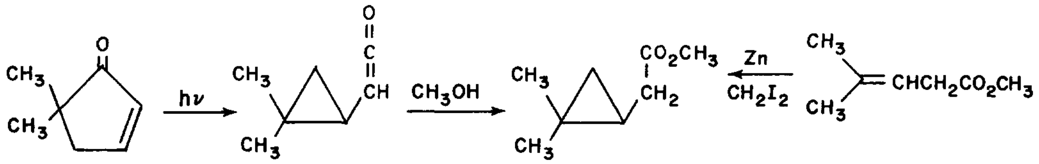
The bimolecular photochemistry of cyclopentenone has played a key role in the study of photodimerization mechanisms.[3] We wish to describe a rather general intramolecular photoisomerization of cyclopentenones which, in appropriate systems, completely overwhelms the bimolecular pathway.

Irradiation of a 0.5% solution of 5,5-diphenylcyclopent-2-enone[4] (I) in 3:2 acetonitrile-water for three days[5] in a Pyrex vessel resulted in 78% conversion (by titration) to acidic product. Workup produced in 52% yield a crystalline $C_{17}H_{16}O_2$ carboxylic acid[6] having spectroscopic properties suggestive of 2,2-diphenylcyclopropaneacetic acid (II). The identity of the photoacid was confirmed by an independent synthesis of II proceeding from the diazoketone[7] III using a photochemical Wolff rearrangement.



I II III

In a similar experiment a 0.1% methanolic solution of 5,5-dimethylcyclopent-2-enone[8] (IV) was irradiated to give in 62% yield a methyl ester identified as VI by independent synthesis from methyl pyroterebate[10] (VII) using the Simmons-Smith reaction.[11] The photochemical pathway to ester VI was demonstrated by the following observations. A 0.1% solution of ketone IV in n-pentane was irradiated at 15° for 3 hours.[9] Direct examination at room temperature of the infrared (ir) spectrum of the resulting solution revealed a sharp band of medium intensity at 2110 cm^{-1}. Treatment of the solution with excess methanol at room temperature for 16 hours resulted in complete loss of the 2110 cm^{-1} band and formation of a new strong band at 1750 cm^{-1}. Gas-liquid chromatography (glc)[12] of the crude product remaining after removal of solvent showed three components in the (uncorrected) ratio 13:66:21; these were separated and purified by preparative glc. From ir, nmr, and retention time the first of these was identified as starting ketone IV and the second, as the methyl ester VI. The data clearly point to the intermediacy of the ketene V in this reaction.

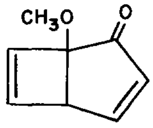


IV V VI VII

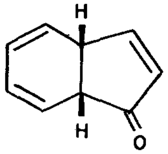
Direct irradiation of cyclopentenone itself in pentane has permitted spectroscopic detection of minute amounts of the presumed cyclopropylketene; here this pathway seems to be followed only to the extent of a few percent. The photorearrangement of ketones I and IV can be efficiently sensitized by benzophenone, a result indicating that triplet excited states are converted to the ketenes in good yield. Preliminary attempts to quench the rearrangement have been made using 2,3-dimethyl-1,3-butadiene in the concentration range 0.05 - 0.2 molar. The diene had no effect on the rearrangement quantum yield for I and only partially quenched the process from IV. The possibilities of a singlet component or of a fast triplet mechanism in the photochemistry of these ketones are under investigation.

The postulated transformation exemplified by IV → V is a reverse, photochemical example of the quite general vinylcyclopropane - cyclopentene rearrangement[13] and may be regarded also as a "homocyclobutenone" ring opening.[14] It is noteworthy that this pathway is not followed in the photochemistry of the related ketone VIII,[15] although it remaines as one possible route for the conversion of *cis*-8,9-dihydroindenone (IX) to the methyl ester X upon photolysis[16] in methanol.

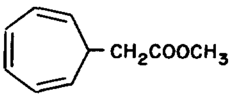
We are continuing our investigations of this rearrangement in these and other systems.



VIII



IX



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FOOTNOTES AND REFERENCES

(1) Correspondence may be addressed to either of these authors.

(2) Fellow of the Alfred P. Sloan Foundation.

(3) *Inter alia*, P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966); J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5671 (1966); P. de Mayo, J-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); P. de Mayo, A. A. Nicholson, and M. Tchir, *ibid.*, **47**, 711 (1969); and P. J. Wagner and D. J. Bucheck, *ibid.*, **47**, 713 (1969).

(4) P. N. Craig and I. H. Witt, *J. Am. Chem. Soc.*, **72**, 4925 (1950).

(5) An external 140 watt medium-pressure Hanovia utility lamp, model 30620, was employed.

(6) This product melted at 97-98°; its nmr spectrum exhibited a 2-proton complex doublet centered at δ 1.3 (cyclopropyl CH_2), a broad 3-proton multiplet at δ 2.1 (other aliphatic protons), and a strong peak at δ 7.3 arising from the 10 aromatic protons.

(7) The diazoketone III, mp 117-118°, was prepared in high yield from the chloride of 2,2-diphenylcyclopropanecarboxylic acid using excess diazomethane in ether.

(8) The ketone IV was prepared from 2,2-dimethylcyclopentanone (H. O. House and B. M. Trost, J. Org. Chem., 30, 2502 (1965)) by the α-bromoketal procedure of E. W. Garbisch, Jr., ibid., 30, 2109 (1965).

(9) A 450 watt medium-pressure Hanovia mercury arc, type L, no. 679A-36, with a Pyrex filter, was employed.

(10) Ester VII was obtained by diazomethane esterification of pyroterebic acid (A. A. Goldberg and R. P. Linstead, J. Chem. Soc., 2343 (1928)) and was used without rigorous purification.

(11) H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 81, 4256 (1959); and R. S. Shank and H. Shechter, J. Org. Chem., 24, 1825 (1959).

(12) All glc was carried out on a Varian Aerograph Autoprep using a 20 ft x 0.25 in. stainless steel column packed with 30% SE-30 on 60/80 Chromosorb W. Typical operating conditions were a column temperature of 140° and a helium flow rate of 100 ml/min.

(13) C. D. Gutsche and D. Redmore, Adv. Alicyclic Chem., Supp. 1, 163 (1968). See also L. A. Paquette, G. V. Meehan, and R. F. Eizember, Tetrahedron Lett., 995 (1969).

(14) J. E. Baldwin and M. C. McDaniel, J. Am. Chem. Soc., 90, 6118 (1968).

(15) O. L. Chapman and J. D. Lassila, ibid., 90, 2449 (1968).

(16) E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, Helv. Chim. Acta, 50, 297 (1967).