The Photoisomerization of 3-Cyclooctenones[1]

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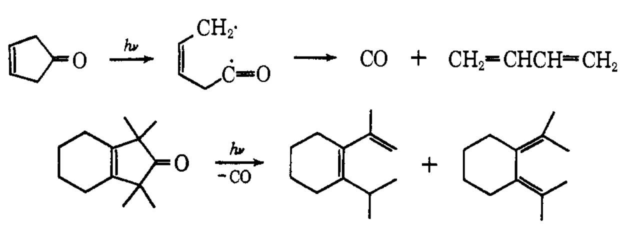
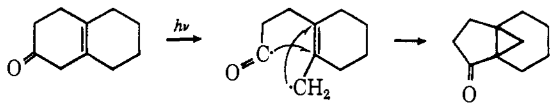
Abstract: 3-Cyclooctenone and its 6-oxa analog have been found to rearrange principally to 2-vinylcyclohexanone derivatives upon irradiation. Data are presented in support of the proposal that the formation of 2-vinylcyclohexanones as well as the minor products stems from an initial Norrish type I photochemical process followed by transannular rebonding or hydrogen abstraction.

As part of the surge of interest in organic photochemistry, the photochemical behavior of monocyclic five-, six-, seven-, and eight-membered α,β-unsaturated ketones has been examined and is now recognized to be highly dependent upon the ring size of the carbonyl-containing substrate. Whereas 2-cyclopentenone[3] and 2-cyclohexenone derivatives[4] dimerize quite readily, 2-cycloheptenone[5] and 2-cyclooctenone[6] are converted to the corresponding highly strained *trans* isomers.[7] Despite the extensiveness of our knowledge regarding such conjugated cycloalkenones, the photochemistry of the related β,γ-unsaturated cycloalkenones had not been studied when this investigation was initiated. We have had occasion to examine the ultraviolet irradiation of 3-cyclooctenone (**1**) and its 7-oxa analog **2** and wish now to report on the results of this study.

The photolability of these eight-membered cyclic ketones was anticipated in view of the demonstrated enhancement of n → π* absorption generally associated with such molecules.[8] In addition, past investigations have shown that certain bicyclic β,γ-unsaturated ketones undergo rearrangement when exposed to ultraviolet light under appropriate conditions.[9] More recently, preliminary reports have dealt with the photoinduced reactions of isomesityl oxide[10] and 2,3,3-trimethyl-1-penten-4-one,[11] acyclic examples of such nonconjugated ketones. The choice of 3-cyclooctenones was founded on the expectancy of unique transannular reactions in these medium-sized rings, and thus represented part of our continuing interest in transannular phenomena.[12] These expectations have been realized.

Since the inception of this work, reports dealing with the photolysis of 3-cyclopentenones[13] and 3-cyclohexenones[14] have appeared. Irradiation of the n → π* band of 3-cyclopentenones results solely in highly efficient conversion to derivatives of 1,3-butadiene and carbon monoxide. In direct contrast to this behavior, 3-cyclohexenones are rearranged in good yield under similar conditions to ring-contracted cyclopropyl ketones.





Results

3-Cyclooctenone (**1**) was prepared by the mild acid hydrolysis of 1-dimethylamino-1,3-cyclooctadiene.[12c] The irradiation of **1** was conducted in a variety of solvents (see Table I) using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) fitted with a Vycor filter. The photolysis was followed by withdrawal of small aliquots at various time intervals and examination of these by vapor phase chromatography. Careful monitoring of the photochemical rearrangement indicated that the rate of disappearance of **1** was relatively rapid at the outset but gradually diminished to a point where a photostationary state appeared to be reached.[15] The various irradiations were found to give rise to two photoisomers which were readily separated by preparative gas chromatography.

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[2] Alfred P. Sloan Foundation Research Fellow, 1965–1967.

[3] P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962); P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966); J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5672 (1966).

[4] For example, H. Ziffer, N. E. Sharpless, and R. O. Kan, *Tetrahedron*, 22, 3011 (1966), and pertinent references cited therein.

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[6] P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

[7] In contrast, irradiation of *trans*-2-cyclododecenone is reported to produce the conjugated *cis* isomer in addition to some β,γ-unsaturated ketone: H. Nozaki, T. Mori, and R. Noyori, *Tetrahedron*, **22**, 1207 (1966).

[8] For general discussions of the intensification of n → π* absorption in β,γ-unsaturated ketones, consult A. Moskowicz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962); D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., Sect. B*, 215 (1967).

[9] G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960); R. Criegee and H. Furrer, *Chem. Ber.*, **97**, 2949 (1964); D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963); G. O. Schenk and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963); E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967).

[10] N. C. Yang and D.-M. Thap, *Tetrahedron Letters*, 3671 (1966).

[11] E. F. Kiefer and D. A. Carlson, *ibid.*, 1617 (1967).

[12] (a) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **87**, 1561 (1965); (b) L. A. Paquette and R. W. Begland, *ibid.*, **87**, 3784 (1965); (c) L. A. Paquette and R. W. Begland, *ibid.*, **88**, 4685 (1966); (d) L. A. Paquette and L. D. Wise, *ibid.*, in press; (e) L. A. Paquette and M. L. Wise, *Tetrahedron*, in press.

[13] J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966); L. D. Hess and J. N. Pitts, *J. Am. Chem. Soc.*, **89**, 1973 (1967).

[14] J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967); J. R. Williams and H. Ziffer, *ibid.*, 469 (1967).

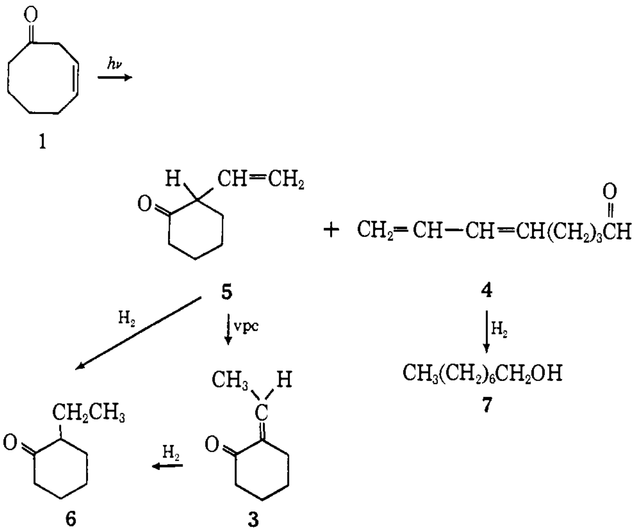
[15] In an independent study, Professor Jack Crandall, Indiana University, has demonstrated the existence of a photoequilibrium involving **1** and **5**. We thank Professor Crandall for informing us of his results prior to publication.

Table I. Representative Time and Percentage Composition Values for the Photorearrangement of 3-Cyclooctenone (**1**)

Solvent	Time, hr	Photolysate compn, %^{a}		
		1	3	4
Pentane	3	65	27	8
	5.5	48	42	10
	9	28	45	7
Ether	3	68.5	10.5	1.5
	7	60	20	3
	22	21	31	8
Methanol	3	56	34	10
	6	32	49	19
Methanol (0.1 *M* in added naphthalene)	7	53	38	8
Piperylene	7	79	*b*	*b*
	26	45	*b*	*b*

[a] In runs performed other than in methanol solvent, small amounts of a viscous polymer were obtained with increasing duration of the irradiation. Cyclooctane was employed throughout as the internal standard. [b] New peaks presumably due to reaction of **1** and/or **4** (**5**) with piperylene (not investigated) were seen to be produced. Only very small quantities of **3** and **4** were noted.

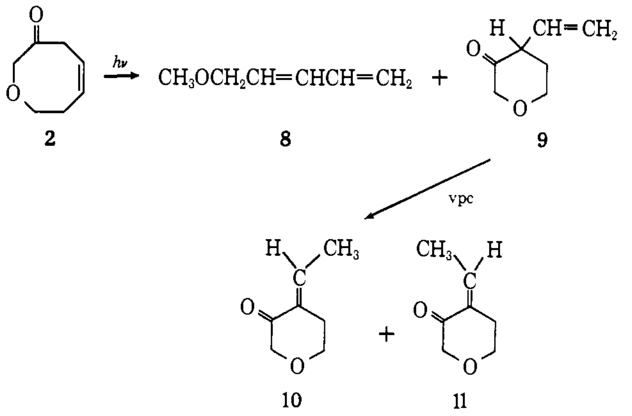
The major product was assigned structure **3** on the basis of its molecular weight (*m/e* 124), spectral data, and subsequent catalytic hydrogenation to 2-ethylcyclohexanone (**6**). The infrared spectrum in CCl_4 shows a strong carbonyl band at 1700 cm^{-1} and the ultraviolet spectrum in isooctane displays maxima at 236 (ϵ 5400) and 280 mμ (ϵ 130). Nmr studies in carbon tetrachloride indicated, *inter alia*, the presence in **3** of a methyl group (doublet of triplets, J = 7.5 and 1.5 cps) centered at δ 1.80 and a lone vinyl proton (quartet of triplets, J = 7.5 and 1.5 cps) centered at δ 5.80. The methyl substituent was assigned the *syn* configuration by comparison with the chemical shift data of ketones **10** and **11** (see below).



The minor product was shown to be aldehyde **4**. In agreement with this formulation, this substance exhibited a mass spectral molecular ion peak at *m/e* 124, an intense infrared (CCl_4) carbonyl stretching band at 1745 cm^{-1}, a lone ultraviolet peak (isooctane) at 224 mμ (ϵ 24,500), and a compatible nmr spectrum. Conclusive evidence was derived from its exhaustive catalytic hydrogenation to 1-octanol (**7**).

Careful scrutiny of the nmr spectrum of the crude photolysate obtained by careful evaporation of the solvent indicated that although the anticipated amounts of unreacted **1** and aldehyde **4** were present, absorption bands assignable to **3** were totally absent. Rather, the spectrum suggested the presence of 2-vinylcyclohexanone (**5**). On the basis of these data and because catalytic hydrogenation of such a mixture afforded only cyclooctanone, 2-ethylcyclohexanone, and 1-octanol in the expected ratio, we have concluded that **4** and **5** are the primary photoproducts of 3-cyclooctenone (**1**) and that **3** arises because of a rapid and quantitative isomerization of **4** during the gas chromatographic process.

In an effort to determine the generality of this photorearrangement, the photochemical behavior of **2** was studied. In a typical experiment, irradiation of a dilute pentane solution of **2** for 1 hr under very similar conditions led to the formation of a photolysate mixture which contained (vpc analysis) 27% unreacted **2**, 12% **8**, 57% of a mixture of ketones and **10** and **11** (ratio 65:35), and a trace of a carbonyl compound which has not been characterized. Diene **8** proved to be a highly volatile liquid; however, sufficient pure material was isolated to permit the obtention of mass (*m/e* 98) and infrared ($\nu_{\max}^{\mathrm{CCl_4}}$ 1645 cm^{-1}) spectra. Compounds **10** and **11** were isomeric with the starting material. Their nmr spectra (in CCl_4) confirmed the structural assignments and clearly indicated their *syn-anti* relationship. Thus, the spectrum of **10** displays a singlet for the isolated methylene group at δ 3.98, a triplet (J = 5 cps) of relative area 2 at δ 3.78 for the $-OCH_2CH_2-$ protons, a quartet of triplets (J = 7.5 and 1.5 cps, relative area 1) centered at δ 6.82 for the vinyl proton, and a doublet of triplets (J = 7.5 and 1.5 cps, 3 H) at δ 1.75 for the methyl group. In addition, the triplet (J = 5 cps) centered at δ 2.60 and assignable to the two allylic ring protons clearly demonstrates the existence of additional long-range coupling.

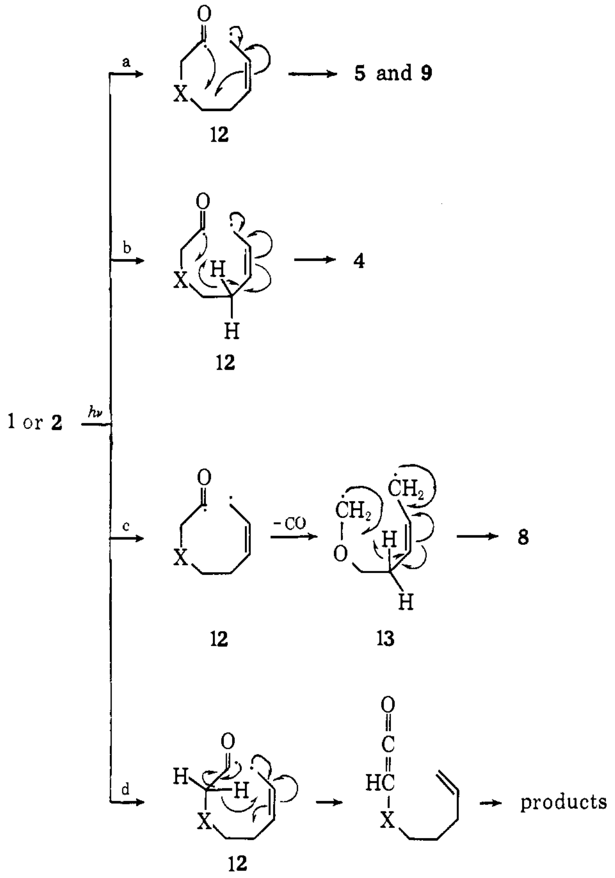


The multiplicities of the peaks in the case of **11** are nearly identical, but the following changes in chemical shifts are to be noted: 3.92, 3.76, 5.90, 2.06, and 2.60, respectively. In view of these data, the *syn*-vinyl proton in **10** is seen to be deshielded by 0.92 ppm relative to the same substituent in **11**. Similarly, the *syn*-methyl group of **9** is deshielded by 0.31 ppm when compared to the same group in its *anti* counterpart (**11**).

In this instance also, the available evidence indicated that the 2-vinylcyclohexanone derivative **9** was the precursor of **10** and **11**.

Discussion

The molecular changes involved in the photorearrangement of **1** and **2** may adequately be explained in terms of a primary Norrish type I process leading to the biradical **12**. *A priori*, the possibility exists that this species may react further by means of four mechanistically plausible paths (a–d) each involving five- or six-centered transition states. Bonding at the alternate terminus of the allylic radical moiety (path a) has been demonstrated to be the preferred mode of reorganization for both **1** and **2**. Intramolecular transannular abstraction of an allylic hydrogen atom by the acyl radical (path b) is quite pronounced in the 3-cyclooctenone system. Apparently, however, this reaction in the case of **2** is not observed under our conditions due to the increased propensity for decarbonylation (path c) presumably caused by the added stability associated with α-alkoxy radicals such as **13**.[16] The operation of an intramolecular hydrogen shift in **13** leads to **8**. The mechanistic rationalization outlined in path d was not observed herein.



On the basis of the spectral data for **1** and **2** the reaction may be formulated as occurring by means of $n \rightarrow \pi^*$ excitation. The question then arises whether singlet or triplet species are responsible for the subsequent rearrangements. The photolysis of **1** in pentane does not appear to be sensitized by benzophenone (E_T = 69 kcal/mole), 2-acetonaphthone (E_T = 59 kcal/mole), or fluorenone (E_T = 53 kcal/mole), nor quenched by anthracene (E_T = 42 kcal/mole). However, quantitative studies were complicated by competitive absorptions. Quenching was observed in the case of piperylene solvent (Table I),[17] but because destruction of starting material was evidenced in this instance, the absence of products may not be meaningful. Furthermore, although quenching of a reaction by piperylene solvent has been commonly taken as evidence for the intermediacy of triplet intermediates, recent data[18] suggest that this medium is also effective in the quenching of singlet states. Therefore formulation of the multiplicity of the title reaction at this time could best be provisional, and considerable further work is required before clarification of this point becomes available.

Of interest was the observation that irradiation of **1** and **2** did not produce derivatives of *trans*-3-cyclooctenone or cyclooctanone, possible products of intramolecular energy transfer.[19]

In view of the novelty of the 3-cyclooctenone rearrangement and especially because the limited available data suggest that 3-cyclopentenones and 3-cyclohexenones react from their photoexcited states in a manner not paralleled by the medium-ring systems (at least after the α-cleavage step), the photochemistry of a wide variety of β,γ-unsaturated mesocyclic ketones and related compounds is presently under investigation in this laboratory.

Experimental Section[20]

3-Cyclooctenone (1). To a solution of 20 g of 50% fluoroboric acid in 100 ml of water was added 10 g (0.07 mole) of 1-dimethylamino-1,3-cyclooctadiene.[12c] The solution was refluxed for 1 hr, cooled, and extracted with three 50-ml portions of ether. The organic extracts were combined, washed with sodium bicrabonate and water, and dried over magnesium sulfate. The solution was concentrated and distilled to yield 7.5 g (90%) of clear colorless **1**, bp 85–86° (11 mm), $n^{24}\mathrm{D}$ 1.4870; $\nu_{\max}^{\mathrm{CCl_4}}$ 1710 and 1653 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ 284 sh (45), 292 (50), 300 (55), 310 (40), and 320 mμ (ϵ 25) [lit.[21] bp *ca.* 80° (12 mm); $\lambda_{\max}^{\mathrm{EtOH}}$ 286 mμ (114)]; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.8 (complex multiplet, 6 H, aliphatic methylene groups), 2.4 (multiplet, 2 H, $\mathrm{C}H_2$-C=O), 3.1 (multiplet, 2 H, =$\mathrm{CHC}H_2$C=O), and 5.7 (complex multiplet, 2 H, vinyl protons).

Irradiation of 3-Cyclooctenone (1). A. Preparative Scale. Two grams (0.015 mole) of **1** dissolved in 500 ml of purified pentane was irradiated for 90 min under a nitrogen atmosphere with a 450-w medium-pressure Hanovia Type L mercury arc in an immersion well apparatus fitted with a Vycor filter. The reaction mixture was carefully concentrated at 0° and the residue (1.95 g) was subjected to preparative vpc separation [10 ft × 0.25 in. copper column packed with 15% SE-30 on Chromosorb W (60–80 mesh)] at 140°.

The first material to be eluted was 5,7-octadien-1-al (**4**), bp 35° (5 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.5–2.6 (complex multiplet, 6 H, methylene protons), 4.85–6.60 (multiplet, 5 H, vinyl protons), and 9.80 (aldehyde proton).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 76.99; H, 9.77.

The second product was *syn*-2-ethylidenecyclohexanone (**3**), bp 40° (1 mm), $n^{25}\mathrm{D}$ 1.4812. The spectral parameters are discussed in the text.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.09; H, 9.77.

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(16) C. Walling and M. J. Mintz, *J. Am. Chem. Soc.*, **89**, 1515 (1967)

(17) These results may be misleading in the sense that lessened yields can be expected in a given time when the quencher is also competing for light.

(18) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966).

(19) H. Morrison, *Tetrahedron Letters*, 3653 (1964); H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965); R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966).

(20) The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were recorded with a Cary Model 14 spectrometer. The nmr spectra were determined with a Varian A-60 spectrometer and the mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 ev.

(21) N. Heap and G. H. Whitham, *J. Chem. Soc., Sect. B*, 164 (1966).

Catalytic hydrogenation of *ca.* 50-mg samples of **3** and **4** at 50 psig in a Parr shaker over 10% palladium on charcoal at 30° for 2 days in ether solution produced 2-ethylcyclohexanone and 1-octanol, respectively. The authenticity of the structures of the reduced materials was derived by comparison of vpc retention times on two columns, infrared spectra, and nmr spectra.[22]

B. Analytical Scale. A small sample of **1** and an approximately equimolar amount of cyclooctane were dissolved in the appropriate solvent (already containing the sensitizer or quencher if used in the run) and the resulting concentrations were calibrated with an Aerograph A90P gas chromatograph. The solution was placed in a quartz test tube which was affixed to the exterior of the immersion well. The solution was placed under an atmosphere of nitrogen and the tube was sealed with a rubber septum. The progress of the reaction was followed by removal of small aliquots with an appropriate syringe at specified time intervals; the aliquots were analyzed by vpc.

Hydrogenation of Crude Photolysate Mixture. Crude photolysate mixture (500 mg) was hydrogenated as above. After filtration to remove the catalyst, the solution was concentrated and submitted to preparative vpc (SE-30). The three products were characterized as cyclooctanone (derived from residual 3-cyclooctenone), 2-ethylcyclohexanone (derived from **5**), and 1-octanol (derived from **4**).

Irradiation of 2. Two grams of **2** was dissolved in 500 ml of pentane and irradiated as before for 60 min. The reaction mixture was concentrated at 0° and subjected to preparative vpc [10 ft × 0.25 in. copper column packed with 15% QF-1 on Chromosorb W (60–80 mesh)] at 140°.

The first product which was rapidly eluted from the column was identified as 5-methoxy-1,3-pentadiene (**8**). Because of the high volatility of **8**, sufficient material was isolated to permit obtention of an infrared spectrum ($\nu_{\max}^{\mathrm{CCl_4}}$ 1645 cm^{-1}) and a mass spectrum (*m/e* 98, remainder of fragmentation pattern in agreement).

For the purpose of elemental analysis, isomeric ketones **10** and **11** were collected from the gas chromatogram as a mixture (peaks seriously overlapped). Redistillation of the collected material in a molecular still afforded a colorless liquid.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.92; H, 7.93.

Nmr spectra of **10** and **11** were obtained on samples derived from the resubmission of the purified mixture to preparative vpc (SE-30 column, 120°). The respective nmr spectra are discussed in the text.

Acknowledgment. The authors wish to thank the Elanco Products Co. and the Benzol Products Co. for the generous gifts of chlorodimethyl acetal and benzyl alcohol, respectively, which materials were employed in the synthesis of **2**.

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[22] We wish to thank Dr. Kenneth Greenlee, Chemical Samples Co., for a generous sample of authentic 2-ethylcyclohexanone.

The Photochemistry of 3-Cyclooctenone[1a]

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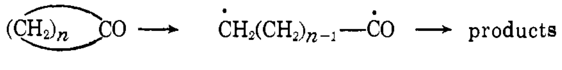
Abstract: The solution photochemistry of 3-cyclooctenone has been examined under several sets of reaction conditions. The main photolysis products are 2-vinylcyclohexanone and 5,7-octadienal. The separate irradiation of 2-vinylcyclohexanone produces 3-cyclooctenone and the same acyclic aldehyde. 5,7-Octadienal does not revert to its precursors photochemically. 2-Vinylcyclohexanone is labile to both heat and acid, which convert it to the isomeric *cis*- and *trans*-2-ethylidenecyclohexanones. The photochemical transformations encountered in this work appear to be best described in terms of an initial Norrish type I cleavage followed by subsequent reactions of the diradical thus formed.

The photochemical behavior of cyclic saturated ketones has been the subject of extensive study.[2] Although much remains to be learned about the electronic details of such photochemical transformations, there has emerged a fair understanding of the potential reactivity of this class of compounds. In general, most of the photochemistry of cyclic ketones appears to be best described as involving preliminary Norrish type I bond cleavage to give a diradical intermediate as illustrated below. Various straightforward recombination and disproportionation reactions of this reactive intermediate account for the great majority of known photoconversions. In contrast, the photochemistry of α,β-unsaturated cyclic ketones is, on the whole, of a decidedly different and more complex nature.[3]



As part of an over-all program designed to evaluate the photochemical interaction of formally nonconjugated chromophores contained within the same molecule, we have examined the photolysis of 3-cyclooctenone (**1**). Several other β,γ-unsaturated cyclic ketones have been studied,[4] but the published work has centered almost exclusively on rigid polycyclic mole-

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[1] (a) Partial support of this work was provided by grants from the National Science Foundation (GP 6610) and the Public Health Service (GM 12860). (b) National Defense Education Act Title IV Predoctoral Fellow, 1965–1967.

[2] (a) R. Srinivasan, *Advan. Photochem.*, 1, 83 (1963); (b) O. L. Chapman, *ibid.*, 1, 365 (1963); (c) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 377–427; (d) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 71–93.

[3] K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966), provides a recent review of this area.

[4] (a) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960); (b) P. E. Eaton, *Tetrahedron Letters*, 3695 (1964); (c) R. Criegee and H. Furrer, *Chem. Ber.*, **97**, 2849 (1964); (d) R. L. Cargill, M. E. Beckham, A. E. Seibert, and J. Dorn, *J. Org. Chem.*, 30, 3647 (1965); (e) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Am. Chem. Soc.*, **88**, 1330 (1966); (f) J. R. Williams and H. Ziffer, *Chem. Commun.*, **194**, 469 (1967); (g) D. I. Shuster, F. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, 30, 2262 (1965); (h) D. E. Bays and R. C. Cookson, *J. Chem. Soc., Sect. B*, 226 (1967).