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.

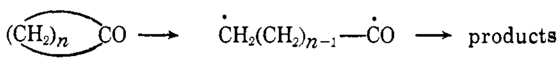
The Photochemistry of 3-Cyclooctenone[1a]

J. K. Crandall, J. P. Arrington,[1b] and John Hen

Contribution No. 1505 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received July 10, 1967*

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]



$$(CH_2)_n\,CO \longrightarrow \dot{C}H_2(CH_2)_{n-1}\text{—}\dot{C}O \longrightarrow \text{products}$$

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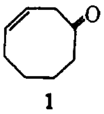
[1] (a) Partial support of this work was provided by grants from the National Science Foundation (GP 6610) and the Public Health Service (GM 12860). (b) National Defense Education Act Title IV Predoctoral Fellow, 1965–1967.

[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).

cules and it was therefore of interest to compare the photochemistry of these compounds with a flexible analog such as **1**.

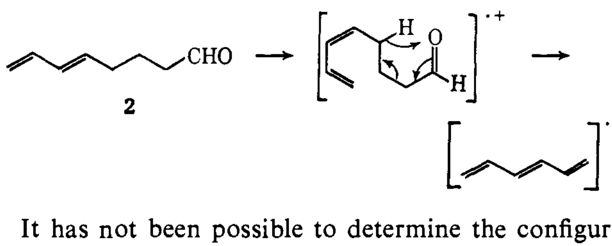


1

Results

Irradiation of 3-cyclooctenone as a 1% solution in cyclohexane or benzene using a 450-w Hanovia lamp with a Vycor filter rapidly effected partial conversion into two major photoproducts as determined by analytical gas chromatography (gc). Interestingly, the ratio of these two materials appeared to depend on the reaction time. Preparative gc, on the other hand, resulted in the isolation of *three* major components. Two of these were new materials not originally present in the photolysis product, while the remaining constituent was the first of the primary photoproducts. Preparative gc did not yield a component with a retention time identical with the second photoproduct by analytical gc, indicating that this compound was unstable to the isolation conditions.

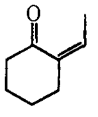
The stable photoproduct was shown to be 5,7-octadienal (**2**). Its infrared spectrum indicates the presence of an unconjugated aldehyde (3.66, 5.80 μ) and a conjugated diene system (6.05, 6.24 μ) with a terminal vinyl group (10.0, 11.1 μ). The ultraviolet spectrum is as expected for a monosubstituted diene (λ_{max} 223 mμ (ε 23,200)), while the nmr spectrum confirms the presence of the aldehyde group by a one-proton absorption at τ 0.4 as a closely spaced triplet (J = 1 cps) and shows a total of five protons in the olefinic region. The mass spectrum of **2** is relatively simple with a strong molecular ion at m/e 124 and the base peak at m/e 80 (M − 44). The latter ion most probably arises by a McLafferty rearrangement[5] from the molecular ion in which the positive charge is found on the conjugated hexatriene moiety in contrast to its usual residence on the oxygen-containing fragment, presumably because of the extra stability of the charged olefin fragment in this instance. Further chemical evidence for the assigned structure of **2** is found in the reduction studies described below.



2

It has not been possible to determine the configuration about the internal double bond of **2**. While the product might be expected to be a mixture of *cis* and *trans* isomers, especially since it is obtained from a photochemical reaction, the fact that **2** is homogeneous to a variety of gc columns and conditions should be noted. Likewise the corresponding alcohol obtained by lithium aluminum hydride reduction (*vide infra*) is also a single peak by gc.

The other two materials isolated from the photolysis mixture by preparative gc were identified as *cis*- and *trans*-2-ethylidenecyclohexanone (**3** and **4**), respectively, by their spectroscopic properties (see Experimental Section). Compound **4** was also compared with an authentic sample.[6] Differentiation between the two isomers was made on the basis of nmr data. The *cis* isomer displays its olefinic proton as a quartet of triplets at τ 4.4 (J = 7, 1.5 cps), whereas the *trans* compound shows a similar pattern shifted downfield to τ 3.4 owing to the placement of this proton in the deshielding region of the neighboring carbonyl group.[7]



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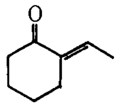
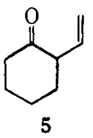


4

The logical precursor of these secondary products is 2-vinylcyclohexanone (**5**) and subsequent experimentation has established that **5** is, in fact, the second photoproduct derived from **1**. A photolysis of **1** was carried out in methanol and the crude reaction mixture was subjected to catalytic hydrogenation. The resulting mixture yielded 2-ethylcyclohexanone and *n*-octanal, the expected reduction products of **5** and **2**, respectively. Lithium aluminum hydride reduction of the crude photoproduct from a run in cyclohexane gave *trans*-2-vinylcyclohexanol (**6**), *cis*-2-vinylcyclohexanol (**7**), and 5,7-octadienol (**8**) in addition to small amounts of 3-cyclooctenol (**9**) and an additional alcohol discussed below. The infrared spectrum of **8** shows hydroxy (3.0 μ), diene (6.05, 6.24 μ), and terminal vinyl (10.0, 11.1 μ) functions. Its nmr spectrum indicates five olefinic protons (τ 3.1–5.3), six methylene protons (τ 7.9, 2 H; 8.5, 4 H), and a primary alcohol (τ 6.0, 1 H; 6.5, 2 H, t, J = 7 cps). The stereochemistry of the internal double bond is again unspecified.



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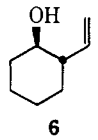
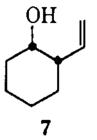


6



7

An authentic sample of **6**, obtained by the addition of vinyllithium to cyclohexene oxide, was shown to be identical with the material secured above. Careful chromic acid oxidation of **6** gave a modest yield of 2-vinylcyclohexanone which could be satisfactorily purified under rigorously controlled conditions. The nmr spectrum is in full accord with the assigned structure, while the infrared shows a 5.84-μ carbonyl band and the typical vinyl absorptions. As expected, **5** produced **6** and **7** in the same ratio as found in the lithium aluminum hydride reduction of the photolysis mixture. Furthermore, although **5** gave a peak with the same retention time as the second photoproduct from **1** on analytical gc, it was converted smoothly to a mixture of **3** and **4** in a 5:1 ratio upon attempted preparative gc under the conditions used to isolate the photolysis products. A similar conversion was effected by heating

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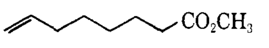
[5] F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 123–121.

[6] J. E. Dubois and M. Dubois, *Compt. Rend.*, **256**, 715 (1963).

[7] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, pp 78–79.

at elevated temperatures or by stirring with acidic alumina.

Several minor products isolated during the course of the reduction experiments are noteworthy. The catalytic hydrogenation of the crude methanol photolysate also yielded methyl octanoate which was apparently derived from methyl 7-octenoate (**10**), since this material could be isolated as 9% of the total product from a photolysis in methanol. Compound **10** has infrared absorption for ester (5.75, 8.4, 8.6 μ) and vinyl (10.1, 11.0 μ) functions and its nmr shows vinyl (τ 4.35, 1 H; 5.0, 2 H), methyl ester (τ 6.4, 3 H), and five methylene (τ 7.6–8.9) groupings. The hydride reduction of a cyclohexane photolysis, in addition to the products described above, yielded 7-octen-1-ol (**11**) as 7% of the mixture. Spectral examination again provided structural information indicating vinyl (6.1, 10.1, 11.0 μ; τ 4.3, 1 H and 5.1, 2 H), primary alcohol (3.0 μ; τ 5.9, 1 H, and 6.5, 2 H, t, $J = 7$ cps), and five methylene (τ 7.8–8.9) groups.



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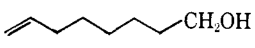


11

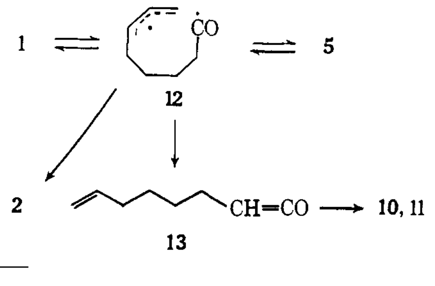
The availability of pure 2-vinylcyclohexanone allowed the photochemistry of this photoisomer of **1** to be studied. As expected from mechanistic considerations, photolysis of **5** gave a reaction mixture from which 3-cyclooctenone and aldehyde **2** were isolated. Lithium aluminum hydride reduction of the crude photoproduct mixture generated **6**, **7**, **8**, **9**, and **11** in almost exactly the same ratio as found in the experiment utilizing **1** as the starting material.

Finally, although aldehyde **2** does decompose in an ill-defined manner on prolonged irradiation, it does not regenerate either of its photochemical precursors.

Discussion

The photochemical isomerization of saturated cyclic ketones to open-chain unsaturated aldehydes (*e.g.*, cyclopentanone to 4-pentenal) is perhaps the most common photoreaction of this class of molecules since it occurs extensively in both vapor and condensed phases.[2] Although a concerted mechanism has been seriously considered for this transformation,[2a] the most recent data support a stepwise conversion proceeding by way of a Norrish type I bond homolysis of the excited molecule.[8] The intermediate diradical formed in this process then undergoes an intramolecular disproportionation to yield the unsaturated aldehyde product. Chart I illustrates an adaptation of this mechanism to describe the results of the present study.

Chart I



The experimental data require a photoequilibration between ketones **1** and **5** and an irreversible process leading to aldehyde **2**.[9] The irreversible reaction can logically emanate from either of the two ketones or from an intermediate in the interconversion of these photoisomers. Concerted mechanisms can be written for the observed transformations within the framework of these limitations, but a more satisfactory description utilizes diradical **12** as a common branching point. Preferential cleavage of the allylic bond of **1** and **5** is dictated by radical stability considerations. Radical recombination in **12** can occur at either end of the allylic radical and in this fashion the interconversion of **1** and **5** can take place. The predominance of **5** at photoequilibrium[10] is probably at least partly attributable to the favorability of ring closure to the cyclohexane skeleton. Disproportionation between the radical centers in **12** by hydrogen atom transfer is expected to be a slower and essentially irreversible process. 1,5-Hydrogen migration to the acyl radical center from the methylene group adjacent to the allylic radical moiety transforms **12** to aldehyde **2** in a manner similar to that proposed for the generation of aldehydes from saturated cyclic ketones.

Several of the rigid β,γ-unsaturated ketones which have been examined to date[4] also undergo allylic isomerization of the **1** to **5** variety and reversibility has been confirmed in several cases.[4a–d] There are, in addition, several examples of cleavage-mixed recombination reactions of *acyclic* β,γ-unsaturated ketones which appear to proceed *via* discrete free-radical intermediates.[11] Thus, postulation of an initial Norrish type I reaction not only provides a satisfactory rationale for the restricted class of compounds under consideration but it establishes an interrelationship with the much larger body of knowledge on saturated ketones in general.[2c]

An alternate mode of disproportionation of **12** can be visualized which leads to ketene **13**; in this instance a 1,5-hydrogen shift occurs from the methylene group next to the acyl radical to the near end of the allylic radical function. (Transfer to the other end of this moiety is not expected since an unfavorable 1,7-hydrogen shift would be required.) The ketene is implicated in the formation of 7-octenoate (**10**) in the methanol photolysis of **1** and 7-octen-1-ol (**11**) from the hydride reductions of the crude photolysates from **1** and **5**. There is ample precedent for the production of acyclic acids and acid derivatives *via* the corresponding ketenes from cyclic ketones.[12] Products derived from ketene intermediates are not usually found in photolyses in nonnucleophilic solvents, but this is probably because the free ketene is lost during product isolation.[13] Lithium aluminum hydride reduction apparently preserves the ketene product in the present study by converting it to the alcohol.[14]

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(8) R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965); H. M. Frey, *Chem. Ind.* (London), 947 (1966).

(9) The best data for the ratio of **1**:**5** at photoequilibrium is obtained from the hydride reduction experiments which indicate ratios of 7:40 and 6:42 using **1** and **5**, respectively, as starting materials.

(10) The differences in light absorption and quantum efficiencies are also factors here.

(11) (a) E. F. Kiefer and D. A. Carlson, *Tetrahedron Letters*, 1617 (1967); (b) N. C. Yang and D. M. Thap, *ibid.*, 3671 (1966); (c) H. Morrison, *ibid.*, 3653 (1964).

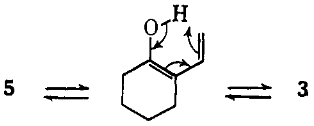
(12) G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965).

(13) Private communication of unpublished work, W. F. Erman.

(14) The initial reduction product of **13** is expected to be the enolate of the corresponding aldehyde; hydrolysis and rapid reduction of the

Although information regarding the primary processes involved in the photochemistry of **1** and **5** would be of substantial interest, sufficient evidence is not available to warrant detailed speculation at this time, and this aspect of the over-all problem must await further experimentation. However, it can be noted parenthetically that there is no evidence for the involvement of the neighboring double bond in these electronic processes other than to facilitate bond cleavage. At least there is no concrete manifestation of energy transfer or chemical interaction between the two chromophoric systems available from this study.[15]

A brief comment on the thermal and acid-catalyzed isomerization of 2-vinylcyclohexanone is in order. Preponderance of *cis*-2-ethylidenecyclohexanone (**3**) in the isomerization mixture is probably significant in view of the expected greater thermodynamic stability of the *trans* isomer. We conclude that **3** is the kinetic product of an isomerization which takes place by a 1,5-hydrogen migration in the appropriate enol form of **5**. Further random isomerization then leads to **4**.[16]



Experimental Section

General. Nmr spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride as solvent. Infrared spectra were obtained on Perkin-Elmer 137 and 137-G instruments, and were run on neat samples unless otherwise noted. Gas chromatography (gc) was performed on Aerograph A600, A1200 (analytical), and A700 (preparative) instruments. Analytical columns were 5 ft × $^1/_8$ in. 15% diethylene glycol succinate on 80–100 Chromosorb W and both 8 ft × $^1/_8$ in. and 5 ft × $^1/_8$ in. 15% Carbowax 20M on 60–80 Chromosorb W; preparative columns were 10 ft × $^3/_8$ in. 30% FFAP on 60–80 Chromosorb W or 20 ft × $^3/_8$ in. 15% polyethylene glycol succinate on 60–80 Chromosorb W unless otherwise noted. Mass spectra were obtained at 70 ev on an AEI-MS 9 instrument. Analyses were performed by Midwest Microlab, Inc. Anhydrous magnesium sulfate was used for all drying operations.

3-Cyclooctenone (1).[17] To a stirred, cooled solution of 12.2 g of 3-cyclooctenol (**9**) in 100 ml of acetone was added 60 ml of 8 *N* chromic acid dropwise over 0.5 hr The resulting mixture was stirred for 0.5 hr, poured into water, and extracted with five 30-ml portions of pentane. The pentane solution was washed with water and dried, and the solvent was removed by distillation. Distillation of the residue under reduced pressure yielded 4.2 g (34%) of **1**, bp 83–86° (15 mm); ultraviolet spectrum:[18] $\lambda_{\max}^{\text{hexane}}$ 292 mμ (ε 47); $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 290 mμ (ε 60). There is no evidence for a second discrete maximum above 220 mμ.

***trans*-2-Vinylcyclohexanol (6)** To a solution of 19.6 g of cyclohexene oxide in 100 ml of tetrahydrofuran under a nitrogen atmosphere was added 120 ml of commercial 2.1 *M* vinyllithium in tetrahydrofuran. The mixture was stirred at reflux temperature for 30 hr, poured into 350 ml of ice–water, and extracted with six 100-ml portions of pentane. The combined extracts were washed with water and dried, and the solvent was removed by distillation. The residue was distilled through a short-path distillation head to give 19.8 g (79%) of *trans*-2-vinylcyclohexanol, bp 44–47° (2 mm). The product was found to contain 5% of 2-cyclohexenol by gc separation and comparison with an authentic sample. Gc-isolated **6** shows infrared bands at 2.95, 3.22, 5.49 (w), 6.10, 9.48, 10.1, and 11.0 μ, and nmr absorption as a complex three-proton multiplet characteristic of a vinyl group from τ 3.9 to 5.2, a two-proton absorption consisting of a sharp singlet superimposed over a broad multiplet at 6.9 (C*H*O*H*), and a nine-proton methylene absorption extending from 7.9 to 9.1.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.31; H, 11.08.

2-Vinylcyclohexanone (5). To a stirred, ice-cold solution of 12.6 g of *trans*-2-vinylcyclohexanol (**6**) in 150 ml of acetone was added 40 ml of 8 *N* chromic acid dropwise. The resulting mixture was stirred for 0.5 hr, poured into 150 ml of water, and extracted with five 60-ml portions of pentane. The pentane was washed twice with water and dried, and the solvent was removed on a steam bath. The residue was distilled through a short-path distillation head to yield 3.50 g (28%) of **5**, bp 35° (0.3 mm). A sample was further purified by preparative gc on a 5 ft × 0.25 in. column of 20% SE-30 silicone gum rubber on 60–80 Chromosorb W at 85°; infrared spectrum: 3.24, 5.84, 6.10, 10.1, and 11.0; nmr: a three-proton resonance typical of a terminal vinyl group with resonances centered at τ 4.0 (C*H*=CH$_2$) and at 5.0 (CH=C*H*$_2$), a broad one-proton absorption at 7.05 (C*H*CH=CH), and broad eight-proton methylene absorption from 7.5 to 8.6. The ultraviolet spectrum (hexane) of a >90% pure sample of **5** containing a small amount of **3** showed $\lambda_{\max}$ 296 mμ (ε 20).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.18; H, 9.70.

Photolysis of 3-Cyclooctenone (1). A solution of 4.0 g of 3-cyclooctenone in 400 ml of cyclohexane was irradiated with a 450-w medium-pressure Hanovia Type L mercury-vapor lamp in an immersion-well apparatus using a Vycor filter. The solution was degassed by bubbling nitrogen through it prior to photolysis and a positive nitrogen pressure was maintained during the photolysis. The sample was irradiated until the two products were present in approximately equal amounts (*ca.* 2 hr, **1** still present), as determined by gc (5 ft × $^1/_8$ in. Carbowax, 120°). The solvent was removed by evaporation on a steam bath, and the residue was distilled through a short-path distillation head (0.2 mm). The yield of crude photoproduct was 3.5 g (88%). The use of benzene as solvent gave similar results.

Three products were isolated by preparative gc, in contrast to the two products shown to be present by analytical gc. The first product was 5,7-octadienal (**2**); infrared spectrum: 3.22, 3.31, 3.66, 5.80, 6.05, 6.23, 9.95, and 11.06 μ; nmr: a one-proton triplet (*J* = 1 cps) at τ 0.4 (C*H*O), a complex five-proton multiplet from 3.5 to 5.2 (C=C*H*), and a six-proton multiplet from 7.4 to 8.6 (C*H*$_2$); ultraviolet spectrum (hexane): $\lambda_{\max}$ 223 mμ (ε 23,200).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.19; H, 9.92.

The second product was *cis*-2-ethylidenecyclohexanone (**3**);[6] infrared spectrum: 5.94, 6.15, 7.27, 8.14, 8.8, 11.2, and 12.15 μ; nmr: a one-proton quartet (*J* = 7 cps), each peak of which is further split into a triplet (*J* = 1.5 cps) at τ 4.4 (C=C*H*), and two broad absorptions at 7.7 and 8.2, which together integrate for 11 protons; ultraviolet spectrum (hexane): $\lambda_{\max}$ 233 mμ (ε 6420).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.51; H, 9.80.

The third product was identified as *trans*-2-ethylidenecyclohexanone (**4**);[6] infrared spectrum: 5.94, 6.18, 7.29, 8.00, 8.80, and 12.3 μ; nmr: a one-proton quartet (*J* = 7 cps), each peak of which is further split into a triplet (*J* = 2 cps) at τ 3.4 (C=C*H*), and two broad absorptions at 7.7 and 8.2, which integrate for four and seven protons, respectively. The ultraviolet spectrum (hexane) showed a peak at $\lambda_{\max}$ 237 mμ (ε 7150). This material was identical in its spectroscopic properties with an authentic sample.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.68; H, 9.98.

That neither of the ethylidenecyclohexanones was a primary photolysis product was demonstrated by analytical gc comparison with the crude photoproduct mixture.

Catalytic Hydrogenation of the Photoproducts of 1. A solution of 500 mg of the crude photoproduct mixture (obtained from photolysis of 3-cyclooctenone in methanol) in 25 ml of methanol was hydrogenated at atmospheric pressure using 5% palladium on carbon as catalyst. After 18 hr the catalyst was removed by filtration and the filtrate was poured into water and extracted four times

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aldehyde by excess hydride during work-up may account for the complete reduction of **13** to **11**.

(15) *cis–trans* isomerization of the double bond in **1**, reduction of the double bond,[4e] addition of external olefin,[4e] or excessive photostability are possible consequences of energy transfer.

(16) During the preparation of this manuscript we learned of a similar study by L. A. Paquette and R. F. Eizember [*J. Am. Chem. Soc.*, **89**, 6205 (1967)]. We wish to acknowledge a helpful exchange of information with Professor Paquette regarding this independent work which agrees in substantial detail with our own.

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

(18) Reference 17 gives $\lambda_{\max}^{\text{EtOH}}$ 286 mμ (ε 114).

Table I

m/e	**2**	**5**	**1**	**3**	**4**	*m/e*	**2**	**5**	**1**	**3**	**4**
39	22.6	27.5	32.8	35.2	29.6	69	7.8	5.2	1.4	7.5	4.8
40	5.1	8.7	9.0	11.6	10.0	70	2.2	...	1.4	..c	1.9
41	33.3	65.6	25.8	31.8	23.8	77	5.9	...	3.6	...	3.7
42	5.9	7.0	9.3	6.1	5.5	78	3.7	...	5.1	...	1.3
43	28.8	3.9	3.0	17.4	3.0	79	22.2	9.8	19.4	22.3	9.7
44	3.3	...	1.2	...	3.4	80	100.0	29.8	100.0	29.8	2.8
45	...	9.2	...	...	...	81	9.4	21.2	19.2	44.8	37.6
46	...	31.7	...	...	...	82	4.2	4.5	8.5	...	6.5
50	3.1	...	2.3	...	2.2	83	2.2	...	1.7	...	4.1
51	4.1	3.9	4.6	7.2	5.1	84	2.2	...	...	...	1.3
52	3.3	2.4	2.9	...	3.1	91	2.6	...	6.0	...	2.4
53	8.5	15.1	15.4	21.2	18.7	93	...	...	1.4	...	2.3
54	15.7	23.2	48.9	22.3	18.9	95	11.5	12.7	27.7	18.2	10.0
55	8.9	19.4	16.2	25.8	24.6	96	2.0	7.1	4.2	11.0	10.8
56	4.4	9.2	2.0	...	3.7	97	...	2.1	...	...	2.1
57	3.3	100.0	...	...	1.6	98	...	...	...	...	4.4
58	14.5	4.5	...	6.7	...	105	...	...	1.9	...	...
59	...	6.4	...	...	...	108	...	...	...	...	1.0
60	...	3.4	...	...	...	109	...	8.5	...	26.6	15.7
64	7.1	...	...	...	...	110	...	...	...	...	5.2
65	3.3	...	3.6	...	4.0	112	1.8	...	...	...	...
66	...	4.7	3.7	10.5	10.8	124	10.4	37.3	36.9	100.0	63.5
67	25.9	48.5	48.5	91.6	100.0	125	0.8	3.5	2.9	9.6	5.4
68	10.9	17.8	13.8	30.3	28.2						

with pentane. The pentane was dried and the solvent removed by distillation. Separation by preparative gc yielded octanal, 2-ethylcyclohexanone, and methyl octanoate, each of which was identified by comparison of its infrared spectrum with that of a known sample. In addition a fourth component, amounting to *ca.* 10% of the product mixture, was isolated. Its infrared spectrum suggested that it was a saturated acetal (bands at 7.30, 9.40, and 9.52 μ), possibly the dimethyl acetal of octanal.

The methyl octanoate apparently resulted from an additional product formed as 9% of the mixture (13% **1**, 37% **2**, 41% **5**) when the photolysis was carried out in methanol; this was isolated and identified as methyl 7-octenoate[19] (**10**) on the basis of its spectral properties; infrared spectrum: 3.24, 5.75, 6.10, 8.4, 8.6, 10.1, and 11.0 μ; nmr: a one-proton multiplet at τ 4.35 ($CH{=}CH_2$), a two-proton multiplet centered at 5.0 ($CH{=}CH_2$), a three-proton singlet at 6.4 (CH_3O), and a broad ten-proton absorption from 7.6 to 8.9.

Reduction of the Photoproducts of 1. To a stirred, ice-cold slurry of 1 g of lithium aluminum hydride in 50 ml of anhydrous ether was added the photoproduct mixture from the photolysis of 3 g of 3-cyclooctenone (irradiation was halted when the two products were present in approximately equal amounts). After addition was complete the ice bath was removed, and stirring was continued for 3 hr. The mixture was hydrolyzed with dilute hydrochloric acid, the layers were separated, and the aqueous layer was extracted with 40-ml portions of ether. The ether solution was washed with water and dried, and the solvent was removed by flash evaporation. The products were isolated by preparative gc.

The first product (42%) was identified as *trans*-2-vinylcyclohexanol (**6**) by comparison of its infrared and nmr spectra with those of an authentic sample.

The second product (10%) is assigned as *cis*-2-vinylcyclohexanol (**7**); infrared spectrum: 2.95, 3.25, 6.11, 9.48, 10.0, 10.3, and 11.0 μ; nmr: a one-proton multiplet at τ 4.2 ($CH{=}CH_2$), a two-proton multiplet centered at 5.0 ($CH{=}CH_2$), a broad one-proton absorpton at 6.25 ($CHOH$), a one-proton, temperature-dependent singlet at 7.3 (OH), and a broad nine-proton absorption from 7.7 to 9.1.

The third product (7%) is identified as 7-octen-1-ol[20] (**11**) on spectroscopic grounds; infrared spectrum: 3.0, 3.24, 6.10, 9.5, 10.1, and 11.0 μ; nmr: a one-proton multiplet at τ 4.3 ($CH{=}CH_2$), a two-proton multiplet at 5.1 ($CH{=}CH_2$), a temperature-dependent singlet at 5.85 (OH), a two-proton triplet (J = 7 cps) at 6.5 (CH_2OH), and a broad ten-proton methylene absorption from 7.8 to 8.9.

The fourth component (35%) was 5,7-octadienol (**8**); infrared spectrum (CCl_4): 3.0, 3.21, 3.29, 5.57 w, 5.82 w, 6.05, 6 24, 9.49, 10.0, and 11.1 μ; nmr: a five-proton complex multiplet from τ 3.1 to 5.3 (olefinic hydrogens), a one-proton, temperature-dependent singlet at 6.0 (OH), a two-proton triplet (J = 7 cps) at 6.5 (CH_2OH), and multiplets at 7.9 and 8.5, which together integrate for six protons (CH_2).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.92; H, 11.09.

The fifth component (6%) was 3-cyclooctenol (**9**), identified by comparison with authentic material.

Two other components, together constituting less than 2% of the total mixture, were not isolated.

Reduction of 2-Vinylcyclohexanone (5). To an ice-cold slurry of 0.5 g of lithium aluminum hydride in 50 ml of anhydrous ether was added 265 mg of 2-vinylcyclohexanone in 10 ml of anhydrous ether. After addition was complete, the ice bath was removed and stirring was continued for 3 hr. Hydrolysis was effected by the addition of 35 ml of 10% hydrochloric acid and the resulting mixture was extracted with four 40-ml portions of ether. The ether solution was washed with water and dried, and the solvent was removed on a flash evaporator. Gc analysis of the crude product showed three products in a relative ratio of 1:10:3. The products were isolated by preparative gc and identified as 2-cyclohexenol (from 5% 2-cyclohexenone impurity in the starting material), *trans*-2-vinylcyclohexanol, and *cis*-2-vinylcyclohexanol, respectively, by comparison of infrared spectra.

Photolysis of 2-Vinylcyclohexanone (5). A solution of 1 g of 95% pure 2-vinylcyclohexanone in 100 ml of cyclohexane was photolyzed in the same manner as described above for 3-cyclooctenone for about 1 hr. Gc analysis of the product mixture indicated the presence of 5,7-octadienal (57%), 2-vinylcyclohexanone (34%), and 3-cyclooctenone (9%). The products isolated were 5,7-octadienal, 3-cyclooctenone, *cis*-2-ethylidenecyclohexanone, and *trans*-2-ethylidenecyclohexanone.

Gas Chromatographic Isomerization of 2-Vinylcyclohexanone (5). When 2-vinylcyclohexanone was injected into the gas chromatograph under conditions used for separation of the photoproducts, only *cis*- and *trans*-2-ethylidenecyclohexanones were collected in a ratio of *ca.* 5:1.

Reduction of the Photoproducts of 2-Vinylcyclohexanone (5). The crude photoproduct from irradiation of 1 g of **5** in cyclohexane was reduced in the same manner as described above for the photoproducts of 3-cyclooctenone. The products were *trans*-2-vinylcyclohexanol (40%), *cis*-2-vinylcyclohexanol (9%), 7-octen-1-ol (8%), 5,7-octadienol (36%), and 3-cyclooctenol (7%).

Alumina-Catalyzed Isomerization of 2-Vinylcyclohexanone (5). To a slurry of 0.14 g of acidic alumina (Guilini) in 20 ml of hexane and six drops of acetic acid was added 0.44 g of **7** and the resulting mixture was stirred at reflux for 5 days. The solid was removed by filtration and washed with hexane. The hexane was removed by

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[19] J. Colonge and P. Lasfargues, *Bull. Soc. Chim. France*, 177 (1962).

[20] A. C. Cope and J. K. Hecht, *J. Am. Chem. Soc.*, **84**, 4872 (1962).

distillation, leaving 0.21 g of crude material, which was shown by gc to consist of two components in a 4:1 ratio. The products were isolated by preparative gc and were found to be the *cis-* and *trans*-2-ethylidenecyclohexanones isolated above.

Photolysis of 5,7-Octadienal (2). A 1% solution of 2 (40 mg) in benzene was irradiated in a Rayonet photochemical reactor using 3500-A lamps. The photolysis was followed for 84 hr, in which time most of the starting material had disappeared. No products were detected at any time which might have been 3-cyclooctenone (**1**) or 2-vinylcyclohexanone (**5**). Under the same conditions both **1** and **5** gave essentially the same photomixtures as observed with the Hanovia system in a shorter period of time.

Mass Spectra. Mass spectra of the major compounds encountered in this work are tabulated in Table I. The values of peaks in abundance greater than 1% are given as percentage of the base peak.

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Photochemistry of Quercetin Pentamethyl Ether

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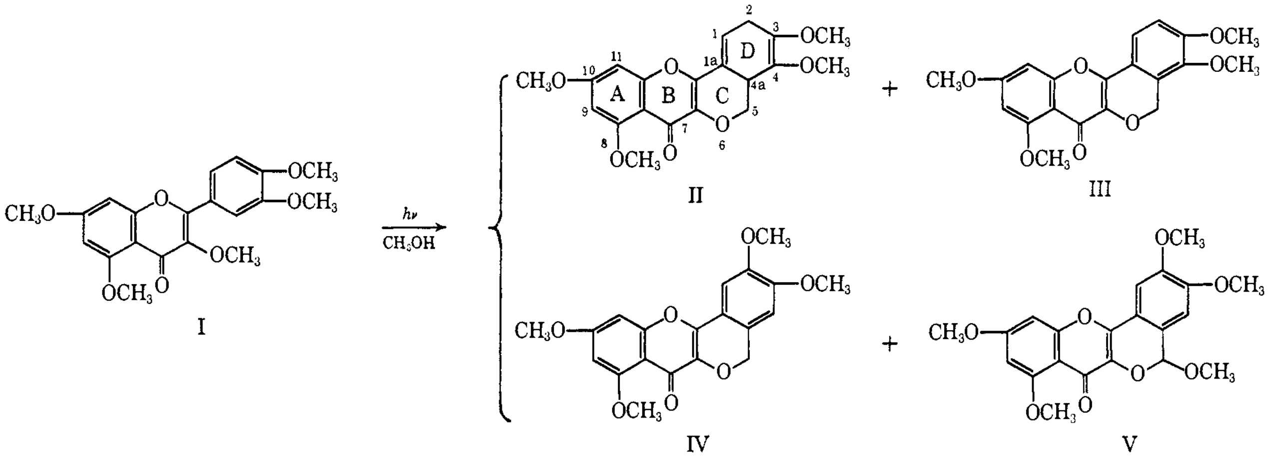
Abstract: Ultraviolet (350 $m\mu$) irradiation of quercetin pentamethyl ether (I) in methanol gave four photoproducts: lumimethylquercetin (II), α-photomethylquercetin (III), β-photomethylquercetin (IV), and methoxy-β-photomethylquercetin (V). The structures of these compounds were established by spectroscopic and chemical means. Possible mechanisms, one of which involves a novel photocycloaddition process, are proposed.

Flavonoid compounds[1] occur widely in plants and are often exposed to sunlight for long durations of time. The possibility that these compounds may act as photodynamic transferring agents (sensitizers or quenchers) for specific chemical transformations in plants is worthy of consideration.[2] The photochemistry of flavonoid compounds has not been investigated. Since quercetin is one of the better known flavonoids occurring in many plant families, its pentamethyl ether was chosen to initiate our program on a systematic study of the photochemistry of the flavonoids.



Results and Discussion

This report deals with the isolation and characterization of the four crystalline products, II, III, IV, and V, isolated from the photochemical reaction of quercetin pentamethyl ether (I) in methanol irradiated at 350 $m\mu$ and postulates possible mechanisms for their formation.

The first fluorescent compounds, lumimethylquercetin (II, R_f 0.67),[3] was isolated in 16% yield, mp 198–200°, from the irradiation product mixture by adsorption and chromatographic separations on silica gel. Mass spectroscopic and chemical analyses indicated that although II has the same molecular weight and empirical formula as its parent compound I, it contains only four methoxy groups. Evidence for the presence of a conjugated carbonyl function in V was provided by its ultraviolet spectrum [$\lambda_{\max}^{\mathrm{MeOH}}$ 344 and 264 $m\mu$ (ϵ

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(1) For recent reviews on the chemistry of flavonoid compounds see (a) T. A. Geissman, "The Chemistry of Flavonoid Compounds," The MacMillan Co., New York, N. Y., 1962, and (b) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworth & Co. (Publishers), Ltd., London, 1963.

(2) Flavone is known to be a sensitizer for *cis–trans* isomerization of stilbene (G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964)) and light-induced *trans–cis* conversion of β-D-glucosyl O-hydroxycinnamic acid in leaves has been reported (F. A. Haskins, L. G. Williams, and H. J. Gorz, *Plant Physiol.*, **39**, 777 (1964)).

(3) All tlc analyses reported here were performed on starch-bound silica gel eluted with 20% 2-propanol in ethyl acetate.