

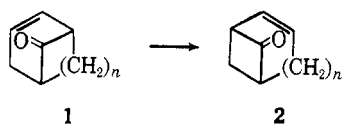
Photochemistry of β,γ -Unsaturated Bicyclic Ketones. A Novel Synthesis of Bridged Cyclobutanones

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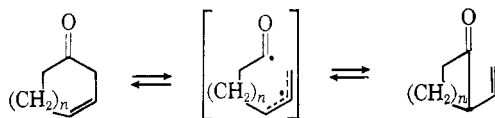
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Abstract: β,γ -Unsaturated bicyclic ketones of type **1** are converted by ultraviolet irradiation to bicyclic cyclobutanones of type **2** in good yield. Specifically, each of the ketones **7**, **9**, and **11** on irradiation with a broad-spectrum mercury arc lamp undergoes rearrangement to the cyclobutanones **8**, **10**, and **12**, respectively. After a short period of irradiation the ketones reach an apparent photostationary state in which the ratios of **8**:**7**, **10**:**9**, and **12**:**11** are 2:1, 1.7:1, and 1.5:1, respectively. Since ketones of type **1** ($n > 1$) are accessible by classic syntheses, the conversion of **1** \rightarrow **2** represents a practical approach to the synthesis of bicyclic four-membered ring ketones in general.

Bicyclic four-membered ring ketones, β,γ -unsaturated, of type **2**, though sporadically confronted in essential oils,¹ are extremely difficult to synthesize due to their unusual lability to base and acid.^{2,5-8} We have found that β,γ -unsaturated bicyclic ketones of type **1** in general are converted smoothly by ultraviolet irradiation to cyclobutanones of type **2**. Since the former ketones **1** are accessible by classic syntheses the conversion of **1** \rightarrow **2** represents a practical approach to the synthesis of bicyclic four-membered ring ketones in general.



Although bicyclic ketones when exposed in a suitable solvent to ultraviolet irradiation may undergo a variety of photochemical reactions depending upon the structure of the molecule and the environment of the carbonyl function,⁹ four isolated reports¹⁰⁻¹³ suggested to us that β,γ -unsaturated cyclic ketones may undergo a general type reaction: *i.e.*, cleavage of the carbon-carbon bond located allyl to the double bond and α to the carbonyl with subsequent double bond migration and recyclozation.



(1) For example, chrysanthemone (**11**) from the oil of *chrysanthemum indium*,² *chrysanthemum Sinense*,³ and *Zieria Smithii*.⁴

(2) J. de Pascual Teresa, H. Sanchez Bellido, and I. Sanchez Bellido, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), Ser. B., **58**, 339 (1962).

(3) M. Kotake and H. Nonaka, *Ann.* **607**, 153 (1957).

(4) A. R. Penfold, G. R. Ramage, and J. L. Simonsen, *J. Chem. Soc.*, 1496 (1939).

(5) E. P. Blanchard, Jr., *Chem. Ind.* (London), 293 (1958).

(6) R. M. Dodson, J. R. Lewis, W. P. Webb, E. Wenkert, and R. D. Youssefeyeh, *J. Am. Chem. Soc.*, **83**, 938 (1961), and references cited therein.

(7) For examples of synthetic approaches unique to specific type β,γ -unsaturated bicyclic cyclobutanones, see ref 6 and 8.

(8) J. J. Hurst and G. H. Whitam, *J. Chem. Soc.*, 2864 (1960).

(9) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); O. L. Chapman, *ibid.*, **1**, 323 (1963).

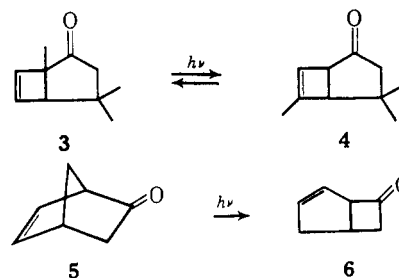
(10) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

(11) P. E. Eaton, *Tetrahedron Letters*, 3695 (1964).

(12) R. L. Cargill, L. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

(13) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963).

Thus 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one (**3**) and 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one (**4**) (and related compounds possessing the general bicyclo[3.2.0]hept-6-ene-2-one structure^{11,12}) are interconverted on irradiation with ultraviolet light.¹⁰ Similarly, dehydronorcamphor (**5**) is converted to bicyclo[3.2.0]hept-2-en-7-one (**6**) on ultraviolet irradiation, although the reverse process apparently does not ensue.¹⁴



In view of these reports we examined the photochemical behavior of several readily prepared β,γ -unsaturated bicyclic ketones with the hope of extending the synthetic versatility of this reaction.

Each of the ketones **7**, **9**, and the simplest homolog of the series—**11**—on irradiation with a broad spectrum mercury arc lamp was rearranged to the ketones **8**, **10**, and **12**, respectively. After a short period of irradiation the ketones reached an apparent photostationary state in which the ratios of **8**:**7**, **10**:**9**, and **12**:**11** were 2:1, 1.7:1, and 1.5:1, respectively. Specifically, irradiation of a solution of 1.50 g of bicyclo[3.3.1]non-2-en-9-one (**7**), conveniently prepared from cyclohexanone,¹⁵ in cyclohexane for 60 min with a 200-w Hanovia mercury arc lamp using a Vycor filter afforded a mixture of the ketone **7** (27%) and bicyclo[5.1.1]non-2-en-9-one (**8**, 62%). Further irradiation did not appreciably alter the ratio of **7**:**8** but gave a poorer recovery of the ketones due to polymer formation. Similarly a photostationary state was reached after 90-min irradiation of 1.00 g of bicyclo[3.2.1]oct-2-en-8-one (**9**).^{15,16} The ketone **9** (20%) and bicyclo[4.1.1]oct-2-en-8-one (**10**, 44%) were accompanied by a significant quantity (17%) of an unidentified aldehyde. Finally, irradiation of 273 mg of the ketone **11**^{8,17} for a period of 20 min led

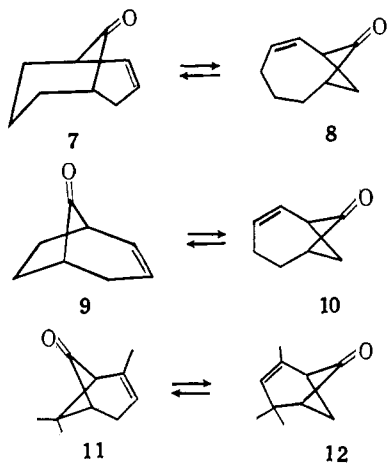
(14) On further irradiation the ketone **6** is converted to cyclopentadiene and ketene, apparently at a faster rate than reversion to **5**.¹³

(15) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(16) N. A. LeBel and L. A. Spurlock, *ibid.*, **20**, 215 (1964).

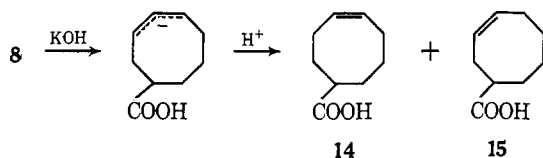
(17) W. F. Erman, *J. Am. Chem. Soc.*, **89**, 3828 (1967).

to a photochemical equilibrium mixture of **11** (12%) and 2,4,4-trimethylbicyclo[3.1.1]hept-2-en-6-one (**12**, 18%).¹⁸ In like manner, irradiation of each of the ketones **8** and **12** afforded the ketones **7** and **11**, respectively, clearly showing that the process is reversible for these two isomers.



Structure Proof of Products. Structure determination of the ketone **12** is described in a separate communication.¹⁷ The infrared spectrum of both ketones **8** and **10** showed typical cyclobutanone absorption¹⁹ at $5.61\ \mu$. The presence of *cis* olefin was established from the characteristic broad bands at $13.94\ \mu$ in **8** and at 13.5 and $13.9\ \mu$ in **10**. Characteristic peaks for *trans* olefin at 10.0 – $10.5\ \mu$ were conspicuously absent from the spectra of both **8** and **10**. The nmr spectra of **8** and **10** were strikingly similar and were consistent with the assigned structures—*i.e.*, the two vinyl protons appeared as unresolved multiplets at τ 3.8–4.65, the two bridgehead protons at τ 6.2–6.9, and the methylene protons in the τ 7.3–8.5 region. Because molecular weight determinations and elemental analyses indicated that the compounds **8** and **10** were homologs of the same basic structure, chemical proof of structure will be described for only ketone **8**.

That β,γ -unsaturated bridge cyclobutanones of type **8** are readily cleaved by methanolic potassium hydroxide has been firmly established.^{2,5,8} Cleavage of **8** by hydroxide ion should yield a mixture of the two acids **14** and **15**. Indeed, treatment of **8** with 2 *N* methanolic potassium hydroxide at room temperature for 16 hr

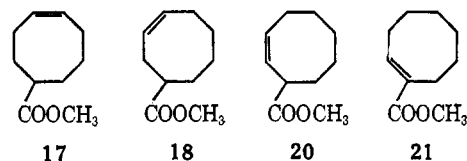


with subsequent diazomethane esterification gave a mixture of two methyl esters in the ratio 60:40 in 82% yield. The corresponding saturated derivative, bicyclo[5.1.1]nonan-8-one (**16**), was unaffected by the same base treatment. This implies that the double bond in **8** must be β,γ to the ketone, thus providing a driving force for cleavage by stabilizing an incipient carbanion in the transition state.

(18) Other products of this reaction are discussed in detail in the accompanying paper.¹⁷

(19) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 149.

The structures of the two esters, obtained from **14** and **15**, above, were rigorously defined by the following experiments. Catalytic hydrogenation of the ester mixture afforded exclusively methyl cyclooctanecarboxylate (**19**), identical in every respect with an authentic sample prepared by diazomethane esterification and hydrogenation of the known *cis*-4-cyclooctene-1-carboxylic acid.²⁰ The ester mixture, then, must contain two of the four possible isomers **17**, **18**, **20**, **21**. The presence of the Δ^4 isomer **17** (60%) in this mixture was established by comparison with the authentic sample above. The Δ^1 isomer **21** can be eliminated as a possible product by spectral evidence since no α,β unsaturation was ob-



served in the infrared or nmr spectrum of the mixture. The Δ^2 isomer **20** was synthesized independently by metalation of cyclooctene, subsequent carboxylation, and diazomethane methylation. Although the gas chromatography retention time and infrared spectrum of this material and the second ester were identical, the nmr spectra were strikingly different. In the nmr spectrum of the Δ^2 isomer **20** the tertiary allyl proton α to the ester function is revealed as a multiplet centered at τ 6.4–6.8. An expansion of the τ 6.0–7.0 region of the nmr spectrum of the ester mixture derived from base cleavage of **8** and subsequent diazomethane esterification indicated complete absence of isomer **20**. Thus the second isomer (40%) of the mixture must be the Δ^3 isomer **18**.

Discussion

A priori, it is difficult to explain why the four-membered ring ketones exceed the six-membered ring ketones in the product mixture at a point when an apparent photostationary state is attained. In the case of the interconversion of the 5/4-fused ring ketones **3** and **4**, Büchi¹⁰ has already emphasized that product distribution cannot be related to the relative thermodynamic stability of products but must be related to the photochemical properties of the molecule. The interconversion of β,γ -unsaturated bicyclic ketones (*i.e.*, **1** \rightleftharpoons **2**) unquestionably involves initial $n \rightarrow \pi^*$ photoexcitation of the carbonyl and cleavage of the carbon-carbon bond located allyl to the double bond and α to the carbonyl.⁹ Whether this cleavage occurs concerted with bond formation¹⁰ or whether an intermediate completely dissociated species²¹ is involved in this steady-state interconversion is germane to the discussion but a point not fully understood. That the $n \rightarrow \pi^*$ band of nonplanar β,γ -unsaturated ketones shows a bathochromic shift and increased intensity relative to the corresponding saturated ketones is well known.²² That this intensification is a consequence of the π orbi-

(20) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

(21) For a brief discussion of the mechanism by which these species may arise see H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4533 (1962).

(22) For a critical discussion of this phenomenon see J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 164–168.

tals of the carbonyl and the oxygen nonbonding orbitals pointing toward one another in space seems well defined.²² Each of the β,γ -unsaturated ketones previously reported to undergo photochemical transformation by α cleavage and recyclization shows a bathochromic shift and some intensification of the $n \rightarrow \pi^*$ band relative to normal saturated ketones. However, there seems to be little correlation between the wavelength and intensity of $n \rightarrow \pi^*$ absorption with product distribution. The two ketones **7** and **9**, in fact, show $n \rightarrow \pi^*$ extinction coefficients no greater than that expected for saturated ketones. Furthermore, Dreiding models reveal little difference between the spacial relationship of the double bond and π orbitals of the six-membered ring ketones **7** and **9** and the corresponding four-membered rings **8** and **10**. Although the efficiency of the process may well be affected by the proximity in space of the oxygen and olefinic π orbitals, there is no reason to believe that planar β,γ -unsaturated ketones will not undergo the same type reaction. Whether product distribution can be predicted by treating the intermediate transition as a completely dissociated diradical can be tested only after study of the photochemical behavior of bicyclic ketones possessing radical stabilizing or destabilizing substituents on the γ position of the olefin function.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus or on a micro hot stage and are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer and ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Nuclear magnetic resonance spectra were run as 10% solutions in carbon tetrachloride (unless stated otherwise) on a Varian A-60 or HA-100 spectrometer using tetramethylsilane as an internal reference by Dr. T. J. Flaunt and associates of these laboratories. Chemical shifts are recorded as parts per million on the τ scale, coupling constants as cycles per second. Nuclear magnetic resonance data are recorded in the order: chemical shift (multiplicity, where s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, coupling constant) [integration], interpretation. Molecular weights were determined on a Bendix Model 12-100 Time-of-Flight mass spectrometer or Atlas CH-4 mass spectrometer by Dr. J. H. Collins and associates of these laboratories. Gas chromatography separations were made on one of two columns unless otherwise stated: column 1: a 10 ft \times 0.25 in. stainless steel column packed with 20% GE-SF-96 silicone oil on 70–80 mesh Chromosorb W HMDS; column 2: a 10 ft \times 0.25 in. stainless steel column packed with 20% Reoplex 400 on 60–80 mesh Chromosorb W HMDS. Microanalyses were performed by T. Atanovich and associates of these laboratories and by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Bicyclo[3.3.1]non-2-en-9-one (7). This compound was prepared according to the method of Foote and Woodward.¹⁵ From 200 g of cyclohexanone there was obtained 31.0 g of colorless prisms, mp 96–99°. This material was sublimed twice (70° (15 mm)) to afford 16.0 g (6% yield based on cyclohexanone) of ketone **7** as colorless needles, mp 100–101.5° (lit.¹⁵ mp 98–99°).

Bicyclo[3.2.1]oct-2-en-8-one (9). This ketone was prepared according to the method of Foote and Woodward¹⁵ with the exception that the acid hydrolysis of the ethylene ketal was performed as described by LeBel and Spurlock.¹⁶ From 168.0 g of cyclopentanone there was obtained 15.8 g (6% yield based on cyclopentanone) of bicyclo[3.2.1]oct-2-en-8-one (**9**) as a colorless liquid, bp 70° (4 mm) (lit.¹⁶ bp 69–70° (5 mm)).

Bicyclo[5.1.1]non-2-en-9-one (8). An oxygen-free, 1% solution (1.50 g in 150 ml) of bicyclo[3.3.1]non-2-en-9-one (**7**) (mp 100–101.5°) in cyclohexane was irradiated in a nitrogen atmosphere with a 200-w Hanovia mercury arc lamp using a Vycor filter for 1 hr. The cyclohexane solution was passed through a column packed with 50 g of silica gel and eluted with an additional 200 ml of cyclo-

hexane. Evaporation of the cyclohexane afforded 1.4 g (93%) of soft crystals. Gas chromatography on column 2 at 130° with a helium flow of 60 cc/min showed four peaks: peak 1 (1.0%), retention time 1.5 min, unidentified; peak 2 (4%), retention time 9 min 25 sec, infrared $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 5.80 (carbonyl), unidentified; peak 3 (29%), bicyclo[3.3.1]non-2-en-9-one (**7**), retention time 12 min 20 sec (a sample of **9** collected by preparative glpc under the conditions described above showed mp 100–101.5°, and was identical in every respect—infrared spectrum, gas chromatography retention time, nmr spectrum—with an authentic sample prepared as outlined above); peak 4 (67%), bicyclo[5.1.1]non-2-en-9-one (**8**), retention time 13 min 10 sec. A sample collected by preparative glpc showed mp 75.0–76.0°; infrared spectrum: $\lambda_{\text{max}}^{\text{CCl}_4}$ 5.61 (carbonyl), λ_{max} 13.94 (cis olefin); ultraviolet spectrum: $\lambda_{\text{max}}^{\text{EtOH}}$ 299 m μ (ϵ_{max} 45); nmr spectrum: τ 3.8–4.65 (m) [1.9] olefinic protons, τ 6.2–6.9 (m) [1.8] bridgehead protons, τ 7.3–8.5 (m) [8.3] four methylene protons, two allyl protons, two bridge protons.

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}$: C, 79.3; H, 8.9. Found: C, 79.0; H, 8.9.

In a separate irradiation experiment carried out as described above the reaction mixture was sampled at various time intervals. The results of this experiment are shown in Table I. The per cent composition of **7** and **8** was shown by glpc on column 2.

Table I

Irradiation period, min	% 7	% 8	Ratio 7 : 8
15	58.6	39.6	1.5:1
30	50.3	48.4	1:1
60	32.6	65.6	1:2
90	30.0	63.1	1:2.1
120	29.5	55.6	1:1.9

Preparation of Bicyclo[5.1.1]nonan-9-one (16). A solution of 968 mg of the mixture obtained from the irradiation of bicyclo[3.3.1]non-2-en-9-one (**7**), above, in 20 ml of absolute ethanol was hydrogenated in the presence of 20 mg of 5% palladium-on-charcoal on a Parr low-pressure hydrogenator at 50 psi initial hydrogen pressure with shaking for a period of 1 hr. The catalyst was removed by filtration and the ethanol evaporated under reduced pressure to yield 645 mg (67%) of a white semisolid. Gas chromatography on column 2 at 130° with a helium flow of 70 cc/min showed four peaks: peak 1 (3%), retention time 12 min 0 sec, unidentified; peak 2 (47%), bicyclo[5.1.1]nonan-9-one (**16**), retention time 16 min 15 sec (a sample collected by preparative glpc under the above conditions showed mp 96–98°; infrared spectrum: $\lambda_{\text{max}}^{\text{CCl}_4}$ 5.60 (carbonyl); nmr spectrum: τ 6.6–7.2 (m) [2] tertiary bridgehead protons adjacent to carbonyl, τ 7.7–8.7 (m) [12] methylene protons. *Anal.* Calcd for $\text{C}_9\text{H}_{14}\text{O}$: C, 78.2; H, 10.2. Found: C, 78.0; H, 10.2; peak 3 (41%), retention time 18 min 40 sec, bicyclo[3.3.1]nonan-9-one (**27**), collected by preparative gas chromatography as above and identified by comparison with a sample of the ketone **22** prepared from the pure bicyclo[3.3.1]non-2-en-9-one (**7**), below; peak 4 (10%), retention time 26 min, unidentified.

Treatment of Bicyclo[5.1.1]nonan-9-one (16) and Bicyclo[3.3.1]nonan-9-one (26) with Methanolic Potassium Hydroxide. A solution of 645 mg of a 60:40 mixture of ketones **16** and **26** in 20 ml of 10% methanolic potassium hydroxide was stored at room temperature for 16 hr. After dilution with 50 ml of cold water (0–5°) the basic solution was extracted with ether (three 25-ml portions) and the ethereal layer washed with water (two 25-ml portions) and dried over magnesium sulfate. Evaporation of ether afforded 485 mg (75%) of colorless semisolid, which on analysis by gas chromatography on column 2 at 130° showed no change in product composition. The two ketones **16** and **22** were isolated by preparative gas chromatography and identified by comparison with the ketones **16** and **22** from the direct reduction above.

Bicyclo[4.1.1]oct-2-en-8-one (10). An oxygen-free solution of 1.00 g of bicyclo[3.2.1]oct-2-en-8-one (**10**) in cyclohexane was irradiated in a nitrogen atmosphere with a 200-w Hanovia mercury arc lamp using a Vycor filter for 90 min. Evaporation of the cyclohexane yielded 950 mg (95%) of light yellow liquid. Gas chromatography on a 10 ft \times 0.25 in. column packed with 20% ethylene glycol succinate polymer on 60–80 mesh Chromosorb W-HMDS with a helium flow of 60 cc/min at 150° showed five peaks: peak 1

(7%), retention time 6 min 30 sec, unidentified; peak 2 (18%), retention time 7 min 20 sec, unidentified; peak 3 (27%), retention time 11 min 40 sec, bicyclo[3.2.1]oct-2-en-8-one (9), identical in every respect (glpc retention time, infrared, nmr) with an authentic sample of bicyclo[3.2.1]oct-2-en-8-one prepared as described above; 2,4-dinitrophenylhydrazone, mp 176–177° [lit.¹³ mp 175–176°]; peak 4 (46%), retention time 13 min 0 sec, bicyclo[4.1.1]oct-2-en-8-one (10) (a sample collected by preparative glpc under the above conditions showed infrared: $\lambda_{\text{max}}^{\text{film}}$ 5.61 (carbonyl), λ_{max} 6.1, 13.5, 13.9 (*cis* olefin); nmr: τ 4.0–4.5 (m) [1.89], τ 6.3–6.8 (m) [1.89], τ 7.2–8.4 (m) [6.26] (Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}$: C, 78.65; H, 8.25. Found: C, 77.7; H, 7.9); the 2,4-dinitrophenylhydrazone was recrystallized from ethanol in needles, mp 153.5–155.5°; peak 5 (3%), retention time 19 min 20 sec, unidentified.

Treatment of the Mixture Obtained from the Irradiation of Bicyclo[3.3.1]non-2-en-9-one (7) with Base. A 900-mg portion of the mixture obtained from the irradiation of bicyclo[3.3.1]non-2-en-9-one, as outlined above, was dissolved in 20 ml of 10% methanolic potassium hydroxide and allowed to stand at room temperature for 16 hr. After dilution with 50 ml of ice water the basic solution was extracted with ether (three 25-ml portions), and the ethereal layer was washed with water (two 25-ml portions) and dried over magnesium sulfate. Evaporation of the ether yielded 200 mg (22%) of a yellow solid, mp 95–98°. A sample of this solid was identical—infrared, glpc retention time, mixture melting point—with an authentic sample of bicyclo[3.3.1]non-2-en-9-one prepared as described above. The basic layer was acidified with concentrated hydrochloric acid and the resulting liquid extracted with ether (three 25-ml portions), washed with four 25-ml portions of water, and dried over magnesium sulfate. Evaporation of the ether gave 500 mg (56%) (82% yield based on the four-membered ketone present) of acid product as a yellow liquid, infrared spectrum: $\lambda_{\text{max}}^{\text{film}}$ 5.89 (carbonyl), λ_{max} 14.2 (*cis* olefin). The acid was treated without further purification with diazomethane to yield 500 mg (92%) of light yellow liquid which was distilled from a modified Hickman apparatus, bp 60–70° (0.5 mm), to yield 460 mg of colorless liquid; infrared spectrum: $\lambda_{\text{max}}^{\text{film}}$ 5.77 (carbonyl), 8.2, 8.35, 8.6 (ester), 6.08, 13.35, 14.0 (*cis* olefin). Gas chromatography on a 150-ft capillary column 0.01 in. in diameter coated with polyphenyl ether polymer with programmed temperature 100–180° at a rate of 5°/min with a flow rate of 58.71 cc of He/min showed three peaks: peak 1 (1.5%), relative retention volume, 0.825, unidentified; peak 2 (39%), relative retention volume 0.968, methyl Δ^3 -cyclooctene-1-carboxylate (structure proof described in the text of this report); peak 3 (59%), relative retention volume 1.000, methyl *cis*-4-cyclooctene-1-carboxylate. The relative retention volume of this ester on the 150-ft capillary column described above was identical with a sample of methyl *cis*-4-cyclooctene-1-carboxylate prepared as described below.

Methyl *cis*-4-Cyclooctene-1-carboxylate (17). Treatment of *cis*-4-cyclooctene-1-carboxylic acid (14)²⁰ (*p*-phenacyl ester, mp 118–119° (lit.²⁰ mp 120–121°)) with excess diazomethane afforded the ester 17, bp 61° (0.6 mm), in 86% yield; infrared: $\lambda_{\text{max}}^{\text{film}}$ 5.77 (carbonyl), λ 8.2–8.6 (ester), 6.08, 13.4, 14.0 (*cis* olefin); nmr τ 4.2–4.5 (m) [1.8] vinyl protons, τ 6.41 (s) [2.9] methyl ester, τ 7.4–8.05 (m), and τ 8.05–8.70 (m) [11.4] allyl, tertiary proton α to carbonyl, methylene protons.

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2$: C, 71.4; H, 9.6. Found: C, 71.2; H, 9.7.

Preparation of Methyl Cyclooctanecarboxylate (19). A. From Methyl *cis*-4-Cyclooctene-1-carboxylate (17). A solution of 5.55 g of methyl *cis*-4-cyclooctene-1-carboxylate in 75 ml of absolute methanol was hydrogenated in the presence of 500 mg of 10% palladium on charcoal in a Parr rocking hydrogenator at 50 psi and 27° for a period of 3 hr. Filtration of catalyst, evaporation of the solvent, and short-path distillation produced 3.80 g (68%) of methyl cyclooctanecarboxylate (19) as a colorless liquid, bp 47° (0.3 mm); infrared spectrum: $\lambda_{\text{max}}^{\text{film}}$ 5.77 (carbonyl), λ 8.4–8.6 (ester). The ester was purified for analysis by preparative gas chromatography on column 2 at 146° and 60 cc of He/min; nmr spectrum: τ 6.45 (s) [2.9] methyl ester, τ 7.6 (m) [0.9] tertiary proton adjacent to carbonyl, τ 8.0–8.8 (m) [14.2] methylene protons.

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.6; H, 10.6. Found: C, 70.9; H, 10.5.

B. By Reduction of Hydroxide Cleavage Product of Bicyclo[5.1.1]non-2-en-9-one (8). A solution of 200 mg of the ester mixture obtained from hydroxide opening of the ketone 8, as described above, in 20 ml of absolute ethanol was hydrogenated in the presence of 20 mg of 10% palladium-on-charcoal catalyst on a Parr hydrogenator with shaking at 50 psi initial pressure for a period of 2 hr.

The catalyst was removed by filtration and the ethanol was evaporated to yield 190 mg (95%) of light yellow liquid. Gas chromatography on column 2 at 146° with a helium flow of 60 cc/min showed four peaks: peak 1 (3%), retention time 3 min 30 sec, unidentified; peak 2 (2%), retention time 6 min 10 sec, unidentified; peak 3 (89%), retention time 7 min 25 sec, methyl cyclooctanecarboxylate; peak 4 (7%), retention time 9 min 20 sec, unidentified. A sample of the third peak was collected by preparative glpc. The infrared and nmr spectra of this sample were superimposable with those of an authentic sample of methyl cyclooctanecarboxylate prepared by hydrogenation of the known methyl 4-*cis*-cyclooctene-1-carboxylate. A 50:50 mixture of these esters when analyzed by gas chromatography under the above conditions displayed a single symmetrical peak.

Methyl Cyclooct-2-ene-1-carboxylate (20). Butylpotassium²³ was prepared in excess cyclooctene (200 g) from 17.72 g (0.454 g-atom) of potassium and 21.0 g (0.227 mole) of butyl chloride at 0–10°. This mixture was maintained at –20° for 3 hr and allowed to warm to room temperature over a period of 16 hr. Carbonation by pouring over excess solid carbon dioxide provided 9.5 g (27%) of acidic product which was converted to the corresponding methyl ester with diazomethane. Gas chromatography on column 2 at 150° with a helium flow of 70 cc/min showed 5 peaks: peak 1 (13%), retention time 1 min 40 sec, unidentified; peak 2 (2%), retention time 2 min 50 sec, unidentified; peak 3 (0.5%), retention time 4 min, unidentified; peak 4 (1%), retention time 4 min 30 sec, unidentified; peak 5 (84%), retention time 8 min 38 sec, methyl Δ^2 -cyclooctene-1-carboxylate (20). Further purification by fractional distillation through an 18-in. Nester and Faust spinning-band column afforded a material that was 99% pure by glpc, bp 49° (0.5 mm); infrared spectrum: $\lambda_{\text{max}}^{\text{film}}$ 5.77 (carbonyl), 8.2–8.4, 8.6 (ester), 6.05, 13.1, 14.2 (*cis* olefin); nmr: τ 4.1–4.4 (m) [1.8] olefin protons, τ 6.32 (s) [3.2] methyl ester, τ 6.4–6.8 (m) [1.0] tertiary allyl proton adjacent to carbonyl, τ 7.7–8.1 (m) [2.0] allyl protons, τ 8.1–8.9 (m) [7.9] methylene protons; mass spectrum: parent ion peak *m/e* 168.

Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2$: C, 71.4; H, 9.6. Found: C, 71.4; H, 9.6.

Nmr spectrum of the 39:59 mixture of methyl Δ^3 - and Δ^4 -*cis*-cyclooctene-1-carboxylates from base cleavage of ketone 10 showed τ 4.2–4.5 (m) [2.05] olefin protons, τ 6.39 (s), τ 6.41 (s) [3.01] methyl esters, τ 7.4–7.9 (m) [5.2] allyl protons and tertiary proton adjacent to carbonyl, τ 8.0–8.8 (m) [5.76] methylene protons. A blow-up of the τ 6–7 region showed no signal for the tertiary allyl proton adjacent to the carbonyl that is present in methyl Δ^2 -cyclooctene-1-carboxylate (20).

Bicyclo[4.1.1]octan-8-one (23).—A 1.000-g portion of the mixture obtained from the irradiation of bicyclo[3.2.1]oct-2-en-8-one containing 53% ketone 10 and 37% ketone 9, as described above, was dissolved in 20 ml of absolute ethanol, mixed with 0.020 g of 5% palladium-on-charcoal catalyst, and shaken on the Parr low-pressure hydrogenator under 50 psi of hydrogen for 2 hr. The catalyst was removed by filtration and the ethanol was evaporated to yield 800 mg of light yellow liquid. Gas chromatography of this liquid on a 10 ft \times 0.25 in. diameter column packed with 20% ethylene glycol succinate polymer on 60–80 mesh Chromosorb W-HMDS with a helium flow of 65 cc/min at 150° showed five peaks: peak 1 (2%), retention time 3 min 30 sec, unidentified; peak 2 (6%), retention time 4 min 45 sec, unidentified; peak 3 (36%), retention time 6 min 40 sec, bicyclo[4.1.1]octan-8-one (23) (a sample of the third peak was collected by preparative glpc under the above conditions as a colorless liquid, the infrared spectrum of which showed $\lambda_{\text{max}}^{\text{film}}$ 5.61 (carbonyl); the nmr spectrum showed signals at τ 6.5–7.0 (multiplet) [1.8 protons] bridgehead protons, τ 7.9–8.7 (multiplet) two cyclobutane and eight methylene protons. This compound was analyzed as the 2,4-dinitrophenylhydrazone derivative, mp 164–165°, after one recrystallization from ethanol. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$: C, 55.3; H, 5.3; N, 18.4. Found: C, 55.3; H, 5.1; N, 18.8; peak 4 (55%), retention time 7 min 55 sec, bicyclo[3.2.1]octan-8-one (a sample collected by preparative glpc had mp 138–140°, lit. 140–141°¹⁸); peak 5 (0.9%), retention time 9 min 15 sec, unidentified.

Irradiation of Bicyclo[5.1.1]non-2-en-9-one (8). A solution of 25 mg of bicyclo[5.1.1]non-2-en-9-one (8), mp 74–75.5°, in 20 ml of cyclohexane was irradiated with a 200-w Hanovia mercury arc lamp for a period of 0.75 hr. Gas chromatographic analysis of an aliquot of the reaction mixture on a 10 ft \times 0.125 in. column packed with 20% Reoplex on 100–120 mesh Chromosorb W-DMCS at 150° with a helium flow of 65 cc/min showed three peaks: peak 1 (6%), retention time 10 min 55 sec, unidentified; peak 2 (18%), retention time 13 min 50 sec, bicyclo[3.3.1]non-2-en-9-one (7) (a sample

of **7** collected by preparative glpc under the conditions described above showed mp 95–98°; a mixture melting point with an authentic sample of **7**,^{1b} mp 95–98°, showed no depression, mp 95–98°; peak 3 (76%), retention time 14 min 50 sec, bicyclo-[5.1.1]non-2-en-9-one (**8**) (a sample of **8** collected by preparative glpc under the above conditions showed mp 74–75.5°; a mixture

melting point with a sample of starting **8**, mp 74–75.5°, showed no depression, mp 74–75.5°).

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Photoinduced Reactions. VI. The Photochemical Formation of the Ketone Tautomer of a Phenol from 2,4,6-Tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone^{1,2}

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Abstract: A reinvestigation of the photochemical transformation of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (**I**) to an isomeric photoketone and a photophenol, to which structures **II** and **IIIa** had been previously assigned, respectively, was carried out. The structure of the photoketone was revised to **IV** which is the ketone tautomer of a phenol **VIb** derived from **IV**. Structure **IIIa** for the photophenol was confirmed. A lumiketone **II**, which was shown to be an intermediate leading onward to the photoketone and the photophenol, was also isolated. Evidence is reported for the $n\text{--}\pi^*$ excitation in the primary process of the reaction.

In a previous publication³ we reported that irradiation of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (**I**) in methanol or ether with a low-pressure mercury lamp give a photoketone, C₁₉H₃₂O₂, isomeric to **I**, and a photophenol, C₁₅H₂₄O₂, in low yields, along with a trace of 2,4,6-tri-*t*-butylphenol, and structures **II** and **IIIa** were assigned, respectively. In the present paper we wish to report the results obtained from the reinvestigation of this reaction; *i.e.*, the photoketone has the revised structure **IV** which is the ketone tautomer of a phenol **VIb**.

Irradiation of **I** in various organic solvents with a high-pressure mercury lamp (Pyrex filter) yielded a mixture of the photoketone⁴ and the photophenol in high yields. These results are summarized in Table I. It should be noted that the ratio of the photophenol to the photoketone decreases with the increase of the polarity of the solvents. The role of the solvent in this reaction will be discussed later.

The structure of the photophenol which had been previously assigned as **IIIa** was strongly supported by nmr analysis of its methyl ether **IIIb**. In the nmr spectrum of **IIIb**, two *t*-butyl (τ 8.63), two methoxyl (τ 6.15), and two aromatic protons (τ 3.05) are magnetically equivalent. With other possible structures of 3,4- and 5,6-di-*t*-butylguaiacols³ (**IXa** and **IXb**), it would be difficult to explain such a magnetic equivalence.

Pyrolysis or acid-catalyzed reaction of the photoketone resulted in the elimination of a *t*-butyl group to

Table I. The Yields of Photophenol **IIIa** and Photoketone **IV** on Irradiation of **I** in Various Solvents

Expt no.	Solvent	Yields, % ^c		
		IIIa	IV	IIIa:IV
1	Petroleum ether ^a	41	51	0.83
2	Ether ^a	35	46	0.75
3	Benzene ^a	38	53	0.72
4	Pyridine ^a	35	56	0.64
5	Ethyl acetate ^a	33	53	0.62
6	N,N-Dimethylformamide ^a	18	81	0.22
7	Benzene-methanol (1:1) ^a	9	80	0.11
8	Methanol ^a	2	62	0.03
9	Ether ^b	28	29 ^d	...
10	Methanol ^b	3	29 ^d	...

^a With a high-pressure mercury lamp using a Pyrex filter. ^b With a low-pressure mercury lamp using a Vycor filter. ^c The yields were based on the consumed **I** and were estimated by vpc analysis (see Experimental Section). ^d 2,4,6-Tri-*t*-butylphenol was formed in 3–4% yield.

yield a crystalline phenol **Va** which, on methylation, gave 4,6-di-*t*-butylresorcinol dimethyl ether (**Vb**) (Scheme I).⁵ Treatment of the photoketone with sodium hydride in dimethyl sulfoxide or with sodium methoxide in methanol gave an anion **VIa**. Hydrolysis of **VIa** yielded a phenol **VIb**, which could not be isolated in a pure form, but was easily oxidized by air to a ketone hydroperoxide **VIII**. The nmr spectrum of phenol **VIb** shows six singlets at τ 3.02 (1 H, aromatic proton), 5.06 (1 H, phenolic hydroxyl), 6.43 (3 H, methoxyl), 8.45 (9 H, *t*-butyl), 8.58 (9 H, *t*-butyl), and 8.65 (9 H, *t*-butyl). Mild treatment of phenol **VIb** with hydrobromic acid-acetic acid (1:24) afforded **Va**. Methylation of anion **VIa** gave a tri-*t*-butyldimethoxybenzene, the structure of which can be assigned as either 2,4,6-**VIc** or 4,5,6-tri-*t*-butylresorcinol

(5) M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).

(1) Part V: T. Matsuura and K. Ogura, *Bull. Chem. Soc. Japan*, **40**, 945 (1967).

(2) This work was supported in part by U. S. Public Health Service Research Grant AM 07955, from the National Institute of Arthritis and Metabolic Diseases.

(3) T. Matsuura, *Bull. Chem. Soc. Japan*, **37**, 564 (1964).

(4) Irradiation of the photoketone with a high-pressure mercury lamp for a longer time gave a new compound, the structure of which is being studied and will be reported in a forthcoming paper.