Photochemical Reactions of Simple Cyclopentenones

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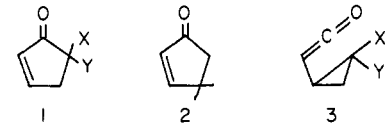
Abstract: The preparation and photolysis of simple cyclopentenones **1a–1d** and **2** have been investigated. Two new photochemical reactions were found; these are the rearrangement of **1a–1d** to cyclopropylketenes, isolated as esters **4** and **5**, and closure of a 1,4 biradical (**10**) onto the double bond to form bicyclic ketones **8** and **9**. In addition, examples of several other photochemical transformations were observed, leading to aldehydes **7** (α cleavage), alcohols **11** and **12** (collapse of a 1,4 biradical), cyclopentenone (type II cleavage), and solvent adducts of two sorts (**13** and **20**). Independent syntheses of several products (**4a**, **4e**, **8**, **13**, and **20**) are described.

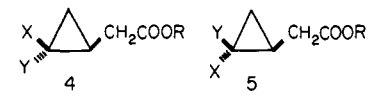
While photocycloaddition reactions of cyclopentenone have received[2–5] intensive study, virtually nothing is known about light-induced rearrangements of this compound or its simple derivatives.[6] Indeed, very few such compounds particularly suited to photochemical investigation (such as **1a**) have ever been prepared. Our investigations in this area are described below; these have yielded not only examples of a number of known rearrangements observed here for the first time in cyclopentenones, but also several cases of new photochemical transformations. We describe first photochemical results and then experiments concerned with preparation of both starting materials and photoproducts.

Photochemical Experiments. The ketones examined most thoroughly are the four C-5-substituted cyclopentenones **1a–1d**;[7] in addition some results with 4,4-dimethylcyclopentenone (**2**)[8] and the parent **1e** are of interest. Pentane, methanol, or *tert*-butyl alcohol solutions of these compounds at concentrations low enough ($\leq$1 mg/ml) to discourage dimerization were irradiated through Pyrex ($\lambda > 2800$ Å) or uranium glass[9] ($\lambda > 3300$ Å) filters. The latter was particularly useful in protecting saturated ketone products from secondary photolytic destruction. For slower reacting ketones, *tert*-butyl alcohol gave cleaner reaction mixtures than did methanol, presumably through suppression of reactions initiated by hydrogen abstraction. Irradiated reaction mixtures were analyzed and the components separated preparatively by vapor phase chromatography (vpc). The results, which are discussed below, are presented in Table I. Yield figures are only approximate and are given as percentages of the volatile products, which amounted to some 75–90% of the starting material.



1 2 3

a, X=Y=CH_3, R=CH_3
b, X=C_2H_5, Y=H, R=$C(CH_3)_3$
c, X=n-C_3H_7, Y=H, R=$C(CH_3)_3$
d, X=OC_2H_5, Y=H, R=CH_3
e, X=Y=H, R=CH_3



4 5

The first reaction uncovered by this approach was the novel rearrangement of these ketones to the cyclopropylketenes **3**, isolated and identified as the corresponding methyl or *tert*-butyl esters **4**.[10] Thus photolysis of **1a** in methanol gave largely **4a**, the structure of which was secured both from its spectroscopic (ir, 220-MHz nmr) properties as well as through independent synthesis reported below. The intermediacy of cyclopropylketene **3a** was clear from a parallel irradiation in pentane as solvent. Direct examination of the ir spectrum of the irradiated solution revealed a sharp band of medium intensity at 2110 cm^{-1}. Treatment of this pentane solution with excess methanol at room temperature for 16 hr resulted in complete replacement of the 2110-cm^{-1} absorption by a new strong band at 1750 cm^{-1}; subsequent isolation gave **4a**. In similar fashion photolysis of **1b–1d** in the appropriate alcohol as solvent gave cyclopropane esters. In each of these cases both possible diastereomeric esters, **4b–4d** and **5b–5d**, were found. For the pair from **1d** the configuration of each ester (**4d** and **5d**) could be tentatively assigned from nmr spectra by making use of earlier data,[11] which indicated that for the trans

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

(3) J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, 89, 4944 (1967).

(4) P. de Mayo, J-P. Pete, and M. Tchir, *Can. J. Chem.*, 46, 2535 (1968).

(5) R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, 1, 301 (1969).

(6) The vapor phase photolysis of cyclopentenone has been reported to yield carbon monoxide, $\Phi_{CO} \sim 0.004$: L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 89, 1973 (1967). A rearrangement of uncertain mechanism involving a C-3-substituted cyclopentenone is described by B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 46, 2473 (1963).

(7) Preparation of ketones **1a–1c** is discussed below; **1d** was prepared as described by C. H. DePuy, R. D. Thurn, and M. Isaks, *J. Org. Chem.*, 27, 714 (1962).

(8) This compound was prepared by the acid-catalyzed dehydration of the corresponding acyloin, 4,4-dimethyl-2-hydroxycyclopentanone (**39**), as described by R. S. Rouse and W. E. Tyler, III, *ibid.*, 26, 3525 (1961). We have confirmed the more recent finding of A. J. Bellamy, *J. Chem. Soc. B*, 449 (1969), that this dehydration leads to a mixture of **2** and 2,3-dimethyl-2-cyclopentenone. Preparation of the acyloin **39** is given by H. Kwart and J. A. Ford, Jr., *J. Org. Chem.*, 24, 2060 (1959).

(9) 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. Amer. Chem. Soc.*, 86, 3197 (1964).

(10) In a preliminary communication this rearrangement of **1a** was reported along with completely independent experiments by Professor A. S. Kende and his coworkers on the analogous rearrangement of 5,5-diphenylcyclopentenone: W. C. Agosta, A. B. Smith, III, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Lett.*, 4517 (1969).

(11) U. Schöllkopf and W. Pitteroff, *Chem. Ber.*, 97, 636 (1964), and references cited therein.

Table I. Photoproducts from Cyclopentenones

Starting ketone	Products (rel yield) Cyclopropane esters	Aldehydes	Reaction with solvent	Type II	Bicyclo[3.2.0] system	Bicyclo[2.2.1] system
1a	**4a** (76%)	**7a** (24%)	**20**[a]			
1b	**4b** **5b**					
1c	**4c** (45)% **5c** **4d** (25%)				**11** (11%)	**8** (44%)
1d	**5d**	**7d** (3%)		**1e** (6%)	**12** (49%)	**9** (17%)
2			**13**			

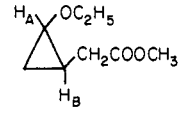
[a] Only in the presence of benzophenone.

Table II. Nmr Spectra of **9** and **9a**

Position	Signal, δ — **9**	**9a**
K	1.19 (d, J_{EK} = 6 Hz, 3 H)	
G	1.56 (dd, J_{FG} = 11 Hz, J_{AG}[a] ~ 2 Hz, 1 H)	
C	1.86 (dd, J_{BC} = 17 Hz, J_{CF} = 4 Hz, 1 H)	
F	1.99 (m, J_{FG} = 11 Hz, J_{CF} = 4 Hz, J_{AF}[b] ~ 2 Hz, 1 H)	
B	2.06 (dd, J_{BC} = 17 Hz, J_{BD} = 4 Hz, 1 H)	
D	2.45 (m, J_{BD} = 4 Hz, J_{DF}[c] ~ 2 Hz, 1 H)	
E	3.79 (q, J_{EK} = 6 Hz, 1 H)	3.54 (d, J_{EX} = 7 Hz)
X		3.81 (m, J_{EX} = 7 Hz, $J_{DX} \neq 0$)
A	3.93 (d, J_{AG}[d] = 2 Hz, 1 H)	3.92 (d, J_{AG}[d] = 2 Hz)

[a] Or J_{DG}. [b] Or J_{DF}. [c] And/or J_{DG}. [d] Or J_{AF}.

isomer of **6**, H_A should appear upfield and J_{AB} should be smaller relative to the cis compound. Neither cyclopentenone itself, **1e**, nor its 4,4-dimethyl derivative **2** gave cyclopropylketene products on irradiation. Synthetic samples of both anticipated products, **4e** and **4a**, respectively, were available, and less than 1% of these esters would have been detected. This suggests that the rearrangement of **1** to **3** proceeds *via* initial α cleavage followed by rebonding of C-5 to C-3. α cleavage of ketones is well known to be strongly favored by substitution α to the carbonyl[12] and must occur more readily in **1a–1d** than in **1e** or **2**.



6

XYC=CH–CH=CH–CHO

7

In keeping with the expected facility of α cleavage in **1a**, 5-methylsorbaldehyde (**7a**) was also produced on irradiation of this ketone. The photoproduct was identical with a synthetic sample, which, both from its mode of preparation[13] and its nmr spectrum,[14] clearly is the trans isomer. Although the immediate product from **1a** should be *cis*-**7a**, there is ample opportunity during irradiation and subsequent isolation for either photochemical or thermal conversion to the more stable trans isomer. Only from **1d** of the other cyclopentenones investigated was an aldehyde **7d** isolated, and here the amount was too small for rigorous identification.

A second novel reaction we have observed occurs in **1c** and **1d** and leads to the bridged bicyclic ketones **8** and **9**, respectively.[15] In the propyl ketone **1c** this is a significant pathway, accounting for 44% of the product. The structure of **8** was first surmised from its ir and nmr spectra; there is carbonyl absorption at 1750 cm^{-1} and the methyl protons appear as a doublet, J = 6 Hz, at 1.08 ppm. Independent synthesis detailed below supported this conclusion and firmly established the exo stereochemistry of the methyl group. The constitution of **9** rests on analysis[16] of its 220-MHz nmr spectrum (see Table II) and the presence of ir carbonyl absorption at 1768 cm^{-1}. The assignment of exo configuration to the C-3 methyl group is not only consistent with the stereochemistry proved for **8**, but is also required by the observed lack of coupling between H_E and H_D (expected[16] for *endo*-H_E, J_{DE} = 0–2 Hz, and for *exo*-H_E, J_{DE} = 3–4 Hz). This assignment is nicely supported by the nmr spectrum of parent bicyclic ketone **9a**.[17] The three signals at lowest field in **9a** can be assigned as recorded in Table II by making use of the expected downfield shift of exo protons relative to the corresponding endo protons. Both the chemical shifts of H_X and H_E in **9a**, as well as the extent of their spin–spin coupling with H_D, indicate

(12) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969), and references cited therein; D. S. Weiss, N. J. Turro, and J. C. Dalton, *Mol. Photochem.*, 2, 91 (1970); J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564 (1970).

(13) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, 28, 692 (1963).

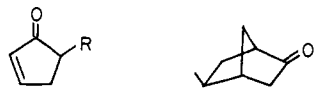
(14) J-P. Schirmann, J. Dreux, and J. Doris, *Bull. Soc. Chim. Fr.*, 3896 (1967), and observations in this laboratory. The 220-MHz nmr spectrum of **7a** is recorded in the Experimental Section.

(15) A preliminary communication concerning this reaction has appeared: A. B. Smith, III, and W. C. Agosta, *Chem. Commun.*, 343 (1971).

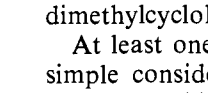
(16) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 230, 288, and 334, and references cited therein.

(17) L. A. Spurlock and R. G. Fayter, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. ORGN 108. Our measurements were made on a sample of **9a** generously provided by Professor Spurlock.

clearly that H_E of photoproduct **9** must be an endo proton.



1c, R = $CH_2CH_2CH_3$
1d, R = OCH_2CH_3



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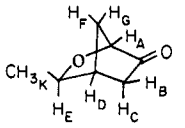
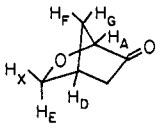
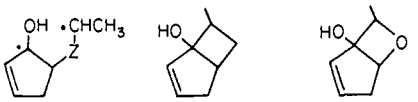


9



9a

An attractive pathway for formation of **8** and **9** is through the type II biradical **10**[18] formed on abstraction of γ-hydrogen by carbonyl oxygen. Cyclization of **10** at the double bond furnishes the product directly as its enol. Only the exo isomers **8** and **9** were obtained, and in models it appears that closure to these rather than the endo isomers would be sterically favored. This novel cyclization is seen then as simply a process vinylogous to the well-established collapse of biradicals such as **10** to four-membered rings.[18] This latter transformation also occurs with **8** and **9** and leads to **11** and **12**. In addition type II cleavage[18] of the biradical intermediate **10** occurs to a very limited extent with **1d**, as shown by isolation of a small amount of cyclopentenone from this irradiation. Neither cyclopentenone nor products corresponding to **8** and **11** were found in photolysis of **1b**, a result presumably reflecting the reduced stability[19] of the side-chain radical center in this instance.



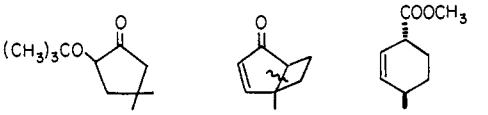
10, Z = CH_2 or O

11

12

Overall, the distribution of products from these ketones (**1a–1d**) can be accounted for qualitatively by simple hypotheses. α cleavage occurs when substitution at C-5 favors it and results in rearrangement to a cyclopropyl ketene **3** and some aldehyde **7**. With appropriate stabilization of the radicals involved, γ-hydrogen abstraction will compete with α cleavage and lead to loss of the side chain, formation of four-membered rings, and vinylogous formation of the bicyclo[2.2.1] system. When neither of the above is an attractive process, other slower reactions dominate the picture. We noted above that **2** fails to rearrange to **3a**. Both **2** and **1e** undergo mainly photoreduction of the double bond on irradiation in *n*-pentane or methanol. If this is suppressed in turn by use of *tert*-butyl alcohol as solvent, **2** yields a solvent adduct, **13**, the structure of which was deduced from spectroscopic properties and confirmed by independent synthesis. This reaction represents a novel photochemical α addition ("anti-Michael") of an alcohol to an α,β-unsaturated ketone.[20] In contrast, the photolysis of 5,5-dimethylcyclohexenone in *tert*-butyl alcohol has been reported[21] to yield the β adduct, 3-*tert*-butoxy-5,5-dimethylcyclohexanone.

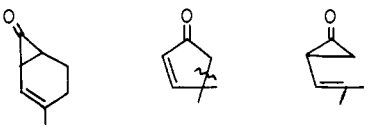
At least one other factor needs to be added to these simple considerations for extension to more complex systems. This is the bond weakening effect of steric strain, which can alter reaction paths in photochemical, just as in thermal, rearrangements. Transformation of the bicyclic cyclopentenone **14** to ester **15** on irradiation in methanol, for example, is believed to involve a cyclopropanone intermediate **16**[22] and thus presumably requires a β cleavage in **14**. We have not, however, detected any product arising from analogous rearrangement of **2** (**17** to **18**), implying necessity of the four-membered ring in **14**. Relief of ring strain in rearrangement of **14** is apparently significant in determining the reaction path.



13

14

15



16

17

18

There remains one phototransformation to be described. Attempts to sensitize photolysis of **1a** in methanol using benzophenone led to reduced yields of **4a** and **7a** and formation of an adduct of **1a** with solvent. Benzophenone-sensitized irradiation of cyclopentenone itself in isopropyl alcohol was reported[23] some years ago to lead to **19**, and our product then should be the analogous hydroxy ketone, **20**. This structure was compatible with ir and nmr data, and we have confirmed the assignment by an independent synthesis discussed below. Several considerations compelled us to confirm the structure of **20** with care. First, the proof[23] of structure for **19** seemed possibly open to question. Second, at the time of the experiment there was considerable uncertainty concerning the mechanism of this reaction; formation of **19** and **20** appeared[4] to involve a cyclopentenone triplet reached by energy transfer from benzophenone (E_T = 69 kcal/mol). Third, there are proved examples of both α and β addition of solvent to unsaturated ketones under various conditions. As mentioned above, **2** gives **13**, and the Δ^4-3-keto steroid **21** adds toluene α to give **22**,[24a] while the Δ^{16}-20-keto compound **23** adds ethanol β to give **24**.[24b] For the addition of solvent cyclohexane to cyclopentenone both possible structures, **25**[3] and **26**,[24a] have been advocated. This collection

(18) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

(19) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

(20) For heterocyclic analogs of cyclopentenones, however, the situation is apparently less straightforward; see, for example, T. H. Koch and R. J. Sluski, *Tetrahedron Lett.*, 2391 (1970).

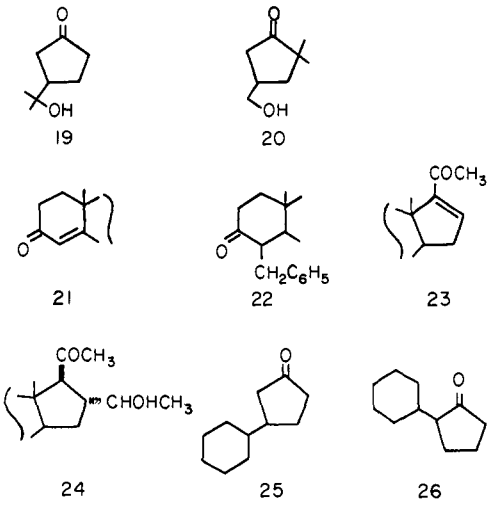
(21) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

(22) R. L. Cargill and A. B. Sears, *J. Amer. Chem. Soc.*, **92**, 6084 (1970).

(23) M. Pfau, R. Dulou, and M. Vilkhs, *C. R. Acad. Sci. Paris*, **254**, 1817 (1962).

(24) (a) D. Beluš, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969); (b) I. A. Williams and P. Bladon, *Tetrahedron Lett.*, 257 (1964).

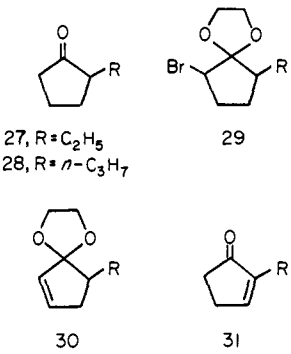
of uncertainties led us to the synthesis of **20** as mentioned above.

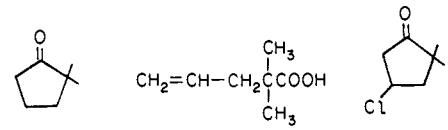


It is now clear, however, that there is no cyclopentenone triplet low enough to be sensitized by benzophenone, and that the first triplet of cyclopentenone and its simple derivatives has an energy of 73–74 kcal/mol.[5,25] The formation of **19** and **20** is most simply viewed as a reaction of ground-state ketone with radicals derived from solvent through hydrogen abstraction[26] by triplet benzophenone, the pathway originally suggested by Pfau.[23] Radical additions to α,β-unsaturated ketones are known[27] to occur preferentially at the β position.

Preparative Experiments. Apart from low-yield syntheses of the methyl[28] and hexyl[29] compounds, C-5-monoalkylated cyclopentenones are unknown. Our preparation of the 5-ethyl and 5-propyl ketones (**1b** and **1c**) is convenient and proceeds from the readily available[30] cyclopentanones **27** and **28**. Treatment of these precursors with bromine in dry ethylene glycol following the carefully developed procedure of Garbisch,[31] resulted in bromination largely at the methylene group and concomitant formation of the ethylene ketal. This intermediate (**29**) underwent smooth dehydrobromination[31] in strong hot base to yield unsaturated ketal **30**. Mild hydrolysis with aqueous oxalic acid freed the carbonyl group and provided **1b** and **1c** in about 40% overall yield. Small amounts (2–4%) of the isomeric 2-alkyl ketones (**31**) were obtained as side products.

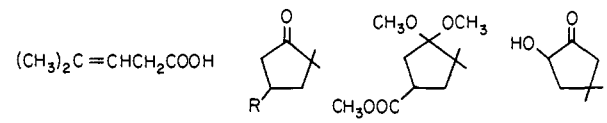
We have prepared the α-disubstituted ketone **1a** by two routes.[32] The first involved application to 2,2-dimethylcyclopentanone (**32**) of the bromination–dehydrobromination sequence[31] used above. Preparation[33] of **32** was sufficiently tedious, however, to render this route unsatisfactory. A more palatable alternative employed 2,2-dimethyl-4-pentenoic acid (**33**), available[34] upon allylation of lithium α-lithioisobutyrate. This acid was converted to its acyl chloride and then cyclized to **1a** in a Friedel–Crafts reaction. Some of the related β-chloro ketone (**34**) accompanied the cyclopentenone.





Turning to preparation of photoproducts, we reached the cyclopropane acetate **4a** in two steps from pyroterebic acid **35**.[35] Esterification using ethereal diazomethane and then Simmons–Smith reaction[36] with methylene iodide gave **4a** without difficulty.[37] The parent ester **4e** was similarly available from methyl vinylacetate.

Ketone **1a** served as starting material for independent synthesis of the methanol adduct **20**. Treatment of **1a** with excess diethylaluminum cyanide[38] in benzene led to quantitative Michael addition of hydrogen cyanide. The product **36** was hydrolyzed in strong base to the keto carboxylic acid **37**,[39] with protection of the ketone carbonyl as the ethylene ketal during the reaction. Acid **37** was converted to the ketal ester **38** with methyl orthoformate and then reduced with lithium aluminum hydride. Brief treatment of the product with aqueous acid furnished the desired hydroxy ketone **20**.



The *tert*-butyl ether **13** was prepared by acid-catalyzed addition[40] of isobutylene to the corresponding acyloin **39**.[8]

(25) R. O. Loutfy and P. de Mayo, *Chem. Commun.*, 1040 (1970).
(26) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem. Soc.*, **83**, 2795 (1961).
(27) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 275–276, and references cited therein.
(28) M. Mousseron, R. Richaud, and R. Granger, *Bull. Soc. Chim. Fr.*, 625 (1946).
(29) P. A. Plattner and A. St. Pfau, *Helv. Chim. Acta*, **20**, 1474 (1937); R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *J. Amer. Chem. Soc.*, **70**, 1379 (1948).
(30) R. Mayer in "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press, New York, N. Y., p 101.
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(37) Independent related syntheses in this series are given by M. J. Jorgenson, *Chem. Commun.*, 137 (1965), and J. W. Wilson and V. S. Stubblefield, *J. Amer. Chem. Soc.*, **90**, 3423 (1968).
(38) W. Nagata and M. Yoshioka, *Tetrahedron Lett.*, 1913 (1966).
(39) An earlier synthesis of this acid is given by J. C. Bardhan, S. K. Banerji, and M. K. Bose, *J. Chem. Soc.*, 1127 (1935).
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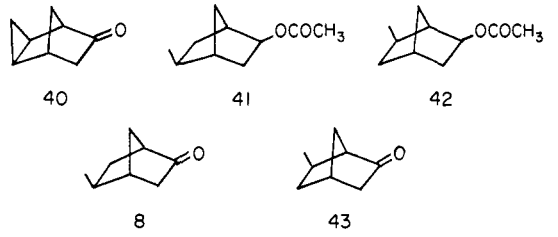
The norcamphor derivative **8** was synthesized from the known[41] tricyclic ketone **40**. Catalytic hydrogenation of **40** over platinum in acetic acid led to cleavage of the cyclopropane and concomitant reduction of the carbonyl group. The resulting mixture was acetylated and the esters **41** and **42** then separated with some difficulty by vpc. Each acetate was saponified, and the resulting alcohols were directly oxidized to give *exo*-5-methyl-2-norbornanone (**8**) and *exo*-6-methyl-2-norbornanone (**43**).



40 41 42

8 43

In closing we note that the qualitative observations reported here open, in their usual way, a variety of mechanistic problems. We have found, for example, that the rearrangement leading to cyclopropylketenes (**3**) can be sensitized by propiophenone ($E_T \sim 74.6$ kcal/mol[42]) and quenched in part by 2,3-dimethyl-1,3-butadiene ($E_T \sim 60$ kcal/mol[43]). The mechanistic significance of these experiments remains unclear, however. Singlet–triplet splitting in simple cyclopentenones is apparently quite small ($E_S \sim 75$ kcal/mol,[5,44] $E_T \sim 73$–74 kcal/mol[5,25]), and the importance of thermal population of the excited singlet state from the triplet will require specific consideration. The complications introduced into benzophenone photochemistry by a parallel situation there already have received attention.[45] At this more physical level satisfactory understanding of the photochemistry of cyclopentenones must await further experimentation.

Experimental Section

Materials and Equipment. Solvents for photochemical experiments were Matheson Coleman and Bell pentane (98%) and *tert*-butyl alcohol (chromatoquality) and Merck methanol (anhydrous reagent). All vpc was done using a Varian Aerograph Model 700 Autoprep or Model A-90-P3 with one of the following columns: A, 30% QF-1, 10 ft × 3/8 in.; B, 30% Carbowax, 10 ft × 3/8 in.; C, 30% SE-30, 20 ft × 1/4 in.; D, 30% PDEAS, 10 ft × 3/8 in.; E, 30% QF-1, 50 ft × 1/4 in. The column oven was operated at 90–190°, and helium carrier gas flow rate was 100–120 ml/min. Unless otherwise noted both ir and nmr spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 237B spectrophotometer and the latter on a Varian Model A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Ultraviolet spectra were obtained for solutions in 95% ethanol using a Cary Model 14 PM spectrophotometer. Melting points are corrected.

Photochemical experiments were carried out with a Hanovia Model L mercury lamp (no. 679A-36) in a quartz immersion well using either Pyrex 7740 or uranium glass (Corning no. 3320) as filter.

General Procedure for Irradiations. A solution of the cyclopentenone (0.25–1 mg/ml) in pentane, methanol, or *tert*-butyl alcohol was flushed with dry nitrogen for 15–30 min and then irradiated for the stated time at about 15° under nitrogen and with magnetic stirring. Pentane photolyses were monitered by ir using 1.0 mm cells. At the end of the irradiation period 1 ml of methanol was added, and the solution was stirred for several hours, after which the ir spectrum was redetermined. Photolyses in alcohol solvents were worked up by addition of water and extraction with pentane, which was then washed with brine and dried over sodium sulfate. Careful removal of pentane through a long Vigreux column left the product as an oil, which was then analyzed and purified by vpc.

Photolysis of 5,5-Dimethyl-2-cyclopentenone (1a). A solution of 199 mg of **1a** in 170 ml of pentane was irradiated through Pyrex for 3 hr, after which its ir spectrum showed absorption at 2110 cm^{-1} (m). Addition of 122 mg of methanol (2.1 equiv based on **1a**) caused slow replacement of this band by new absorption at 1750 cm^{-1} (s). An aliquot of the resulting solution was examined by vpc and found to contain ester **4a**, aldehyde **7a**, and unreacted **1a** in the ratio 5.2:1.7:1. Calibrated vpc measurements indicated a 63% yield of **4a**. Preparative vpc gave 71 mg of **4a**, which was shown by ir, nmr, mass spectrum, and vpc retention time to be identical with authentic **4a**. Aldehyde **7a** was purified by vpc on column D and shown to be identical with an authentic sample[13] by ir, nmr, and vpc retention time: nmr (220 MHz) δ 1.88 (s, 6 H), 5.90 (dd, J_{12} = 8 Hz, J_{23} = 15 Hz, 1 H), 6.04 (m, 1 H), 7.27 (dd, J_{23},J_{34} = 11 Hz, 1 H), 9.45 (d, J_{12} = 8 Hz, 1 H).

When a solution of 67 mg of **1a** in 60 ml of methanol was irradiated through Pyrex for 3 hr, **4a** was formed in 63% yield, just as in pentane.

A solution of 68 mg of **1a** and 402 mg of benzophenone (recrystallized, mp 48.0–49.5°) in 65 ml of methanol was irradiated for 3 hr. After 75% of the solvent was removed through a Vigreux column, a solid (benzophenone reduction products) precipitated and was filtered off and discarded. Removal of the remaining solvent and flash distillation (190° (20 mm)) gave an oil which was purified by vpc on column C. This product was shown to be identical with authentic **20** by comparison of ir and nmr spectra.

Photolysis of 5-Ethyl-2-cyclopentenone (1b). Irradiation of a solution of 188 mg of **1b** in 200 ml of *tert*-butyl alcohol through Pyrex for 3 hr followed by work-up gave 180 mg of a light yellow oil. Vpc on column B indicated a 1:1 mixture of *tert*-butyl esters **4b** and **5b** with almost complete destruction of **1b**. For the first eluted of these esters, **4b** or **5b**, the following characteristics were observed: ir 3045 (w), 2960–2945 (w), 2920 (w), 2860 (w), 1737 (s), 1140 (w) cm^{-1}; nmr (220 MHz) δ 0.26 (m, 2 H), 0.49 (broad m, 1 H), 0.73 (broad m, 1 H), 0.98 (t, J = 7 Hz, 3 H), 1.27 (broad m, 2 H), 1.45 (s, 9 H), 1.96 (m, 1 H), 2.20 (m, 1 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.62; H, 11.02.

For the second eluted ester, **5b** or **4b**, the following characteristics were observed: ir 3050 (w), 2965–2950 (w), 2920 (w), 2860 (w), 1737 (s), 1140 (s) cm^{-1}; nmr (220 MHz) δ −0.22 (m, 1 H) [0.68 (m), 0.99 (t, J = 8 Hz), 1.30 (broad m), 1.44 (s)] 17 H, 2.15 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.48; H, 10.98.

When **1b** was irradiated in methanol through Pyrex or in pentane through uranium glass, one component of the photolysate was 2-ethylcyclopentanone, as shown by comparison of ir, nmr, and vpc retention time with authentic material. Careful examination of the vpc data from photolysis in *tert*-butyl alcohol, methanol, or pentane, including co-injection of authentic material, indicated that no norcamphor (<1%) was formed in these photolyses.

Photolysis of 5-Propyl-2-cyclopentenone (1c). A solution of 408 mg of **1c** in 400 ml of *tert*-butyl alcohol was irradiated through uranium glass for 6 hr. Work-up gave 393 mg, vpc analysis of which on columns B and C indicated the presence of four monomeric products in the ratio 2.7:1.7:4.1:1.0. The data below are given in order of elution of these products from column B under analytical conditions.

The first two products were the diastereomeric 2-propylcyclopropane acetic acid *tert*-butyl esters **4c** and **5c**. For the first, the following was observed: ir 3050 (w), 2950 (s), 2925 (m), 2865 (m), 1740 (s), 1140 (s) cm^{-1}; nmr (220 MHz) δ 0.25 (m, 1 H), 0.44–1.44, 0.95 (broad m, t, 5 H), 1.44 (s, 9 H), 1.71–2.43 (broad m, 7 H).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.82; H, 11.23.

For the second ester, the following characteristics were observed:

(41) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 30, 2278 (1965).

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ir 3050 (w), 2970 (m), 2955 (m), 2920 (m), 2860 (w), 1738 (s), 1142 (s) cm^{-1}; nmr (220 MHz) δ −0.22 (m, 1 H), 0.57–1.44, 0.95, 1.44 (broad m, t, J = 7 Hz, s, 19 H), 2.15 (d, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.81; H, 11.22

Fraction three was **5**-*exo*-methylbicyclo[2.2.1]heptan-2-one (**8**): ir 2950 (m), 2900 (m), 2870 (m), 1755 (s), 1400 (m), 1150 (m), 1040 (m) cm^{-1}; nmr (220 MHz) δ 0.81–1.51, 1.08 (broad m, d, J = 7 Hz, 4 H), 1.51–2.22 (m, 6 H), 2.29 (m, 1 H), 2.49 (m, 1 H); nmr (^{13}C)[46] (parts per million upfield from CS_2, in dioxan-C_6F_6) −21.9, 142.3, 147.7, 150.5, 158.0, 158.9, 159.4, 171.1; mass spectrum *m/e* 124.08868 (M^+, calcd for $C_8H_{12}O$: 124.08881).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.41; H, 9.96.

The 2,4-dinitrophenylhydrazone of **8** was prepared, mp 130–134°, from methanol; mass spectrum *m/e* 304.1185 (M^+, calcd for $C_{14}H_{16}N_4O_4$: 304.1171).

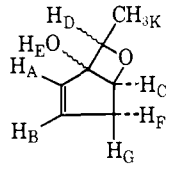
The fourth component, 7-methylbicyclo[3.2.0]hept-2-en-1-ol (**11**), was found to be quite unstable: ir 3610 (m), 3550 (broad, w), 3040 (m), 2960 (s), 2920 (s), 2905 (m), 2860 (m), 2835 (m), 1608 (w) cm^{-1}; nmr (220 MHz) δ 1.09–1.36, 1.16 (m, d, J = 7 Hz, 5 H), 1.57 (m, 1 H), 2.04 (m, 1 H), 2.32 (m, 1 H), 2.60 (m, 2 H), 5.62 (broad, 1 H), 5.82 (broad, 1 H), plus a small signal due to impurity, 3.36 (m); mass spectrum *m/e* 124.08832 (M^+, calcd for $C_8H_{12}O$: 124.08881).

Photolysis of 5-Ethoxy-2-cyclopentenone (1d). A solution of 190 mg of **1d**[7] in 200 ml of pentane was irradiated through Pyrex glass for 2 hr, after which the ir spectrum of an aliquot showed absorption at 2110 cm^{-1}. Addition of 1 ml of methanol caused disappearance of this band. Work-up gave 182 mg, vpc analysis of which on columns A and D indicated the presence of six monomeric products in the ratio 2.5:1.0:18:11:4.9:6.5. The data below are given in order of the elution of these products from column A under analytical conditions.

The first product was shown to be 2-cyclopentenone by comparison of its ir spectrum and vpc retention time with those of an authentic sample.

The second component was presumed to be **7d** from its ir spectrum: 3090 (w), 2970 (m), 2920 (m), 2810 (w), 2710 (w), 1728 (s), 1615 (s) cm^{-1}; it was not further characterized.

The third component was 7-methyl-6-oxabicyclo[3.2.0]hept-2-en-1-ol (**12**): ir 3610 (m), 3380 (broad, m), 3060 (w), 2970 (m), 2930 (m), 1610 (w), 1138 (s) cm^{-1}; nmr (220 MHz) δ 1.38 (d, J_{DH} = 7 Hz, 3 H, H_K), 2.39 (m, J_{FG} = 18 Hz, $J \sim 2$ Hz, 1 H, H_F), 2.64 (m, J_{FG} = 18 Hz, $J \sim 4$ Hz, 1 H, H_G), 3.00 (broad s, 1 H, H_E), 4.49 (q, J_{DH} = 7 Hz, 1 H, H_D), 4.87 (d, J_{CG} = 5 Hz, 1 H, H_C), 5.70 (m, 1 H, H_A or H_B), 5.97 (m, 1 H, H_B or H_A); mass spectrum *m/e* 126.0685 (M^+, calcd for $C_7H_{10}O_2$: 126.0681).



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Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.78; H, 8.07.

The fourth product was *cis*-2-ethoxycyclopropaneacetic acid methyl ester (**4d**): ir 3070 (w), 2970 (m), 1742 (s), 1180 (m), 1140 (s) cm^{-1}; nmr (220 MHz) δ 0.23 (m, 1 H), 0.67 (m, 1 H), 1.05, 1.15 (m, s, 4 H), 2.35 (t, J = 7 Hz, 2 H), 3.20 (m, $w_{1/2}$ = 18 Hz, 1 H, H_A), 3.46, 3.64 (q, J = 7 Hz, s, 5 H).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.74; H, 8.90.

The fifth component was *trans*-2-ethoxycyclopropaneacetic acid methyl ester (**5d**): ir 3075 (w), 2970 (m), 2945 (m), 2865 (w), 1746 (s), 1140 (m) cm^{-1}; nmr (220 MHz) δ 0.29 (m, 1 H) 0.76 (m, 1 H), 1.12 (t, J = 8 Hz, m, 4 H), 1.98 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 1 H), 2.20 (dd, J_1 = 16 Hz, J_2 = 7 Hz, 1 H), 2.93 (m, $w_{1/2}$ = 14 Hz, 1 H, H_A), 3.46 (q, 2 H), 3.64 (s, 3 H).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.86; H, 8.83.

The final component was 3-*exo*-methyl-2-oxabicyclo[2.2.1]-heptan-6-one (**9**): ir 2975 (m), 2910 (w), 1770 (s), 1036 (m), 937 (m), 837 (m) cm^{-1}; nmr (220 MHz), see Table II; mass spectrum *m/e* 126.0692 (M^+, calcd for $C_7H_{10}O_2$: 126.0681).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.83; H, 8.14.

Photolysis of 2-Cyclopentenone (1e). A solution of 509 mg of **1e** (freshly distilled and >99.5% pure by vpc) in 2000 ml of pentane was irradiated through Pyrex for 3 hr. After treatment with methanol, vpc analysis of the photolysis mixture on column D indicated the presence of at least 17 components. Coinjection of this mixture with **4e** produced a new peak eluted at a retention time different from any of these.

Photolysis of 4,4-Dimethyl-2-cyclopentenone (2). A solution of 500 mg of **2**[8] in 2000 ml of *tert*-butyl alcohol was irradiated through uranium glass for 36 hr. Work-up and vpc on column B showed at least six components in the ratio 3.2:1.0:6.8:9.4:3.9:12.3. The first component was 3,3-dimethylcyclopentanone, as shown by comparison of ir and vpc retention time with authentic material.[47] The second component was unreacted **2**. Components 3, 5, and 6 were assumed to be dimeric, since each contained signals for four methyl groups in its nmr spectrum. Component 4 was shown to be **13** by comparison of ir and nmr spectra with authentic **13**, prepared as described below, mp 56–57°.

5,5-Dimethyl-2-cyclopentenone (1a). A. From 2,2-Dimethylcyclopentanone (32). On a 6.0-g scale ketone **32**[33] was brominated and dehydrobrominated and the ketal was hydrolyzed following closely the procedure of Garbisch.[31] At the bromoketal stage 11.65 g (92%) was obtained. This gave 7.96 g of unsaturated ketal which was hydrolyzed as needed to **1a**, spectroscopic properties identical with those of the material prepared by route B below.

B. From 2,2-Dimethyl-4-pentenoic Acid (33). A mixture of 10.0 g of acid **33**[34] and 12 ml of thionyl chloride was heated at 100° for 1 hr and then excess thionyl chloride was removed *in vacuo*. The crude acyl chloride in 50 ml of CS_2 was added dropwise to 11.0 g of $AlCl_3$ in 50 ml of CS_2. This mixture was stirred at reflux for 2.5 hr, poured onto ice, and then extracted into ether. This was washed with aqueous $NaHCO_3$, water, and brine, and then dried. Removal of solvent and distillation gave 4.08 g of **1a** (bp 90° (70 mm)) and 3.49 g of 4-chloro-2,2-dimethylcyclopentanone (**34**, bp 100° (20 mm)). Both compounds were purified by preparative vpc. Spectroscopic properties of **1a**: ir 2960 (m), 1712 (s), 1587 (m), and 1115 (m) cm^{-1}; nmr (60 MHz) δ 1.05 (s, 6 H), 2.51 (t, 2 H), 6.08 (dt, 1 H) 7.50 (dt, 1 H); uv (ethanol) λ_{max} 217 (9250), 316 nm (44).

Anal. Calcd for $C_7H_{10}O$: C, 76.38; H, 9.26. Found: C, 76.32; H, 9.15.

A 2,4-dinitrophenylhydrazone was prepared: mp 176–178° (lit.[32] mp 172–173°).

Purified **34** showed the following properties: ir 1755 cm^{-1}; nmr (220 MHz) δ 1.05, 1.07 (s, s, 6 H), 2.18 (m, 2 H) 2.45 (m, 2 H), 4.10 (m, 1 H). By double resonance the signal at 4.10 ppm was shown to be coupled to both the 2.18- and the 2.45-ppm signals.

Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found: C, 57.30; H, 7.59.

5-Ethyl-2-cyclopentenone (1b). On a 10.0-g scale 2-ethylcyclopentanone[30] was brominated and dehydrobrominated following the procedure of Garbisch.[31] At the bromoketal stage 17.78 g (85%) was obtained. It was important to keep this material cold before addition of methanolic NaOH to prevent spontaneous dehydrobromination; the HBr thus formed in the absence of neutralizing base promoted rapid resinification. Dehydrobromination gave 9.64 g of unsaturated ketal, which was directly dissolved in 130 ml of ether and hydrolyzed by stirring at room temperature for 5 hr with 60 ml of saturated aqueous oxalic acid. From this was recovered a brown oil which on distillation (bp 90–100° (40 mm)) yielded 4.00 g of colorless oil. This was further purified by vpc: yield 39%; ir 1715 (s), 1588 (w), 1338 (m) cm^{-1}; nmr (220 MHz) δ 0.95 (t, J = 7 Hz, 3 H), 1.41 (m, 1 H), 1.82 (m, 1 H), 2.27 (m, 2 H), 2.87 (m, 1 H), 6.09 (m, 1 H), 7.57 (m, 1 H).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.16; H, 9.10.

(46) This nmr (^{13}C) spectrum is in quite good agreement with that recently published for 8 by J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970). In addition we have directly compared the ir spectrum of 8 with that of authentic 5-*endo*-methyl-2-norbornanone (J. A. Berson, A. W. McRowe, R. G. Bergman, and D. Houston, *ibid.*, **89**, 2563 (1967)) and found them to be significantly different. The spectrum of the authentic ketone was kindly furnished by Professor Jerome A. Berson.

(47) The authentic ketone was prepared by Mr. William W. Lowrance, Jr., following the procedure of H. Pines, F. J. Pavlik, and V. N. Ipatieff *ibid.*, **73**, 5738 (1951).

5-Propyl-2-cyclopentenone (1c). This compound was prepared from 2-propylcyclopentanone[30] just as **1b** above: yield 41%; ir 1713 (s), 1587 (w), 1335 (m) cm^{-1}; nmr (220 MHz) δ 0.95 (t, J = 7.5 Hz, 3 H), 1.36 (m, 3 H), 1.75 (m, 1 H), 2.27 (m, 2 H), 2.87 (m, 1 H), 6.20 (m, 1 H), 7.72 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.54; H, 9.81.

2,2-Dimethylcyclopropaneacetic Acid Methyl Ester (4a). Using ethereal diazomethane, 1.14 g of pyroterebic acid (**35**)[35] was esterified, and the resulting crude product was added to a solution of 2.67 g of methylene iodide, 0.65 g of zinc–copper couple, and a crystal of iodine in 3.1 ml of ether.[36] After 35-hr reflux the reaction was worked up to give 1.07 g of oil which by vpc was a mixture of methyl pyroterebate and **4a**. The latter was collected and purified by preparative vpc: ir 2945 (m), 1748 (s), 1180 (m), 1165 (s) cm^{-1}; nmr (60 MHz) δ 0.27–1.04, 1.03, 1.08 (m, s, s, 9 H), 2.24 (d, J = 7 Hz, 2 H), 3.63 (s, 3 H); mass spectrum m/e 142.10013 (M^+, calcd for $C_8H_{14}O_2$: 142.09937).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.46; H, 10.20.

Cyclopropaneacetic Acid Methyl Ester (4e). This ester was prepared as **4a** above using vinylacetic acid in place of **35**. A sample was purified by preparative vpc: ir 1748 (s) cm^{-1}; nmr (60 MHz) δ 0.03–1.33 (m, 5 H), 2.17 (d, J = 7 Hz, 2 H), 3.67 (s, 3 H).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.15; H, 8.89.

3,3-Dimethyl-4-oxocyclopentanecarbonitrile (36). A solution of 267 mg of **1a** in 5 ml of dry benzene was cooled to 0°, and approximately 4 equiv of diethylaluminum cyanide[38] in 8 ml of benzene was added over a period of 15 min. After being stirred for 3.25 hr with warming to room temperature, this mixture was poured into 0.0125 M NaOH aqueous and extracted with ether. The ether extract was washed with water and brine and dried. Removal of ether left 334 mg (100%) of thick oil. Vpc on column A yielded an analytical sample: mp 42–43°; ir 2970 (m), 2925 (w), 2870 (w), 2240 (w), 1755 (s), 1465 (m), 1455 (sh), 1410 (w), 1370 (w), 1325 (w), 1215 (w), 1100 (m), 1070 (w) cm^{-1}.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.91; H, 8.18; N, 10.16.

3,3-Dimethyl-4-oxocyclopentanecarboxylic Acid (37). A solution of 54 mg of **36** in 10 ml of dry benzene, 30 μl of dry ethylene glycol, and several crystals of p-toluenesulfonic acid was heated at reflux, and water was removed with a Dean-Stark trap. After 72 hr the solution was poured into saturated aqueous $NaHCO_3$ and extracted with ether. The ether was washed with water and brine and dried. The crude ketal nitrile was dissolved in 2 ml of 1.2 M aqueous NaOH and 0.5 ml of methanol, and the solution was heated at reflux for 45 hr and then partitioned between water and ether. The water layer was then acidified and the product extracted into ether, which was washed and dried. Removal of solvent left 13 mg of oil which crystallized. Recrystallization twice from cyclohexane gave an analytical sample: mp 96–98° (lit.[39] mp 93°); ir 3500–2400 (broad, m), 1740 (s), 1712 (s) cm^{-1}.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.39; H, 7.72.

3,3-Dimethyl-4-oxocyclopentanemethanol (20). A solution of 23 mg of acid **37** in 1 ml of dry methanol and 2 ml of methyl orthoformate was treated under nitrogen with two drops of acetyl chloride and then allowed to stand at room temperature for 86 hr. It was then poured into pentane containing excess solid anhydrous Na_2CO_3 and allowed to stand overnight. Removal of the solid and then evaporation of the pentane left an oil which was dissolved in 2 ml of ether and added dropwise under nitrogen to 8.2 mg of $LiAlH_4$ in 2 ml of ether. This mixture was stirred at room temperature for 8 hr and then ethyl acetate was added to destroy excess hydride. The reaction was worked up[48] to give **20** as an oil (100%) which was purified by vpc on column B: ir 3640 (w), 3460 (broad, m), 2955 (m), 1740 (s), 1070 (m), 1030 (m) cm^{-1}; nmr (220 MHz) δ 1.01, 1.05 (s, s, 6 H), 1.53 (m, 1 H), 1.95 (m, 2 H), 2.39 (m, 2 H), 3.00 (broad s, 1 H), 3.58 (m, 2 H); mass spectrum m/e 142.0992 (M^+, calcd for $C_8H_{14}O_2$: 142.0994).

2-*tert*-Butoxy-4,4-dimethylcyclopentanone (13). In 10 ml of CH_2Cl_2 was dissolved 262 mg of acyloin **39**,[8] and 100 μl of phosphoric acid–boron trifluoride complex was added. Then at −20° 20 ml of isobutylene was condensed into the mixture, which was then placed on a Parr shaker and allowed to warm to room temperature.[40] After 1 hr the mixture was poured into 2 M ammonium chloride and the product was extracted into CH_2Cl_2, which was then dried. Removal of the solvent yielded 388 mg of an oil which was chromatographed on grade II neutral alumina. After elution of hydrocarbon oligomers with 200 ml of pentane, ether caused elution of 148 mg of **13** as a white solid which was further purified on column B: mp 57–57.5°; ir 2970 (sh), 2960 (s), 2925 (m), 2890 (m), 1760 (s), 1460 (m), 1380 (m), 1365 (m), 1360 (sh), 1183 (m), 1105 (m), 1075 (m) cm^{-1}; nmr (220 MHz) δ 1.07 (s, 3 H), 1.16 (s, 12 H), 1.62 (dd, J_1 = 14 Hz, J_2 = 7 Hz, 1 H), 1.96–2.08 and 2.00 (m, s, 3 H), 3.88 (t_{app}, $J_1 = J_2$ = 7 Hz, 1 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.80; H, 10.98.

Treatment[40] of 63 mg of ether **13** with 1 ml of trifluoroacetic acid for 10 min at room temperature, followed by neutralization with saturated aqueous $NaHCO_3$ and extraction into ether, gave 32 mg (73%) of an oil, which after purification on column E was shown to be **39** by comparison of ir spectrum and vpc retention time with those of authentic material.

Dehydration of 4,4-Dimethyl-2-hydroxycyclopentanone (39). The procedure of Rouse and Tyler[8] gave 5.90 g of oil, bp 82–90° (45 mm), from 8.13 g of **39** in hot polyphosphoric acid. An aliquot of this oil was examined by vpc on column C and found to consist of 4,4-dimethyl-2-cyclopentenone (**2**) (retention time 6.5 min) and a second product (12.5 min) in the ratio 4:1. Each was purified by preparative vpc. Compound **2** gave the following spectra: ir 2960 (m), 1720 (s), and 1580 (w) cm^{-1}; nmr (60 MHz) δ 1.25 (s, 6 H), 2.14 (s, 2 H), 5.92 (d, J = 6 Hz, 1 H), 7.36 (d, J = 6 Hz, 1 H); 2,4-dinitrophenylhydrazone of **2**, mp 168–169° from methanol (lit.[49] mp 163–164°). The second product was identified as 2,3-dimethyl-2-cyclopentenone by the following characteristics: ir 1708 (s), 1660 (m), 1625 (s) cm^{-1}; nmr (60 MHz) δ 1.63 (m, 3 H), 2.03 (broad s, 3 H), 1.88–2.75 (m, 4 H) (both ir and nmr are in accord with published[50] values); 2,4-dinitrophenylhydrazone, mp 227.5–229° (lit.[51] mp 226–227°); oxime, mp 120.5–121.5° (lit.[51] 120.5°).

Synthesis of *exo*-Bicyclo[3.2.1.0^{2,4}]octan-6-one (40). Jones oxidation[52] of 5-norbornen-2-ol followed by Simmons–Smith reaction[36] yielded **40**,[41] which was purified on column A: ir 3070 (w), 3010 (w), 2960 (w), 2910 (w), 1752 (s), 1310 (m), 1135 (m) cm^{-1}; 2,4-dinitrophenylhydrazone, mp 175–178° from methanol (lit.[41] mp 170–173° dec).

Synthesis of *exo*-5- and *exo*-6-Methylbicyclo[2.2.1]heptan-2-ones (8 and 43). A solution of 491 mg of **40** and 200 mg of platinum oxide in 5 ml of glacial acetic acid was hydrogenated at a pressure of 50 lb/in.^{2} for 10 hr. Two subsequent additions of 100 mg of platinum oxide and further hydrogenation, each time for 5 hr, led to complete reduction. The catalyst was then filtered and water added. The solution was extracted five times with ether and the combined ether extracts were washed with water, aqueous $NaHCO_3$, and water, and dried. Removal of ether yielded 463 mg of oil, which was acetylated with acetic anhydride–pyridine (1:1) for 30 hr at 4°. Isolation of the mixture of acetates, followed by vpc on column E, yielded acetates **42** and **41** (order of elution) in the ratio 2:1. Hydrolysis of each acetate in a 1:1 mixture of methanol and 15% aqueous NaOH for 24 hr at room temperature, followed by Jones oxidation[52] at 0°, gave ketones **43** and **8**, respectively.

Ketone **43** was purified on column B: ir 2980 (s), 2965 (sh), 2865 (m), 1750 (vs), 1405 (m), 1155 (m) cm^{-1}; nmr (220 MHz) δ 1.04 (d, J = 7 Hz, 3 H), 1.11–1.38 (m, 1 H), 1.52–2.08 (m, 6 H), 2.18 (broad s, $w_{1/2}$ = 5 Hz, 1 H), 2.61 (broad, $w_{1/2}$ = 10 Hz, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.45; H, 9.73.

The 2,4-dinitrophenylhydrazone of **43** was prepared: mp 160–162° from methanol; mass spectrum m/e 304.1174 (M^+, calcd for $C_{14}H_{16}N_4O_4$: 304.1171).

Ketone **8** as prepared here had ir and nmr spectra identical with those of **8** obtained from photolysis of **1c**, with the exception that the nmr spectrum of the synthetic sample showed it to be contaminated with approximately 5% of **43**.

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Some Aspects of the Photochemical and Mass Spectral Behavior of Bridgehead Acetone Derivatives

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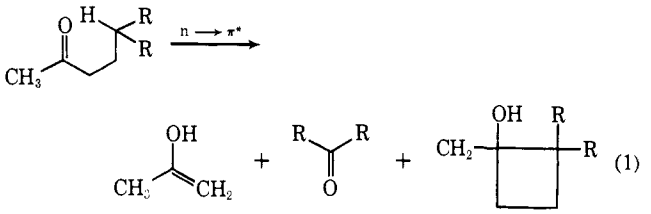
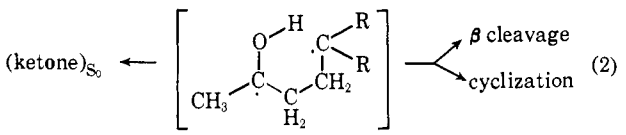
Abstract: The behavior of the following ketones was examined under conditions of irradiation with ultraviolet light ($\lambda > 260$ nm) and under electron impact in a mass spectrometer: 1-norbornylacetone (**2**), 1-bicyclo[2.2.2]-octenylacetone (**7**), 1-bicyclo[2.2.2]octylacetone (**12**), 1-bicyclo[3.3.1]nonylacetone (**17**), and 1-adamantylacetone (**18**). The principal irradiation products were the cyclobutanols derived from intramolecular hydrogen abstractions followed by cyclization. The most significant fragmentations in the mass spectrometer led to the formation of $M^+ - 58$ ions in contrast to the usual behavior of acetone derivatives. The differences between these systems and acyclic analogs are attributed to the strain associated with introduction of double bonds at bridgeheads.

The mechanism of the type II photoelimination reaction of aliphatic ketones has received considerable attention over the past few years.[1,2] It has been found that ketones having γ-hydrogen atoms undergo cleavage at the β bond with formation of an olefin and an enol, and, to a lesser extent, cyclobutanols (eq 1). These reactions are believed to involve biradical



(1)

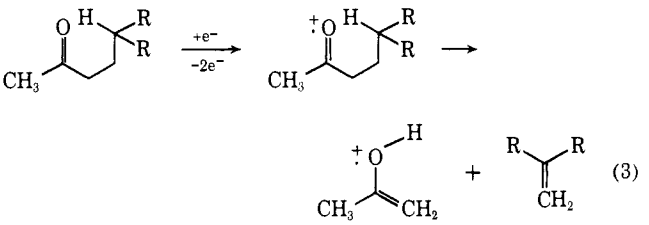
intermediates which may be formed by hydrogen abstraction by either singlet or triplet excited states of the carbonyl groups. The quantum efficiencies of these reactions have been rationalized in terms of the partitioning of these biradicals[2] (eq 2).



(2)

The objective of this research was directed toward enlarging our understanding of the scope of this reaction. Specifically, we sought to determine the structural factors which affect the relative efficiencies of the product-forming steps in eq 2. For this purpose, we chose to examine the photochemical behavior of the following ketones: 1-norbornylacetone (**2**), 1-bicyclo[2.2.2]octenylacetone (**7**), 1-bicyclo[2.2.2]octylacetone (**12**), 1-bicyclo[3.3.1]nonylacetone (**17**), and 1-adamantylacetone (**18**). The choice of these compounds was dictated by the expected gradation[3] in ease of formation of the different bridgehead olefins which could be formed as a result of type II eliminations. Cyclobutanol formation, on the other hand, was expected to be considerably less sensitive to the changes in the carbon skeletons.

As a sequel, a comparison of the photochemical results was to be made with the fragmentation processes induced by electron impact. In simple systems it has been noted that ketones having γ-hydrogen atoms undergo McLafferty cleavages (eq 3) in the mass spectrometer. Several investigators have commented[4] on these similarities and an approximate correlation between quantum yields of photoeliminations and efficiency of McLafferty cleavages has been noted. It was anticipated that information bearing on the generality of this correlation would be available from these studies. Furthermore, the scope of the McLafferty



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