Table I. ^{13}C Spin-Lattice Relaxation Times of $[RN(CH_3)_3]^+Br^-$ in Aqueous Solution at 34°

R	Concn, M	Type of solution	NT_1, sec[a] CH_3	CH_2	CH_2	$(CH_2)_k$	CH_2	CH_2	CH_2	$N(CH_3)_3$
n-Hexyl ($k = 0$)	1.0	Molecular	14.3	8.6	6.3		5.2	5.0	4.4	6.0
n-Octyl ($k = 2$)	0.2	Molecular[b]	12.9		7.8	4.7[c]		4.7	4.7	6.3
n-Octyl ($k = 2$)	2.0[d]	Spherical micelles	10.3	2.9	2.4	1.6[c]	1.0	1.0	0.90	2.6
n-Hexadecyl[e] ($k = 10$)	0.4[f]	Rod-shaped micelles	8.4		1.2			0.68	0.54	1.8

[a] N is the number of directly attached hydrogens. T_1 values are accurate to ±10%. Unless otherwise indicated, all NT_1 values are those of totally resolved carbon resonances. [b] Predominantly molecular. Several values of the critical micelle concentration in the range 0.1–0.3 M have been reported: P. Mukerjee and K. J. Mysels, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 36, 103 (1971). [c] Two-carbon resonance. [d] Critical micelle concentration is about 0.1–0.3 M (see footnote *b*). [e] At 41°. [f] Critical micelle concentration is about 10^{-3} M (see reference in footnote *b*).

methylene group upon micellation is comparable to that for transfer of a methylene group of an alkane from water to the pure hydrocarbon.[26] Second, the rotational correlation times for stable free radicals dissolved in micelles are only slightly longer than those for the same species in aqueous solution.[26-29] Third, tumbling rates for dyes dissolved in micelles as measured by depolarization of fluorescence are sufficiently rapid to accord with a liquid-like interior for the micelle.[30,31] Finally, differential ultraviolet spectroscopy of micelles formed from chromophoric surfactants suggests a fluid environment for the chromophoric group.[32]

It should be noted that our ^{13}C T_1 values are weighted averages of the T_1 values of unassociated and micellar species.

$$1/T_1 = x_f/T_{1f} + x_m/T_{1m} \quad (2)$$

Here T_1 is the measured ^{13}C T_1 value, T_{1f} and T_{1m} are the relaxation times of free and micellar molecules, respectively, and x_f and x_m are the corresponding mole fractions. Equation 2 is valid when exchange between the free and micellar environment is rapid with respect to $1/T_1$, a condition satisfied here.[33] As a result of the fact that rotational motion of free molecules is faster than that of those in a micellar environment

$$1/T_{1f} < 1/T_{1m} \quad (3)$$

Introduction of eq 3 into (2) yields

$$T_1 > T_{1m} \quad (4)$$

Thus, our observed T_1 values are upper limits to T_{1m}. Consequently, the actual shortening of T_1 at the polar end of the molecule when going from unassociated to micellar species is even greater than our numbers indicate. However, the difference between T_1 and T_{1m} is not expected to be great for the micellar systems we have studied, because x_f is approximately equal to the critical micelle concentration, and thus is much smaller than x_m[34] (Table I).

(24) G. Stainsby and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 587 (1950).
(25) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic, New York, N. Y., 1963, p 52.
(26) A. S. Waggoner, O. H. Griffith, and C. R. Christensen, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1198 (1967).
(27) J. Oakes, *Nature (London)*, **231**, 38 (1971).
(28) N. M. Atherton and S. J. Stach, *J. Chem. Soc., Faraday Trans. 2*, **68**, 374 (1972).
(29) G. P. Rabold, *J. Polymer Sci., Part A-1*, **7**, 1187 (1969).
(30) M. Shinitzky, A. C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, **11**, 2106 (1971).
(31) M. T. Flanagan and S. Ainsworth, *Biochim. Biophys. Acta*, **168**, 16 (1968).
(32) S. J. Rehfeld, *J. Colloid Interface Sci.*, **34**, 518 (1970).
(33) N. Muller in "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Press, New York, N. Y., 1973, Chapter 1.
(34) P. Mukerjee and K. J. Mysels, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **36**, 103 (1971).

Photochemical Rearrangements of α-Methylene Ketones

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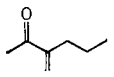
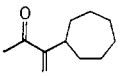
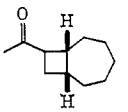
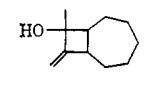
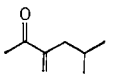
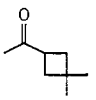
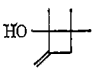
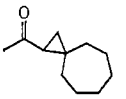
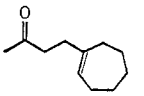
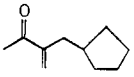
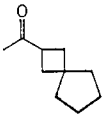
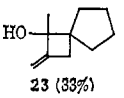
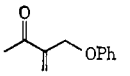
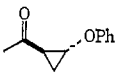
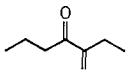
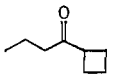
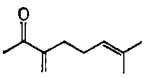
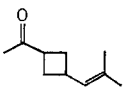
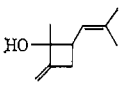
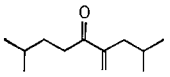
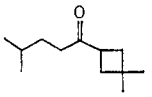
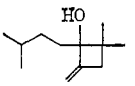
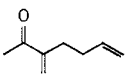
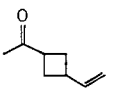
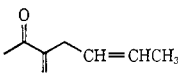
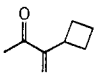
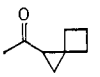
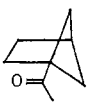
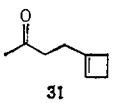
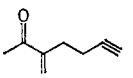
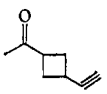
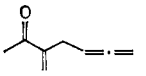
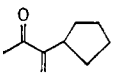
Abstract: Preparation and irradiation of 18 α-methylene ketones are described. The resulting products, which are summarized in Table I, are isomeric cyclobutyl ketones, cyclopropyl ketones, and 2-methylenecyclobutanols, formation of which may be explained by eq 1 and 2. In many cases the reaction leads from readily prepared substrates to useful yields of cyclobutyl ketones, including simple, bicyclic, and spirocyclic systems.

In this report we describe the preparation of a variety of open chain α-methylene ketones and identification of the products formed on their irradiation. The results, summarized in Table I and discussed in detail below,[1] can be accounted for by eq 1 and 2. The former involves generation of the familiar type II biradical[2] through carbonyl abstraction of γ hydrogen and sub-

(1) Two preliminary communications concerning portions of this work have appeared: W. L. Schreiber and W. C. Agosta, *J. Amer. Chem. Soc.*, **93**, 6292 (1971); R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 729 (1972). For photochemical α-cleavage reactions of α-methylene ketones, see D. L. Dean and H. Hart, *J. Amer. Chem. Soc.*, **94**, 687 (1972).

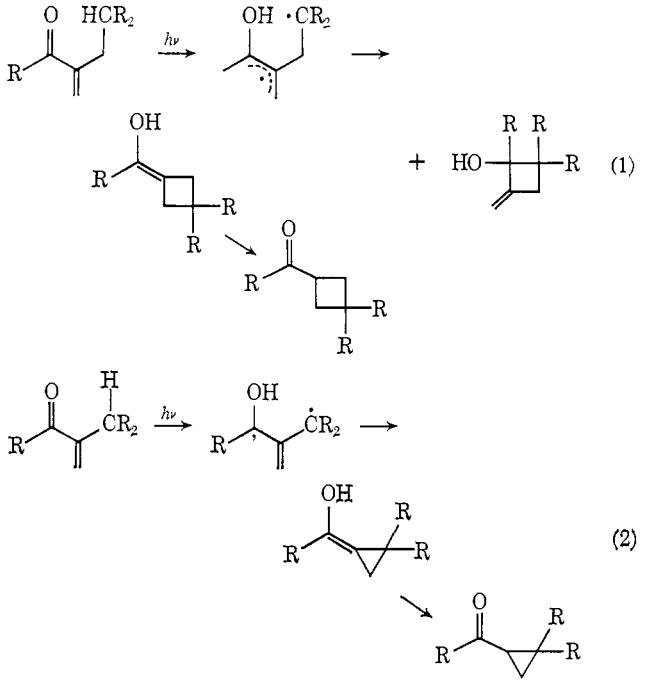
(2) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971), and references cited therein.

Table I. Products of Photolysis of α-Methylene Ketones

α-Methylene ketones	Products (% yield)	α-Methylene ketones	Products (% yield)
 1	 19 (37% trans, 24% cis)	 10	 37 (28% endo, 3% exo)  38 (10%, 2 isomers)
 2	 20 (68%)  21 (19%)		 39 (24%)  40
 3	 22 (51%)  23 (33%)	 11	 41 (17%)
 4	 24 (27%)	 12	 42 (24% trans, 26% cis)  43 (23%)
 5	 25 (67%)  26 (12%)	 13	 44 (12% trans, 15% cis)  45 (20%)
 6	 27 (2% trans, 21% cis)  28 (31%)		 46 (6%)  47 (17% trans, 10% cis)
 7	 29 (8% endo, 5% exo)  30 (8%)		 48 (8%)
	 31	 14	 49 (11% trans, 16% cis)  50 (22%)
 8	32 (12%) 33 (7%)	15	51 (57%)
	34 (34%) 35	16	52 (87%)
9	36 (58% endo, 6% exo)	17	Polymer
		18	Polymer

sequent closure of this species either on the carbon atom of the methylene group to yield a cyclobutyl ketone as its enol, or else on the carbonyl carbon to form a 2-methylenecyclobutanol. The alternative path shown in eq 2 requires transfer of β hydrogen to the oxygen atom and then closure to the enol of a cyclopropyl ketone. While cyclobutanols are common products of type II processes,[2] the isomerizations yielding cyclobutyl and cyclopropyl ketones have not been observed previously.

Preparation of α-Methylene Ketones. Several different methods were employed in preparing ketones



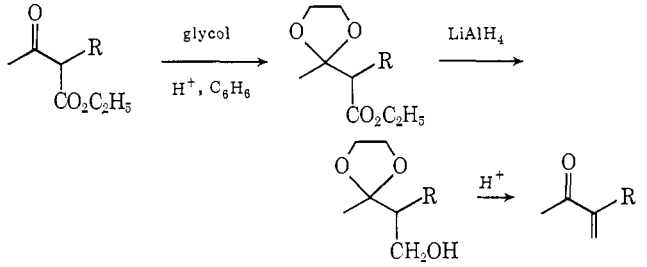
(1)

(2)

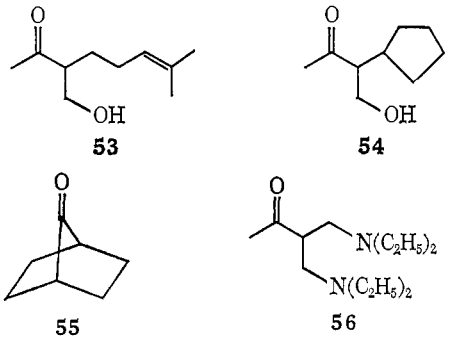
1–18. Most generally useful was the acid-catalyzed Mannich reaction[3] of formaldehyde, diethylamine or piperidine hydrochloride, and the appropriate saturated ketone, followed by thermal β elimination from the Mannich base. This served for synthesis of **1–5**, **13**, and **15–17**, of which **16**[4] had been previously prepared in this manner. Despite reports to the contrary,[5] it was our experience that this Mannich reaction did not lead to clean, high yield substitution at the methylene position of methyl ketones. In our hands these ketones frequently reacted indiscriminately at the methyl and the methylene positions to give mixtures of the two possible α-methylene derivatives as well as α,α'-dimethylene ketones (such as **15**).[6] Again contrary to report,[5] α-methylene ketones with branching at the β carbon, such as **6–10**, could not be prepared by this method, since only the isomeric α'-methylene compounds were formed. Quite similar difficulties already have been detailed by others.[7]

Ketones **6**, **9**, and **10** were prepared from alkylated acetoacetic esters as summarized in Scheme I below in which R is isopropyl, cyclohexyl, or cycloheptyl.

Scheme I



Alkylation, followed by ketalization, reduction with lithium aluminum hydride, and mild acid hydrolysis of the ketal led to the β-hydroxy ketone. This was dehydrated directly in hot benzene containing *p*-toluenesulfonic acid, giving the desired compound in acceptable yield. The method had been used earlier for **6**.[7] Modification of this sequence was necessary for **12** and **14** since the acidic conditions of the final β elimination led to reactions involving the distant double or triple bond. In these cases the unsaturated hydroxy ketone **53** or the related acetylene was treated with *p*-toluenesul-

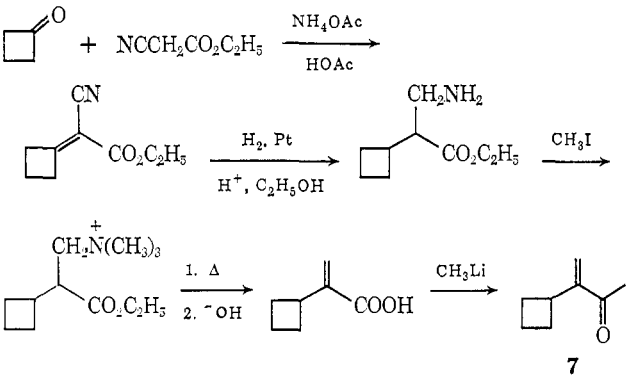


fonyl chloride in pyridine, first in the cold and then at elevated temperature. This permitted base-catalyzed elimination of tosylate and led to **12** and **14** without difficulty.

For **8** simple condensation of cyclopentylacetone[8] with formaldehyde in base gave **54**, which was dehydrated using *p*-toluenesulfonic acid in benzene as described above.

Another approach was developed for two cases (**7** and **18**) in which the above methods were inappropriate. This is illustrated for **7** in Scheme II and

Scheme II



involved initial condensation[9] of cyclobutanone with cyanoacetic ester. The resulting product[10] was hydrogenated in acidic ethanol to yield an amino ester. This was quaternized with methyl iodide, pyrolyzed, and saponified, giving the substituted acrylic acid. Reaction[11] of this acid with methyllithium in ether led to the desired ketone **7**. A similar sequence beginning with 7-norbornanone (**55**)[12] furnished **18** by way of analogous intermediates.

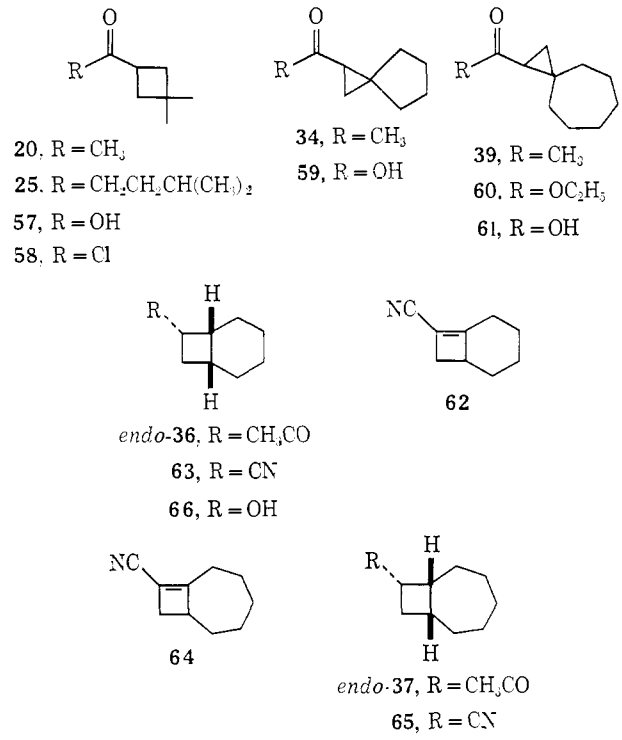
(3) F. F. Blicke, *Org. React.*, **1**, 303 (1942).
(4) M. Muehlstaedt, L. Zach, and H. Belwer-Reinhardt, *J. Prakt. Chem.*, **29**, 158 (1965).
(5) G. S. Mironov, M. I. Farberov, and I. M. Orlova, *Zh. Prikl. Khim. (Leningrad)*, **36**, 654 (1963); M. I. Farberov and G. S. Mironov, *Dokl. Akad. Nauk SSSR*, **148**, 1095 (1963).
(6) Several of these side products were characterized; complete details are given in the Experimental Section.
(7) T. A. Spencer, D. S. Watt, and R. J. Friary, *J. Org. Chem.*, **32**, 1234 (1967), give a more complete discussion of this matter, with particular reference to preparation of **6**.
(8) G. A. R. Kon, *J. Chem. Soc.*, **119**, 810 (1921).
(9) A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenbergh, *J. Amer. Chem. Soc.*, **63**, 3452 (1941).
(10) C. D. Nenitzescu, A. M. Glats, M. Gavet, and I. Pogany, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 301 (1963).
(11) M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).
(12) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964). A simple procedure for preparation of **55** is given in the Experimental Section.

Finally, phenoxy ketone **11** was available on treatment of diamine **56** first with excess methyl iodide and then with sodium phenoxide in dimethyl sulfoxide, a procedure adapted from the reported[13] preparation of the related methoxy ketone.

Photolysis Products from α-Methylene Ketones. Dilute (~1 mg/ml, ~0.007 *M*) benzene or pentane solutions of these compounds **1–18** were irradiated under conditions minimizing secondary photolysis of the saturated ketones formed. The results collected in Table I include all volatile products found in greater than 5% yield. Figures given as yields were determined by calibrated vpc measurements and are based on converted starting material. All products were isolated and purified by preparative vpc, including in most cases separation of the cis–trans mixtures of cyclobutyl ketones frequently encountered. However, the cis–trans mixture of methyl 2-methylcyclobutyl ketones (**27**), as well as that of the 3-methyl isomer **19**, could not be separated under any vpc conditions tried. The structures assigned to all products are fully consistent with their ir and 220-MHz nmr spectra, which were compared where possible with previous measurements. All these spectroscopic data are reported, and appropriate literature is cited, in the Experimental Section. Stereochemical assignments for cis–trans pairs of ketones rest on base-catalyzed equilibration. Since the cyclization reactions leading to cyclobutyl and cyclopropyl ketones are novel, the structures of several of these products were confirmed by independent syntheses which are outlined in the paragraphs below. In addition, authentic comparison samples of a number of products were prepared by known alternative routes.

Ketone **20** was available by addition of methyllithium[11] to 3,3-dimethylcyclobutanecarboxylic acid (**57**),[14] while reaction[15] of the related acyl chloride **58** with diisoamylcadmium gave **25**. Similarly, cyclobutanecarbonyl chloride reacted with dipropylcadmium to furnish authentic **24**, and methyllithium reacted with spiro[2.4]heptane-1-carboxylic acid (**59**)[16] giving **34**, while lower homolog **30** was prepared analogously from spiro[2.3]hexane-1-carboxylic acid.[16] Addition[16] of diazoacetic ester to methylenecycloheptane[17] led to **60**, which was saponified to the acid **61**, and this was treated with methyllithium to provide authentic **39**.

A sample of 7-*endo-cis*-bicyclo[4.2.0]octyl methyl ketone (*endo*-**36**) was independently prepared from the related unsaturated nitrile **62**.[18] Hydrogenation of the double bond of **62** over palladium on carbon furnished the *endo-cis*-nitrile **63**, which on reaction with methylmagnesium bromide followed by hydrolysis yielded *endo*-**36**. The identical procedures applied to the higher homolog **64**[18] led *via* **65** to *endo*-**37**. The stereochemistry assigned to *endo*- and *exo*-**36** and to *endo*- and *exo*-**37** is consistent with the results of base-catalyzed equilibration (>80% exo isomer at equilibrium



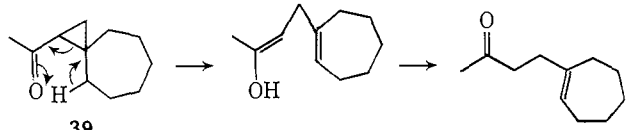
in both cases), and also with the expected course of catalytic hydrogenation of **62** and **64**. In each instance the anticipated cis addition of hydrogen to the more accessible side of the double bond should lead to the endo-cis series, as depicted in structures **63** and **65**. Furthermore, Baeyer–Villiger oxidation[19] of *endo*-**36** with peroxytrifluoroacetic acid and subsequent saponification yielded *endo-cis*-bicyclo[4.2.0]octan-7-ol (**66**). The ir spectra of this alcohol from *endo*-**36** and of its derived phenylurethane (mp 119–120.5°) were identical with those of authentic **66** and its derivative (lit.[20] mp 119.5–120°).

The cis and trans isomers of **47** were prepared by the route outlined above in Scheme I, starting with alkylation of acetoacetic ester by crotyl bromide as previously described.[21]

There are several minor products peripheral to the discussion below which may be considered here. One is the bicyclo[2.1.1]hexyl ketone **48**, which arises from intramolecular cycloaddition in **13**. Closely related transformations have been known for some time;[22] the structural assignment here follows these precedents and is supported by comparison of the nmr spectrum of **48** with data for other bicyclo[2.1.1]hexanes.[23] The

(13) V. B. Piskov, *J. Gen. Chem. USSR*, **33**, 3676 (1963).
(14) K. B. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).
(15) D. A. Shirley, *Org. React.*, **8**, 28 (1954).
(16) L. M. Konzelman and R. T. Conley, *J. Org. Chem.*, **33**, 3828 (1968). We thank Dr. Robert T. Conley, Wright State University, for a generous sample of **59**.
(17) O. Wallach, *Justus Liebigs Ann. Chem.*, **345**, 146 (1906); R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(18) I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 2165 (1964).
(19) W. D. Emmons and G. B. Lucas, *J. Amer. Chem. Soc.*, 77, 2287 (1955).
(20) A. C. Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962). We are grateful to Professor Gleason, Middlebury College, who generously provided these spectra, as well as those of the exo alcohol and phenylurethane.
(21) T. I. Temnikova and B. A. Ershov, *Zh. Obshch. Khim.*, **32**, 2436 (1962), and references cited therein.
(22) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963); R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **89**, 407 (1967), and references cited therein.
(23) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Amer. Chem. Soc.*, **84**, 1594 (1962); J. Meinwald and R. A. Chapman, *ibid.*, **90**, 3218 (1968); T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **37**, 1148 (1972). A formal alternative is the isomeric bicyclo[2.2.0]hexane. These compounds give distinctly different nmr spectra: R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961); W. Lüttke and V. Schabacker, *Justus Liebigs Ann. Chem.*, **698**, 86 (1966); R. Srinivasan and F. I. Sonntag, *Tetrahedron Lett.*, 603 (1967); W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 1014 (1968).

remaining side products are the γ,δ-unsaturated ketones **31**, **35**, and **40**. These arise from secondary thermal or photochemical ring opening of cyclopropyl ketones **30**, **34**, and **39**, respectively, in a process that has already been studied in depth by others.[24] At vpc temperatures below 100° thermal formation of **35** and **40** could be suppressed; higher temperatures permitted partial or complete conversion of the cyclopropyl ketones **34** and **39** to these rearrangement products. Similarly, photochemical formation of **31** and **35** occurred only in prolonged photolyses. Authentic samples of all three of these compounds were available through photolysis or thermolysis of the pure spiroketones. Fifteen minutes at 185°, for example, sufficed for quantitative rearrangement of **39** to **40**.

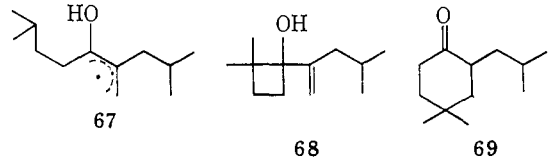


39 40

Discussion

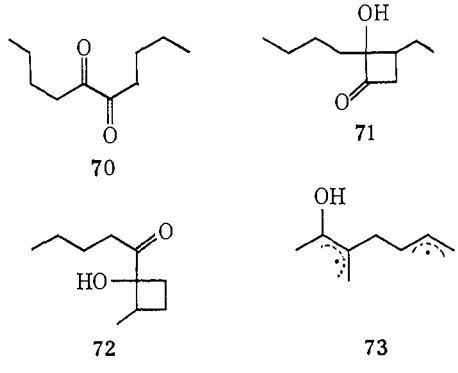
The most significant conclusion from Table I is that for a variety of structural types photolysis of α-methylene ketones offers a useful synthesis of cyclobutyl ketones. With only two exceptions (**15** and **16**), one of which is a cross-conjugated dienone, the alternative closure to 2-methylenecyclobutanols was less important or even absent. In no case was δ hydrogen transferred, although the opportunity existed in compounds which yielded no other volatile products (**17** and **18**).[25] Also no transfer of γ' hydrogen took place in the two compounds (**4** and **5**) having γ and γ' hydrogen situated in similar environments. It was conceivable that **5** yield biradical intermediate **67**, which could collapse either to the cyclobutanol **68** or to 4,4-dimethyl-2-isobutylcyclohexanone (**69**). We observed neither of these possible products (<1%).[26] This specificity is reminiscent of that noted[27] earlier in the photochemical rearrangement of α-diketones; photolysis of 5,6-decanedione (**70**), for example, leads only to the cyclobutanone **71**, and not to **72**. In this earlier work such selectivity was considered to reflect a more readily attainable transition state for hydrogen transfer leading to **71** rather than **72**. The argument[27] may be applicable also to the present results, and stated for ketone **5** it is as follows. The transition state for unobserved γ'-hydrogen transfer (see **67**) requires proper alignment for one more methylene group than does the transition state leading to γ-hydrogen transfer (see eq 1), which is the observed process. Presumably the loss of rotational freedom and the attendant entropy of activation for arrangement of this additional methylene group is sufficient to suppress abstraction of γ' hydrogen.

In the photolysis of **10** there was no evidence for formation of the trans-fused ketones isomeric with **37**, although there is thought to be little difference in the stability of *cis*- and *trans*-bicyclo[5.2.0]nonane.[28]



67 68 69

The alternative β abstraction (see eq 2 above) occurred only when the β hydrogen was tertiary (**6**, **7**, **8**, and **10**) or otherwise activated (**11**). This unusual process is also undoubtedly favored in these molecules by the α-methylene group. Rates of hydrogen abstraction by excited carbonyl oxygen are known[2] to reflect the stability of the resulting radicals, and an α-methylene group should provide considerable stabilization to a β radical center. The biradical of eq 2 is at least formally a derivative of trimethylenemethane, a ground state triplet species with an estimated delocalization energy of approximately 34 kcal/mol.[29] The behavior of **9**, which in contrast with **8** and **10** yielded little or no (<4%) cyclopropyl ketone, demonstrates, however, that the reaction is sensitive to the specific structure of the ketone. It is not yet clear whether this difference in behavior of **9** stems from simple ground state steric factors or is due to more subtle effects of structure on the properties of intermediates involved in these reactions. The products from **6**, **7**, **8**, and **10** do demonstrate for the first time that transfer of β and γ hydrogens can take place competitively.[30] These results also lend support to the suggestion[31] that the photoenolization of α-diketones[32] may proceed by a similar process.

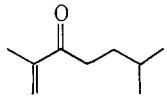


70 71 72 73

(24) R. M. Roberts, R. M. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967), and references cited therein; W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).

(25) Several examples of δ abstraction by carbonyl oxygen are on record: L. M. Stephenson and J. L. Parlett, *ibid.*, **36**, 1093 (1971), and references cited therein.

(26) Related to this is the observation that 6-methyl-2-methylene-3-heptanone (i) is photochemically stable under the conditions used for



i

ketones **1–18**: A. B. Smith, III, unpublished observations in this laboratory.

(27) W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962).

(28) N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

(29) F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970); P. Dowd, *Accounts Chem. Res.*, **5**, 242 (1972), and references cited therein.

(30) For previous reports of β-abstraction reactions, see A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 107 (1970); A. Padwa and W. Eisenhardt, *ibid.*, **93**, 1400 (1971); J. R. Scheffer, J. Trotter, R. A. Westradowski, C. S. Gibbons, and K. S. Bhandari, *ibid.*, **93**, 3813 (1971); J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. H. Wiekenkamp, *ibid.*, **94**, 285 (1972).

(31) N. J. Turro and T-J. Lee, *ibid.*, **92**, 7467 (1970).

(32) J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967); R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970); R. G. Zepp and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 7466 (1970).

Abstraction of γ hydrogen in **13** according to eq 1 would lead to a biradical which is depicted in **73** as a bisallylic species. Formation of the allylically rearranged cyclohexenes **45** and **46**, as well as olefins **47**, on photolysis of **13** provides strong evidence for such an intermediate.[33] It is noteworthy that in pentane both *cis*- and *trans*-**47** were formed, while in benzene only the cis isomer was obtained. A similar allylically stabilized intermediate can explain the isomerization of acetylene **14** to allene **50**. Also consistent with eq 1 and synthetically advantageous is the preferential formation of the cis or endo isomer of cyclobutyl ketones **27**, **29**, **32**, **36**, and **37**. This is in keeping with kinetically controlled protonation[34] of an initially formed enol (see eq 1) from the less hindered side. In each instance the cis compound was largely epimerized by base to the more stable trans isomer. As expected on this basis, there were formed more nearly equal amounts of the cis and trans isomers of the 3-substituted cyclobutyl ketones **19**, **42**, and **44**. Here protonation is almost equally favorable from either side, and the resulting isomeric ketones differ little in stability.[35]

Several questions remain open concerning these transformations. Stereochemical assignments for the methylenecyclobutanols must be secured along with further information to substantiate or modify the mechanistic pathways proposed in eq 1 and 2. The qualitative results recorded here, however, already suggest that photolysis of readily available α-methylene ketones frequently can lead to useful yields of simple, bicyclic, and spirocyclic cyclobutyl ketones.

Experimental Section

Materials and Equipment. All vpc was carried out using a Varian Aerograph Model 700 Autoprep or Model A-90-P3 with one of the following columns: A, 25% QF-1, 10 ft; B, 25% SE-30, 10 ft; C, 25% Carbowax 1500, 10 ft; D, 25% QF-1, 20 ft; E, 25% Carbowax 20M, 20 ft; F, 10% SE-30, 15 ft; G, 15% QF-1, 15 ft; H, 25% QF-1, 10 ft; J, 10% QF-1, 5 ft. Column J was prepared using 60–80 Chromosorb W in 0.25-in. stainless steel tubing; all other columns employed 45–60 Chromosorb W in $^3/_8$-in. aluminum tubing. Unless otherwise noted, column oven was operated at 85–200°, and helium carrier gas flow rate was 100–150 ml/min. Unless otherwise noted, 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 A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Solutions were dried over Na_2SO_4 or $MgSO_4$; melting points are corrected; boiling points are uncorrected. Yields of photoproducts were determined by calibrated vpc measurements and are based on unrecovered starting material. All compounds were obtained as colorless oils unless otherwise noted.

3-Methylene-2-hexanone (1). A mixture of 5.0 g (50 mmol) of 2-hexanone, 6.1 g (50 mmol) of piperidine hydrochloride, and 4.5 g (50 mmol) of 37% aqueous formaldehyde was heated on a steam bath overnight. The resulting solution was concentrated on a rotary evaporator, and the residue was destructively distilled at 200–260° (aspirator) until all volatile material was collected. The distillate was dissolved in ether and washed with 10% aqueous HCl and saturated aqueous $NaHCO_3$. After drying the solvent was distilled through a Vigreux column to yield a pale yellow oil, and the products were isolated by preparative vpc on column B. 3-Methylene-2-hexanone (**1**) (47%): ir 3090, 2960, 2930, 2870, 1679, 1620, 1360, 1135, and 923 cm^{-1}; nmr (60 MHz) δ 0.90 (t, J = 7 Hz), 1.10–1.62 (m, 2 H), 2.03–2.37 (m, 2 H), 2.24 (s, 3 H), 5.62 (dd, $J_1 = J_2$ = 1 Hz, 1 H), and 5.87 (d, J = 1 Hz, 1 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.72; H, 10.79.

1-Hepten-3-one (28%): ir 3090, 2960, 2925, 2870, 1705, 1687, 1613, 1395, 973, and 943 cm^{-1}; nmr (60 MHz) δ 0.63–1.84 (m, 7 H), 2.47 (br t, J = 7 Hz, 2 H), 5.65 (dd, J_1 = 4 Hz, J_2 = 8 Hz, 1 H) and 6.17 (m, 2 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.77; H, 10.71.

4-Methylene-1-hepten-3-one (14%): ir 3095, 3025, 2960, 2930, 2865, 1672, 1660, 1620, 1605, 1404, 1100, 1033, 1023, 970, 955, and 923 cm^{-1}; nmr (60 MHz) δ 0.91 (t, J = 7 Hz, 3 H), 1.18–1.75 (m, 2 H), 2.29 (br t, J = 6.5 Hz, 2 H), 5.60 (dd, J = 2.5, 10.5 Hz, 1 H), 5.64 (br s, 1 H), 5.88 (1 H), 6.18 (m, 1 H), 6.90 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.56; H, 9.88.

5-Methyl-3-methylene-2-hexanone (2). A mixture of formaldehyde (36.6 g of 37% aqueous solution, 0.25 mol), diethylamine hydrochloride (27.2 g, 0.25 mol), 5-methyl-2-hexanone (28.4 g, 0.25 mol), and 0.85 ml of concentrated HCl was heated in a stainless steel bomb at 100° for 1.5 hr. The reaction was worked up as for **1** above, and the products were separated on column C to give pure samples of each; **2**: ir 3090 (w), 2960 (m), 1682 (s), 1622 (w), 930 (m), 862 (m) cm^{-1}; nmr (60 MHz) δ 0.88 (d, J = 5.5 Hz, 6 H), 1.38–2.05 (m, 1 H), 2.14 (d, J = 6.5 Hz, 2 H), 2.28 (s, 3 H), 5.70 (m, 1 H), 5.99 (m, 1 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.26; H, 11.32.

6-Methyl-1-hepten-3-one: ir 3090 (w), 2960 (s), 1705 (ms), 1685 (s), 1620 (m), 983 (m), 950 (m) cm^{-1}; nmr (60 MHz) δ 0.91 (d, J = 5 Hz, 6 H), 1.20–2.00 (m, 3 H), 2.53 (t, J = 7.5 Hz, 2 H), 5.74 (d of d, 1 H), 6.15–6.40 (m, 2 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.26; H, 11.21.

6-Methyl-4-methylene-1-hepten-3-one (15): ir 3090 (w), 2960, 1675 (s), 1660 (m), 1623 (m), 1612 (m), 1037 (ms), 976 (m), 965 (w), 930 (m) cm^{-1}; nmr (60 MHz) δ 0.87 (d, J = 6 Hz, 6 H), 1.35–2.20 (m, 1 H), 2.23 (d, J = 6.5 Hz, 2 H), 5.50–5.88 (m, 2 H), 5.94 (s, 1 H), 6.20 (d of d, 1 H), 6.90 (d of d, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.91; H, 10.20.

4-Cyclopentyl-3-methylene-2-butanone (3). From 4-cyclopentyl-2-butanone[36] this ketone was prepared as described for **1** above and isolated using column C: ir 3090, 2950, 2865, 1680, 1623, 1445, 1425, 1355, 1145, 1100, and 920 cm^{-1}; nmr (220 MHz) δ 0.98–1.16 (m, 2 H), 1.40–1.76 (m, 6 H), 1.91 (m, 1 H), 2.20 (m, 2 H), 2.24 (s, 3 H), 5.68 (t, J = 1 Hz, 1 H), and 5.91 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.72; H, 10.75.

3-Methylene-4-heptanone (4). This compound was prepared as described for **1** above. Preparative vpc on column C gave both the mono- and dimethylene products; **4** (71%):[37] ir 3085, 2960, 2930, 2870, 1680, 1625, 1460, 1405, 1375, 1112, 1000, and 920 cm^{-1}; nmr (60 MHz) δ 0.55–3.01 (m, 12 H), 5.62 (dd, J = 1, 1 Hz, 1 H), and 5.87 (d, J = 1 Hz, 1 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.18.

3,5-Dimethylene-4-heptanone (18%): ir 3080, 2965, 2930, 2875, 1655, 1620, 1455, 1430, 1075, 990, and 915 cm^{-1}; nmr (60 MHz) δ 1.03 (t, J = 7.5 Hz, 6 H), 2.34 (br q, J = 7.5 Hz, 4 H), and 5.52 (AB, J = 1.5 Hz, 4 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.36; H, 10.05.

2,8-Dimethyl-4-methylene-5-nonanone (5). This compound was prepared as described for **2** above and purified on column C: nmr (60 MHz) δ 0.86 (d, J = 5 Hz) and 0.92 (d, J = 5 Hz, 12 H), 1.5 (m, 4 H), 2.1 (m, 2 H), 2.62 (t, J = 7 Hz, 2 H), 5.61 (m, 1 H), 5.93 (br s, 1 H).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.03; H, 12.32.

(33) Allylic rearrangement in the simple type II reaction of appropriate ketones was reported by N. C. Yang, A. Morduchowitz, and D-D. H. Yang [*J. Amer. Chem. Soc.*, **85**, 1017 (1963)], who interpreted the result as implying a biradical intermediate. For a dissenting view, see K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964).

(34) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **79**, 6554 (1957), and references cited therein.

(35) N. L. Allinger and L. A. Tushaus [*J. Org. Chem.*, **30**, 1945 (1965)] have shown that methoxide-catalyzed equilibration of methyl 3-methylcyclobutanecarboxylate leads to a mixture in which the cis isomer predominates, 61:39. We have used this result, which is that predicted by conformational analysis, in assigning configuration to cis and trans isomers of **19**, **42**, **44**, and **49**.

(36) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogic, and M. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).

(37) L. K. Evans and L. K. Gillam, *J. Chem. Soc.*, 815 (1941).

3-Methylene-6-hepten-2-one (13). This ketone was prepared from 6-hepten-2-one[38] following the procedure described for **1** above and purified on column C: ir 3075, 2975, 2920, 2845, 1680, 1640, 1625, 1430, 1360, 1130, 985, 920, and 902 cm^{-1}; nmr (220 MHz) δ 2.12 (m, 2 H), 2.24 (s, 3 H), 2.30 (br t, J = 7.5 Hz, 2 H), 4.98–5.12 (m, 2 H), 5.72–5.93 (m, 1 H), 5.80 (br s, 1 H), and 6.02 (s, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.33; H, 9.79.

5,5-Dimethyl-3-methylene-2-hexanone (17). This compound was prepared from 5,5-dimethyl-2-hexanone[39] as described for **1** above and purified on column C: ir 3085, 2955, 2905, 2860, 1685, 1620, 1470, 1460, 1360, 1160, 1105, 925 cm^{-1}; nmr (220 MHz) δ 0.82 (s, 9 H), 2.21 (s, 2 H), 2.27 (s, 3 H), 5.62 (s, 1 H), and 5.98 (s, 1 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.18; H, 11.33.

3-Cyclohexyl-3-buten-2-one (9). Ethyl 2-cyclohexylacetoacetate[40] (1.06 g, 5.41 mmol) was treated with 0.28 ml (5.2 mmol) of ethylene glycol and 100 mg of *p*-toluenesulfonic acid in refluxing benzene with water separation. The resulting solution was washed with saturated aqueous $NaHCO_3$, dried, and evaporated to a greenish oil. Nmr confirmed that ketalization had occurred: (60 MHz) δ 1.23 (t, J = 7 Hz), 1.39 (s), 3.87 (s), 4.07 (partially obscured q, J = 7 Hz). The oil was dissolved in ether, dried over $MgSO_4$, and added dropwise to 300 mg (8.83 mmol) of lithium aluminum hydride in ether. After the mixture was heated for 0.75 hr, an ether solution of 2 ml of methanol was added followed by aqueous HCl to acidity. The mixture was stirred at room temperature for 2 hr. The layers were separated; the organic phase was dried and evaporated. At this point nmr indicated the presence of a hydroxy ketone: (60 MHz) δ 2.13 (s), 2.83 (s), 3.67 (m), no vinyl H. This material was heated at reflux in benzene (water separation) containing 100 mg of *p*-toluenesulfonic acid for 1 hr, by which time water was no longer being produced. The solution was washed with saturated aqueous $NaHCO_3$, dried, and evaporated. Bulb-to-bulb distillation of the residue gave 612 mg (78%) of slightly yellow oil which was purified on column C: ir 3010 (w), 2935, 2852, 1683, 1621 (wm), 978 (m), 880 (wm) cm^{-1}; nmr (60 MHz) δ 0.70–2.00 (m, 10 H), 2.23 (s, 3 H), 2.30–2.80 (m, 1 H), 5.60 (m, 1 H), 5.88 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 8.97; H, 10.47.

3-Cycloheptyl-3-buten-2-one (10). This was synthesized (93%) from ethyl cycloheptylacetoacetate, prepared as described below, using the procedure given for **9**; purified on column C: ir 3090 (w), 2935 (s), 1685 (s), 1624 (wm), 1355 (m), 923 (m) cm^{-1}; nmr (60 MHz) δ 0.85–2.05 (m, 12 H), 2.26 (s, 3 H), 2.42–2.99 (m, 1 H), 5.68 (m, 1 H), 5.92 (s, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 19.71; H, 11.07.

Ethyl 2-Cycloheptylacetoacetate. Ethyl acetoacetate was dissolved in ethanol containing 1 equiv of KOH. Addition of ether precipitated the potassium salt which was collected and dried *in vacuo*. Cycloheptyl iodide[41] (12.5 g, 5.58 mmol) was dissolved in 40 ml of diglyme along with 9.50 g (5.65 mmol) of the above potassium salt and the solution was heated on a steam bath for 2.5 hr. The usual work-up gave 5.75 g (45%) of colorless oil, bp 105–109° (0.5 mm), purified on column J: ir 2935, 1735 (sh), 1715, 1175, 1142 cm^{-1}; nmr (60 MHz) δ 0.80–2.50 (m, with t (J = 7 Hz) at 1.30, 16 H), 2.14 (s, 3 H), 3.20 (d, J = 9 Hz, 1 H), 4.19 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.22; H, 10.01.

7-Methyl-3-methylene-6-octen-2-one (12). This ketone was prepared from ethyl isohexenylacetoacetate[42] following the procedure described above for **9** as far as the hydroxy ketone stage. Dehydration of the hydroxy ketone was effected by treating 1.92 g of this intermediate with 2.38 g of tosyl chloride in 20 ml of pyridine at 0°. The mixture was stirred at 5° for 19 hr and then heated 4 hr at 100°. The resulting solution was worked up with water and ether. Ether extracts were washed with 10% aqueous $CuSO_4$, water, and brine and then dried. Bulb-to-bulb distillation of the residue after removal of solvent afforded 1.23 g of oil [bp 90–105° (5 mm)] which was purified on column C: ir 3090, 2970, 2925, 2850, 1683, 1625 1430, 1370, 1360, 1128, 1110, 922, and 875 cm^{-1}; nmr (220 MHz) δ 1.56 (br s, 3 H), 1.65 (br s, 3 H), 2.02 (m, 2 H), 2.22 (br t, J = 8 Hz, 2 H), 2.25 (s, 3 H), 5.04 (m, 1 H), 5.68 (br s, 1 H), and 5.90 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.56. Found: C, 78.91; H, 10.36.

3-Methylene-6-heptyn-2-one (14). This ketone was prepared from ethyl 2-acetyl-5-hexynoate, prepared as given below, following the procedure described above for **12**. An analytical sample was obtained on column C: ir 3310, 3095, 2925, 2115, 1680, 1630, 1430, 1365, 1180, 1120, and 930 cm^{-1}; nmr (220 MHz) δ 1.78 (t, J = 2.5 Hz, 1 H), 2.22–2.32 (m, 2 H), 2.28 (s, 3 H), 2.41 (br t, J = 6.5 Hz, 2 H), 5.80 (br s, 1 H), and 5.98 (s, 1 H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.85; H, 8.18.

3-Cyclopentyl-3-buten-1-one (8). A mixture of 9.3 g (75 mmol) of cyclopentylacetone,[8] 5.6 ml (75 mmol) of 37% aqueous formaldehyde, and 2 NaOH pellets in 10 ml of 95% ethanol was stirred at room temperature for 43 hr. The resulting yellowish solution was made strongly acidic with *p*-toluenesulfonic acid. A 100-ml portion of benzene was added, and the mixture was refluxed with water separation until no more water was produced. The benzene solution was washed with saturated aqueous $NaHCO_3$ and dried. After distillation of the solvent through a Vigreux column the orange residue was short-path distilled to yield 7.72 g (75%) of colorless liquid, bp 93–101° (25 mm). Pure **8** was collected on column C: ir 3095, 2950, 2860, 1682, 1625, 1347, 1260, 1110, and 920 cm^{-1}; nmr (220 MHz) δ 1.20–1.34 (m, 2 H), 1.57–1.68 (m, 4 H), 1.79–1.92 (m, 2 H), 2.26 (s, 3 H), 2.86 (m, 1 H), 5.66 (d, J = 1 Hz, 1 H), and 5.88 (s, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.14; H, 10.22.

3-Cyclobutyl-3-buten-2-one (7). A solution of 0.72 g (5.7 mmol) of α-methylenecyclobutaneacetic acid, prepared as described below, in 10 ml of ether was cooled in ice, and 9 ml of 1.9 *M* methyllithium in ether was added dropwise with stirring during 15 min. After the mixture was stirred at room temperature for 2 hr, appropriate work-up and bulb-to-bulb distillation at 95–105° (50 mm) afforded 0.60 g (85%) of colorless 3-cyclobutyl-3-buten-2-one (**7**). An analytical sample was obtained on column C: ir 3095, 2980, 2940, 2865, 1680, 1625, 1360, 1275, 1230, 1140, and 920 cm^{-1}; nmr (220 MHz) δ 1.65–2.22 (m, 6 H), 2.24 (s, 3 H), 3.32 (m, 1 H), 5.61 (d, J = 1.5 Hz, 1 H), and 5.91 (s, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.39; H, 9.88.

α-Methylenecyclobutaneacetic Acid. A solution of 3.60 g (21.8 mmol) of cyclobutylidenecyanoacetic acid ethyl ester[10] in 50 ml of absolute ethanol containing 2.5 ml of concentrated HCl was hydrogenated over 200 mg of PtO_2 at room temperature and 50 psi[43] overnight. The catalyst was removed by suction filtration, and the filtrate was concentrated on a rotary evaporator. The pale yellow residue was dissolved in 25 ml of water and made basic with saturated aqueous Na_2CO_3. This mixture was extracted twice with ether, and after drying the extracts were concentrated on a rotary evaporator. Bulb-to-bulb distillation at 70–75° (0.5 mm) afforded 2.22 g (60%) of colorless α-aminomethylcyclobutaneacetic acid ethyl ester: ir 3400, 2980, 2940, 2865, 1730, 1615, 1365, 1240, 1190, 1165, 1145, and 1015 cm^{-1}; nmr (60 MHz) δ 0.90 (s, 2 H), 1.25 (t, J = 7 Hz, 3 H), 1.72–2.78 (m, 9 H), and 4.10 (q, J = 7 Hz, 2 H). This was used directly in the following step. A mixture of 1.97 g (11.5 mmol) of amino ester, 2.90 g (34.5 mmol) of $NaHCO_3$, and 4.90 g (34.5 mmol) of methyl iodide in 25 ml of methanol was heated at reflux with stirring for 42 hr. A 1.5-g portion of methyl iodide was added after 12 and 24 hr. The resulting mixture was concentrated on a rotary evaporator, and the residue was destructively distilled at 150–200° (0.3 mm). The distillate was dissolved in ether and washed with 5% aqueous HCl and saturated aqueous $NaHCO_3$. After drying with Na_2SO_4 the solvent was distilled through a Vigreux column to leave 1.20 g (68%) of slightly yellow α-methylenecyclobutaneacetic acid ethyl ester. The analytical sample was obtained on column C: ir 3095, 2975, 2940, 2865, 1717, 1627, 1440, 1356, 1280, 1260, 1230, 1210, 1165, 1135,

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1030, and 925 cm^{-1}; nmr (220 MHz) δ 1.29 (t, J = 7 Hz, 3 H), 1.71–2.00 (m, 4 H), 2.08–2.23 (m, 2 H), 3.25 (m, 1 H), 4.13 (q, J = 7 Hz, 2 H), 5.43 (dd, J = 1.5, 1.5 Hz, 1 H), and 6.07 (dd, J = 1.5, 1.5 Hz, 1 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.08; H, 9.26.

This ester was saponified in methanol using 10% aqueous KOH. The usual work-up and bulb-to-bulb distillation at 75–85° (0.3 mm) gave analytically pure α-methylenecyclobutaneacetic acid: ir 3375–2230, 2980, 2940, 1695, 1625, 1425, 1287, 1230, 1170, 1150, and 935 cm^{-1}; nmr (60 MHz) δ 1.72–2.42 (m, 6 H), 2.98–3.52 (m, 1 H), 5.60 (t, J = 1.5 Hz, 1 H), 6.30 (t, J = 1.5 Hz, 1 H), and 12.49 (s, 1 H).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.61; H, 8.10.

3-(7-Norbornyl)-3-buten-2-one (18). This ketone was available from α-methylene-7-norboraneacetic acid, prepared as described below, and methyllithium, following the procedure given above for **7**. An analytical sample was obtained on column C: ir 3095, 2950, 2910, 2865, 1682, 1623, 1472, 1348, 1298, 1270, 1197, 1177, 1150, 1105, 953, and 925 cm^{-1}; nmr (220 MHz) δ 1.10–1.29 (m, 4 H), 1.47–1.58 (m, 2 H), 1.64–1.76 (m, 2 H), 2.25 (s, 5 H), 2.51 (br, 1 H), 5.71 (d, J = 2 Hz, 1 H), and 5.94 (s, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.30; H, 9.81.

7-Norbornanone (55). A solution of 10.0 g of commercially available 7-*tert*-butoxynorbornadiene in 25 ml of methanol was hydrogenated over 250 mg of 5% Pd/C at room temperature and 50 psi and worked up in the usual manner to give 9.93 g (97%) of crude 7-*tert*-butoxynorbornane: nmr (60 MHz) δ 0.9–1.9 (m, 10 H), 1.14 (s, 9 H), 3.66 (br s, 1 H). A 9.9-g sample of this ether was treated[44] with 30 ml of trifluoroacetic acid at room temperature for 30 min, and then worked up with ice cold saturated aqueous $NaHCO_3$ and ether. This yielded 5.88 g (96%) of waxy 7-norbornanol, which was oxidized directly with chromium trioxide–pyridine complex in CH_2Cl_2.[45] The yield of **55** was 5.09 g (88 or 82% overall): ir (CCl_4) 2960, 2875, 1845, 1780, 1745, 1128 cm^{-1} (lit.[12] ir 1843, 1783, 1745 cm^{-1}).

Ethyl 7-Norbornylidenecyanoacetate. In 3 ml of benzene, 2.20 g of ketone **55**, 2.26 g of cyanoacetic ester, 100 mg of ammonium acetate, and 0.2 ml of acetic acid were heated at reflux with water separation.[9] The same amounts of catalysts were added three times with an additional hour's heating each time. An additional 1.0 g of cyanoacetic ester was added and the above procedure repeated. Bulb-to-bulb distillation of the resulting orange oil gave 1.78 g (43%) of desired ethyl ester as a colorless viscous oil. This was purified on column F to afford an analytically pure white solid: mp 57.0–58.5°; ir 2965, 2865, 2220, 1735, 1652, 1360, 1305, 1260, 1240, 1195, 1130, 1080, 1050, and 1015 cm^{-1}; nmr (220 MHz) δ 1.41 (t, J = 7 Hz, 3 H), 1.61 (m, 4 H), 1.88 (m, 4 H), 3.02 (br, 1 H), 3.86 (br, 1 H), and 4.35 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.17; H, 7.26; N, 6.69.

Ethyl α-Aminomethyl-7-norbornaneacetate. A 1.68-g sample of the above nitriloester was hydrogenated as described above. Bulb-to-bulb distillation at 100–110° (0.4 mm) yielded 1.11 g (64%) of colorless oil which was further purified on column F: ir 3400, 2955, 2870, 1730, 1615, 1470, 1455, 1365, 1300, 1250, 1190, 1165, 1140, and 1015 cm^{-1}; nmr (60 MHz) δ 0.98–2.44 (m, 14 H), 1.27 (t, J = 7 Hz, 3 H), 2.82 (br d, J = 6.5 Hz, 2 H), and 4.14 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.15; H, 9.92; N, 6.52.

Ethyl α-Methylene-7-norbornaneacetate. The amino ester described above was quaternized and destructively distilled as in the preparation of α-methylenecyclobutaneacetic acid above. Distillation at 50–60° (0.3 mm) followed by vpc on column C gave a pure colorless oil: ir 3100, 2955, 2905, 2865, 1718, 1623, 1297, 1270, 1260, 1195, 1175, 1155, 1118, 1022, and 930 cm^{-1}; nmr (220 MHz) δ 1.14–1.34 (m, 4 H), 1.33 (t, J = 7 Hz, 3 H), 1.57–1.83 (m, 4 H), 2.32 (br, 2 H), 2.54 (br, 1 H), 4.16 (q, J = 7 Hz, 2 H), 5.52 (dd, J = 2, 2 Hz, 1 H), and 6.12 (dd, J = 2, 2 Hz, 1 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.37.

α-Methylene-7-norbornaneacetic Acid. Saponification of the above ester gave the desired acid, mp 123–124°, from hexane: ir 3380–2260, 2950, 2905, 2865, 1695, 1620, 1415, 1300, 1280, 1205, 1165, 1125, and 940 cm^{-1}; nmr (220 MHz) δ 1.14–1.35 (m, 4 H), 1.56–1.80 (m, 4 H), 2.39 (br, 2 H), 2.52 (br, 1 H), 5.66 (dd, J = 2, 2 Hz, 1 H), and 6.34 (dd, J = 2, 2 Hz, 1 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.10; H, 8.83.

3-Methylene-4-phenoxy-2-butanone (11). A 6.84-g (30 mmol) portion of diamine **56**, prepared as previously described,[13] was cooled in ice, and 17.0 g (120 mmol) of methyl iodide was added dropwise with stirring during 15 min. Stirring was continued overnight while the cooling bath was allowed to warm to room temperature. The resulting chunky white solid was crushed in a mortar, and the excess methyl iodide was removed *in vacuo* to yield 14.7 g (96%) of crude dimethiodide. This material was dissolved in 50 ml of dimethyl sulfoxide, and a solution of 6.96 g (60 mmol) of sodium phenoxide in 50 ml of dimethyl sulfoxide was added with stirring. After 28 hr at 65° the red reaction mixture was poured into water and extracted three times with ether. The combined extracts were washed twice each with 5% aqueous NaOH and water and once with saturated aqueous NaCl. After the extracts were dried, the solvent was removed on a rotary evaporator. Bulb-to-bulb distillation of the residue at 110–120° (0.2 mm) afforded 2.00 g (38%) of pale yellow enone **11**. Preparative vpc on column A gave an analytical sample: ir 1680, 1600, 1585, 1495, 1290, 1240, 1210, 1045, 935, and 675 cm^{-1}; nmr (220 MHz) δ 2.33 (s, 3 H), 4.68 (t, J = 1.5 Hz, 2 H), 6.15 (m, 2 H), 6.70–7.20 (m, 5 H).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.61; H, 6.82.

General Procedure for Photolyses. Photochemical experiments were carried out on benzene solutions (1 mg/ml) of the ketone using one of the following procedures: A, a solution in a toroidal vessel was irradiated with Hanovia Model L mercury lamp No. 679A-36 in a quartz immersion well using Corning No. 3320 uranium glass as filter; B, a solution in a cylindrical vessel equipped with a cold finger was irradiated in a Rayonet RPR-100 reactor equipped with 16 RPR-3500 Å lamps. In either case the solution was flushed with dry nitrogen for 30 min before irradiation and kept under nitrogen during irradiation. In procedure A the apparatus was customarily wrapped in aluminum foil and immersed in a water bath at 15–20°. Any variation in these procedures is noted in the details given below. After irradiation, the solvent was evaporated through a Vigreux column, and both analysis and purification of products were effected by vpc on the column indicated.

Photolysis of 3-Methylene-2-hexanone (1). A solution of 74 mg of **1** was photolyzed 72 hr by procedure A. Vpc on column D showed that 96% of **1** was consumed, and that the sole volatile product (61%) was a 64:36 (nmr) mixture of *trans*- and *cis*-**19**. These could not be separated under any conditions tried: ir 2955, 2925, 2860, 1713, 1355, 1160 cm^{-1}; nmr (220 MHz) δ 1.03 and 1.12 (d, J = 6 Hz, 3 H), 1.64–1.83 (m, 2 H), 1.97 and 2.01 (s, 3 H), 2.14–2.41 (m, 3 H), and 2.89–3.21 (m, 1 H); the signals at δ 1.03 and 1.97 corresponded to the cis isomer, and those at δ 1.12 and 2.01 to the trans isomer. The cis–trans mixture was equilibrated in 0.5 ml of 2 M methanolic KOH at room temperature for 3 hr. This was worked up with water and pentane; the pentane was dried and removed to leave the product as a colorless oil, which was a 35:65 mixture of *trans*- and *cis*-**19**.[35]

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.72; H, 10.48.

Photolysis of 5-Methyl-3-methylene-2-hexanone (2). Irradiation of 70 mg of **2** for 64 hr following procedure A with pentane as solvent led to 90% conversion and two products isolated using column H. Ketone **20** (68% yield) was identical with a sample prepared as described below. 1,4,4-Trimethyl-2-methylenecyclobutanol (**21**, 19% yield) gave the following data: ir 3620 (m), 3475 (w), 3070 (w), 2960 (s), 2865 (m), 1680 (w), 880 (s) cm^{-1}; nmr (60 MHz) δ 1.02 and 1.07 (s, 6 H), 1.22 (s, 3 H), 1.55 (s, exchanges with D_2O, 1 H), 2.12 (m, 2 H), 4.77 (m, 1 H), 5.02 (m, 1 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.03; H, 11.34.

3,3-Dimethylcyclobutyl Methyl Ketone (20). Treatment of 3,3-dimethylcyclobutanecarboxylic acid[14] (mp (*p*-bromophenacyl ester) 88.5–90.5°, lit.[14] mp 89–90°) with methyllithium as described above for **7** gave ketone **20** (column H): ir 2955 (s), 1718 (s), 1355 (m), 1170 (m) cm^{-1}; nmr (60 MHz) δ 1.06 (s) and 1.18 (s) (6 H), 1.35–2.25 (m) and 1.99 (s) (7 H), 2.75–3.45 (m, 1 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.16; H, 11.36.

Photolysis of 4-Cyclopentyl-3-methylene-2-butanone (3). Photolysis according to procedure B for 42 hr led to 95% conversion

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and two products from column G. The first was 1-methyl-2-methylenespiro[3.4]octan-1-ol (**23**, 33%): ir 3610, 3475, 3070, 2950, 2865, 1675, 1445, 1420, 1365, 1310, 1235, 1150, 1115, 1060, 940, and 875 cm^{-1}; nmr (220 MHz) δ 1.25 (s, 3 H), 1.27–1.46 (m, 2 H), 1.51–1.80 (m, 7 H), 2.16 (m, 2 H), 4.68 (m, 1 H), and 4.97 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.84; H, 10.44.

The second product was methyl spiro[3.4]oct-2-yl ketone (**22**, 51%): ir 2950, 2850, 1712, 1445, 1420, 1350, and 1162 cm^{-1}; nmr (220 MHz) δ 1.46–1.67 (m, 8 H), 1.94 (ddd, J_{AB} = 9.5 Hz, J_{AX} = 8.5 Hz, $J_{AB'}$ = 2 Hz, 1 H) 1.98 (s, 3 H), 2.08 (ddd, J_{AB} = 9.5 Hz, J_{BX} = 9 Hz, $J_{BA'}$ = 2 Hz, 1 H], and 3.02 (tt, $J_{AX} \approx J_{BX} \approx$ 9 Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.83; H, 10.79.

Photolysis of 3-Methylene-4-heptanone (4). Photolysis was carried out using procedure B. After 116-hr irradiation, vpc on column E indicated 91% conversion to at least nine minor products which were not further investigated and 27% of cyclobutyl propyl ketone (**24**) which was identical with a sample prepared as described below.

Cyclobutyl Propyl Ketone (24). Cyclobutanecarboxylic acid was allowed to react with thionyl chloride, and the crude acyl chloride was added directly to dipropylcadmium prepared in the usual way[15] at 0°. Work-up with ether and water gave 77% of pale yellow product which was purified on column D: ir 2965, 2870, 1712, 1455, 1355, 1235, 1120, and 975 cm^{-1}; nmr (220 MHz) δ 0.89 (t, J = 7 Hz, 3 H), 1.55 (m, 2 H), 1.76–2.27 (m, 6 H), 2.22 (t, J = 7 Hz, 2 H), and 3.14 (m, 1 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.96; H, 11.31.

Photolysis of 2,8-Dimethyl-4-methylene-5-nonanone (5). Ketone **5** was irradiated for 40 hr according to procedure A to essentially complete conversion. Two products were isolated on column H. The first was 3,3-dimethylcyclobutyl isopentyl ketone (**25**, 67%), identical with a synthetic sample described below. The second product was 1-isopentyl-4,4-dimethyl-2-methylene-1-cyclobutanol (**26**, 12%): ir 3620 (m), 3480 (w), 3070 (w), 2960 (s), 2875 (s), 1680 (w), 1470 (m), 880 (m); nmr (60 MHz) δ 0.92 (d, J = 5 Hz, 6 H), 1.05 and 1.08 (s, 6 H), 1.45 (m, 6 H), 2.10 (m, 2 H), 4.80 (m, 1 H), 4.95 (m, 1 H); mass spectrum 182.1670 (M^+, calcd for $C_{12}H_{22}O$, 182.1670).

3,3-Dimethylcyclobutyl Isopentyl Ketone (25). This ketone was prepared from 3,3-dimethylcyclobutanecarboxylic acid[14] and diisopentylcadmium as described above for **24**. A pure sample was obtained using column H: ir 2960, 1718, 1464, 1364 cm^{-1}; nmr (60 MHz) δ 0.89 (d, J = 5 Hz, 6 H), 1.05 (s, 3 H), 1.17 (s, 3 H), 1.20–2.50 (m, 9 H), 2.75–3.45 (m, 1 H).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.18; H, 12.31.

Photolysis of 4-Methyl-3-methylene-2-pentanone (6). This ketone[7] was photolyzed for 407 hr according to procedure A. Analysis on column D indicated 82% conversion and two products. The first of these was 2,2-dimethylcyclopropyl methyl ketone (**28**, 31%), identical with an authentic sample.[24] The second product was a 1:9 mixture (nmr) of *trans*- and *cis*-2-methylcyclobutyl methyl ketones (**27**, 23%):[46] ir 2960, 1713, 1405, and 1165 cm^{-1}; nmr (220 MHz) δ 0.99 (d, J = 7 Hz, 3 H), 1.40–1.55 (m, 1 H), 1.66–1.85 (m, 1 H), 1.97 (s, 3 H), 2.01–2.17 (m, 1 H), 2.32–2.48 (m, 1 H), 2.64–2.84 (m, 1 H), and 3.28 (m, 1 H); the trans isomer was indicated by a singlet at δ 1.99. The individual isomers could not be separated by vpc under any conditions tried. Equilibration of this mixture as described above for **19** gave a 59:41 mixture (nmr) of trans and cis isomers, respectively.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.72; H, 10.78.

Photolysis of 3-Cyclobutyl-3-buten-2-one (7). A 353-mg sample of **7** was photolyzed using procedure B for 189 hr, by which time a large amount of polymer coated the walls of the reaction vessel. Vpc on column G indicated 90% conversion of **7** and formation of 8% of *endo*- and 5% of *exo*-bicyclo[2.2.0]hex-2-yl methyl ketones (**29**)[47] and a mixture of 5% methyl spiro[2.3]hex-1-yl ketone (**30**) and 3% 4-(1-cyclobuten-1-yl)-2-butanone (**31**). These last two compounds were separated by reinjection onto column C.

For *endo*-**29** the following data were obtained: ir 2970, 2940, 2845, 1712, 1350, 1170, and 1163 cm^{-1}; nmr (220 MHz) δ 1.90 (s, 3 H), 1.96–2.11 (m, 1 H), 2.14–2.48 (m, 4 H), 2.52–2.78 (m, 2 H), 3.07–3.24 (m, 1 H), and 3.36–3.50 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.31; H, 9.77.

For *exo*-**29** the following data were obtained: ir 2975, 2935, 2845, 1712, 1350, 1173, and 1157 cm^{-1}; nmr (220 MHz) δ 1.98 (s, 3 H), 2.02–2.12 (m, 3 H), 2.42–2.72 (m, 4 H), 2.78–2.90 (br, 1 H), and 3.16–3.27 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.16; H, 9.72.

Equilibration of *endo*-**29** as described for **19** above gave a 64:36 mixture (nmr) of exo and endo isomers, respectively. Ketones **30** and **31** were identified by comparison of ir and nmr spectra with data from authentic samples prepared as described below.

Methyl Spiro[2.3]hex-1-yl Ketone (30). Spiro[2.3]hexane-1-carboxylic acid ethyl ester was prepared as previously described[16] from methylenecyclobutane and ethyl diazoacetate and purified on column D: ir 3070, 2980, 2950, 1725, 1438, 1395, 1378, 1310, 1240, 1198, 1148, 1100, and 1035 cm^{-1}; nmr (220 MHz) δ 0.91 (dd, J_{AB} = 5 Hz, J_{AC} = 8 Hz, 1 H), 1.10 (dd, J_{AB} = J_{BC} = 5 Hz, 1 H), 1.25 (t, J = 7 Hz, 3 H), 1.45 (dd, J_{AC} = 8 Hz, J_{BC} = 5 Hz, 1 H), 1.94–2.28 (m, 6 H), and 3.97–4.13 (m, 2 H).

Hydrolysis of the crude spiro ester in aqueous methanolic KOH afforded a 7% overall yield of spirohexane-1-carboxylic acid:[16] ir 3560–2200, 2980, 2950, 1695, 1435, 1310, 1280, 1250, 1230, 1215, 1100, and 935 cm^{-1}; nmr (220 MHz) δ 1.03 (dd, J_{AB} = 4 Hz, J_{AC} = 8 Hz, 1 H), 1.51 (dd, J_{AC} = 8 Hz, J_{BC} = 5 Hz, 1 H), 1.95–2.30 (m, 6 H), and 12.50 (br, 1 H).

This carboxylic acid was converted to ketone **30** with methyllithium as described above for **7**. An analytical sample was prepared on column C: ir 3070, 2980, 2950, 1598, 1423, 1385, 1345, 1305, 1240, 1195, 1160, 1100, 1075, and 945 cm^{-1}; nmr (220 MHz) δ 0.92 (dd, J_{AB} = 4 Hz, J_{AC} = 8 Hz, 1 H), 1.20 (dd, J_{AB} = 4 Hz, J_{BC} = 5 Hz, 1 H), 1.82 (dd, J_{AC} = 8 Hz, J_{BC} = 5 Hz, 1 H), 1.90–2.25 (m, 6 H), and 2.14 (s, 3 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.25; H, 9.94.

4-(1-Cyclobuten-1-yl)-2-butanone (31). A solution of 75 mg of **30** in 75 ml of pentane was photolyzed following procedure B, except that the light source was 16 RPR-3000 Å reactor lamps. After 5.5 hr ir and vpc analysis indicated that about half the starting material was consumed to yield a nearly equal amount of cyclobutenyl ketone. A small amount of white solid coated the walls of the reaction vessel. An analytical sample of **31** was obtained on column C: ir 3040, 2950, 2920, 2840, 1723, 1627, 1425, 1350, 1153, 900, and 840 cm^{-1}; nmr (220 MHz) δ 2.06 (s, 3 H), 2.16–2.50 (m, 8 H), and 5.61 (br s, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.54; H, 9.70.

Photolysis of 3-Cyclopentyl-3-buten-2-one (8). A 314-mg sample of **8** was photolyzed for 36 hr according to procedure B to 37% conversion. Vpc on column D gave three products. The first of these was 6-methyl-7-methylenebicyclo[3.2.0]heptan-6-ol (**33**, 7%), which was further purified on column E: ir 3615, 3485, 3060, 2945, 2950, 1673, 1275, 1020, 930, and 880 cm^{-1}; nmr (220 MHz) δ 1.39 (s, 3 H), 1.39–1.98 (m, 7 H), 2.55 (m, 1 H), 3.01 (br, 1 H), 4.61 (d, J = 2 Hz, 1 H), and 5.00 (d, J = 2 Hz, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.13; H, 10.35.

The second product was methyl spiro[2.4]hept-1-yl ketone (**34**, 34%), which was identical with the authentic sample prepared as described below.

The third product was methyl *endo-cis*-bicyclo[3.2.0]hept-6-yl ketone (**32**, 12%), which was further purified on column E: ir 2945, 2850, 1710, 1465, 1445, 1435, 1350, 1190, and 1165 cm^{-1}; nmr (220 MHz) δ 1.28–2.00 (m, 6 H), 1.93 (s, 3 H), 2.12–2.35 (br, 2 H), 2.72 (m, 1 H), 3.02 (m, 1 H), and 3.25 (m, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.14; H, 10.21.

Equilibration of **32** as described for **19** above afforded an 86:14 mixture (nmr) of exo and endo isomers, respectively. The exo isomer, indicated by a methyl signal at δ 1.99, was not present in the photolysis mixture. Treatment of this equilibration mixture with semicarbazide reagent gave the exo ketone semicarbazone, mp 192–

(46) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 3671 (1961).

(47) R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **34**, 1916 (1969). We thank Professor McDonald, Kansas State University, for 60-MHz nmr spectra of mixtures of *endo*- and *exo*-**29**, with which the data reported here are in substantial agreement.

193°, from aqueous methanol (mp (authentic sample)[48] and mmp 191–193°).

When the photolysis of **8** was prolonged to 129 hr (92% completion), there was obtained in addition to the above products 4-(cyclopenten-1-yl)-2-butanone (**35**, 7%). This was purified on column E and was identical with a sample prepared as described below.

Methyl Spiro[2.4]hept-1-yl Ketone (34). This ketone was prepared (85%) from spiro[2.4]heptane-1-carboxylic acid[16] and methyllithium as described above for **7** and purified on column A: ir 3060, 2990, 2950, 2860, 1699, 1385, 1345, 1165, and 1080 cm^{-1}; nmr (220 MHz) δ 0.94 (dd, J_{AB} = 4 Hz, J_{AX} = 8 Hz, 1 H), 1.29 (dd, J_{AB} = 4 Hz, J_{BX} = 6 Hz, 1 H), 1.61–1.74 (m, 8 H), 1.89 (dd, J_{AX} = 8 Hz, J_{BX} = 6 Hz, 1 H), and 2.14 (s, 3 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.06; H, 10.12.

4-(Cyclopenten-1-yl)-2-butanone (35). Photolysis of **34** using procedure B resulted in slow destruction of substrate and formation of **35**, minor volatile products, and much polymer. A pure sample of **35** yielded the following data: ir 3045, 2950, 2845, 1725, 1650, 1440, 1355, 1150, and 937 cm^{-1}; nmr (220 MHz) δ 1.78–1.92 (m, 2 H), 2.06 (s, 3 H), 2.15–2.35 (m, 6 H), 2.49 (t, J = 7 Hz, 2 H), and 5.25 (br, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.33; H, 10.36.

Photolysis of 3-Cyclohexyl-3-buten-2-one (9). A 70-mg sample of **9** was photolyzed using procedure A for 40 hr. Vpc on column C indicated 68% conversion of **9** and formation of two products which were isolated. These were *endo*-**36** (58%) and *exo*-**36** (6%), each identical with authentic material prepared as detailed below.

***endo*- and *exo*-Bicyclo[4.2.0]oct-7-yl Methyl Ketones (*endo*- and *exo*-36).** To a solution of nitrile **63** (675 mg, 5.00 mmol) in 9 ml of ether was added 3.0 ml of 3 *N* methylmagnesium bromide, and the mixture was heated at reflux for 4 hr. The reaction vessel was cooled in an ice bath as saturated NH_4Cl was added, and the two phase mixture was stirred at room temperature for 1 hr. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were dried and evaporated to give 744 mg (98%) of yellow oil which gave mainly two peaks on vpc (column C) in the ratio of 1:4. The minor component was *exo*-**36**: ir 2935, 1713, 1445, 1350, 1162 cm^{-1}; nmr (220 MHz) δ 1.00–2.20 (m, 11 H), 1.98 (s, 3 H). 2.48 (m, 1 H), 3.04 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.95. Found: C, 78.70; H, 10.97.

The major component was *endo*-**36**: ir 2935, 1713, 1463, 1370, 1350, 1190, 1175 cm^{-1}; nmr (220 MHz) δ 0.80–2.40 (m, 11 H), 1.92 (s, 3 H), 2.59 (m, 1 H), 3.00 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.95. Found: C, 78.78; H, 10.60.

Separate samples of *endo*-**36** and *exo*-**36** were dissolved in 1.5 ml of methanol and 1.0 ml of 10% aqueous KOH. After 3 hr at room temperature the materials were recovered by dilution with water and extraction with pentane. The organic solutions were dried and evaporated. Analysis of the residues by vpc (column C) and by nmr at 220 MHz showed that each sample had been converted to the same mixture of ketones, *endo*-**36** and *exo*-**36**, in the ratio 1:5.

Bicyclo[4.2.0]octane-7-carbonitrile (63). A methanol solution of 1.33 g (10.0 mmol) of the unsaturated nitrile **62**[18] containing 250 mg of 5% Pd/C was hydrogenated at 1 atm to yield 1.24 g (92%) of colorless, sweet-smelling oil: bp 103–105° (aspirator); ir 2940, 2860, 2230 (m), 1465 (m), 1450 (m) cm^{-1}; nmr (220 MHz) δ 0.80–2.85 (m, 12 H), 2.98 (m, 1 H). Analytically pure material was prepared on column C.

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 80.11; H, 9.70; N, 10.35.

Baeyer–Villiger Oxidation of *endo*-36. To a slurry of 360 mg (2.54 mmol) of Na_2HPO_4 was added 1.0 ml of 1.0 *N* peroxytrifluoroacetic acid in methylene chloride.[19] The ketone (75 mg, 0.49 mmol) was then added in 1 ml of methylene chloride. The mixture was stirred and heated at reflux for 0.5 hr and then partitioned between additional methylene chloride and aqueous Na_2CO_3. The organic layer was dried and evaporated leaving 85 mg of an oil. The oil was saponified in aqueous methanolic KOH to give 49 mg (79%). This was purified on column C (>90% one peak). The ir spectra of the purified product and its phenylurethane derivative (mp 119–120.5°, lit.[20] 119.5–120°) were virtually identical with the spectra of authentic *endo*-bicyclo[4.2.0]octan-7-ol and its phenylurethane, respectively.[20]

Photolysis of 3-Cycloheptyl-3-buten-2-one (10). A 200-mg sample of this ketone was photolyzed following procedure A for 72 hr to 90% conversion. Vpc on column D at 95° gave five products described below. At higher temperatures (~175°) **39** was absent, and its rearrangement product, 4-(cyclohept-1-enyl)-2-butanone (**40**), was obtained instead. This was identical with a synthetic sample prepared as described below.

The first two products were *endo*- and *exo*-*cis*-bicyclo[5.2.0]-non-8-yl methyl ketones (*endo*- and *exo*-**37**), in 28 and 3% yields, respectively. These were identical with authentic samples prepared as described below.

Two isomers of 8-methyl-9-methylenebicyclo[5.2.0nonan-8-ol (**38**) were obtained as a mixture which was separated on column E to give **38a** (6%), ir 3610 (m), 3360 (m), 3060 (w), 2920 (s), 1676 (m), 1445 (m), 878 (m) cm^{-1}; nmr (220 MHz) δ 1.09–1.82 (m, 11 H), 1.26 (s, 3 H), 1.82–2.02 (m, 1 H), 2.83 (m, 1 H), 4.61 (d, J = 2.5 Hz, 1 H), 4.82 (d, J = 2.5 Hz, 1 H); mass spectrum 166.1374 (M^+, calcd for $C_{11}H_{18}O$, 166.1358); and **38b** (4%), ir 3610 (m), 3470 (w), 3060 (w), 2920 (s), 1672 (m), 1180 (m), 877 (ms) cm^{-1}; nmr (220 MHz) δ 1.00–1.39 (m, 6 H), 1.31 (s, 3 H), 1.63–1.90 (m, 3 H), 1.93–2.10 (m, 2 H), 2.10–2.26 (m, 1 H), 2.75 (m, 1 H), 4.67 (d, J = 2.5 Hz, 1 H), 4.95 (d, J = 2.5 Hz, 1 H); mass spectrum 166.1379 (M^+, calcd for $C_{11}H_{18}O$, 166.1358).

The final product was methyl spiro[2.6]non-1-yl ketone (**39**, 24%), which was identical with an authentic sample prepared as described below.

***endo*- and *exo*-Bicyclo[5.2.0]non-8-yl Methyl Ketone (*endo*- and *exo*-37).** Nitrile **65** (750 mg, 5.00 mmol) was treated with methylmagnesium bromide and worked up as was done with **63**. This gave a crude yield of 831 mg of yellow oil from which the predominant products were obtained by vpc on column D or E. Column E offered the better separation but it appeared that some epimerization was occurring on this column. Nmr of the crude material indicated a mixture of endo and exo isomers in the ratio 60:40. Purified *endo*-**37** yielded the following: ir 2920 (s), 1713 (s), 1457 (m), 1349 (m), 1167 (m) cm^{-1}; nmr (220 MHz) δ 0.80–2.16 (m, 12 H), 1.95 (s, 3 H), 2.28–2.49 (m, 1 H), 2.65–2.85 (m, 1 H), 3.19 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.47; H, 10.99.

For *exo*-**37** the following were found: ir 2920 (s), 1715 (s), 1460 (wm), 1448 (wm), 1357 (m), 1347 (m), 1167 (m) cm^{-1}; nmr (220 MHz) δ 0.98–1.94 (m, 11 H), 1.97 (s, 3 H), 2.20–2.41 (m, 2 H), 2.45–2.62 (m, 1 H), 2.65–2.78 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.41; H, 10.82.

Treatment of the above ketones with aqueous methanolic KOH as described for ketones **36** gave equilibrium mixtures of *endo*- and *exo*-**37** in the ratio 1:8.

***endo*-*cis*-Bicyclo[5.2.0]nonane-8-carbonitrile (65).** Unsaturated nitrile **64**[18] (1.40 g) was hydrogenated over 250 mg of 5% Pd/C in methanol at about 1 atm to provide 1.28 g (90%) of colorless oil: bp 70–72° (0.3 mm); ir 2935 (s), 2035 (wm), 1457 (m) cm^{-1}; nmr (220 MHz) δ 0.80–2.90 (m, 14 H), 3.07 (m, 1 H). A sample was purified on column C.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.59; H, 10.13; N, 9.31.

Spiro[2.6]nonane-1-carboxylic Acid Ethyl Ester (60). A mixture of 2.20 g (20.0 mmol) of methylenecycloheptane,[17] 2 ml of *n*-octane, and 0.20 g of copper bronze[49] was stirred and heated at reflux in an oil bath. A solution of 2.50 ml (23.9 mmol) of ethyl diazoacetate and 2 ml of *n*-octane was added dropwise over a period of 1.25 hr.[16] Refluxing was continued for a few minutes after the addition and the mixture was cooled and filtered. The solvent was removed through a Vigreux column at aspirator pressure. The residue was distilled to give 3.08 g (79%) of colorless product, bp 64–66° (0.2 mm). Vpc on column C gave analytically pure material: ir 3070 (w), 2030, 1730, 1160 cm^{-1}; nmr (220 MHz) δ 0.77 (d of d, J_1 = 4, J_2 = 8 Hz, 1 H), 1.06 (m, J_1 = 4, J_2 = 6 Hz, 1 H), 1.26 (t, J = 7 Hz, 3 H), 1.10–2.08 with d of d (J_1 = 6, J_2 = 8 Hz) at 1.43 (m, 13 H), 4.08 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.57; H, 10.33.

Spiro[2.6]nonane-1-carboxylic Acid (61). Ethyl ester **60** (2.61 g,

(48) R. Granger, J. Boussinesq, J.-P. Girard, and J.-C. Rossi, *Bull. Soc. Chim. Fr.*, 2801 (1969). We thank Professor Granger and Dr. Girard for generously providing this material. The ir spectra of the two samples were also essentially identical.

(49) J. E. Hodgkins and R. F. Flores, *J. Org. Chem.*, **28**, 3356 (1963).

13.3 mmol) was saponified in aqueous methanolic KOH. Distillation gave 2.00 g (89%) of analytically pure viscous oil: bp 110° (0.5 mm); ir 3400–2250 (m), 2930, 1695, 1445, 1425, 1210 cm^{-1}; nmr (220 MHz) δ 0.88 (d of d, $J_1 = 4$, $J_2 = 8$ Hz, 1 H), 1.16 (m, $J_1 = 4$, $J_2 = 6$ Hz, 1 H), 1.00–2.15 with d of d ($J_1 = 6$, $J_2 = 8$ Hz) at 1.50 (m, 13 H), 12.05 (broad, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.50; H, 9.62.

Methyl Spiro[2.6]non-1-yl Ketone (39). A 336-mg sample of **61** was converted to **39** as described above for **7**. Pure material was obtained from column J at 95°: ir 3070 (w), 2930, 1699, 1370, 1170 cm^{-1}; nmr (220 MHz) δ 0.73 (d of d, $J_1 = 4$, $J_2 = 8$ Hz, 1 H), 1.22 (d of d, $J_1 = 4$, $J_2 = 6$ Hz, 1 H), 1.23–1.68 (m, 12 H), 1.77 (d of d, $J_1 = 6$, $J_2 = 8$ Hz, 1 H), 2.20 (s, 3 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.61; H, 10.92.

4-(1-Cycloheptenyl)-2-butanone (40). When cyclopropyl ketone **39** was subjected to vpc on column H at 180° essentially only one peak was observed. Collection of the material provided the rearranged ketone **40**: ir 3040 (w, shoulder), 2920, 1719, 1437, 1350, 1150 cm^{-1}; nmr (220 MHz) δ 1.37–1.53 (m, 4 H), 1.67–1.82 (m, 2 H), 1.97–2.22 with s at 2.05 (m, 7 H), 2.27 (broad t, $J = 8$ Hz, 2 H), 2.40 (t, $J = 8$ Hz, 2 H), 5.49 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.55; H, 11.15.

Heating a sample of **39** at 180–185° for 15 min gave material whose ir spectrum showed that it had rearranged quantitatively to **40**.

Photolysis of 3-Methylene-4-phenoxy-2-butanone (11). A solution of 405 mg of **11** in 350 ml of benzene was photolyzed for 262 hr following procedure B. A large amount of orange solid lined the walls of the reaction vessel. The yellow solution was washed three times with 10% aqueous Na_2CO_3, twice with water, and once with saturated aqueous NaCl. After drying with Na_2SO_4 the resulting colorless solution was concentrated on a rotary evaporator. Vpc analysis indicated that 90% of the starting material was consumed to give only methyl *trans*-2-phenoxycyclopropyl ketone **41** in 17% yield. The product was isolated by preparative vpc on column F and was shown to be identical with an authentic sample prepared as described below.

Methyl *trans*-2-Phenoxycyclopropyl Ketone (41). In our hands preparation of methyl 2-phenoxycyclopropyl ketone from 890 mg of the crude carboxylic acid (mp 88–99°) following the procedure reported by Julia[50] gave 613 mg (70%) of ketone, bp 90–95° (0.2 mm). Preparative vpc on column F gave analytically pure trans ketone: ir 1700, 1600, 1587, 1490, 1425, 1380, 1237, 1160, 950, 875, and 675 cm^{-1}; nmr (220 MHz) δ 1.38 (ddd, $J_{AD} = 5$, $J_{AB} = 9$, $J_{AE} = 4$ Hz, 1 H, H_A), 1.55 (m, 1 H, H_B), 2.14 (ddd, $J_{AD} = 6$, $J_{BD} = 4$, $J_{DE} = 2$ Hz, 1 H, H_D), 2.30 (s, 3 H), 3.91 (ddd, $J_{AE} = 4$, $J_{BE} = 6$, $J_{DE} = 2$ Hz, 1 H, H_E), 6.82–6.95 (m, 3 H, *m*- and *p*-ArH), 7.23 (t, $J = 8$ Hz, 2 H, *o*-ArH).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.98; H, 6.91.

Equilibration of ketone **41** as described above for **19** afforded a 90:10 mixture of trans and cis isomers, respectively. The cis ketone was indicated by an acetyl methyl singlet at δ 2.04 ppm.

Photolysis of 7-Methyl-3-methylen-6-octen-2-one (12). A solution of 147 mg of enone **12** was photolyzed following procedure B for 42 hr. A small amount of yellow solid was observed in the reaction vessel. Vpc analysis indicated that 98% of the enone was consumed to yield 23% of one isomer of 1-methyl-2-isobutenyl-4-methylenecyclobutan-1-ol (**43**) and 26% of methyl *cis*- and 24% of methyl *trans*-3-isobutenylcyclobut-1-yl ketones (**42**), isolated on column G. Cyclobutanol **43** was reinjected onto column C to give an analytical sample: ir 3610, 3570, 3070, 2970, 2920, 1675, 1430, 1365, 1320, 1175, 1125, 1050, 935, and 875 cm^{-1}; nmr (220 MHz) δ 1.34 (s, 3 H), 1.51 (br s, 3 H), 1.71 (br s, 1 H), 1.77 (br, s, 3 H), 1.96–2.09 (m, 1 H), 2.54–2.70 (m, 1 H), 2.86 (ddd, $J_{AB} = J_{AD} = 3$ Hz, $J_{AX} = 9$ Hz, 1 H, H_A), 4.71 (m, 1 H), 4.98 (m, 1 H), and 5.03 (br d, $J_{AX} = 9$ Hz, 1 H, H_X).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.56. Found: C, 78.58; H, 10.74.

The second product was *cis*-**42**: ir 2970, 2925, 2850, 1713, 1440, 1370, 1350, 1170, and 930 cm^{-1}; nmr (220 MHz) δ 1.54 (br s, 3 H), 1.63 (br s, 3 H), 1.81–1.99 (m, 2 H), 1.96 (s, 3 H), 2.16–2.32 (m, 2 H), 2.77–3.03 (m, 2 H), and 5.02 (br d, $J = 8$ Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.56. Found: C, 78.97; H, 10.76.

The third product was *trans*-**42**: ir 2965, 2930, 2850, 1712, 1435, 1420, 1370, 1350, and 1160 cm^{-1}; nmr (220 MHz) δ 1.54 (br s, 3 H), 1.75–1.97 (m, 2 H), 2.01 (s, 3 H), 2.32–2.45 (m, 2 H), 2.94–3.17 (m, 2 H), and 5.20 (br d, $J = 8$ Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.56. Found: C, 79.10; H, 10.72.

Equilibration of a sample of *trans*-**42** as described for **19** above afforded a 72:28 mixture (nmr) of cis and trans isomers, respectively.

Photolysis of 3-Methylene-6-hepten-2-one (13). A solution of 405 mg of **13** in 400 ml of pentane was photolyzed following procedure B for 42 hr. No solid was observed in the reaction vessel. Vpc analysis indicated that 89% of enone **13** was consumed to yield 6% of 1-methyl-6-methylenecyclohex-3-en-1-ol (**46**), 17% of a 60:40 mixture (nmr) of *cis*- and *trans*-**47**, respectively, 27% of a 56:44 mixture (nmr) of methyl *cis*- and *trans*-3-vinylcyclobut-1-yl ketone (*cis*- and *trans*-**44**), 8% of methyl bicyclo[2.1.1]hex-1-yl ketone (**48**), and 20% of cyclohex-3-en-1-yl methyl ketone (**45**), all isolated on column G. The cis and trans ketones **44** were separated by reinjection onto column G. Methyl *cis*-3-vinylcyclobut-1-yl ketone (*cis*-**44**): ir 3080, 2980, 2935, 2860, 1715, 1635, 1420, 1350, 1165, 980, and 900 cm^{-1}; nmr (220 MHz) δ 1.93–2.09 (m, 2 H), 1.98 (s, 3 H), 2.15–2.34 (m, 2 H), 2.78 (m, 1 H), 2.97 (m, 1 H), 4.85–4.98 (m, 2 H), and 5.73–5.89 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.23; H, 9.86.

Methyl *trans*-3-vinylcyclobut-1-yl ketone (*trans*-**44**): ir 3075, 2980, 2935, 2850, 1712, 1635, 1420, 1350, 1160, 980, and 900 cm^{-1}; nmr (220 MHz) δ 1.91–2.08 (m, 2 H), 2.02 (s, 3 H), 2.30–2.44 (m, 2 H), 2.82–2.95 (m, 1 H), 3.00–3.15 (m, 1 H), 4.90–5.01 (m, 2 H), and 5.83–5.99 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.30; H, 9.94.

Equilibration of *trans*-**44** as described for **19** above afforded a 66:34 mixture (nmr) of cis and trans isomers, respectively.

Cyclohex-3-en-1-yl methyl ketone (**45**) was identical (ir, nmr) with an authentic sample:[51] ir 3025, 2970, 2840, 1713, 1650, 1430, 1365, 1345, 1210, 1150, 700, and 615 cm^{-1}; nmr (220 MHz) δ 1.41–1.63 (m, 1 H), 1.78–1.98 (m, 1 H), 2.02–2.18 (m, 4 H), 2.08 (s, 3 H), 2.34–2.56 (m, 1 H), and 5.58 (br s, 2 H).

1-Methyl-6-methylenecyclohex-3-en-1-ol (**46**) gave the following data: ir 3605, 3460, 3085, 3025, 2970, 2955, 1653, 1420, 1365, 1125, 1090, 1000, 950, 890, 860, and 620 cm^{-1}; nmr (220 MHz) δ 1.27 (br, 1 H), 1.30 (s, 3 H), 2.18 (br, 2 H), 2.88 (br, 2 H), 4.69 (br s, 1 H), 4.92 (br s, 1 H), and 5.52 (br s, 2 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.39; H, 9.72.

Photolysis of **13** in benzene gave *cis*-**47** exclusive of the trans isomer. Both isomers were prepared independently as detailed below. A mixture of *cis*- and *trans*-**47** from photolysis in pentane was hydrogenated over 5% Pd/C in methanol at room temperature and 1 atm to give as sole product 3-methyl-2-heptanone. This was identical (ir, nmr) with the authentic sample prepared as detailed below.

Bicyclo[2.1.1]hex-1-yl methyl ketone (**48**) gave the following data: ir 2970, 2870, 1700, 1350, 1265, and 1190 cm^{-1}; nmr (220 MHz) δ 1.23–1.28 (m, 2 H), 1.75 (br, 6 H), 2.01 (s, 3 H), and 2.44 (br, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.23; H, 9.86.

***cis*- and *trans*-3-Methylene-5-hepten-2-one (*cis*- and *trans*-47).** These ketones were prepared from ethyl 2-crotylacetoacetate[21] following the procedure given above for **12**. Commercial crotyl bromide was used in the first step, and the final product was a 4:1 mixture (nmr) of trans and cis isomers which was separated by vpc on a 40 ft × 0.25 in. column of Carbowax 20M. Data for *trans*-**47**: ir 3085, 3020, 2960, 2915, 2850, 1680, 1625, 1430, 1420, 1360, 1250, 1110, 960, 935, and 925 cm^{-1}; nmr (220 MHz) δ 1.65 (br d, $J = 6$ Hz, 3 H), 2.25 (s, 3 H), 2.85 (br d, $J = 6$ Hz, 2 H), 5.25–5.48 (m, 2 H), 5.66 (br s, 1 H), and 5.89 (s, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.15; H, 9.66.

Purified *cis*-**48** gave the following data: ir 3090, 3020, 2970, 2915, 2850, 1680, 1625, 1425, 1360, 1255, 1105, 960, 935, 925, and 670 cm^{-1}; nmr (220 MHz) δ 1.61 (br d, $J = 7$ Hz, 3 H), 2.26 (s, 3 H), 2.92 (br d, $J = 7$ Hz, 2 H), 5.24–5.39 (m, 1 H), 5.44–5.62 (m, 1 H), 5.67 (br s, 1 H), and 5.90 (s, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.39; H, 9.77.

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3-Methyl-2-heptanone. Hydrogenation of 504 mg of authentic **47** in 10 ml of methanol over 10 mg of 5% Pd/C gave 92% of 3-methyl-2-heptanone. An analytical sample was obtained on column C: ir 2960, 2925, 2870, 2855, 1720, 1455, 1350, and 1140 cm^{-1}; nmr (220 MHz) δ 0.90 (t, J = 7 Hz, 3 H), 0.98 (d, J = 7 Hz, 3 H), 1.14–1.69 (m, 6 H), 2.02 (s, 3 H), and 2.37 (m, 1 H).

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.93; H, 12.76.

Photolysis of 3-Methylene-6-heptyn-2-one (14). A solution of 152 mg of **14** in 150 ml of pentane was irradiated for 61 hr following procedure B. A large amount of yellowish solid coated the walls of the reaction vessel. Vpc analysis indicated that 98% of the starting enone was consumed to yield 24% of a 90:10 mixture (vpc) of 3-methylene-5,6-heptadien-2-one (**50**) and starting material, respectively, and 11% of *trans*- and 16% of *cis*-3-ethynylcyclobutyl methyl ketone (**49**). The products were isolated on column G. Allene **50** was separated from the small amount of **14** by reinjection onto column C. A sample of **14** was prepared under identical vpc conditions and was shown by ir and nmr to contain none of allene **50**. Allene **50** gave the following data: ir 3095, 2985, 2915, 1963, 1685, 1627, 1425, 1360, 1310, 1248, 1180, 1115, 1097, 925, and 835 cm^{-1}; nmr (220 MHz) δ 2.27 (s, 3 H), 2.86–2.94 (m, 2 H), 4.58–4.66 (m, 2 H), 5.04 (m, 1 H), 5.77 (br s, 1 H), and 5.94 (s, 1 H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.67; H, 8.37.

trans-**49** gave the following data: ir 3310, 2985, 2945, 2855, 2110, 1715, 1425, 1355, 1230, 1175, and 1160 cm^{-1}; nmr (220 MHz) δ 2.14–2.32 (m, 2 H), 2.41–2.56 (m, 2 H), 2.84–3.01 (m, 1 H), and 3.20–3.36 (m, 1 H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.58; H, 8.18.

cis-**49** gave the following data: ir 3310, 2990, 2945, 2865, 2110, 1715, 1450, 1430, 1415, 1355, 1220, and 1175 cm^{-1}; nmr (220 MHz) δ 2.00 (s, 4 H), 2.19–2.50 (m, 4 H), and 2.77–3.09 (m, 2 H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.83; H, 8.28.

Equilibration of *trans*-**49** following the procedure described for **19** above afforded a 66:34 mixture (nmr) of *cis*- and *trans*-**49**.

Photolysis of 6-Methyl-4-methylene-1-hepten-3-one (15). Irradiation of 70 mg of **15** in 70 ml of pentane for 4 hr through Pyrex following procedure A led to 98% conversion. Vpc on column C indicated formation of a single product in 57% yield. In a similar experiment using a uranium glass filter the same product was obtained and no others. This was identified as 1-vinyl-3,3-dimethyl-2-methylenecyclobutan-1-ol (**51**): ir 3605 (m), 3465 (w), 3070 (wm), 2955 (s), 1680 (wm), 1635 (w), 990 (m), 925 (m), 913 (m), 880 (s) cm^{-1}; nmr (60 MHz) δ 1.03 and 1.10 (s, 6 H), 1.80 (s, exchanges with D_2O, 1 H), 2.17 (m, 2 H), 4.85–5.45 (m, 4 H), 5.94 (d of d, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.46.

Photolysis of 2-Methylenecyclododecanone (16). A solution of 300 mg of enone **16**, prepared as previously described,[4] in 300 ml of benzene was photolyzed following procedure A for 121 hr to complete conversion. The solvent was distilled through a Vigreux column to afford a pale yellow solid in 87% yield. This was recrystallized from pentane, mp 86.5–88°, to afford colorless 12-methylenebicyclo[10.2.0]dodecan-1-ol (**52**): ir 3610, 3455, 2930, 2845, 1675, 1470, 1435, and 880 cm^{-1}; nmr (220 MHz) δ 1.25–1.81 (m, 17 H), 2.01–2.28 (m, 2 H), 2.41–2.51 (m, 1 H), 4.73 (dd, J = 2, 2 Hz, 1 H), and 4.97 (dd, J = 2, 2 Hz, 1 H).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.47: H, 11.46.

Photolysis of 5,5-Dimethyl-3-methylene-2-hexanone (17). Under the conditions employed for **4**, a solution of 55 mg of **17** in 55 ml of benzene was photolyzed for 142 hr. A large amount of yellow solid coated the reaction vessel. Vpc analysis indicated no distinct volatile products, and no further investigation was attempted.

Photolysis of 3-(7-Norbornyl)-3-buten-2-one (18). A 111-mg sample of **18** was photolyzed following procedure B for 281 hr. A large amount of white solid coated the reaction vessel. Vpc analysis indicated no distinct volatile products, and no further investigation was attempted.

Ethyl 2-Acetyl-5-hexynoate. An 8.45-g portion of acetoacetic ester was added dropwise to a stirred ice-cold solution prepared from 1.54 g of sodium and 30 ml of absolute ethanol. To this was added 9.32 g of 4-bromo-1-butyne[52] in one portion. A white precipitate soon appeared, and the mixture was heated at reflux overnight. Solvent was removed at reduced pressure and the remaining paste was extracted twice with ether, which was then washed with water and brine and dried. Distillation of the yellow residue after removal of solvent gave 2.66 g (23%) of colorless oil, bp 123–126° (10 mm). An analytical sample was obtained on column G: ir 3310, 2980, 2930, 2110, 1750, 1725, 1440, 1430, 1365, 1355, 1235, 1140, 1035, and 1010 cm^{-1}; nmr (220 MHz) δ 1.28 (t, J = 7 Hz, 3 H), 1.85 (t, J = 2.5 Hz, 1 H), 1.89–2.06 (m, 2 H), 2.14–2.25 (m, 2 H), 2.19 (s, 3 H), 3.57 (t, J = 7 Hz, 1 H), and 4.16 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.90; H, 7.60.

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