# Abstraction of Allylic Hydrogen *vs.* Other Processes in the Photochemistry of Three Doubly Unsaturated Ketones

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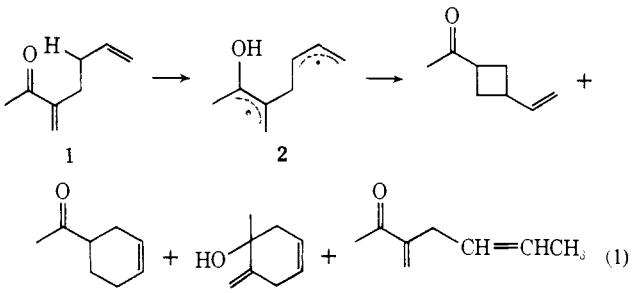
**Abstract:** Preparation and photolysis of three ketones, **3**, **12**, and **27**, are described. **3** yields the product of allylic rearrangement **5** and the [2 + 2] cycloadduct **6**. **12** is isomerized to **17**–**20** through transfer of both allylic and nonallylic $\gamma$ hydrogen, and also to **21**, through transfer of $\beta$ hydrogen. Secondary rearrangement of **21** yields **22**. From ketone **27** there was obtained only dienal **28** through formation of oxetane **29** and subsequent thermal opening. The results indicate that the possibility of forming stabilized biradical intermediates such as **2** and **4** does not control the qualitative photochemistry of these ketones. Products derivable from such intermediates may be formed, but only in competition with other processes. Structures of the various products were established by a combination of spectroscopic and chemical methods.

During an investigation into the photochemistry of $\alpha$-methylene ketones we observed that irradiation of 3-methylene-6-hepten-2-one (**1**) yielded a number of products which could be explained as arising from collapse of the bisallylic radical intermediate **2** (eq 1).[1,2]




(1)

This observation, together with reports concerning similar intermediates in other reactions,[3,4] encouraged us to explore the photolysis of additional unsaturated ketones which might follow pathways related to eq 1. We were particularly interested in learning whether pathways involving such bisallylic radicals were highly favorable in competition both with abstraction of nonallylic hydrogen, as well as with [2 + 2] cycloaddition reactions. The complex effects involved are not yet sufficiently well understood to allow prediction of preferred photochemical pathways and of the distribution of photoproducts in such situations,[5] although it is just this sort of information that is needed in order to evaluate the preparative usefulness of these reactions. The results described below indicate that the possibility of forming such stabilized intermediates does not suffice to control qualitative photochemical behavior; such pathways may be followed, but only in effective competition with alternative processes. Photochemical experiments are described first, followed by preparative work.

We first examined the behavior of 5-allyl-1-cyclopenten-1-yl methyl ketone (**3**), a compound in which $\gamma$ abstraction with formation of stabilized intermediate **4** appears sterically quite favorable. Irradiation of **3** in pentane led to the *trans*-propenyl ketone **5** (50%[6]) and methyl tricyclo[3.3.0.0$^{2,7}$]oct-1-yl ketone (**6**, 13%[6]) as the only volatile products. In benzene as solvent the yields were **5** (31%[6]) and **6** (36%[6]). The double bond isomerization leading to **5** appears to proceed through the desired bisallylic intermediate **4**, which undergoes disproportionation with allylic rearrangement of hydrogen in the side chain. The structure and stereochemistry of **5** follow from its spectra and the fact that partial hydrogenation of both **3** and **5** yielded the propyl-substituted product, **7**. It is noteworthy that various other possible products from **4** (see eq 1) are absent, and that there is an effect of solvent on the competition between hydrogen abstraction and [2 + 2] cycloaddition. This cycloaddition itself is interesting in that it represents a new means of reaching a tricyclic system first prepared in 1908. Previous photochemical syntheses[3,7] of this ring system have depended upon intramolecular cycloadditions of vinylcyclohexenes such as carvone (**8**) (the original example), with formation of new bonds as indicated in **9**; the present example, on the other hand, utilizes the unsaturation of an allylcyclopentene, with closure of the alternative pair of cyclobutane bonds, as shown in **10**. The structure of **6** was suggested by its spectroscopic properties and confirmed through Wolff–Kishner reduction to the tricyclic hydrocarbon **11**, which was independently prepared as outlined in a later paragraph.

The second dienone investigated was **12**. This ketone was chosen because it offers abstractable allylic

(1) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Amer. Chem. Soc.*, **95**, 4873 (1973). For a mechanistic study pointing to singlet biradical intermediates in these and related abstraction reactions of $\alpha$-methylene ketones, see R. A. Cormier and W. C. Agosta, *ibid.*, **96**, 618 (1974).

(2) In addition there is formed from **1** a small amount of [2 + 2] product, bicyclo[2.1.1]hex-1-yl methyl ketone.

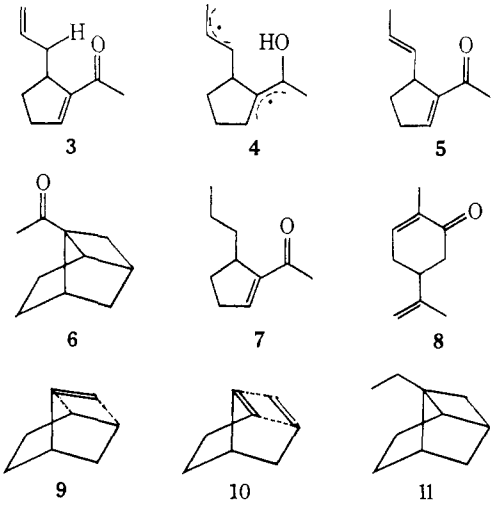
(3) W. F. Erman and T. W. Gibson, *Tetrahedron*, **25**, 2493 (1969); T. S. Cantrell and J. S. Solomon, *J. Amer. Chem. Soc.*, **92**, 4656 (1970).

(4) J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. H. Wiekenkamp, *J. Amer. Chem. Soc.*, **94**, 285 (1972); J. R. Scheffer, J. Trotter, R. E. Gayler, and C. A. Bear, *Tetrahedron Lett.*, 2871 (1973).

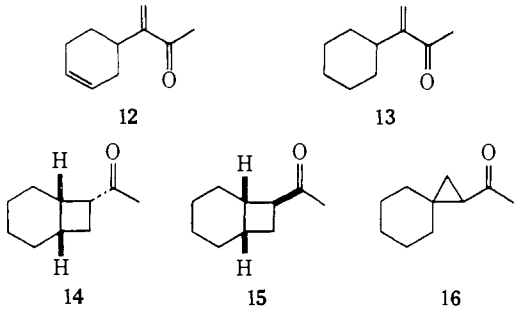
(5) Both the number of steps involved and their reversibility lead to these difficulties. Thus rapid abstraction of hydrogen does not assure effective transformation by way of the species formed. While quantitative data are not yet available for substrates from which bisallylic intermediates are possible, the point can be illustrated with data obtained with phenones. In these systems carbonyl abstraction of allylic $\gamma$ hydrogen is some 3.85 times faster than that of simple alkyl $\gamma$ hydrogen, but the quantum yield for reaction (type II photoelimination) is lower for the allylic than for the saturated compound (0.26 compared with 0.33). For further discussion, see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971), and references cited therein.

(6) Yields of photoproducts are based on converted starting material and were determined by calibrated vpc measurements.

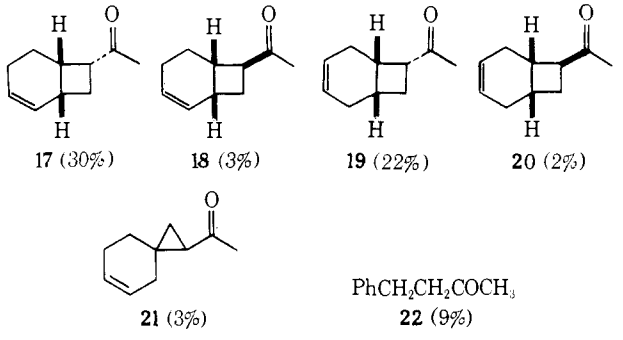
(7) G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1908); G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.*, **79**, 4741 (1957); J. Meinwald and R. A. Schneider, *ibid.*, 87, 5218 (1965); G. L. Hodgson, D. F. MacSweeney, and T. Money, *J. Chem. Soc., Chem. Commun.*, 236 (1973).



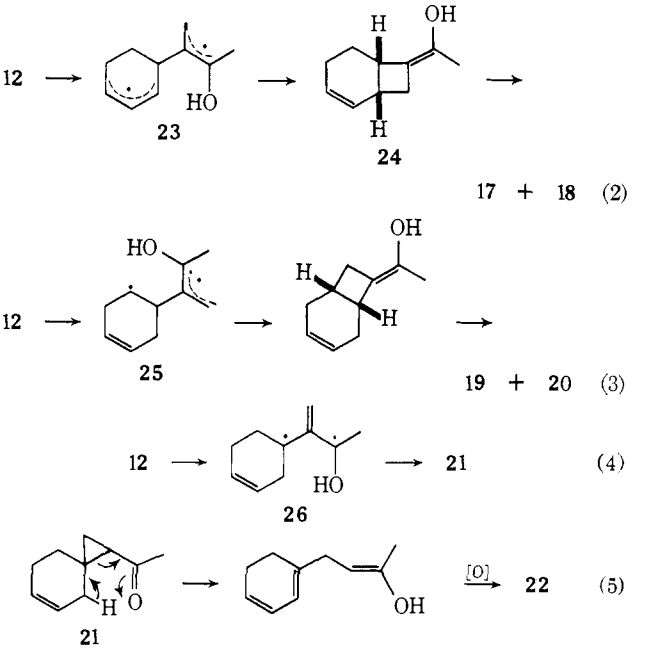
and nonallylic $\gamma$ hydrogens in very similar stereochemical situations. Its behavior was expected to be interesting in comparison with that of the cyclohexyl analog **13**. As we have previously reported,[1] **13** is isomerized on irradiation to a mixture of **14** and **15**. Little, if any, of the spiro ketone **16** is formed, although analogous



cyclopropanes are seen in related systems. Irradiation of **12** in benzene gave rise to the six products, **17**–**22**.



The plausible [2 + 2] cycloaddition product, which once again is ketone **6**, was absent. All of these products are reasonable on the basis of previous experience with **13** and related $\alpha$-methylene ketones. Abstraction of allyic $\gamma$ hydrogen in **12** can lead to **23**, which may collapse to enol **24**. Protonation of **24** should occur largely from the exo side, leading to preferential formation of **17** rather than the thermodynamically more stable **18**. The other pair of bicyclic ketones **19** and **20** can be accounted for similarly, but through initial abstraction of the alternative, nonallylic $\gamma$ hydrogen, as illustrated in **25**. We have previously suggested that spiro ketones such as **21** result from abstraction of $\beta$ hydrogen (see **26**), collapse to the enol, and ketonization.[1] **21** was obtained as the mixture of isomers expected from this sequence. These three competing processes are shown in eq 2–4. Benzylacetone (**22**)



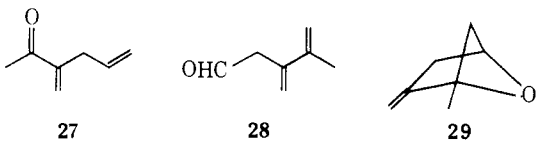
doubtless results from secondary thermal or photochemical ring opening[1,8,9] of **21** with subsequent, adventitious oxidation of the cyclohexadiene formed (eq 5). We note that more $\beta$ abstraction occurs with **12** (12%) than with **13** (<4%). Thus, the double bond of **12** leads to an increase in effective transfer of $\beta$ hydrogen but causes only slight selectivity (1.37:1) in effective abstraction of allylic rather than nonallylic $\gamma$ hydrogen.

The structures of these products from **12** were secured in the following manner. The four bicyclo[4.2.0]octenes **17**–**20** were readily separated by preparative vpc into endo (**17** and **19**) and exo (**18** and **20**) pairs. Hydrogenation of each pair gave a single product in high yield, **14** from **17** and **19**, and **15** from **18** and **20**, identical in each case with an authentic sample.[1] A second and more difficult vpc separation furnished the double bond isomers from each pair. Tentative assignment of the double bond position in each isomer was possible from nmr spectra, as well as from the relative amount of each obtained from **12**. These assignments were verified by independent syntheses of **17** and **18** which are detailed below. The structure of **21** rests on its spectroscopic properties, and **22** was compared with an authentic sample.

We next examined the photochemical behavior of 3-methylene-5-hexen-2-one (**27**). Through abstraction of $\beta$ hydrogen this ketone could have shown behavior parallel to its higher homolog **1**. On irradiation in pentane, however, **27** was smoothly transformed into a mixture which yielded a single volatile product in 54%[6] yield on preparative vpc. This was collected and identified as 4-methyl-3-methylene-4-pentenal (**28**) through ir, nmr, and uv measurements. The rearrangement may be explained as an intramolecular Paternò–Büchi reaction[10] leading to the bicyclic oxetane **29**, followed by thermal rupture of the four-membered ring in the

(8) R. M. Roberts, R. M. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 89, 1404 (1967), and references cited therein.
(9) W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, 34, 1849 (1969).
(10) D. R. Arnold, *Advan. Photochem.*, 6, 301 (1968).

opposite fashion. This interpretation is supported by our finding that there is spectroscopic evidence of **28** only after the photolysate is heated at 50–60° or subjected to vpc. Efforts to isolate the unstable primary product were not successful. While **27** then behaves quite differently from **1**, the observed cycloaddition has good analogy in related systems. Irradiation of α-diketone **30** yields **31**,[11] and 5-hexen-2-one (**32**) is isomerized photolytically to both possible oxetanes **33** and **34** (although **34** was too unstable to permit isolation).[12]



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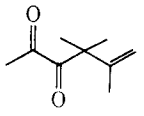

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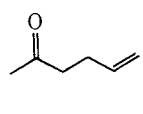

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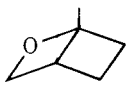

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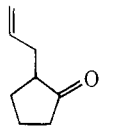
**Preparative Experiments.** Ketone **3** was available from 2-allylcyclopentanone (**35**).[13] Formation of the cyanhydrin and subsequent dehydration furnished an approximately 1:1 mixture of unsaturated nitriles **36** and **37**. These could be separated by preparative vpc for characterization or hydrolyzed directly using potassium hydroxide in isopropyl alcohol.[14] This hydrolysis led to a mixture of roughly equal amounts of three carboxylic acids, **38a–40a**, which were separated and characterized as their methyl esters **38b–40b**. Hydrol-



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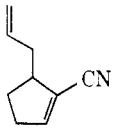

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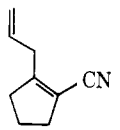

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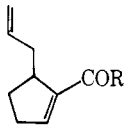

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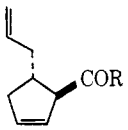

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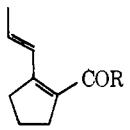

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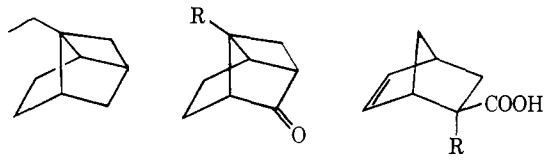
a, R = OH
b, R = $OCH_3$
c, R = $CH_3$

ysis of **38b** with carbonate and then reaction of the acid directly with methyllithium[15] in ether gave the desired ketone **38c** (≡**3**). Alternatively, it was more convenient for preparative purposes to treat the original mixture of acids **38a–40a** with methyllithium and then to separate the three methyl ketones **38c–40c** thus formed. Only single stereoisomers of **39b** and **39c** were observed; since similar cis-substituted cyclopentenes readily undergo epimerization to their trans isomers in base,[16] **39b** and **39c** can be assigned the trans stereochemistry shown. In a separate experiment base-catalyzed equilibration of **38b** showed that there is almost no preference for conjugation of the double bond in this system (**38b**:**39b** = 54:46, $K_{eq}$ = 0.85). This is ascribable to steric inhibition of resonance by the adjacent allyl substituent in the α,β-unsaturated isomer **38b**, since the parent methyl cyclopentenecarboxylate system is largely conjugated at equilibrium ($K_{eq}$ = 0.06[17]). The same effect is apparent in the reduced intensity of uv absorption of ketone **38c** [$\lambda_{max}^{EtOH}$ 238 nm (ε 8300), compared with 239 nm (13,000) reported[18] for 1-cyclopenten-1-yl methyl ketone]. The extended conjugation of **40b** and **40c** leads to uv absorption at 270 nm (ε 19,400) and 291 (14,500), respectively. Only the *trans*-propenyl isomers were found, as indicated by both ir and nmr spectra.

In order to substantiate the structure of tricyclic ketone **6** we required an unimpeachable synthesis of its reduction product **11**. An attractive solution to this problem lay in preparation of **11** by way of **41a**. Synthesis of the related methyl compound **41b** from **42b** has been well described,[19] and we used this sequence with only trivial modification for preparation of **41a** from **42a**. Thus, acid-catalyzed rearrangement of **42a**[20] furnished lactone **43**, hydride reduction of which gave a diol, **44**. This could be partially acetylated to form chiefly the desired primary acetate **45**, which was separated from the related diacetate on alumina. Jones oxidation[21] then furnished the acetoxy ketone **46**, and saponification of this ester gave ketol **47** which was in mobile equilibrium with the related hemiketal **48**. **47–48** was converted to tosylate **49**, and this underwent cyclization to **41a** on treatment with sodium hydride in hot glyme. Wolff–Kishner reduction led to **11**, identical with the sample from photoproduct **6**. In both preparations of **11** the final step was removal of a carbonyl function. Since the amounts of the ketones available were rather limited, and both the ketone starting materials and the hydrocarbon product are relatively volatile compounds, we adopted particular conditions for these Wolff–Kishner reductions. A useful procedure which gave excellent results involved heating a mixture of 15–25 mg of ketone, ethylene glycol, sodium glycolate (prepared using sodium hydride), and excess 97% hydrazine in a sealed tube at 195° for several hours. Work-up with pentane and water gave **11** in 75–82% yield in each case with no other volatile products. On a slightly larger scale the preformed semicarbazone of **41a** was reduced to the hydrocarbon under similar conditions.

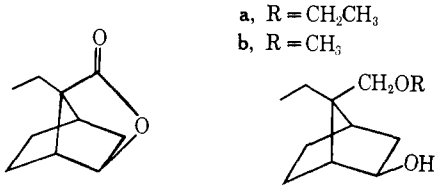
The second substrate, ketone **12**, was prepared from

(11) R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970).
(12) N. C. Yang, N. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965).
(13) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **26**, 3112 (1961).
(14) Use of methanol as solvent led to acidic products which showed methoxyl absorption in their nmr spectra. This incorporation of solvent, presumably by Michael addition before hydrolysis, did not occur with isopropyl alcohol.
(15) M. J. Jorgenson, *Org. React.*, 18, 1 (1970).
(16) P. R. Brook and A. J. Duke, *J. Chem. Soc. C*, 1764 (1971).
(17) S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, **35**, 3352 (1970).
(18) I. Heilbron, E. R. H. Jones, J. B. Toogood, and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).
(19) J. A. Berson, D. S. Donald, and W. J. Libbey, *J. Amer. Chem. Soc.*, **91**, 5580 (1969).
(20) W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Amer. Chem. Soc.*, 80, 5488 (1958).
(21) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953); C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).



11 41 42

a, R = $CH_2CH_3$
b, R = $CH_3$



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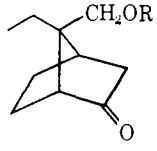
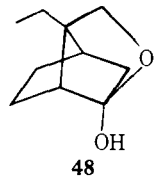
44, R = H
45, R = $COCH_3$





46, R = $COCH_3$
47, R = H
49, R = tosyl

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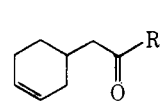
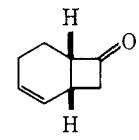


50, R = OH
51, R = $CH_3$



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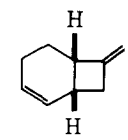

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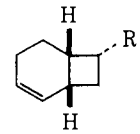
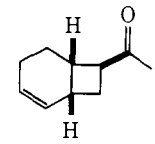


17, R = $COCH_3$
54, R = $CH_2OH$
55, R = COOH
56, R = $COOCH_3$



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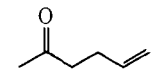

57

3-cyclohexene-1-acetic acid (**50**).[22] Reaction of **50** with methyllithium furnished the methyl ketone **51**; condensation of this with formaldehyde in base and subsequent acid-catalyzed dehydration of the ketol gave **12**. The photoproducts **17** and **18** were synthesized from the related cyclobutanone **52**.[23] Wittig reaction with triphenylphosphonium methylide in dimethyl sulfoxide[24] gave **53**. Hydroboration using 9-borabicyclo[3.3.1]nonane[25] (9-BBN) and subsequent peroxide oxidation furnished the primary alcohol **54**, which was treated directly with Jones reagent[21] to form the carboxylic acid **55**. This acid was fully characterized as the ester **56** obtained with diazomethane, and it was converted to the desired ketone **17** with methyllithium. Equilibration of **17** in base gave largely the exo isomer **18** (86:14). This experiment confirmed that **17** and its precursors **54** and **55** have the endo stereochemistry predicted if hydroboration of **53** occurs preferentially, as expected,[25] from the less hindered exo side.

Finally, **27** was available through acid-catalyzed Mannich reaction[26] of allylacetone (**57**), formaldehyde, and piperidine, followed by destructive distillation of the resulting ammonium salt.

## Experimental Section

**Materials and Equipment.** All vpc and spectroscopic equipment has been previously described.[1] Columns used in the present work are: A, 25% Carbowax 1500, 10 ft; B, 15% Carbowax 20M, 40 ft; C, 25% QF-1, 20 ft; D, 10% SE-30, 15 ft; E, 15% SE-30, 15 ft. All were prepared in $^3/_8$-in. aluminum tubing using 45–60 Chromosorb W, except column B, which is 0.25 in. in diameter. Solutions were dried over $Na_2SO_4$ or $MgSO_4$; melting points are corrected; boiling points are uncorrected. All compounds were obtained as colorless oils unless otherwise noted.

**General Procedure for Photolyses.** Photochemical experiments were performed and worked up as previously described,[1] using a Rayonet RPR-204 reactor equipped with four RUL-3500-Å lamps.

**Photolysis of Methyl 5-Allyl-1-cyclopenten-1-yl Ketone (3).** A solution of 351 mg of **3** in 350 ml of pentane was irradiated for 4 hr. Vpc analysis indicated that 73% of the starting material was consumed to yield 13% of methyl tricyclo[3.3.0.$0^{2,7}$]oct-1-yl ketone (**6**) and 50% of methyl 5-(*trans*-propenyl)-1-cyclopenten-1-yl ketone (**5**), isolated on column A.

Ketone **6**: ir 2960, 2870, 1698, 1455, 1350, 1255, 1200, 1080, 925, 900, 855, and 830 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.20–1.47 (m, 2 H), 1.53–1.83 (m, 5 H), 1.88–1.96 (m, 1 H), 2.02 (s, 3 H), and 2.25–2.35 (m, 3 H).[27]

Ketone **5**: ir 3050, 3000, 2935, 1675, 1610, 1425, 1360, 1275, 1245, and 950 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.63 (br d, $J$ = 5 Hz, 3 H), 1.69–1.84 (m, 1 H), 2.00–2.14 (m, 1 H), 2.19 (s, 3 H), 2.31–2.65 (m, 2 H), 3.49 (br, 1 H), 5.25–5.48 (m, 2 H), and 6.57 (br, 1 H).[27]

When **3** was photolyzed in benzene for 21 hr to 90% conversion, 36% of **6** and 31% of **5** were formed.

**Methyl 5-Propyl-1-cyclopenten-1-yl Ketone (7). A. From 3.** A solution of 100 mg (0.67 mmol) of **3** in 2 ml of methanol was hydrogenated over 10 mg of 5% Pd–$BaSO_4$ at room temperature and 1 atm until *ca.* 1 mol of hydrogen was absorbed (~30 min.). The reaction was worked up with water and pentane, and the product was purified on column A: ir 2870, 1673, 1610, 1465, 1430, 1365, 1290, and 1250 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.91 (t, $J$ = 7 Hz, 3 H), 1.03–1.38 (m, 3 H), 1.52–1.73 (m, 2 H), 1.92–2.12 (m, 1 H), 2.20 (s, 3 H), 2.37–2.56 (m, 2 H), 2.89 (br, 1 H), and 6.52 (s, 1 H).[27]

**B. From 5.** In the same way as above, hydrogenation of **5** gave **7**, identical with the sample from **3**.

**Photolysis of 3-(3-Cyclohexen-1-yl)-3-buten-2-one (12).** A solution of 403 mg of **12** in 400 ml of benzene was photolyzed for 119 hr when ir analysis indicated that most of the enone had been consumed. A small amount of white solid appeared on the walls of the reaction vessel. Vpc analysis revealed that 95% of the enone was converted to the following products: 3% of a 57:43 (nmr) mixture of isomers of methyl spiro[2.5]oct-5-en-1-yl ketone (**21**); 5% of a 60:40 (nmr) mixture of methyl *exo-cis*-bicyclo[4.2.0]oct-2-en-7-yl ketone (**18**), and methyl *exo-cis*-bicyclo[4.2.0]oct-3-en-7-yl ketone (**20**); 52% of a 58:42 (nmr) mixture of methyl *endo-cis*-bicyclo[4.2.0]oct-2-en-7-yl ketone (**17**) and methyl *endo-cis*-bicyclo-[4.2.0]oct-3-en-7-yl ketone (**19**); and 9% of benzylacetone (**22**). The products were isolated by preparative vpc on column A. The individual bicyclic ketones were isolated with difficulty by reinjection of the respective endo and exo mixtures onto column B. **17** and **18** were identical with the synthetic samples described later, and **22** was identified by comparison (ir, nmr) with an authentic sample. Data for the other photoproducts follow.

Spiro ketones **21**: ir 3030, 2965, 2925, 1698, 1650, 1255, 1170, 1080, and 640 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.82 (dd, $J_1$ = 4 Hz, $J_2$ = 8 Hz, 1 H), 1.27–1.36 (m, 1 H), 1.62–1.84 (m, 4 H), 1.95–2.16 (m, 3 H), 2.18 and 2.22 (s, 3 H), and 5.62 (br s, 2 H); mass spectrum *m/e* 150.1035 ($M^+$, calcd for $C_{10}H_{14}O$, 150.1044).

Ketone **20**: ir 3025, 2920, 2830, 1710, 1640, 1425, 1350, 1165, and 660 $cm^{-1}$; nmr (220 MHz), $\delta$ 1.05–1.38 (m, 3 H), 1.48–1.66 (m, 1 H), 1.81–2.21 (m, 2 H), 1.97 (s, 3 H), 2.25–2.52 (m, 2 H), 2.62–2.78 (m, 1 H), and 5.83–6.03 (m, 2 H); mass spectrum *m/e* 150.1038 ($M^+$, calcd for $C_{10}H_{14}O$, 150.1044).

(22) W. R. Boehme, *J. Org. Chem.*, **26**, 2107 (1961).
(23) E. J. Corey and T. Ravindranathan, *Tetrahedron Lett.*, 4753 (1971), and references cited therein.
(24) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 28, 1128 (1963).
(25) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280, 5281 (1968).
(26) F. F. Blicke, *Org. React.*, **1**, 303 (1942).
(27) Elemental analysis was consistent with the empirical formula to within ±0.3%.

Ketone **19**: ir 3030, 2940, 2840, 1715, 1640, 1430, 1350, 1145, and 655 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.09–2.29 (m, 6 H), 1.95 (s, 3 H), 2.42–2.88 (m, 2 H), 3.17 (m, 1 H), and 5.46–5.84 [m with d at 5.77 ($J$ = 2 Hz), 2 H]; mass spectrum $m/e$ 150.1061 ($M^+$, calcd for $C_{10}H_{14}O$, 150.1044).

Equilibration of the 58:42 mixture of endo ketones **17** and **19** with KOH in aqueous methanol afforded a mixture containing *ca.* 95% of the exo isomers **18** and **20**; the ratio **18**:**20** was 62:38 (vpc).

Hydrogenation of the mixture of endo ketones **17** and **19** gave a 93% yield of methyl *endo-cis*-bicyclo[4.2.0]oct-7-yl ketone (**14**), identical with an authentic sample. Similarly, hydrogenation of the mixture of exo isomers **18** and **20** afforded 90% of exo ketone **15**, identical with an authentic sample.

**Photolysis of 3-Methylene-5-hexen-2-one (27).** A solution of 498 mg of **27** in 500 ml of pentane was irradiated for 290 hr. A large amount of white solid coated the walls of the reaction vessel. Analysis by vpc revealed that 74% of the starting material was consumed to yield 54% of 4-methyl-3-methylene-4-pentenal (**28**) as the only distinct product. This was isolated on column A: uv (95% EtOH) 228 nm ($\epsilon$ 22,400); ir 3095, 2950, 2805, 2710, 1730, 1600, and 890 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.95 (br s, 3 H), 3.20 (br d, $J$ = 2.5 Hz, 2 H), 4.96 (br s, 1 H), 5.02 (br s, 1 H), 5.11 (br s, 1 H), 5.31 (br s, 1 H), and 9.46 (t, $J$ = 2.5 Hz, 1 H).[27]

No evidence for the aldehyde product was found in the ir and nmr spectra of the crude photolysate. Rather, the nmr spectrum indicated an *ca.* 30:70 mixture, respectively, of starting enone and a product possessing a singlet at $\delta$ 1.47. A sample of the crude photolysate heated at 55° in a sealed tube for 20 min showed a new absorption at 1730 $cm^{-1}$ corresponding to the isolated aldehyde.

**5-Allyl- and 2-Allyl-1-cyclopentene-1-carbonitrile (36 and 37).** A mixture of 31.0 g (0.25) of 2-allylcyclopentanone[13] and 49 g (1 mol) of NaCN in 250 ml of water was cooled in ice, and a solution of 52 g (0.5 mol) of $NaHSO_3$ in 100 ml of water was added dropwise with stirring during 1 hr. After being stirred overnight at 5° the reaction mixture was extracted twice with ether. The combined extracts were washed with saturated aqueous NaCl and dried with $Na_2SO_4$. Concentration on a rotary evaporator afforded 35.9 g (95%) of slightly yellow oily cyanohydrin: ir 3600, 3440, 3070, 2970, 2870, 2225, 1640, 1435, 980, and 905 $cm^{-1}$.

A solution of this material in 100 ml of benzene and 100 ml of pyridine was cooled in ice. A solution of 100 ml of phosphorus oxychloride in 100 ml of pyridine was added dropwise with stirring during 1 hr, whereupon a white solid separated. The cooling bath was then removed, and the reaction mixture was stirred at room temperature for 3 days. The resulting brown mixture was cautiously poured onto ice, and the aqueous layer was extracted with ether. The combined organic solutions were washed with 10% aqueous HCl and saturated aqueous $NaHCO_3$ and dried with $Na_2SO_4$. Concentration on a rotary evaporator followed by short-path distillation afforded 23.2 g (73%) of a colorless oil, bp 102–103° (10 mm). Vpc analysis showed approximately equal amounts of the two nitriles, analytical samples of which were obtained from column C.

5-Allyl-1-cyclopentene-1-carbonitrile (**36**): ir 3075, 2920, 2840 2215, 1645, 1615, 1435, 980, 910, and 835 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.57–1.74 (m, 1 H), 2.02–2.23 (m, 2 H), 2.36–2.54 (m, 3 H), 2.96 (br, 1 H), 5.03 (br d, $J$ = 9 Hz, 1 H), 5.07 (br d, $J$ = 18 Hz, 1 H), 5.62–5.81 (m, 1 H), and 6.53 (dd, $J_1$ = 2 Hz, $J_2$ = 3 Hz, 1 H).[27]

2-Allyl-1-cyclopentene-1-carbonitrile (**37**): ir 3080, 2965, 2860, 2215, 1630, 1425, 975, and 910 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.95 (dddd, all $J$'s ~7.5 Hz, 2 H), 2.44 (br dd, $J_1 \sim J_2 \sim$ 7.5 Hz, 2 H), 2.60 (br dd, $J_1 \sim J_2 \sim$ 7.5 Hz, 2 H), 3.08 (d, $J$ = 6 Hz, 2 H), 5.04 (br d, $J$ = 8 Hz, 1 H), 5.08 (br d, $J$ = 17 Hz, 1 H), and 5.58–5.80 (m, 1 H).[27]

**Conversion of Nitriles 36 and 37 to Ketones 38c, 39c, and 40c.** A mixture of 266 mg (2 mmol) of nitrile **36**, 10 ml of 5% aqueous KOH, and 10 ml of 2-propanol was heated at reflux under a nitrogen atmosphere for 3 days. The reaction mixture was washed with ether and acidified with 10% aqueous HCl. The resulting mixture was extracted twice with ether, and the combined extracts were dried with $Na_2SO_4$. Removal of the solvent on a rotary evaporator yielded 205 mg (67%) of yellow oil. This was treated with excess diazomethane. After standing at room temperature for 30 min the solvent was distilled through a Vigreux column. Bulb-to-bulb distillation of the residue at 125–140° (10 mm) afforded 143 mg (47% overall) of colorless oil. Vpc analysis indicated essentially only two peaks in about equal amounts. Analytical samples were obtained on column A.

5-Allyl-1-cyclopentene-1-carboxylic acid methyl ester (**38b**): ir 3070, 2950, 2840, 1723, 1640, 1627, 1430, 1350, 1290, 1250, 1190, 1085, 985, and 905 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.65–1.80 (m, 1 H), 1.96–2.13 (m, 2 H), 2.35–2.55 (m, 3 H), 2.98 (br, 1 H), 3.66 (s, 3 H), 4.95 (br d, $J$ = 9 Hz, 1 H), 4.97 (br d, $J$ = 18 Hz, 1 H), 5.59–5.80 (m, 1 H), and 6.62–6.67 (m, 1 H).[27]

*trans*-5-Allyl-2-cyclopentene-1-carboxylic acid methyl ester (**39b**): ir 3075, 2995, 2970, 2950, 2910, 2845, 1745, 1645, 1620, 1430, 1185, 1160, 980, 905, and 675 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.94–2.33 (m, 3 H), 2.51–2.73 (m, 2 H), 3.12–3.16 (m, 1 H), 3.62 (s, 3 H), 4.96 (br d, $J$ = 8.5 Hz, 1 H), 4.98 (br, d $J$ = 18 Hz, 1 H), 5.52–5.60 (m, 1 H), and 5.62–5.80 (m, 2 H).[27]

For preparative purposes the mixture of nitriles **36** and **37** was hydrolyzed to yield 67% of crude acidic material. Vpc analysis of the methyl esters, prepared with diazomethane, indicated a mixture composed of 33% ester **38b**, 26% of ester **39b**, and 41% of 2-(*trans*-propenyl)-1-cyclopentene-1-carboxylic acid methyl ester (**40b**). The analytical sample of ester **40b** was obtained from column A: uv (95% EtOH) 270 nm ($\epsilon$ 19,400); ir 3050, 3015, 2950, 2910, 2850, 1712, 1640, 1590, 1428, 1225, 1180, 1110, 1085, and 965 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.75–1.92 (m, 5 H), 2.52–2.68 (m, 4 H), 3.66 (s, 3 H), 5.88 (dq, $J_1$ = 16 Hz, $J_2$ = 7 Hz, 1 H), and 7.24 (br d, $J$ = 16 Hz, 1 H).[27]

The equilibration of **38b** and **39b** was carried out in methanol containing sodium methoxide. Starting with either ester an equilibrium mixture was formed which contained **38b** (54 ± 1%) and **39b** (46 ± 1%) and no other products.

The mixture of acids **38a**–**40a** obtained from hydrolysis of nitriles **36** and **37** was treated directly with methyllithium in ether. The product (68%) was separated on column A into **38c** (40%), **39c** (32%), and **40c** (28%).

**38c** showed the following properties: uv (95% EtOH) 238 nm ($\epsilon$ 8300); ir 3075, 3060, 2940, 2840, 1670, 1640, 1610, 1430, 1365, 1290, 1260, 1180, 980, and 905 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.64–1.79 (m, 1 H), 1.89–2.08 (m, 2 H), 2.21 (s, 3 H), 2.29–2.60 (m, 3 H), 3.00 (br, 1 H), 4.91 (br d, $J$ = 9 Hz, 1 H), 4.94 (br d, $J$ = 17 Hz, 1 H), 5.54–5.75 (m, 1 H), and 6.57 (br s, 1 H).[27]

**39c** showed the following properties: ir 3060, 2965, 2845, 1718, 1640, 1610, 1435, 1348, 1155, 980, 905, 705, and 680 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.95–2.19 (m, 3 H), 2.05 (s, 3 H), 2.49–2.75 (m, 2 H), 3.14 (br, 1 H), 5.08 (br d, $J$ = 10 Hz, 1 H), 5.11 (br d, $J$ = 17 Hz, 1 H), and 5.59–5.84 (m, 3 H).[27]

**40c** showed the following properties: uv (95% EtOH) 291 nm ($\epsilon$ 14,500); ir 3050, 3010, 2960, 2910, 2845, 1675, 1630, 1570, 1430, 1355, 1250, 1220, 985, 965, and 890 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.75–1.91 (m, 5 H), 2.13 (s, 3 H), 2.58 (br dd, $J_1 \sim J_2 \sim$ 8 Hz, 2 H), 2.68 (br dd, $J_1 \sim J_2 \sim$ 7 Hz, 2 H), 5.87 (dq, $J_1$ = 7 Hz, $J_2$ = 16 Hz, 1 H), and 7.12 (br d, $J$ = 16 Hz, 1 H).[27]

Careful hydrolysis of ester **38b** in aqueous methanolic $Na_2CO_3$ (room temperature, 6 days) gave acid **38a** without rearrangement to **39a** (ir, nmr). Treatment of this acid with methyllithium in ether yielded 85% **38c**, identical with the material described above.

***anti*-7-Ethyl-*exo*-2-hydroxynorbornane-*syn*-7-carboxylic Acid $\gamma$-Lactone (43).** This conversion was carried out on 16.60 g of 2-ethyl-5-norbornene-*exo*-2-carboxylic acid (**42a**)[20] as detailed[19] for **42b**, yield 86%. Two recrystallizations from pentane gave an analytical sample: mp 43–44°; ir 2965, 2875, 1783, 1210, 1110, 1095, 1065, 1055, 1020, 995, 975, 955, 925, and 890 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.97 (t, $J$ = 7.5 Hz, 3 H), 1.37–1.77 (m, 7 H), 1.84–2.01 (m, 1 H), 2.12 (br, 1 H), 2.56 (br, 1 H), and 4.46 (br, 1 H); mass spectrum $m/e$ 166.1015 ($M^+$, calcd for $C_{10}H_{14}O_2$, 166.0993).

***anti*-7-Ethyl-*exo*-2-hydroxynorbornane-*syn*-7-methanol (44).** A 3.32-g sample of lactone **43** was reduced with 0.75 g of $LiAlH_4$ in 50 ml of ether at reflux for 2 hr in the usual fashion. Work-up with 0.75 ml of $H_2O$, 0.75 ml of 15% aqueous NaOH, and 2.25 ml of $H_2O$[28] yielded 3.22 g (95%) of a white solid. Recrystallization from ether gave an analytical sample, mp 121–122°, colorless platelets: ir 3610, 3400, 2955, 2870, 1473, 1460, 1210, 1070, 1023, 990, 940, 910, 877, and 850 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.91 (t, $J$ = 7.5 Hz, 3 H), 0.98–1.43 (m, 3 H), 1.46–1.90 (m, 6 H), 2.03 (br, 1 H), 2.88 (br, 1 H), 3.14 (br, 1 H), 3.72 (br, 1 H), and 3.90 (br, 2 H).[27]

***anti*-7-Ethyl-*exo*-2-hydroxynorbornane-*syn*-7-methyl Acetate (45).** A 1.70-ml (1.85 g, 18.1 mmol) portion of acetic anhydride was added to an ice-cold solution of 3.06 g (18.0 mmol) of diol **44** in 10 ml of pyridine. After standing at 5° for 4 days the homogeneous reaction mixture was poured onto ice and made barely acidic with ice-cold 10% aqueous HCl. This mixture was extracted three times with ether. The combined extracts were washed with saturated aqueous $NaHCO_3$ and dried with $Na_2SO_4$. Removal of solvent

(28) V. M. Mićović and M. L. J. Mihailović, *J. Org. Chem.*, 18, 1190 (1953).

afforded 3.41 g of pale yellow viscous oil. This was chromatographed on 75 g of Woelm neutral alumina (activity II); the progress of the chromatogram was followed by ir spectroscopy. Elution with 450 ml of benzene–pentane (1:1) gave 0.97 g (21%) of diacetate as a pale yellow viscous oil showing only one peak on column D. Elution with 250 ml of ether–pentane (1:1) afforded 1.56 g (41%) of pale yellow monoacetate; vpc indicated an 89:11 mixture of primary and secondary monoacetates, respectively. Unreacted diol **44** (0.92 g, 30%) was eluted with 150 ml of ether–pentane and 150 ml of methanol. Analytical samples of monoacetate **45** and diacetate were obtained by preparative vpc on column D.

Monoacetate **45**: ir 3620, 3480, 2955, 2880, 1745, 1475, 1360, 1235, 1074, 1020, 955, 940, and 920 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.87 (t, $J$ = 7 Hz, 3 H), 1.01–1.21 (m, 2 H), 1.30–1.55 (m, 2 H), 1.61–1.80 (m, 4 H), 1.86 (br, 1 H), 1.93 (br, 1 H), 2.00 (s, 3 H), 2.76 (br, 1 H), 3.81 (dd, $J_1$ = 4 Hz, $J_2$ = 8 Hz, 1 H), 4.30 (d, $J$ = 12 Hz, 1 H), and 4.56 (d, $J$ = 12 Hz, 1 H).[27]

Diacetate of **44**: ir 2965, 2885, 1745, 1475, 1360, 1235, 1065, 1025, 975, 950, 925, 890, and 850 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.89 (t, $J$ = 7.5 Hz, 3 H), 1.08–1.32 (m, 2 H), 1.42 (q, $J$ = 7.5 Hz, 2 H), 1.67–2.08 (m, 6 H), 1.94 (s, 3 H), 1.99 (s, 3 H), 4.22 (d, $J$ = 12 Hz, 1 H), 4.29 (d, $J$ = 12 Hz, 1 H), and 4.56 (dd, $J_1$ = 4 Hz, $J_2$ = 8 Hz, 1 H).[27]

***anti*-7-Ethyl-2-ketonorbornane-7-methyl Acetate (46).** A solution of 1.27 g (6.00 mmol) of crude monoacetate from above in 20 ml of acetone was cooled in ice, and 2.67 $M$ Jones reagent[21] was added dropwise with vigorous stirring until a red color persisted. The excess oxidant was destroyed with isopropyl alcohol. Water was added to dissolve the precipitated salts, and the resulting green solution was extracted twice with ether. The combined extracts were washed with water and saturated aqueous $NaHCO_3$ and dried with $Na_2SO_4$. Concentration on a rotary evaporator followed by bulb-to-bulb distillation at 120–125° (1 mm) yielded 1.05 g (83%) of colorless oil. Vpc analysis showed 9% of a single impurity; preparative vpc on column D gave an analytical ample: ir 2965, 2885, 1755, 1475, 1455, 1415, 1380, 1360, 1225, 1025, 920, 900, 870, and 850 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.90 (t, $J$ = 7.5 Hz, 3 H), 1.35–1.59 (m, 4 H), 1.76 (d, $J$ = 18 Hz, 1 H), 1.93–2.06 (m, 2 H), 2.00 (s, 3 H), 2.21 (br d, $J$ = 4 Hz, 1 H), 2.26–2.47 (m, 2 H), and 4.04 (s, 2 H); mass spectrum $m/e$ 210.1278 ($M^+$, calcd for $C_{12}H_{18}O_3$, 210.1255).

***anti*-7-Ethyl-2-ketonorbornane-7-methanol (47).** A solution of 1.00 g (4.76 mmol) of keto acetate **46** in 5 ml of methanol was added to a solution of 330 mg (5.01 mmol) of 85% KOH pellets in 10 ml of methanol, whereupon the mixture became pale yellow. The reaction mixture was heated at reflux overnight, 400 mg (4.76 mmol) of $NaHCO_3$ was added, and the solvent was removed on a rotary evaporator. The residue was dissolved in ether, filtered, and concentrated on a rotary evaporator. Bulb-to-bulb distillation of the pale yellow residue at 105–115° (0.3 mm) afforded 694 mg (87%) of a colorless viscous oil. Vpc indicated a total of ~15% of two impurities, and the analytical sample was obtained from column D: ir 3640, 3425, 2965, 2880, 1750, 1475, 1460, 1325, 1310, 1225, 1115, 1060, 1030, 990, 955, 920, 890, and 850 $cm^{-1}$; nmr (220 MHz, T = 51°) $\delta$ 0.88 (t, $J$ = 7.5 Hz, 3 H), 1.32–1.64 (m, 5 H), 1.71–1.99 (m, 2 H), 2.03 (br d, $J$ = 4 Hz, 1 H), 2.09–2.28 (m, 2 H), 2.71 (s, 1 H), 3.52 (d, $J$ = 12 Hz, 1 H), and 3.61 (d, $J$ = 12 Hz, 1 H); the nmr spectrum determined at ambient temperature was extremely complex and suggested a ~2:1 mixture of keto alcohol **47** and the corresponding hemiketal **48**; mass spectrum $m/e$ 168.1137 ($M^+$, calcd for $C_{10}H_{16}O_2$, 168.1149).

**1-Ethyltricyclo[3.3.0.0$^{2,7}$]octan-6-one (41a).** A 1.00-g (5.25 mmol) portion of tosyl chloride was added to an ice-cold solution of 638 mg (3.80 mmol) of keto alcohol **47**–**48** in 5 ml of pyridine. After being stirred to complete solution, the reaction mixture was allowed to stand overnight at 5°. The resulting mixture was poured into ice–water and extracted twice with ether. The combined extracts were washed with 10% aqueous HCl and saturated aqueous $NaHCO_3$ and dried with $Na_2SO_4$. Removal of the solvent yielded 1.136 g (94%) of pale yellow oily keto tosylate **49**: ir 2970, 2880, 1755, 1600, 1475, 1470, 1372, 1185, 1175, 1090, 970, 945, 870, 855, 825, and 655 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.79 (t, $J$ = 7.5 Hz, 3 H), 1.31–1.56 (m, 4 H), 1.65 (d, $J$ = 18 Hz, 1 H), 1.84–2.12 (m, 4 H), 2.30 (br, 1 H), 2.40 (s, 3 H), 3.66 (d, $J$ = 10 Hz, 1 H), 3.82 (d, $J$ = 10 Hz, 1 H), 7.12 (d, $J$ = 8 Hz, 2 H), and 7.52 (d, $J$ = 8 Hz, 2 H).

A 1-g portion of 50% sodium hydride dispersion in mineral oil was washed four times with pentane and dried under vacuum. A mixture of 1.093 g (3.40 mmol) of tosylate **49** and 350 mg (14.6 mmol) of dry sodium hydride in 25 ml of dimethoxyethane (distilled from lithium aluminum hydride) under nitrogen was placed in an oil bath at 80°. The bath temperature was quickly raised to 100°, and the reaction mixture was allowed to boil at reflux for 8 hr. The resulting mixture was filtered, and the collected solid was washed with wet ether producing very little reaction. The filtrate and washings were poured into water and extracted twice with pentane. The combined extracts were washed with water and saturated aqueous NaCl and dried with $Na_2SO_4$. Distillation of the solvent through a Vigreux column followed by bulb-to-bulb distillation at 130–140° (25 mm) yielded 280 mg (55%) of a colorless camphoraceous liquid and 97 mg of nonvolatile residue. Only trace impurities were indicated by vpc, and the analytical sample was obtained from column A: ir 2965, 2880, 1765, 1460, 1375, 1320, 1285, 1120, 1035, 1000, 973, 958, 930, 920, 895, 875, and 827 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.93 (t, $J$ = 7.5 Hz, 3 H), 1.36–1.63 (m, 4 H), 1.68 (d, $J$ = 8 Hz, 1 H), 1.91–2.13 (m, 3 H), 2.25 (br, 1 H), 2.46 (br, 1 H), and 2.73 (dd, $J_1 \sim J_2 \sim$ 3 Hz, 1 H).[27]

**1-Ethyltricyclo[3.3.0.0$^{2,7}$]octane (11). A. From 41a Semicarbazone.** A 0.5-ml portion of 2 $M$ aqueous semicarbazide hydrochloride was added to 54 mg (0.36 mmol) of ketone **41a** in 1 ml of methanol. Ten micro drops of pyridine was added, and the reaction mixture was warmed on a steam bath until crystals began to separate. After cooling in ice the crystals were filtered, washed with water, and dried under vacuum. The yield of white semicarbazone was 65 mg (88%), mp 196.5–197.5°.

A 23-mg (1 mmol) portion of dry sodium hydride was carefully reacted with 1 ml of freshly distilled ethylene glycol. This solution was added to the above semicarbazone and 0.2 ml (*ca.* 6 mmol) of 97% hydrazine, and the mixture was sealed under vacuum. The reaction mixture was then heated at 195° for 22 hr; nitrogen evolution began immediately. The resulting mixture had a colorless upper layer and a small amount of white precipitate. After cooling in ice the mixture was diluted with water and extracted twice with pentane. The combined extracts were washed twice with water and dried with $Na_2SO_4$. Careful distillation of the solvent through a Vigreux column afforded 36 mg (73% overall) of colorless oil. Vpc analysis showed only one peak, and the analytical sample was obtained from column E: ir 2950, 2870, 1460, 1370, 1295, 1195, 950, 885, 865, and 825 $cm^{-1}$; nmr (220 MHz) $\delta$ 0.87 (t, $J$ = 7 Hz, 3 H), 1.14–1.95 (m, 12 H), and 2.25 (br d, $J$ = 3 Hz, 1 H); mass spectrum $m/e$ 136.1263 ($M^+$, calcd for $C_{10}H_{16}$, 136.1251).

**B. Directly from 41a.** In the same way as above, 15 mg (0.1 mmol) of ketone **41a** was reduced directly with 0.3 ml of 97% hydrazine and 23 mg of sodium hydride dissolved in 1 ml of ethylene glycol. The product (75%) was pure hydrocarbon **11.**

**C. From 6.** Reduction of 24 mg of ketone **6** as described above yielded 82% of **11**, identified by vpc retention time, and comparison of ir and nmr spectra with the authentic hydrocarbon from **41a.**

**3-Cyclohexen-1-yl acetone (51).** Reaction of 3-cyclohexen-1-ylacetic acid[22] with ethereal methyllithium according to the usual procedure yielded 91% of crude ketone, which was purified on column A: ir 3025, 2915, 2840, 1725, 1650, 1430, 1350, 1145, and 635 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.13–1.31 (m, 1 H), 1.52–1.78 (m, 2 H), 1.98–2.19 (m, 4 H), 2.05 (s, 3 H), 2.30 (d, $J$ = 7 Hz, 2 H), and 5.52 (br, 2 H).[27]

**3-(3-Cyclohexen-1-yl)-3-buten-2-one (12).** Base-catalyzed condensation of the above ketone **51** with formaldehyde followed by acid-catalyzed dehydration[1] afforded a 1:1 mixture (vpc) of **12** and starting ketone. Material for analysis and photolysis was obtained on column A: ir 3095, 3025, 2915, 2840, 1685, 1650, 1625, 1430, 1350, 1260, 1200, 1110, 925, and 640 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.31–1.50 (m, 1 H), 1.63–1.87 (m, 2 H), 1.95–2.20 (m, 3 H), 2.28 (s, 3 H), 2.79–2.90 (m, 1 H), 5.63 (br, 2 H), 5.67 (d, $J$ = 1.5 Hz, 1 H), and 5.96 (s, 1 H).[27]

**7-Methylene-*cis*-bicyclo[4.2.0]oct-2-ene (53).** A solution of 2.44 g (20 mmol) of **52**[23] in 10 ml of dimethyl sulfoxide was added to triphenylphosphonium methylide prepared from 35.7 g (100 mmol) of methyl triphenylphosphonium bromide prepared in 150 ml of the same solvent using the procedure of Corey.[24] After 2 hr at 70° the reaction was worked up[24] to give 2.11 g (88%) of distilled diene **53**, bp 80–85° (25 mm). Vpc on column A gave an analytical sample: ir 3070, 3020, 2920, 2845, 1675, 1645, 1430, 865, 705, and 675 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.43–1.61 (m, 1 H), 1.71–1.95 (m, 2 H), 2.09–2.30 (m, 2 H), 2.64–2.78 (m, 1 H), 2.89 (dddd, $J_1 = J_2$ = 2.5 Hz, $J_3$ = 9 Hz, $J_4$ = 15 Hz, 1 H), 3.24 (br, 1 H), 5.18 (m, 2 H), and 5.66–5.82 (m with s at 5.73, 2 H).[27]

***endo-cis*-Bicyclo[4.2.0]oct-2-ene-7-carboxylic Acid Methyl Ester (56).** A 20-ml (16.2 mmol) portion of 0.81 $M$ 9-BBN[25] in tetrahydrofuran was added to a stirred solution of 2.00 g (16.7 mmol) of diene **53** in 10 ml of tetrahydrofuran. After 30 min at room

temperature, 10 ml of 6 *M* NaOH was added, followed by 8 ml of 30% hydrogen peroxide. The reaction mixture was then heated at 60° for 45 min. The resulting mixture was diluted with water and extracted three times with pentane. The combined extracts were washed with water and dried with $Na_2SO_4$. Distillation of the solvent through a Vigreux column yielded 2.83 g of colorless oil. Ir analysis showed the presence of alcohol as well as exocyclic and endocyclic olefin. Without purification this material was oxidized with Jones reagent to yield 32% of crude acid **55**: ir 3725–2330, 3025, 2945, 1705, 1640, 1420, 1235, 1215, 690, and 650 $cm^{-1}$.

A sample of **55** was treated with diazomethane to give 95% of crude ester **56**. Vpc analysis showed *ca.* 10% of a single impurity. An analytical sample of **56** was obtained from column A: ir 3020, 2980, 2950, 2840, 1740, 1640, 1450, 1430, 1360, 1345, 1325, 1230, 1185, 1100, 1075, 1045, 690, and 665 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.48–2.07 (m, 4 H), 2.15–2.28 (m, 2 H), 2.68 (br, 2 H), 3.14 (m, 1 H), 3.61 (s, 3 H), 5.60 (br d, $J$ = 11 Hz, 1 H), and 5.71–5.83 (m, 1 H).[27]

*endo-cis*-**Bicyclo[4.2.0]oct-2-en-7-yl Methyl Ketone (17).** Reaction of acid **55** with methyllithium yielded 89% of an 88:12 mixture (vpc) of endo and exo ketones, **17** and **18**, respectively. Preparative vpc on column A gave an analytical sample of endo ketone **17**: ir 3020, 2975, 2930, 2845, 1712, 1640, 1450, 1430, 1360, 1350, 1225, 1175, 1130, and 690 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.38–1.88 (m, 3 H), 1.91–2.09 (m, 2 H), 1.97 (s, 3 H), 2.23 (m, 1 H), 2.56–2.88 (m, 2 H), 3.21 (m, 1 H), 5.57 (ddd, $J_1 \sim J_2 \sim 3$ Hz, $J_3$ = 10 Hz, 1 H), and 5.67–5.78 (m, 1 H).[27]

*exo-cis*-**Bicyclo[4.2.0]oct-2-en-7-yl Methyl Ketone (18).** Epimerization of the mixture of ketones **17** and **18** described above with KOH in aqueous methanol afforded an 86:14 mixture (vpc) of exo and endo ketones, **18** and **17**, respectively. An analytical sample of exo ketone **18** was obtained from column A: ir 3015, 2920, 2845, 1712, 1645, 1445, 1430, 1350, 1175, 710, and 675 $cm^{-1}$; nmr (220 MHz) $\delta$ 1.43–1.78 (m, 3 H), 2.00 (s, 3 H), 2.06–2.12 (m, 2 H), 2.38 (m, 1 H), 2.49–2.61 (m, 1 H), 2.70–2.84 (m, 1 H), 2.97 (m, 1 H), 5.74 (d, $J$ = 11 Hz, 1 H), and 5.80 (d, $J$ = 11 Hz, 1 H).[27]

**3-Methylene-5-hexen-2-one (27).** A mixture of 9.8 g (0.1 mol) of 5-hexen-2-one (**57**), 12.1 g (0.1 mol) of piperidine hydrochloride, and 7.5 ml (0.1 mol) of 37% formaldehyde was heated on a steam bath for 45 hr. Usual work-up[1] afforded 6.20 g (57%) of pale yellow lachrymatory liquid. Vpc analysis indicated the usual four-component mixture, and material for analysis and photolysis was obtained on column A: ir 3075, 3000, 2975, 2905, 1680, 1640, 1625, 1425, 1360, 1255, 1130, 1110, 985, 965, 925, and 910 $cm^{-1}$; nmr (220 MHz) $\delta$ 2.27 (s, 3 H), 2.94 (br d, $J$ = 7 Hz, 2 H), 4.90–5.03 (m, 2 H), 5.59–5.80 (m, 1 H), 5.64 (br s, 1 H), and 5.92 (s, 1 H).[27]

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# The Synthesis, Stereochemistry, and Nuclear Magnetic Resonance Assignments of Polycyclic Cyclopentanones Obtained by Iron Carbonyl Induced Coupling of Olefins to Carbon Monoxide[1,2]

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**Abstract:** A thermally or photochemically initiated route from olefins to cyclopentanones using iron carbonyl reagents is described. Strained olefins proceed with greatest facility giving up to 77% yields of polycyclic ketones. Both symmetric and unsymmetric ketones are easily prepared by this method. An exo-trans-exo geometry was determined by considering the coupling constant between bridgehead and cyclopentanone ring protons on ketones containing norbornyl systems.

Transformations in which transition metals act to modify organic substrates have evoked considerable interest both because of their utility and the mechanistic information they supply. During the past few years many metal assisted reactions have received particular attention. These include the olefin metathesis reaction,[3,4] cyclodimerization,[4,5] oligomerization,[6] and carbonyl insertion[7,8] reactions. Olefin coupling associated with carbonyl insertion has been briefly reported.[1,9,10] We wish to report observations and conclusions regarding metal-induced dimerization concurrent with carbonyl insertion. The procedure described represents a novel approach to synthesis of the cyclopentane skeleton. Particular attention is

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