

move the inorganic residues. The solvent was removed under reduced pressure to give a crystalline solid. Recrystallization from 95% ethanol gave white needles, mp 124–125°. This material was identical in all respects with a sample of the solid obtained from the oxidation of *N*-benzyl-2,4-diphenylimidazole.

Irradiation of *exo*- (or *endo*-) 2,4,6-Triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene in Methanol. A solution containing 350 mg of the bicycloaziridine in 400 ml of methanol was irradiated for 3 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure left a yellow oil which was subjected to scanning liquid–liquid partition chromatography. The major component of the mixture (140 mg, 40%) was identified as 1-(methoxybenzyl)-2,4-diphenyl-3-imidazoline (25). The same imidazoline could be prepared by treating 1,3,6-triphenyl-2,5-diaza-1,3,5-hexatriene (10) with methanol in the dark.

Irradiation of *endo*-2,4-Diphenyl-6-*p*-nitrophenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (31) in Methanol. A solution containing 900 mg of *endo*-2,4-diphenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (31), mp 173–174° (lit.²³ 174–175°), in 450 ml of methanol was irradiated for 3.5 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left an oil which was purified by liquid–liquid partition chromatography. The major fraction (380 mg, 42%) was recrystallized from 95% ethanol to give 1-*p*-nitrobenzyl-2,4-diphenylimidazole (32) as white needles: mp 116–117°; ir (KBr) 6.62, 7.15, 7.45, 8.45, 10.58, 11.92, 12.30, 12.95, 13.62, and 14.35 μ ; uv (95% ethanol) 268 nm (ϵ 30,800); nmr (100 MHz, CDCl₃) τ 4.82 (s, 2 H), 1.90–3.80 (m, 15 H); *m/e* 220, 95, 81, 71, and 69 (base).

Anal. Calcd for C₂₂H₁₇N₃O₂: C, 74.35; H, 4.82; N, 11.84. Found: C, 74.51; H, 5.00; N, 11.78.

An authentic sample of 32 could be prepared by treating 2,4-diphenylimidazole with *p*-nitrobenzyl bromide. A solution con-

taining 150 mg of 2,4-diphenylimidazole and 150 mg of *p*-nitrobenzyl bromide in 25 ml of xylene was heated at reflux for 15 hr. Removal of the solvent under reduced pressure left a crude red oil which was subjected to preparative thick-layer chromatography. The major component of the mixture amounted to 44 mg (20%) of 1-*p*-nitrobenzyl-2,4-diphenylimidazole (32), mp 116–117°. This material was identical in all respects with that produced from the irradiation of 31.

Irradiation of *endo*- and *exo*-2,4,6-Triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene with Dimethyl Acetylenedicarboxylate. A solution containing 300 mg of diazabicyclohexene 5 (or 6) and 140 mg of dimethyl acetylenedicarboxylate in 60 ml of benzene was irradiated with a 450-W Hanovia mercury lamp for 2.5 hr. Removal of the solvent at 50° under reduced pressure gave a dark oil whose nmr spectrum indicated the complete absence of 2,3-dihydro-2,3,5-triphenylpyrazine. Recrystallization of the oil from 95% ethanol gave a 72% yield of dimethyl (3*R**,7*R**,7*aS**)-7,7*a*-dihydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (34) as a white crystalline solid: mp 123–124°; ir (KBr) 5.80, 6.15, 6.95, 7.95, 10.60, 12.30, 13.40, 14.10, and 14.40 μ ; uv (95% ethanol) 240 nm (ϵ 19,000); nmr (100 MHz, pyridine-*d*₅) τ 6.62 (3 H, s), 6.58 (3 H, s), 4.54 (d, 1 H, *J* = 4.0 Hz), 3.80 (d, 1 H, *J* = 4.0 Hz), 3.62 (t, 1 H, *J* = 4.0 Hz), 1.96–3.02 (m, 15 H); *m/e* 452 (M⁺), 450, 391, 285, 105, and 104 (base).

Anal. Calcd for C₂₈H₂₄O₄N₂: C, 74.32; H, 5.35; N, 6.19. Found: C, 73.94; H, 5.12; N, 6.15.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-24449) and the National Institutes of Health (Grant No. CA-12195-06).

Photochemistry of Cyclopentenones. Hydrogen Abstraction by the β -Carbon Atom

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Abstract: Photochemical isomerization reactions are described for three cyclopentenones, 7, 19, and 24. Irradiation of 7 leads to 8, 9, and 10; 19 gives 21; and 24 leads to 26, 27, and 28. These products are most readily derived from intermediate biradicals 16, 20, and 25, formed by intramolecular abstraction of a side-chain hydrogen atom by the β -carbon atom of the enone system. Direct proof of this hydrogen transfer was obtained using deuterium-labeled 7 (17). Structures of bicyclic products 10 and 21 were proved by photochemical degradation to 15 and 23, respectively, which were independently synthesized. Treatment of acyloin 36 with polyphosphoric acid provided an independent synthesis of 10 through a 1,5-hydride transfer reaction. Preparation of starting cyclopentenones and related compounds is described.

In an earlier investigation¹ into the photochemical reactions of simple cyclopentenones, we observed that irradiation of 4,4-dimethylcyclopentenone (1) in *tert*-butyl alcohol led to 2-*tert*-butoxy-4,4-dimethylcyclopentanone (2). That is, in a cyclopentenone in which type I (α cleavage)² and type II (γ abstraction)^{2,3} processes were disfavored by lack of substitution at C(5), α addition of solvent was a significant photochemical reaction. This is in contrast to previous

reports^{4–6} of light-induced addition of hydroxylic solvent to several unsaturated ketones, including 5,5-dimethylcyclohexenone (3),⁶ a simple homolog of ketone 1. In all these latter cases, the solvent addition is β , leading for example to 4⁶ from 3, and apparently the reaction involves ionic addition of solvent to a photoexcited ketone or some species derived from it.⁴ Apart from these formal Michael reactions, however, both

(1) W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

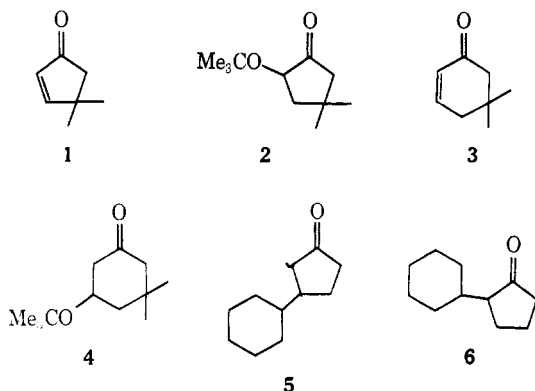
(2) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

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

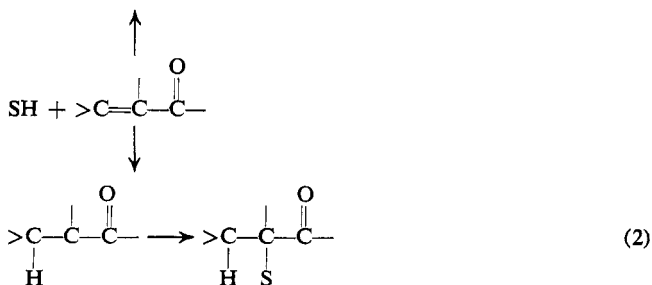
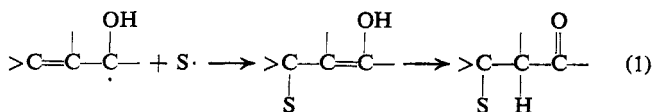
(4) B. J. Ramey and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 3949 (1967); P. de Mayo and J. S. Wasson, *Chem. Commun.*, 970 (1967).

(5) G. Bozzato, K. Schaffner, and O. Jeger, *Chimia*, **20**, 114 (1966); O. L. Chapman, J. B. Sieja, and W. L. Welstead, Jr., *J. Amer. Chem. Soc.*, **88**, 161 (1966); T. Matsuura and K. Ogura, *Bull. Chem. Soc. Jap.*, **40**, 945 (1967).

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



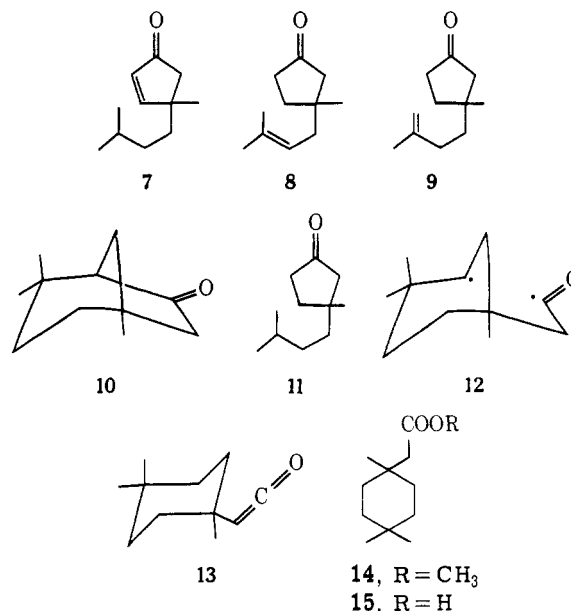
α and β additions of nonhydroxylic solvent to unsaturated ketones have been known⁷ for some time. These additions are believed to involve hydrogen abstraction from solvent either by carbonyl oxygen, leading to β addition (eq 1),⁸ or by the β -carbon atom, leading to α addition (eq 2).^{9,10}



On this basis formation of **2** is most simply regarded as an abstraction of hydroxylic hydrogen¹¹ by the β -carbon atom of excited **1**, followed by collapse of the two resulting radicals, all according to eq 2 ($\text{S} = \text{Me}_3\text{CO}$). We attempted to confirm this view by photolysis of **1** in *tert*-butyl alcohol-*O-d*¹² as solvent, but under these conditions formation of the solvent adduct was completely suppressed. For comparison it would be interesting to know whether similar abstraction occurs in other solvents. In fact, the photolysis of cyclopentenone in cyclohexane to yield cyclohexylcyclopentanone was described¹³ several years ago. Although both structures **5**¹³ (β addition) and **6**⁹ (α addition) have been put forward for this adduct, the matter has never received careful attention. We have reexamined this reaction and find that both **5** and **6** are formed; direct irradiation of cyclopentenone in cyclohexane leads to 22% of **5** and 3% of **6**. Here then both

processes occur, but most of the adduct arises through carbonyl abstraction (eq 1).¹⁴

These observations led us to conjecture that in appropriately constructed cyclopentenones abstraction of hydrogen by the β -carbon atom could be an efficient process. A structurally attractive compound was 4-isopentyl-4-methylcyclopentenone (**7**), in which the type I and type II processes known to be more efficient than hydrogen abstraction from solvent should be minimized by absence of substitution at C(5),¹ and in which the tertiary hydrogen of the isopentyl side chain is located so to favor abstraction through a six-membered transition state by the β -carbon atom. The methyl substituent at C(4) assures that an inconvenient β,γ shift of the double bond is impossible.



We, therefore, prepared **7**¹⁵ and investigated its fate on irradiation.¹⁶ In dilute (1 mg/ml) benzene solution **7** was smoothly isomerized on photolysis through uranium glass ($\lambda > 3300 \text{ \AA}$) to a mixture of three compounds which could be separated and purified by preparative vpc: 59% **8**, 24% **9**, and 11% **10**.¹⁷ With pentane as solvent the overall reaction was faster, but yields were lower, presumably reflecting competitive reactions involving hydrogen abstraction from solvent in this case. It was clear that **8** and **9** had the unaltered carbon skeleton of **7**, since on hydrogenation each gave 3-isopentyl-3-methylcyclopentanone (**11**), an authentic sample of which was available.¹⁵ This result, together with ir and nmr data clearly defining the position of the one double bond in each compound, firmly established structures **8** and **9**. The third isomer appeared to be a saturated, and therefore bicyclic, ketone. Spectroscopic data were consistent with

(7) Several such reactions are noted in ref 1.

(8) I. A. Williams and P. Bladon, *Tetrahedron Lett.*, 257 (1964).

(9) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, 52, 971 (1969).

(10) There is also a mechanistically distinct class of photosensitized solvent additions proceeding *via* sensitizer abstraction from solvent and subsequent β addition of solvent radicals to ground-state unsaturated ketone. For examples in cyclopentenones, see M. Pfau, R. Dulou, and M. Vilks, *C. R. Acad. Sci., Paris*, 254, 1817 (1962), and ref 1.

(11) For discussion of radical abstraction of hydroxyl hydrogen atoms, see E. König, H. Musso, and U.-I. Záhorszky, *Angew. Chem.*, 84, 33 (1972).

(12) M. Morton, J. A. Cala, and I. Piirma, *J. Amer. Chem. Soc.*, 78, 5394 (1956).

(13) J. L. Ruhlen and P. A. Leermakers, *ibid.*, 89, 4944 (1967).

(14) We have also investigated the photoaddition of cyclohexane to cyclohexenone. Here the two modes of abstraction compete somewhat more evenly, although much less adduct is formed: 1.6% 3-cyclohexylcyclohexanone and 0.4% 2-cyclohexylcyclohexanone. Both these products as well as **5** and **6** were identified by comparison of the derived 2,4-dinitrophenylhydrazones or semicarbazones with authentic samples. Details are in the Experimental Section.

(15) All preparative experiments are described in a later section.

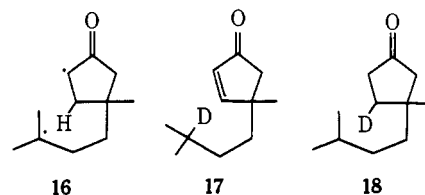
(16) A portion of this work with **7** was described in a preliminary communication: W. L. Schreiber and W. C. Agosta, *J. Amer. Chem. Soc.*, 93, 3814 (1971).

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

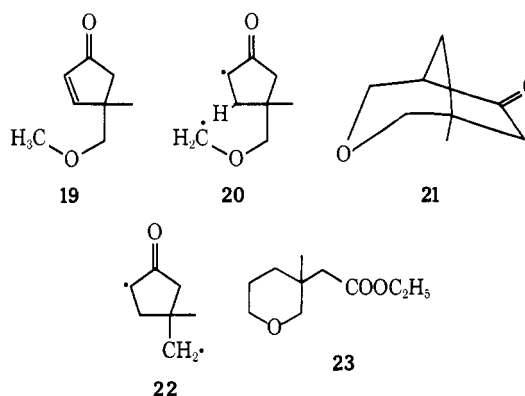
structure **10**, which was shown to be correct by a photochemical degradation. Photolysis of **10** through Pyrex ($\lambda > 2800 \text{ \AA}$) should cause efficient α cleavage to biradical **12**.¹⁸ Subsequent hydrogen transfer could lead to either the monocyclic ketene **13** or the related unsaturated aldehyde having the same skeleton. In the event, irradiation of **10** was carried out in methanol and the methyl ester corresponding to **13**, 1,4,4-trimethylcyclohexanecarboxylic acid methyl ester (**14**), was obtained. Its structure was established by saponification to the corresponding crystalline carboxylic acid **15**, which was identical with a sample prepared by stepwise synthesis.¹⁵ Thus, photolysis of **10** provided a simple and effective means of confirming its structure. Finally, we describe later an independent and nonphotochemical synthesis of **10**, which further corroborates this assignment.

The formation of these three products, **8**, **9**, and **10**, in nearly quantitative yield on irradiation of **7** gave strong support to the original hypothesis that abstraction by the β carbon could be rendered chemically significant. Such abstraction in photoexcited **7** would lead to a biradical intermediate **16**, from which **8** and **9** could arise by a second hydrogen transfer. In models of **16** it appears that such a second hydrogen transfer, from side-chain methylene or methyl to α -carbon atom, is geometrically feasible for both **8** and **9** and that the predominance of **8** is probably due to the usual considerations favoring six-membered cyclic intermediates over those of larger size.¹⁹ Simple collapse of **16** with carbon-carbon bond formation would furnish **10** directly. In order to confirm that the abstraction leading to **16** did in fact occur, we next prepared¹⁵ and irradiated the deuterium-labeled substrate **17**. Photolysis of **17** was much slower²⁰ than that of undeuterated **7**; the same distribution of the three products was apparent by vpc, although yields were somewhat lower. The mixture of products, deuterated **8**, **9**, and **10**, was directly hydrogenated over palladium on carbon and the desired product, deuterated **11**, was isolated and purified by vpc. In the nmr spectrum of **11** the α and β ring protons can be conveniently separated from side-chain resonances using the shift reagent tris(dipivalomethanato)europium [$\text{Eu}(\text{DPM})_3$].²¹ Comparative nmr spectra of deuterated **11** and the authentic undeuterated ketone in solutions containing the shift reagent indicated that one deuterium atom was present and specifically located in the expected β position (**18**). This is then a direct demonstration of specific hydrogen transfer from side-chain to β -carbon atom in the isomerization of **7** to both **8** and **9**.

For a second example of this abstraction process we turned to the methyl ether **19**.¹⁵ Here in intermediate **20** the ether oxygen atom should provide to the



adjacent radical center stabilization comparable³ to that of the tertiary center in **16**, but further reaction of **20** along the paths followed by **16** should lead to a single isomerization product, **21**. Indeed, photolysis of **19** under conditions comparable to those used for **7** gave a 20% yield¹⁷ of **21** along with 7%¹⁷ of another product currently under investigation. While this does represent a virtual doubling in yield of bicyclic product in comparison with formation of **10** from **7**, the total recovery is now far lower. A possible explanation for this result is that **20** may suffer competitive fragmentation²² to formaldehyde and biradical **22**, a species which could cleave further and be lost. The structure of **21** was suggested by its spectroscopic properties, particularly its 220-MHz nmr spectrum which could be analyzed²³ by inspection. This assignment was confirmed by a photochemical degradation parallel to that used above for **10**. Irradiation of **21** in benzene through Pyrex ($\lambda > 2800 \text{ \AA}$) led to a ketene (ir band at 2110 cm^{-1}), which was isolated as ethyl ester **23** after addition of ethanol. This ester was identical with a sample available from independent synthesis.¹⁵



Finally we prepared and irradiated the phenyl-substituted ketone **24**. The products from this photolysis were those expected from the biradical intermediate **25**: *trans*-styrene **26** (43%), *cis*-styrene **27** (13%), and bicyclic ketone **28** (8%).¹⁷ Hydrogenation of both **26** and **27** gave the saturated cyclopentanone **29**, an authentic sample of which was available.¹⁵ This, together with nmr data defining^{23,24} the location and geometry of the double bond in each case, established structures **26** and **27**. The bicyclic structure **28** of the third product from **24** was assigned on the basis of its spectroscopic properties and in analogy with the formation of **10** and **21** described above. The exo stereochemistry shown for the phenyl substituent is

(18) Photolysis of norcamphor follows the analogous course: J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968), and unpublished observations cited therein.

(19) For a study of preferential hydrogen abstraction through a six-membered intermediate in a simple aliphatic system, see J.-Y. Nedelec, M. Gruselle, and D. Lefort, *C. R. Acad. Sci., Paris, Ser. C*, **273**, 1549 (1971).

(20) The complex effects of deuteration on photochemical reactions made it impossible to predict this result with assurance. The problem has been discussed for a type II process by D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966). Several further references are given by A. Padwa and W. Eisenhardt, *ibid.*, **93**, 1400 (1971).

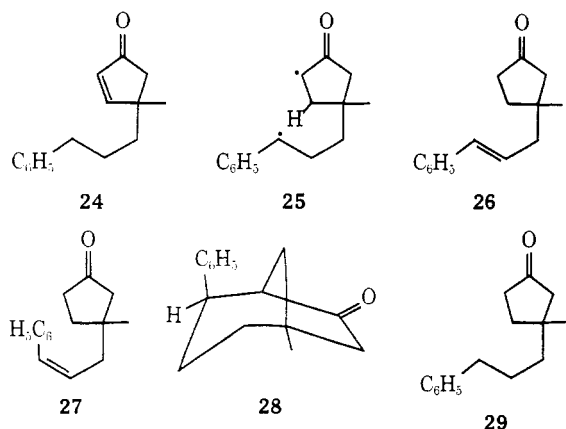
(21) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971), and references cited therein.

(22) See C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967), and references cited therein.

(23) Nmr data are recorded in detail in the Experimental Section and were interpreted with use of L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, and references cited therein.

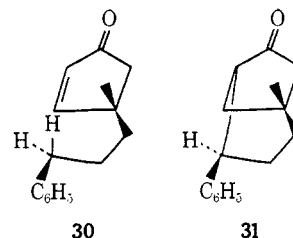
(24) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 115.

suggested by the following considerations. There is a body of coherent data²⁵ indicating that exo and endo groups at C(2) of bicyclo[3.2.1]octane systems behave like ordinary axial and equatorial substituents, respectively, of a chair cyclohexane ring. With this in mind two separate features in the nmr spectrum of **28** lead to the configuration tentatively assigned. First, the five aromatic protons of **28** appear as a broad multiplet (60 Hz at 220 MHz). In 1-*tert*-butyl-4-phenylcyclohexanes of known configuration, protons of an axial phenyl group show similar broad absorption, while those of an equatorial aromatic ring appear as a single sharp signal.²⁶ Second and rather more convincing is the fact that the benzylic proton of **28** appears as an apparent triplet with width at half-height of 11 Hz. This observation is consistent only with an equatorial configuration for this proton, since axial protons with appropriate vicinal couplings typically have width greater than 15 Hz, while for equatorial protons the width is less than 12 Hz.^{23, 26, 27}



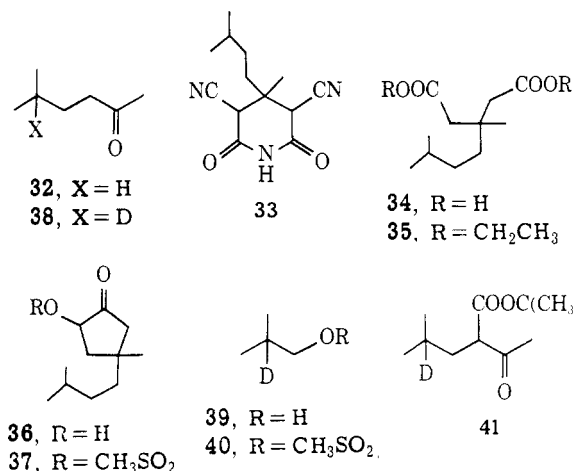
We have previously reported transformations resulting from collapse of 1,4,²⁸ 1,5,¹ and 1,6²⁹ biradicals with creation of a new asymmetric center in a bicyclic system. In each of these cases the stereochemistry at this new center was predominantly or solely that expected in a kinetically controlled reaction dominated by simple steric considerations. The same situation exists in the present conversion of **24** to bicyclic ketone **28**. If initial hydrogen abstraction occurs from conformation **30** in which the phenyl substituent is directed away from the five-membered ring, and if the resulting biradical collapses immediately to the bicyclic product with a minimum of motion, the result is isomer **31**, which is configurationally identical with **28**.

Earlier efforts⁹ at identifying the specific excited state responsible for related abstraction processes suggest that the transformations described for **7**, **19**, and **24** proceed from a π - π^* triplet state.³⁰ As expected for triplet reactions, we have found that the



photochemical rearrangements of cyclopentenone **7** are quenched by low concentrations of 2,3-dimethyl-1,3-butadiene ($E_T \sim 60$ kcal/mol³¹) and may be efficiently sensitized by propiophenone ($E_T \sim 74.6$ kcal/mol³²).³³ The presence of quencher or sensitizer did not materially affect the ratios of products **8**, **9**, and **10**.

Preparative Experiments. Preparation of cyclopentenone **7** began with 5-methyl-2-hexanone (**32**). This ketone was condensed with ethyl cyanoacetate in a Guereschi reaction to yield the glutarimide **33**, which underwent hydrolysis and decarboxylation in acid with formation of 3-isopentyl-3-methylglutaric acid (**34**), all according to a previously described procedure.³⁴ Reductive cyclization of the derived ethyl ester **35**³⁴ on reaction with sodium in liquid ammonia³⁵ led to acyloin **36**. Such acyloins have been previously^{1, 36, 37} dehydrated to cyclopentenones by treatment with acid. In a related case such acid-catalyzed elimination is accompanied,^{1, 37} however, by a substantial amount of rearrangement, as we discuss below in another connection. To avoid difficulties of this sort we carried out the dehydration of **36** by a two-step procedure. Reaction with methanesulfonyl chloride converted the acyloin into **37**, which then smoothly lost methanesulfonic acid in hexamethylphosphoramide at 140° to give the desired cyclopentenone **7**. Similar conditions have been used previously³⁸ for dehydrobromination of α -bromo ketones.



For synthesis of the deuterium-labeled ketone **17**, we required 5-methyl-2-hexanone-5-*d* (**38**), which was

(25) A. A. Youssef, M. E. Baum, and H. M. Walborsky, *J. Amer. Chem. Soc.*, **81**, 4709 (1959); H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

(26) E. W. Garbisch, Jr., and D. B. Patterson, *ibid.*, **85**, 3228 (1963).

(27) A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964), and numerous references cited therein.

(28) W. C. Agosta and D. K. Herron, *J. Amer. Chem. Soc.*, **90**, 7025 (1968). See also in this connection K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964).

(29) A. B. Smith, III, and W. C. Agosta, *J. Org. Chem.*, **37**, 1259 (1972).

(30) See also in this regard W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5474 (1967).

(31) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

(32) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(33) For a caveat concerning discrimination between singlet and triplet processes in cyclopentenones, see ref 1.

(34) G. L. Handley, E. R. Nelson, and T. C. Somers, *Aust. J. Chem.*, **13**, 129 (1960).

(35) The procedure used was adapted from H. Kwart and J. A. Ford, *J. Org. Chem.*, **24**, 2060 (1959).

(36) R. S. Rouse and W. E. Tylor, III, *ibid.*, **26**, 3525 (1961).

(37) A. J. Bellamy, *J. Chem. Soc. B*, 449 (1969).

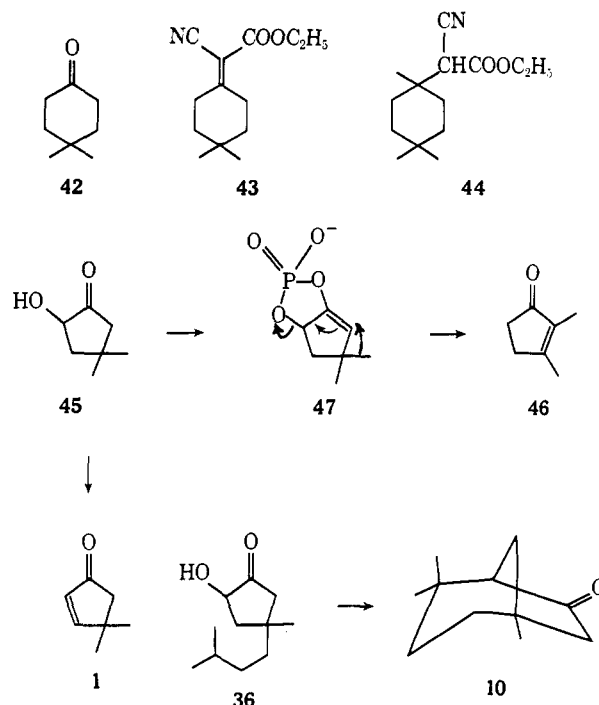
(38) R. Hanna, *Tetrahedron Lett.*, 2105 (1968).

prepared in the following way. Reaction³⁹ of isobutylene with deuterated diborane, formed from lithium deuteride and boron trifluoride etherate, yielded an alkyl borane which was oxidized with basic peroxide to form deuterated isobutyl alcohol **39**.⁴⁰ This was esterified directly with methanesulfonyl chloride in pyridine, and the resulting deuterated isobutyl mesylate **40** was allowed to react in *tert*-butyl alcohol with the potassium salt of *tert*-butyl acetoacetate.⁴¹ The alkylated keto ester **41** thus formed was distilled from 1-naphthalenesulfonic acid⁴¹ to furnish the deuterated ketone **38**. With **38** repetition of the steps described above leading from **32** to **7** now gave **17**. Throughout the sequence of reactions *ir* and *nmr* spectra confirmed that the intermediates differed from those obtained previously only by the presence of one deuterium atom.

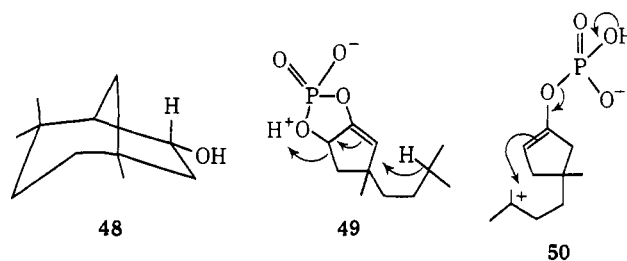
An authentic sample of the cyclopentanone **11** was available through hydrogenation of **7** over palladium on carbon. Reduction⁴² of mesylate **37** using calcium in liquid ammonia also gave **11**, confirming that no unrecognized rearrangement had occurred on conversion of **37** into **7** in hot hexamethylphosphoramide.

Carboxylic acid **15** was prepared by adaptation of a route originally developed⁴³ for 1-methylcyclohexanecarboxylic acid. Condensation⁴⁴ of cyanoacetic ester with 4,4-dimethylcyclohexanone (**42**)⁴⁵ gave the α -cyanoacrylic ester **43**. Conjugate addition of methylmagnesium iodide to **43** proceeded readily in the presence of cuprous chloride to form the expected product **44**. Base-catalyzed hydrolysis of **44** and subsequent thermal decarboxylation of the resulting malonic acid gave **15**.

As we noted above, earlier experience had shown that dehydration in acid of an acyloin such as **36** could be accompanied by rearrangement. Reaction of polyphosphoric acid with the 4,4-dimethyl compound **45**^{1,37} gives a mixture of **1** and **46**. Involvement of the enol is required, and an attractive possibility is the cyclic phosphate **47**. Treatment of **36** with hot polyphosphoric acid, however, yielded neither of the ketones expected in analogy with **45**; in contrast the single product, obtained in 58% yield, was the bicyclic ketone **10**. The identity of this dehydration product with the photochemically derived ketone described above was established by spectral comparisons. In addition, the ketone from each route gave in high yield the same crystalline alcohol on reduction with lithium aluminum hydride. Models show appreciable steric hindrance to endo approach of hydride in **10**, and the alcohol formed is therefore **48**.⁴⁶ To account for formation of **10** from acyloin **36**, we suggest that hydride transfer from the isoamyl side chain (see **49**) takes precedence in this case over both simple dehydration and alkyl



migration, with formation of the tertiary carbonium ion **50**. Internal alkylation of the enol with this ion completes the reaction. There are only a few previous reports⁴⁷ of 1,5-hydride shifts in open chain systems; in the present example the result is a convenient entry into the bicyclo[3.2.1]octane system.



Methyl ether **19** was prepared from the known⁴⁸ related ester **51**. Protection of the ketone carbonyl as the ethylene ketal and subsequent reaction with lithium aluminum hydride furnished the hydroxy ketal **52**. This was alkylated directly with methyl iodide in base, and the resulting ether **53** was subjected to the bromination-dehydrobromination procedure of Garbisch.⁴⁹ Exposure to mild aqueous acid during work-up led to hydrolysis of the ketal and isolation of the desired unsaturated keto ether **19**.

The degradation product in this series, 3-(3-methyl-tetrahydropyran)acetic acid ethyl ester (**23**), could be synthesized from dihydropyran (**54**). Reaction³⁹ first with diborane and then basic peroxide gave the expected⁵⁰ alcohol, tetrahydropyran-3-ol, which was ox-

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(40) For an earlier and different preparation of **39**, see E. L. Eliel and T. J. Prosser, *J. Amer. Chem. Soc.*, **78**, 4045 (1956).

(41) D. S. Breslow, E. Baumgarten, and C. R. Hauser, *ibid.*, **66**, 1286 (1944); R. S. Yost and C. R. Hauser, *ibid.*, **69**, 2325 (1947); W. B. Renfrow and G. B. Walker, *ibid.*, **70**, 3957 (1948).

(42) J. H. Chapman, J. Elks, G. H. Phillips, and L. J. Wyman, *J. Chem. Soc.*, 4344 (1956).

(43) W. Parker and R. A. Raphael, *ibid.*, 1723 (1955).

(44) The method is due to A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenbergh, *J. Amer. Chem. Soc.*, **63**, 3452 (1941).

(45) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963).

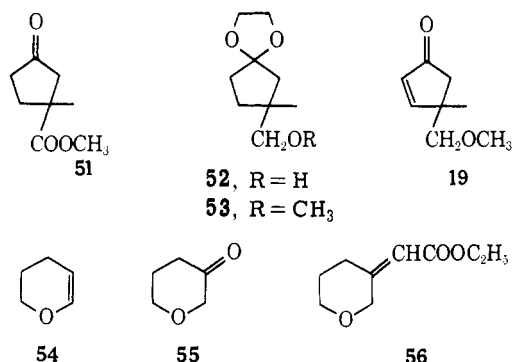
(46) Similar results with norcamphor are on record: P. Hirsjärvi, *Ann. Acad. Sci. Fenn., Ser. A2*, **81** (1957); C. H. DePuy and P. R. Story, *J. Amer. Chem. Soc.*, **82**, 627 (1960).

(47) R. B. Woodward, F. Sondheimer, and Y. Mazur, *ibid.*, **80**, 6693 (1958); J. Colonge and J. C. Brunie, *Bull. Soc. Chim. Fr.*, 1799 (1963); R. K. Hill and R. M. Carlson, *J. Amer. Chem. Soc.*, **87**, 2772 (1965). See also the discussion by J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, p 566-567.

(48) J. D. Roberts, A. K. Jeydel, and R. Armstrong, *J. Amer. Chem. Soc.*, **71**, 3248 (1949); P. T. Lansbury, N. Y. Wang, and J. E. Rhodes, *Tetrahedron Lett.*, 1829 (1971).

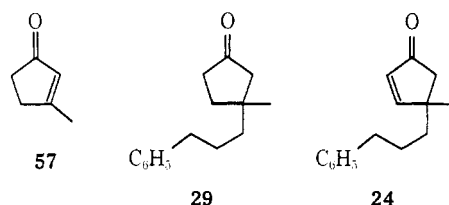
(49) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965). In this connection see also ref 1.

(50) G. Zweifel and J. Plamondon, *ibid.*, **35**, 898 (1970).



idized⁵¹ directly with chromic oxide in pyridine to tetrahydropyran-3-one (**55**).⁵² Wittig reaction⁵³ between this ketone and carbethoxymethylenetriphenylphosphorane catalyzed by benzoic acid⁵⁴ then furnished **56**. Conjugate addition of methylmagnesium iodide, in the presence of the soluble cuprous iodide-tributylphosphine complex,⁵⁵ proceeded smoothly and gave the desired ester **23**.

The third substrate used, the γ -phenylpropylcyclopentenone (**24**), was available from 3-methyl-2-cyclopentenone (**57**).⁵⁶ Conjugate addition of 3-phenylpropylmagnesium bromide using the copper complex noted above gave cyclopentanone **29**, and application of the Garbisch bromination-dehydrobromination sequence⁴⁹ led to **24** without incident.



In summary, these experiments demonstrate that hydrogen abstraction by the β -carbon atom can indeed play a significant role in the photochemistry of cyclopentenones. In a number of cases these abstractions provide synthetically attractive transformations which are otherwise impossible. While the substrates used here for intramolecular abstraction were designed to enhance this mode of reaction, there is no reason to expect it to be limited to these systems. The photochemical cyclization of **58** to **59** reported³⁰ briefly some years ago appears, for instance, to exemplify this transformation in a more complex cyclopentenone. In a future publication we shall describe related transformations of other types of α,β -unsaturated ketones.

(51) For similar oxidation of tetrahydrofuran-3-ol, see J. H. S. Weiland, H. Dijkstra, and A. B. Pik, *Recl. Trav. Chim. Pays-Bas*, **82**, 651 (1963).

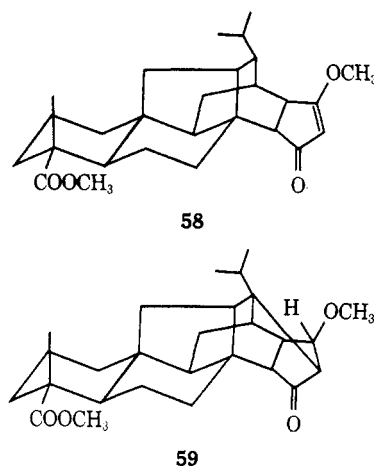
(52) For earlier syntheses of **55**, see G. Bakassian, F. Chizat, D. Sinou, and D. Descotes, *Bull. Soc. Chim. Fr.*, 621 (1969).

(53) A. Maercker, *Org. React.*, **14**, 270 (1965).

(54) C. Rüchardt, S. Eichler, and P. Panse, *Angew. Chem.*, **75**, 858 (1963).

(55) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968), describe the use of this complex in conjugate additions to cyclohexenones. Cuprous chloride catalyzed 1,4 addition of Grignard reagents to α,β -unsaturated esters has been extensively studied by Munch-Petersen: T. Kindt-Larsen, V. Bitsch, I. G. Krogh Andersen, A. Jart, and J. Munch-Petersen, *Acta Chem. Scand.*, **17**, 1426 (1963), and previous papers cited therein.

(56) H. Christol, R. Jaquier, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 1077 (1957).



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, 30% QF-1, 10 ft \times $\frac{3}{8}$ in.; B, 30% SE-30, 10 ft \times $\frac{3}{8}$ in.; C, 30% Carbowax 20M, 10 ft \times $\frac{3}{8}$ in.; D, 10% QF-1, 5 ft \times 0.25 in.; E, 15% SE-30, 15 ft \times $\frac{3}{8}$ in.; F, 30% QF-1, 20 ft \times $\frac{3}{8}$ in.; G, 30% Carbowax 1500, 10 ft \times $\frac{3}{8}$ in. Column D was prepared using 60–80 Chromosorb W in stainless steel tubing; all other columns employed 45–60 Chromosorb W in aluminum tubing. Unless otherwise noted, the column oven was operated at 125–200° and the helium carrier gas flow rate was 120–150 ml/min. Unless otherwise noted, ir and nmr spectra were obtained for CCl_4 solutions, the former on Perkin-Elmer Model 237 B spectrophotometer and the latter on 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. Photochemical experiments were carried out with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well using either Pyrex 7740 or uranium glass (Corning No. 3320) as filter.

Photolysis of 2-Cyclopentenone in Cyclohexane. A solution of 69 mg of 2-cyclopentenone in 70 ml of cyclohexane was irradiated through uranium glass for 9.75 hr. Work-up gave an oil, which showed no hydroxyl absorption in the ir spectrum. Vpc analysis (column G) indicated two volatile monomeric components. The first was shown to be identical with authentic 2-cyclohexylcyclopentanone (**6**) by comparison of ir spectra of the ketone and derived 2,4-dinitrophenylhydrazone, mp 120.5–122°, mmp 120–121°. The second component was shown to be identical with authentic 3-cyclohexylcyclopentanone (**5**) by comparison of the ir spectrum of the ketone; semicarbazone mp and mmp 201–204°. Vpc calibration indicated that 2-cyclohexylcyclopentanone (**6**) and 3-cyclohexylcyclopentanone (**5**) were formed in 3 and 22% yield, respectively.

2-Cyclohexylcyclopentanone (6). The authentic ketone was prepared by alkylation of 2-cyclopentanecarboxylic acid-methyl ethyl ester (a commercial 1:1 mixture) with bromocyclohexane, followed by hydrolysis and decarboxylation. Vpc purification on column G gave pure **6**: ir 2960 (m, sh), 2925 (s), 2859 (m), 1740 (s), 1445 (m), 1400 (m), 1220 (m), 1145 (m) cm^{-1} .

A 2,4-dinitrophenylhydrazone was prepared, mp 120.5–122° (lit.⁵⁶ mp 120–121°).

3-Cyclohexylcyclopentanone (5). To 600 mg (0.025 g-atom) of magnesium turnings and two crystals of iodine in 10 ml of ether was added dropwise 3.86 g (0.02 mol) of cyclohexyl bromide, at a rate as to cause a gentle reflux. When most of the magnesium had reacted the solution was transferred away from the unreacted magnesium. To this solution was added dropwise at 0° 828 mg (0.01 mol) of 2-cyclopentenone in 8 ml of ether. After 2 hr saturated NH_4Cl was added and the mixture was extracted with ether, washed, and dried. Removal of the solvent gave 1.4337 g of an oil which was chromatographed on grade II neutral aluminum. **5** was eluted with ether-pentane and further purified by vpc: ir 2960 (m, sh), 2940 (s), 2850 (m), 1745 (s), 1440 (m), 1255 (m) cm^{-1} .

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.92. Found: C, 79.52; H, 10.91.

A semicarbazone was prepared, mp 201–204° (lit.⁵⁷ mp 186°).

(57) J. v. Braun, E. Kamp, and J. Kopp, *Ber.*, **70**, 1750 (1937).

Anal. Calcd for $C_{12}H_{21}ON_3$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.31; H, 9.55; N, 18.77.

Photolysis of 2-Cyclohexenone in Cyclohexane. A solution of 515 mg of 2-cyclohexenone in 21. of cyclohexane was irradiated for 98 hr through uranium glass. Work-up gave an oil which showed no hydroxyl absorption in the ir spectrum. Vpc analysis on column G indicated at least 11 products. The two solvent adducts were isolated and identified by comparison of ir spectra and derivatives with those of authentic material. 2-Cyclohexylcyclohexanone gave a 2,4-dinitrophenylhydrazone, mp and mmp 131–132°. 3-Cyclohexylcyclohexanone gave a 2,4-dinitrophenylhydrazone, mp and mmp 155–157°. Vpc calibration showed the yields of these adducts to be 0.4 and 1.6% respectively.

Authentic 2-cyclohexylcyclohexanone 2,4-dinitrophenylhydrazone was prepared from the commercially available ketone, mp 131–132° (lit.⁵⁸ mp 172–175°).

Anal. Calcd for $C_{11}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.77; H, 6.84; N, 15.47.

3-Cyclohexylcyclohexanone. The authentic sample was prepared by the same procedure described above for preparation of 5. A 2,4-dinitrophenylhydrazone was prepared, mp 157–159° (lit.⁵⁹ mp 155–157°).

Photolysis of Cyclopentenone 7. A solution of 70 mg of 7 in 50 ml of benzene was irradiated through uranium glass for 5 hr. Removal of solvent through a Vigreux column and then at an aspirator gave a quantitative recovery of material. The extent of conversion of starting ketone (84%) and the yields given below were determined by calibrated vpc. The products were isolated by vpc on column A (given in order of elution).

1,4,4-Trimethylbicyclo[3.2.1]octan-6-one (10) gave an 11% yield. This material had ir and nmr virtually identical with those described below for the product obtained from 36 in polyphosphoric acid. Reduction of the photochemically produced material by lithium aluminum hydride also produced alcohol 48 as indicated by its ir spectrum and mixture melting point with 48 described below.

3-(3-Methyl-2-butenyl)-3-methylcyclopentanone (8): 59% yield; ir 1750, 1675 (w), 840 (w) cm^{-1} ; nmr (60 MHz) δ 1.05 (s, 3 H), 1.15–2.40 with broad s at 1.62 and 1.74 (m, 14 H), 5.16 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.62; H, 11.05.

3-(3-Methyl-3-butenyl)-3-methylcyclopentanone (9): 24% yield; ir 3060 (w), 1750, 1650 (m), 880 (ms) cm^{-1} ; nmr (60 MHz) δ 1.08 (s, 3 H), 1.30–2.50 with broad s at 1.74 (m, 13 H), 4.66 (m, $W_{1/2}$ = 4 Hz, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.59; H, 11.10.

Hydrogenation of photoproducts 8 and 9 over Pd/C in methanol led to cyclopentanone 11 as evidenced by ir and nmr spectral comparisons.

Efficient triplet sensitization of this photolysis was demonstrated. Irradiation through Pyrex for 45 min of a 0.006 M solution of 7 in benzene containing 5.5 mol equiv of propiophenone, which absorbs 80% of the incident light, gave 86% conversion to the above described products. A simultaneously irradiated control ("merry-go-round" apparatus) lacking propiophenone gave a 47% conversion with the same relative distribution of products.

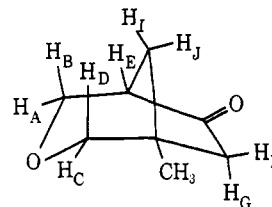
The reaction was efficiently quenched by 2,3-dimethyl-1,3-butadiene. Irradiation through uranium glass for 4.25 hr of 7 in benzene containing 0.1 M quencher led to 5% conversion to the above-described products. A simultaneously irradiated control ("merry-go-round" apparatus) lacking quencher gave 56% conversion.

Photolysis of Ketone 10. 10 (100 mg) was photolyzed through Pyrex in 10 ml of methanol. Two new peaks appeared on vpc (column C) which seemed to be forming in nearly quantitative conversion. After 1.5 hr the reaction was about 95% complete. The solvent was removed through a Vigreux column and the products were isolated by vpc. The minor component (<10%), probably an aldehyde (ir 2720, 1728 cm^{-1}), was not characterized. The major product was 1,4,4-trimethylcyclohexanecarboxylic acid methyl ester (14): ir 2950, 1740, 1158 cm^{-1} ; nmr (60 MHz) δ 0.90 (s, 6 H), 1.00 (s, 3 H), 1.10–1.70 (m, 8 H), 2.20 (s, 2 H), 3.63 (s, 3 H).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.90; H, 11.28.

Photolysis of 4-Isopentyl-4-methylcyclopentenone-3'-d (17). The deuterated cyclopentenone 17 (70 mg) was irradiated in 70 ml of benzene, through uranium glass, for 40 hr. Vpc (column A) indicated roughly the same distribution of products as had been observed on photolysis of 7, with the major product present in about 42% yield. The solvent was removed through a Vigreux column and the residue was passed through a short column of grade V alumina in pentane solution. Again the solvent was evaporated and the residue was dissolved in methanol. The solution was treated with charcoal and filtered through Celite. The mixture was then hydrogenated over 7 mg of 5% Pd/C for 2.5 hr at 1 atm of H_2 . The reaction mixture was then filtered and evaporated and subjected to vpc on column A. The nmr (60 MHz) spectrum of the major component (18) was determined in the presence of the shift reagent $Eu(DPM)_3$ and compared with a similarly determined spectrum of the undeuterated compound 11. The undeuterated compound 11 exhibited the following nmr resonances: δ 2.11 (C(4)-H, broad t, J_{app} = 7.5 Hz, 1.98 H), 2.83 (C(2)-H, s, defined as 2.00 H), 3.10 (C(5)-H, broad t, J_{app} = 7.5 Hz, 2.02 H). For deuterio ketone 18: nmr δ 2.25 (C(4)-H, very broad t, 1.05 H), 3.40 (C(2)-H, s, defined as 2.00 H), 3.70 (C(5)-H, broad d, J_{app} = 7.5 Hz, 2.02 H).

Photolysis of 4-Methyl-4-methoxymethylcyclopentenone (19). A solution of 19 (82 mg) in benzene (80 ml) was irradiated through uranium glass for 18 hr at which time the ir spectrum of an aliquot indicated no enone remaining. After removal of benzene by distillation, vpc analysis on column F of the residue indicated the presence of two components in the ratio 1:4. The minor, first eluted product is still under investigation. The second component (yield 20%) was identified as 21 on the basis of its photochemical degradation (*vide infra*) and the following data: ir 2955 (m), 2850 (w), 1755 (s), 1450 (w), 1395 (w), 1265 (w), 1250 (w), 1210 (w), 1170 (w), 1155 (w), 1100 (s), 1050 (s), 1025 (w), 1000 (w), 920 (w), 905 (m), 860 (w) cm^{-1} ; nmr (220 MHz) δ 3.98 (ddd, J_{AB} = 10, J_{AE} = 2, J_{AJ} = 3 Hz, 60 1 H, H_A), 3.53 (dd, J_{CD} = 11, J_{CJ} = 3 Hz, 1 H, H_C), 3.47 (d, J_{AB} = 10 Hz, 1 H, H_B), 3.44 (d, J_{CD} = 11 Hz, 1 H, H_D), 2.26 (m, 1 H, H_E), 2.18 (dd, J_{FG} = 17, J_{IG} = 3 Hz, 1 H, H_G), 1.86 (d, J_{FG} = 17 Hz, 1 H, H_F), 1.94–1.84 (m, 1 H, H_J), 1.74 (dd, J_{IJ} = 13, J_{IG} = 3 Hz, 1 H, H_I), 1.07 (s, 3 H, CH_3).



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Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.65.

Photolysis of 1-Methyl-3-oxabicyclo[3.2.1]octan-6-one (21). A solution of 21 (40 mg) in benzene (40 ml) was irradiated through Pyrex. Ir spectroscopy was used to monitor the formation of a ketene band at 2110 cm^{-1} , which reached a maximum after 8 hr. Addition of 0.5 ml of absolute ethanol caused this band to be replaced by one at 1740 cm^{-1} . After removal of solvents by distillation, vpc analysis on column F indicated the presence of four components in the ratio of 1:4.2:3.5:2.5. The first component was not collected. The second component was presumed to be 3,6-dihydro-3-methyl-2H-pyran-3-acetaldehyde: ir 3030 (w), 2960 (m), 2830 (m), 2745 (w), 1725 (s), 1455 (m), 1375 (w), 1090 (s), 790 (w) cm^{-1} ; partial nmr (220 MHz) δ 9.74 (t, J = 2 Hz, 1 H), 4.03 (m, 2 H), 3.60 (dd, J_1 = 12, J_2 = 1 Hz, 1 H), 3.31 (d, J = 12 Hz, 1 H). The third component was 3-methyl-3-tetrahydropyranacetic acid ethyl ester (23) having identical ir and 220-MHz nmr spectra and vpc retention time with the independently synthesized material. The fourth component was unreacted starting material.

Photolysis of 4-Methyl-4-(3-phenylpropyl)cyclopentenone (24). A solution of 24 (810 mg) in benzene (850 ml) was placed in two vessels and irradiated through a uranium glass filter for 26 hr, at which time no trace of the starting material could be detected by ir. Removal of the benzene by distillation, column chromatography of the residue on Woelm alumina (100 g to which 5 ml of water was added), and preparative vpc on column F (240°, 200 ml/min)

(58) P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961).

(59) G. P. Kugatova-Shemyakina and V. Vidugiriene, *Zh. Org. Khim.*, **2**, 685 (1966).

(60) For similar long-range couplings in other bicyclo[3.2.1]octanes, see B. Waegell and C. W. Jefford, *Bull. Soc. Chim. Fr.*, 844 (1964).

gave the following compounds (in order of their elution with 9:1 petroleum ether–benzene).

1-Methyl-4-*exo*-phenylbicyclo[3.2.1]octan-6-one (28) (~8%): ir 3035 (w), 2955 (m), 2880 (m), 1750 (s), 1600 (w), 1490 (m), 1455 (m), 1400 (m), 1375 (w), 1285 (m), 1175 (w), 1145 (m), 1040 (m), 1025 (w), 1005 (w), 940 (w), 900 (w), 690 (s) cm^{-1} ; nmr (220 MHz) δ 7.31–7.06 (br, m, 5 H), 3.24–3.17 (m, $W_{1/2}$ = 11 Hz, 1 H), 2.58–2.50 (m, 1 H), 2.20–1.35 (br m, 8 H), 1.14 (s, 3 H); mass spectrum 214.1373 (M^+ , calcd for $C_{15}H_{18}O$, 214.1357).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.67; H, 8.57.

3-Methyl-3-(*cis*-3-phenylprop-2-enyl)cyclopentanone (27) (13%): ir 3030 (w), 2950 (m), 1750 (s), 1485 (w), 1450 (w), 1400 (w), 1375 (w), 1250 (w), 690 (s) cm^{-1} ; nmr (220 MHz) δ 7.33–7.10 (br m, 5 H), 6.55 (d, J = 12 Hz, 1 H), 5.66 (td, J_1 = 12, J_2 = 7 Hz, 1 H), 2.45–2.37 (m, 2 H), 2.20–1.39 (br m, 6 H), 1.08 (s, 3 H).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.21; H, 8.74.

3-Methyl-3-(*trans*-3-phenylprop-2-enyl)cyclopentanone (26) (43%): ir 3030 (w), 2955 (m), 1748 (s), 1598 (w), 1490 (w), 1445 (w), 1400 (w), 1375 (s), 1148 (w), 955 (m), 675 (m) cm^{-1} ; nmr (220 MHz) δ 7.30–7.09 (br m, 5 H), 6.37 (d, J = 16 Hz, 1 H), 6.15 (td, J_1 = 16, J_2 = 7 Hz, 1 H), 2.33–2.12 (m, 4 H), 2.09–1.68 (m, 4 H), 1.12 (s, 3 H).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.10; H, 8.55.

Hydrogenation of *trans*- and *cis*-3-Methyl-3-(3-phenylprop-2-enyl)cyclopentanone (26 and 27). A solution of each unsaturated cyclopentanone (13 mg) in methanol containing a few milligrams of 5% palladium on carbon was hydrogenated at atmospheric pressure for 45 min. Standard work-up gave a product in each case whose 220-MHz nmr and ir spectra were identical with those of 3-methyl-3-(3-phenylpropyl)cyclopentanone (29).

2-Hydroxy-4-isopentyl-4-methylcyclopentanone (36). Sodium (5.00 g, 0.220 g-atom) was dissolved in about 300 ml of ammonia and 200 ml of ether. To this was added 13.6 g (0.050 mol) of diester **35**³⁴ in 80 ml of ether over the course of 2.5 hr. After an additional 1.5 hr of reflux the ammonia was allowed to evaporate overnight under a stream of nitrogen. With the system maintained under nitrogen, 3 *N* HCl was added to acidity. The product was extracted into ether, washed with brine, dried, and evaporated. The residual oil was distilled to provide 7.15 g (78%) of colorless oil: bp 86–87° (0.5 mm); ir 3450 (broad), 1752, 1465, 1088 cm^{-1} ; nmr (60 MHz) δ 0.91 (d, J = 5 Hz, 6 H), 1.10 (s, 3 H), 1.10–2.60 with s at 2.10 (m, 9 H), 3.80 (broad, exchanges with D_2O , 1 H), 3.89–4.41 (m, 1 H). Analytically pure material was obtained by vpc on column A.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.69; H, 11.00.

2-Mesyloxy-4-isopentyl-4-methylcyclopentanone (37). A solution of acyloin **36** (460 mg, 2.50 mmol) in 3 ml of pyridine was cooled in an ice bath as 0.25 ml (3.2 mmol) of methanesulfonyl chloride was added. The mixture was refrigerated overnight and then poured into ice water. The mixture was extracted with ether and the organic layer was washed with aqueous HCl and with saturated $NaHCO_3$. The ether solution was dried and evaporated to an oil. Crystallization of the oil from cold pentane gave 422 mg (64%) of white powdery material, mp 46–52°. Recrystallization from pentane afforded material for elemental analysis, presumably a mixture of stereoisomers: mp 53–57°; ir 2960, 1765, 1365, 1175, 960 cm^{-1} ; nmr (60 MHz) δ 0.91 (d, J = 5 Hz, 6 H), 1.15 (s, 3 H), 1.20–2.70 with s at 2.17 (m, 9 H), 3.10 (s, 3 H), 4.90 (m, 1 H).

Anal. Calcd for $C_{17}H_{28}O_4S$: C, 54.95; H, 8.45. Found: C, 55.27; H, 8.53.

4-Isopentyl-4-methylcyclopentenone (7). Mesylate **37** was prepared as above from 1.84 g of the acyloin **36** and 1.00 g of methanesulfonyl chloride. After evaporation of the ether solution the crude oily mesylate was dissolved in hexamethylphosphoramide and heated in an oil bath at 135–140° for 40 min. The reaction mixture was partitioned between water and ether. The organic layer was washed with saturated $NaHCO_3$, dried, and evaporated. The residual oil was distilled at aspirator vacuum to give 1.15 g (67%) of colorless product: bp 95–99°; ir 1723 cm^{-1} ; nmr (60 MHz) δ 0.88 (d, J = 5 Hz, 6 H), 0.8–2.20 with s at 1.20 (m, 10 H), 5.95 (d, J = 5.5 Hz, 1 H), 7.30 (d, J = 5.5 Hz, 1 H). Analytically pure material was obtained by vpc on column A.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.39; H, 10.94.

Isobutyl-2-*d* Mesylate (40). A solution of deuterioborane was prepared by treating a suspension of LiD in 60 ml of tetrahydro-

furan with 19.0 ml of boron trifluoride etherate.³⁹ Isobutylene was admitted to the reaction vessel and the mixture was stirred under isobutylene for several hours. Aqueous NaOH (12 ml, 3 *N*) was added, carefully at first, and then 12 ml of 30% H_2O_2 was added dropwise as the mixture was stirred in a water bath at 35°. After about 1 hr at this temperature the aqueous layer was saturated with NaCl and the layers were separated. The organic layer was washed with brine. The aqueous solutions were extracted twice with ether and the organic layers were combined for drying over $MgSO_4$. The solvents were evaporated through a Vigreux column. The residue was dissolved in 40 ml of pyridine and treated with 10 ml of methanesulfonyl chloride. The initial heat of reaction was dissipated in an ice bath and the mixture was then kept at room temperature for several hours and overnight at 5°. The dark mixture was poured into ice-water and extracted with ether. The ether layer was washed with aqueous HCl, water, and $NaHCO_3$, dried, and evaporated. Distillation of the residue gave 3.90 g (22% based on LiD) of colorless oil: bp 92–98° (aspirator); nmr (60 MHz) δ 1.00 (t, J = 1 Hz, 6 H), 2.93 (s, 3 H), 3.96 (m, 2 H). Isolation of the intermediate isobutyl alcohol failed to improve the reaction, but it showed that the poor yield occurs at the deuterioboration-oxidation step.

5-Methyl-2-hexanone-5-*d* (38). Equivalent amounts of *tert*-butyl acetate and KOH were combined in methanol and the solvent was evaporated. Trituration of the residue with petroleum ether gave the potassium salt as a light tan powder, which was dried *in vacuo*. Mesylate **40** (3.90 g, 2.5 mmol) was dissolved in 50 ml of *tert*-butyl alcohol along with 5.60 g (28.6 mmol) of the potassium salt and the solution was heated at reflux for 1.5 hr. The mixture was diluted with water and extracted with pentane. The organic solution was washed with water, dried, and evaporated through a Vigreux column to give 5.0 g of an oil. This material was distilled from 100 mg of 1-naphthalenesulfonic acid to yield 1.44 g (39%) of colorless product: ir 2960, 2120 (w), 1725, 1365 cm^{-1} ; nmr (60 MHz) δ 0.87 (t, J = 1 Hz), 2.07 (s), 2.37 (t, J = 7.5 Hz).

4-Isopentyl-4-methylcyclopentenone-3-*d* (17). The deuterated ketone **38** (2.30 g, 20.0 mmol) was converted by the known procedure³⁴ to diacid **34** (2.25 g, 51%): mp 67–69°; nmr (60 MHz) δ 0.85–2.20 with s at 1.00 and 1.32 (m, 13 H), 2.93 (s, 4 H), 12.9 (s, 2 H). This material was esterified in ethanol containing a catalytic amount of sulfuric acid at reflux (through 3A molecular sieves) for 20 hr. The yield of diester **35** was 2.59 g (92%), bp 97–100° (0.5 mm). Conversion of the diester (2.50 g, 9.15 mmol) to the acyloin condensation product **36** was accomplished as described above for the undeuterated compound to give 1.46 g (86%) colorless oil: bp 72–74° (0.1 mm); ir 2465 (broad), 2960, 2135 (w), 1755, 1468, 1082 cm^{-1} ; nmr (60 MHz) δ 0.89 (s, 6 H), 1.00–2.50 with s at 1.12 and 2.10 (m, 11 H), 3.46 (broad s, exchanges with D_2O , 1 H), 3.91–4.42 (m, 1 H). This compound was transformed into enone **17** via the mesylate as described above. The acyloin (1.41 g, 7.62 mmol) gave 0.850 g (67%) of crude enone which was purified as needed by vpc on column A: ir 2960, 2135 (w), 1723 cm^{-1} ; nmr (60 MHz) δ 0.88 (broadened s, 6 H), 0.95–1.80 with s at 1.20 (m, 7 H), 2.07 and 2.12 (s, 2 H), 5.93 (d, J = 5.5 Hz, 1 H), 7.28 (d, J = 5.5 Hz, 1 H).

Hydrogenation of Cyclopentenone 7. Cyclopentenone **7** (50 mg) was reduced in methanol solution over 5 mg of 5% Pd/C, with H_2 at about 1 atm. After removal of catalyst and solvent a quantitative recovery of material was obtained. This was purified for analysis by vpc (column A, one peak), 3-isopentyl-3-methylcyclopentanone **11**: ir 2960, 1748 cm^{-1} ; nmr (60 MHz) δ 0.90 (d, J = 5 Hz, 6 H), 1.02 (s, 3 H), 1.12–1.92 (m, 7 H), 1.94 (s, 2 H), 2.13–2.43 (m, 2 H).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.40; H, 12.04.

Calcium Reduction of Mesylate 37. Calcium (100 mg, 2.50 mg-atoms) was dissolved in about 30 ml of NH_3 and the mesylate **37** (100 mg, 0.382 mmol) was added in a few milliliters of ether. After 40 min 1 ml of methanol was added (carefully) and then several grams of NH_4Cl . The NH_3 was evaporated and the residue partitioned between ether and water. The organic layer was washed with brine, dried, and evaporated to give 75 mg of reddish oil. The major product (53%) isolated by vpc on column A was cyclopentanone **11** as shown by ir and nmr spectra.

(4,4-Dimethylcyclohexylidene)cycanoacetic Acid Ethyl Ester (43). Ethyl cycanoacetate (5.65 g, 50.0 mmol) and 4,4-dimethylcyclohexanone (**42**, 6.30 g, 50.0 mmol)⁴⁶ were combined with 0.60 g of acetic acid and 0.40 g of ammonium acetate in 5 ml of benzene.⁴⁴ The mixture was refluxed with water separation for 1 hr after production of water ceased. The mixture was then diluted with ether, washed with water and saturated $NaHCO_3$, dried, and evaporated. Distillation of the residue afforded 8.54 g (77%) of colorless oil: bp 91–

96° (0.1 mm); ir 2960, 2220 (w), 1735, 1601, 1255, 1220 cm^{-1} . The oil solidified on standing and was recrystallized to analytical purity from pentane, mp 56–57°.

Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.53; H, 8.69; N, 6.23.

(1,4,4-Trimethylcyclohexyl)cycanoacetic Acid Ethyl Ester (44). To a solution of methylmagnesium iodide (22.0 mmol, prepared from 0.535 g of Mg and 1.37 ml of methyl iodide in 25 ml of ether) was added 100 mg of CuCl . After a few minutes the unsaturated ester **43** (4.42 g, 20.0 mmol) was added in 10 ml of ether at a rate that caused refluxing of the solvent. The mixture was then heated at reflux for 1 hr and kept at room temperature for an additional 1 hr. The reaction mixture was treated with saturated NH_4Cl and then partitioned between water and more ether. The organic layer was washed with brine, dried, and evaporated and the residue was distilled to provide 4.27 g (90%) of pale green oil: bp 91–97° (0.1 mm); ir 2935, 2240 (w), 1750, 1248, 1223, 1177 cm^{-1} ; nmr (60 MHz) δ 0.92 (s, 6 H), 1.11 (s, 3 H), 1.03–2.03 with t ($J = 7$ Hz) at 1.33 (m, 11 H), 3.34 (s, 1 H), 4.23 (q, $J = 7$ Hz, 2 H). An analytical sample was obtained by vpc on column D.

Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.72; H, 9.78; N, 5.73.

1,4,4-Trimethylcyclohexanecarboxylic Acid (15). **A. Authentic Sample.** Cyano ester **44** (0.50 g, 2.1 mmol) was dissolved in 4 ml of ethylene glycol along with 0.80 g of KOH, and the mixture was refluxed overnight. The mixture was then diluted with water and washed with ether. The aqueous layer was acidified with concentrated HCl and extracted with ether. The organic layer was washed with brine, dried, and evaporated. The residue was then heated in an oil bath at 200° until no further gas evolution was evident; it was then dissolved in dilute NaOH, washed with ether, and acidified. The product was extracted into ether, washed with brine, dried, and evaporated to give 371 mg of dark oil. Short-path distillation yielded 333 mg (86%) of colorless crystals, mp 46–48°, undepressed on mixture with the acid derived below from photolysis of **10**. Spectroscopic comparisons also verified the identity of these materials.

B. From Photolysis of 10. Methyl ester **14** (31 mg) was saponified in refluxing aqueous alcoholic KOH for 1 hr. The mixture was acidified and the product was isolated by extraction with ether, drying, and evaporation. The residue (23 mg, 80%) crystallized on cooling, mp 47–48.5°. Analytically pure material was obtained on short-path distillation (0.1 mm, water bath at 40°): mp 47.5–48.5°; ir (KBr) 3400–2400 (m), 1710 cm^{-1} ; nmr (60 MHz) δ 0.90–2.0 with s at 0.93 and 1.08 (m, 17 H), 2.18 (s, 2 H), 12.01 (s, 1 H).

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$: C, 71.69; H, 10.94. Found: C, 71.70; H, 10.94.

Reaction of Acyloin 36 in Polyphosphoric Acid. A 2.00-g sample of acyloin **36** was mixed with 33 g of polyphosphoric acid. After 7 hr at room temperature the mixture was heated on a steam bath overnight. The material was then treated with ice and water and the product extracted into ether. The ether solution was washed with water and saturated NaHCO_3 , dried, and evaporated to give 1.73 g of orange oil. Short-path distillation (aspirator pressure, air bath at 120°) yielded 1.05 g (58%) of **10** as a yellow oil: ir 2950 (m), 1745 (s), 1455 (m), 1152 (m) cm^{-1} ; nmr (60 MHz) δ 0.95 (s, 3 H), 1.00 (s, 3 H), 1.13 (s, 3 H), 1.20–2.00 (m, 9 H). Colorless, analytically pure material was obtained from vpc on column A (essentially one peak).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.92. Found: C, 79.59; H, 11.04.

endo-1,4,4-Trimethylbicyclo[3.2.1]octan-6-ol (48). The crude bicyclic ketone **10** (388 mg, 2.00 mmol) was treated with 100 mg (2.91 mmol) of lithium aluminum hydride in 10 ml of ether. After 1 hr the reaction was worked up by sequential addition of 0.10 ml of water, 0.10 ml of 15% NaOH, and 0.30 ml of water. The mixture was filtered and the solvent evaporated to give 372 mg of yellow oil from which the major component (90% of volatile material) was isolated by vpc on column B: ir 3630, 2950 (s), 1452, 1040 cm^{-1} ; nmr (60 MHz) δ 0.93 and 0.97 (s, 6 H), 1.10–2.20 with s at 1.17 (m, 13 H), 4.48 (m, 1 H); mp 51–52.5°.

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$: C, 78.15; H, 11.98. Found: C, 78.39; H, 11.82.

Preparation of 4-Methyl-4-methoxymethylcyclopentenone (19). Ketalization of 3-carboethoxy-3-methylcyclopentanone (7.34 g, 0.0470 mol) was achieved with ethylene glycol (3.36 g, 0.0541 mol) in benzene (100 ml) containing a trace of *p*-toluenesulfonic acid, and the reaction mixture was heated at reflux for 15 hr with continuous removal of water by a Dean-Stark trap. Standard work-up gave 9.59 g of a pale red oil whose ir spectrum showed the presence of

only one carbonyl band at 1735 cm^{-1} . Without further purification the ester (9.59 g, 0.0470 mol) in ether (75 ml) was added to a suspension of lithium aluminum hydride (1.44 g, 0.0379 mol) in ether (150 ml). The reaction was heated at reflux for an additional 0.5 hr and worked up by careful addition of saturated sodium sulfate containing 2 ml of 11% sodium hydroxide solution. After drying and removal of ether *in vacuo*, 7.36 g of a pale yellow oil was obtained; the ir spectrum of this material was transparent in the carbonyl region and contained a hydroxyl band at 3650 cm^{-1} .

To a suspension of sodium hydride (2.32 g of a 53% mineral oil dispersion, 0.0413 mol) in dry dimethyl sulfoxide (45 ml) was added the crude ketal alcohol (7.36 g, 0.0438 mol) in dimethyl sulfoxide (10 ml). It was necessary to heat the reaction to 35° to complete the evolution of hydrogen (~2 hr required). After cooling the mixture in an ice bath, methyl iodide (7.30 g, 0.0514 mol) was added dropwise and the reaction was stirred at room temperature for 2.5 hr. To ensure complete etherification, a small portion of sodium hydride was added to the reaction mixture which stirred for 1 hr and quenched with methyl iodide (2 ml); stirring was continued at room temperature overnight under a nitrogen atmosphere.

The reaction mixture was poured into water (150 ml) and extracted three times with ether. The combined ethereal extracts were washed with water (2 \times 15 ml) and brine (15 ml). After drying and removal of solvents, distillation afforded 6.10 g (70% yield from **51**): bp 91–95° (10 mm); ir 2955 (m), 2880 (m), 1340 (m), 1100 (s) cm^{-1} ; nmr (60 MHz) δ 3.76 (s, 4 H), 3.28 (s, 3 H), 3.07 (s, 2 H), 1.95–1.25 (br m, 6 H), 1.02 (s, 3 H).

The ether ketal was fully characterized by hydrolysis with 10% hydrochloric acid to give 3-methyl-3-methoxymethylcyclopentanone: bp 74–75° (9 mm); ir 2960 (m), 2870 (m), 1750 (s), 1105 (s) cm^{-1} ; nmr (60 MHz) δ 3.20 (s, 3 H), 3.07 (s, 2 H), 2.32–1.52 (br m, 6 H), 1.03 (s, 3 H).

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_2$: C, 67.57; H, 9.93. Found: C, 67.66; H, 9.87.

The procedure of Garbisch⁴⁹ was found to be a more satisfactory method of introducing unsaturation to give 4-methyl-4-methoxymethylcyclopentenone than direct bromination–dehydrobromination. Thus the ketal ether (3.35 g, 18 mmol) was converted to the bromo ketal ether (yield 4.75 g) in ethylene glycol (40 ml) with bromine (2.88 g, 18 mmol). This material was dehydrobrominated with sodium hydroxide (5 g) in methanol (50 ml) heated at reflux for 70 hr. After hydrolysis with 3% sulfuric acid, short path distillation yielded **19** (768 mg, 30%): bp 89–92° (9 mm); ir 2940 (w), 2890 (w), 2870 (w), 1725 (s), 1590 (w), 1190 (w), 1110 (m) cm^{-1} ; nmr (220 MHz) δ 7.35 (d, $J = 6$ Hz, 1 H), 5.98 (d, $J = 6$ Hz, 1 H), 3.30 (s, 3 H), 3.24 (d, $J = 13$ Hz, 1 H), 3.20 (d, $J = 13$ Hz, 1 H), 2.21 (d, $J = 18$ Hz, 1 H), 1.95 (d, $J = 18$ Hz, 1 H), 1.21 (s, 3 H).

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{O}_2$: C, 68.54; H, 8.63. Found: C, 68.69; H, 8.61.

Tetrahydropyran-3-ol. A solution of dihydropyran (25.2 g, 0.30 mol) in ether (150 ml) was hydroborated according to the procedure of Brown.^{49,50} After decomposition of the organoborane and separation of the ethereal phase, the aqueous phase was saturated with salt and extracted twice with ether. After drying and removal of solvent, distillation afforded 9.7 g, bp 78–80° (11 mm). Continuous extraction of the aqueous phase yielded another 11.4 g (total yield, 69%): ir 3630 (w), 3450 (br m), 2940 (s), 2845 (s), 1195 (w), 1090 (s), 1055 (m), 1020 (w), 980 (w), 905 (w), 865 (w) cm^{-1} ; nmr (60 MHz) δ 3.78–2.80 (br m, 6 H), 2.08–1.17 (br m, 4 H).

Tetrahydropyran-3-one (55). Tetrahydropyran-3-ol (3.06 g, 0.03 mol) was oxidized with chromium trioxide in pyridine in a fashion similar to that used for the oxidation of tetrahydrofuran-3-ol.⁵¹ Continuous extraction of the acidified, filtered aqueous phase gave a residue which afforded 1.10 g of **55** after bulb-to-bulb distillation (80°, 10 mm). This material contained 12% butyrolactone and could be purified by vpc: ir 2990 (w), 2875 (w), 1738 (s), 1240 (w), 1100 (s), 910 (s) cm^{-1} ; nmr (60 MHz) δ 3.73 (s, 2 H), 3.63 (br t, $J = 5$ Hz, 2 H), 2.52–1.75 (br m, 4 H). These data are in agreement with published⁵² values.

3-Carboethoxymethylenetetrahydropyran (56). A solution of tetrahydropyran-3-one (**55**) (500 mg, 5 mmol), carboethoxymethylenetriphenylphosphorane (1.83 g, 5.25 mmol), and benzoic acid⁵⁴ (40 mg, 0.33 mmol) in benzene (25 ml) was heated at reflux under a nitrogen atmosphere for 24 hr. The reaction mixture was cooled, poured into water (50 ml), and extracted with ether; after drying and removal of solvents, bulb-to-bulb distillation gave 518 mg of **56** (61%) as the anti isomer: bp ~140° (10 mm); ir 2980 (m), 2845 (m), 1720 (s), 1660 (m), 1375 (m), 1260 (m), 1225 (s), 1190 (s), 1170 (s), 1140 (s), 1080 (s), 1030 (m), 1020 (m) cm^{-1} ; nmr (60 MHz) δ 5.34 (br s, 1 H), 3.92 (q, $J = 6.5$ Hz, 2 H), 3.77 (d, $J = 1$ Hz, 2 H), 3.54

(t, $J = 5$ Hz, 2 H), 2.90 (br t, $J = 6$ Hz, 2 H), 1.87–1.65 (m, 2 H), 1.20 (t, $J = 6.5$ Hz, 3 H). An analytical sample was obtained by vpc on column A (155°, 110 ml/min).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.30; H, 8.31.

On a larger scale, both isomers were formed. The syn isomer nmr spectrum (60 MHz): 5.35 (br s, 1 H), 4.43 (d, $J = 1$ Hz, 2 H), 3.92 (q, $J = 6.5$ Hz, 2 H), 3.52 (t, $J = 5$ Hz, 2 H), 2.32 (br t, $J = 6$ Hz, 2 H), 1.87–1.65 (m, 2 H), 1.20 (t, $J = 6.5$ Hz, 2 H).

3-Methyl-3-tetrahydropyranacetic Acid Ethyl Ester (23). A solution of methylmagnesium iodide was prepared from magnesium (243 mg, 10 mg-atoms) and methyl iodide (1.365 g, 9.58 mmol) in anhydrous ether (15 ml). After cooling to 0° a solution of tetrakisiodo(tri-*n*-butylphosphine)copper⁶¹ (328 mg, 0.833 mmol) in ether (10 ml) was added. The bright yellow reaction mixture was stirred for 5 min before dropwise addition of a solution of **56** (1.432 g, 8.33 mmol) in ether (10 ml) at 0°.

Immediately after completion of the addition, the reaction mixture was poured with rapid stirring into a solution of saturated ammonium chloride containing 1 ml of ammonium hydroxide. After extraction with ether, drying, and removal of the ether, **23** was obtained by preparative vpc (41%) on column G: ir 2945 (m), 2845 (w), 1735 (s), 1460 (w), 1360 (w), 1085 (s), 1025 (m), 970 (w) cm^{-1} ; nmr (220 MHz) δ 4.06 (q, $J = 7$ Hz, 2 H), 3.65–3.55 (m, 1 H), 3.47–3.41 (m, 1 H), 3.35 (d, $J = 12$ Hz, 1 H), 3.13 (d, $J = 12$ Hz, 1 H), 2.47 (d, $J = 14$ Hz, 1 H), 2.12 (d, $J = 14$ Hz, 1 H), 1.72–1.29 (br m, 4 H), 1.24 (t, $J = 7$ Hz, 3 H), 0.96 (s, 3 H).

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.70; H, 9.89.

3-Methyl-3-(3-phenylpropyl)cyclopentanone (29). A solution of 3-phenylpropylmagnesium bromide was prepared from magnesium (4.02 g, 0.165 g-atom) and 1-bromo-3-phenylpropane (29.3 g, 0.15 mol) in ether (130 ml). The reaction mixture was cooled to 0°, and tetrakisiodo(tri-*n*-butylphosphine)copper⁶¹ (2.46 g, 0.00625 mol) was introduced with ether (60 ml), followed by dropwise addition of

3-methylcyclopent-2-enone (12.00 g, 0.125 mol) in ether (75 ml). Upon completion of the addition, the reaction mixture was poured into a solution of saturated ammonium chloride containing a few milliliters of ammonium hydroxide. Extraction with ether, drying, and removal of solvent yielded 29.46 g. The cyclopentanone was isolated from nonketonic material using Girard's reagent T, which afforded, after distillation, **29** (7.50 g, 28%): bp 114–115° (0.1 mm); ir 3040 (w), 2950 (m), 1750 (s), 1600 (w), 1495 (m), 1450 (m), 1400 (m), 1375 (w), 1250 (w), 690 (s) cm^{-1} ; nmr (220 MHz) δ 7.24–7.05 (br m, 5 H), 2.57 (t, $J = 7$ Hz, 2 H), 2.20–2.09 (m, 2 H), 1.95 (d, $J = 18$ Hz, 1 H), 1.86 (d, $J = 18$ Hz, 1 H), 1.75–1.30 (br m, 6 H), 1.01 (s, 3 H). An analytical sample was obtained by preparative vpc on column F (240°, 200 ml/min).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.24. Found: C, 83.39; H, 9.24.

4-Methyl-4-(3-phenylpropyl)cyclopentanone (24). The procedure⁴⁹ of Garbisch was employed in this conversion of the cyclopentanone (1.895 g, 8.75 mmol). At the bromo ketal stage 3.05 g was obtained. Hydrolysis of the unsaturated ketal in ethanol–3% aqueous H_2SO_4 , extraction, drying, and bulb-to-bulb distillation gave the enone (866 mg, 46%): ir 3040 (w), 2950 (m), 1720 (s), 1595 (w), 1490 (w), 1450 (w), 1405 (w), 685 (m) cm^{-1} ; nmr (220 MHz) δ 7.26 (d, $J = 6$ Hz, 1 H), 7.24–7.07 (br m, 5 H), 5.93 (d, $J = 6$ Hz, 1 H), 2.61–2.54 (m, 2 H), 2.17 (d, $J = 18$ Hz, 1 H), 1.97 (d, $J = 18$ Hz, 1 H), 1.71–1.42 (br m, 4 H), 1.19 (s, 3 H). An analytical sample was obtained by preparative vpc on column E.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.94; H, 8.57.

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Generation of Photochemical Intermediates without Light. The Type B Zwitterion. Mechanistic Organic Photochemistry. LXXI¹

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Abstract: 6-Bromo-5,5-diphenylcyclohex-2-en-1-one was synthesized as a precursor to the zwitterion previously postulated as an intermediate in the type B photochemical rearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones. For example, irradiation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one gives a mixture of 2,3-diphenylphenol and 3,4-diphenylphenol. The ratio of phenols now has been found to be a smooth function of solvent polarity with the amount of 3,4 isomer increasing with increasing polarity. Turning to the dark reaction of 6-bromo-5,5-diphenylcyclohex-2-en-1-one with potassium *tert*-butoxide, a reaction designed to generate the Favorski-like zwitterion postulated for the type B photochemical rearrangement, we find that both the 2,3- and the 3,4-diphenylphenols are formed. Even more strikingly, the 2,3-diphenylphenol predominates as in the photochemical process and the ratio of phenols is the same as photochemically. Beyond this, the change in the ratio as a function of solvent polarity is the same for both dark and photochemical runs. Thus, convincing proof is available that the zwitterion B is indeed a true photochemical intermediate.

In 1961 we suggested that the photochemical rearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones to give 2,3- and 3,4-disubstituted phenols and their tautomers (*e.g.*, note eq 1) proceeds *via* the mesoionic zwitterion B.^{2–5} This hypothesis was de-

signed to resolve an inconsistency. On one hand, the triplet $n-\pi^*$ excited state was known to be the species

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