Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left a crude solid which was purified by thick layer chromatography using ethyl acetate as the eluent. Recrystallization of the white solid from acetone gave 4,5-di(β-naphthyl)-1,3-diazabicyclo-[3.1.0]hex-3-ene (**15**) (37%) as a crystalline solid: mp 166–167°; ir (KBr) 6.20, 7.38, 7.52, 9.95, 11.48, 12.01, 13.29 μ; uv (cyclohexane) 226 nm (ε 107,000), 245 (53,200), 253 (48,600), 273 (15,300), 283 (16,100), 292 (12,200), 341 (1,100); nmr ($CDCl_3$, 100 MHz) τ 8.12 (1 H, s), 6.84 (1 H, s), 5.00 (1 H, d, J = 16 Hz), 4.64 (1 H, d, J = 16 Hz), 1.80–2.80 (14 H, m); m/e 334 (M^+), 332 (base), 331, 304, 276, 153, 127.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.27; H, 5.42; N, 8.29.

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate/100 ml of water through the inner jacket.[34] All studies were made at room temperature. Samples were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol[8] or cyclopentanone[35] solutions were used as the chemical actinometer. For cyclopentanone, an actinometer quantum yield of 0.38 was used[35] which gave a reproducible lamp output of 2.01×10^{16} quanta sec^{-1}. After irradiation, the degree of reaction was determined by quantitative vapor phase chromatography. The conversions in the arylazirine series were run to 15% or less. The mass balance in these runs was generally better than 95%.

Competitive studies were carried out photochemically on mixtures of an arylazirine, an internal standard, and two different dipolarophiles in sealed, degassed tubes. The relative reactivities were determined by gas chromatography using the relation

$$k_{rel} = (\log A/A_0)/(\log B/B_0)$$

where A_0 and B_0 are the areas of the two dipolarophiles relative to the internal standard prior to the reaction, and A and B the same quantities after reaction. Relative reactivities of dipolarophiles toward the nitrile ylide generated from *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**16**) were determined in a similar fashion. In a small test tube was added a benzene solution of the two dipolarophiles, an internal standard, and triethylamine. After measuring the area of the peaks corresponding to the dipolarophiles, the solution was allowed to react with *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**16**). Since cycloaddition rates varied considerably between systems, tubes were removed periodically and analyzed by glc until optimum conversion times for analysis had been determined. The final peak areas were determined by glc after *ca.* 40% of the dipolarophiles had been consumed. The results are summarized in Table III.

Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure Xenon lamp, as supplied by the manufacturer. The fluorescence spectra of naphthalene and 2-(β-naphthyl)azirine (**14**) were determined in cyclohexane solution at 25°. The concentration of the substrate was 5×10^{-3} *M*. The solvent was checked for emission each time a spectrum was run. No interference due to solvent was found at any time. All slits were set at 3 mm and excitation was at 335 nm. The naphthylazirine showed a fluorescence maximum at 375 nm and the shape of the emission envelope was essentially identical with that of naphthalene. The singlet lifetime (τ_s) of 2-(β-naphthyl)azirine was measured by single-photon counting and was determined to be 1.5×10^{-9} sec.[24]

Acknowledgment. We gratefully acknowledge support of the work by the National Science Foundation (Grant GP-24449). We also thank Dr. Stuart Clough for some of the quantum yield determinations and Professor N. Turro for the single-photon measurements.

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(35) J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, 1318 (1970).

Photochemical Reactions of 1-Cyclopentenyl and 1-Cyclohexenyl Ketones

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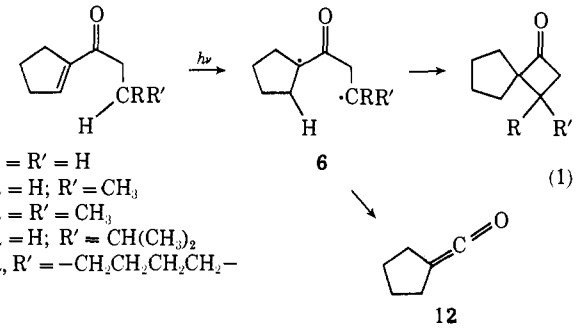
Abstract: Photolysis of several 1-acylcycloalkenes has been investigated and found to lead to three types of rearrangement. Simple ketones **1**–**5**, as well as **22**, undergo hydrogen transfer with formation of spiroketones **7**–**11** and **23** plus some minor products. Cyclohexenyl ketones **25** and **29** give the hexahydrofluorenones **27** and **28** in an electrocyclic reaction, and the doubly unsaturated **35** is isomerized to ketene **43** which can be isolated as esters **36** and **37**. All three processes occur on both direct irradiation and triplet sensitization in preparatively attractive yields.

In a previous report,[1] we described photochemical reactions of cyclopentenones in which a key step is intramolecular transfer of hydrogen to the β carbon atom of the enone system. These findings suggested that related processes might occur in other types of α,β-unsaturated ketones. This has indeed proved to be the case, and we describe below our experience with photolysis of a number of 1-acylcycloalkenes. Apart from hydrogen transfer reactions, two other processes occur in some of these ketones. In several cases the various transformations observed provide synthetically worthwhile routes to useful systems.

The simple alkyl 1-cyclopentenyl ketones **1**–**5** are all available through Friedel–Crafts acylation[2] of cyclopentene with the appropriate carboxylic acid chloride. If irradiation of these compounds leads to the hydrogen abstraction observed in cyclopentenones, the result expected is that shown in eq 1. Abstraction by the β

(1) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 7797 (1972).

(2) N. Jones and H. T. Taylor, *J. Chem. Soc.*, 4017 (1959), and references cited therein.

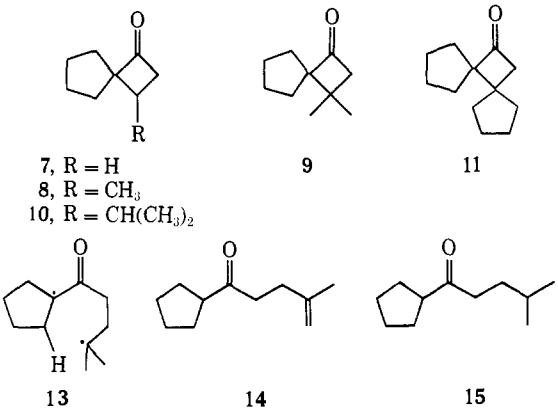


1, R = R′ = H
2, R = H; R′ = CH_3
3, R = R′ = CH_3
4, R = H; R′ = $CH(CH_3)_2$
5, R, R′ = $-CH_2CH_2CH_2CH_2-$

6 (1)

12

carbon atom of the enone system is sterically most reasonable from the β' carbon atom, and the 1,4-biradical formed (**6**) could then collapse to a spiro[3.4]octan-1-one or fragment to a ketene and an alkene. This appears to be correct, for photolysis[3] of ketones **1–5** does furnish the corresponding spiro compounds **7–11**, respectively.[4] Yields of **8–11** are 30–36%,[5] while the yield of the parent **7** is 8%. The reactions are nonetheless attractive preparatively, not only in view of the ready availability of the starting enones, but also because, apart from the easily separated side products noted below, these spiroketones are the only volatile compounds formed. Further evidence supporting eq 1 comes from formation in two cases of the ketene **12**. Infrared monitoring of the irradiation of **3** and **5**, in which the β' carbon atom is tertiary, indicated development of absorption at 2100 cm^{-1} in addition to the cyclobutanone band at 1775 cm^{-1}. After photolysis methanol was added to the benzene solution, and subsequent work-up furnished 25% of methyl cyclopentanecarboxylate, identical with an authentic sample.[6,7]



7, R = H
8, R = CH_3
10, R = $CH(CH_3)_2$

9 11

13 14 15

It is interesting that abstraction from the secondary β' carbon atom of **2** and **4** is as effective as from the tertiary center of **3** and **5**, and that abstraction even of methyl hydrogen is feasible in this reaction.[8] Fragmentation with formation of **12** occurred only when the β' center was tertiary, however. We are currently investigating the possibility that this points to a difference in mechanism leading to ketene and to spiroketone products. The path of eq 1 may prove to be oversimplified, and the actual extent of involvement of biradical intermediates such as **6** remains an open question.

Preparation and irradiation of **4** represent an effort to deflect abstraction from secondary hydrogen through a six-membered intermediate (eq 1) to tertiary hydrogen, with formation of **13** through a seven-membered ring. This effort was partially successful; although the yield of spiroketone **10** was comparable to that of **8**, a new isomerization product **14** was isolated in 10% yield. This appears to result from formation of the desired intermediate **13**, followed by transfer of one of the six methyl hydrogen atoms to the α-radical center. A quite similar sequence occurs in photoisomerization of 4-isopentyl-4-methylcyclopentenone.[1,9]

The structure of **14** was rigorously defined by ir and nmr data requiring an asymmetrically disubstituted ethylene, and by hydrogenation to **15**, which was also available through catalytic reduction of **4**. The structures of spiroketones **7–11** were all strongly supported by spectroscopic data. Nmr signals were present for appropriately situated methyl, geminal dimethyl, and isopropyl groups in **8**, **9**, and **10**, respectively, and all the compounds had cyclobutanone ir absorption at about 1775 cm^{-1}. The ir and nmr data for parent ketone **7** were also in agreement with those found for it in a previous and totally different synthesis.[10] In addition, **9** and **10** were oxidized to the related butyrolactones **16** and **17** with peroxytrifluoroacetic acid,[11] and these lactones were identical with samples independently prepared in the following way. Known[12] acid **18** was converted through an Arndt–Eistert synthesis[13] to the methyl ester **19** of its higher homolog, which furnished **16** on saponification followed by exposure to hot dilute hydrochloric acid. For **17**, the hydroxy ester **20** was prepared by a Reformatsky[14] reaction between α-bromoacetic ester and cyclopentyl isopropyl ketone.[15] Hydrolysis in base and then treatment with sulfuric acid gave a mixture of **17** and the isomeric lactone **21**, presumably by way of the two rearranged carbonium ions or the related olefins. These two lactones, **17** and **21**, were readily separated by preparative vpc.[16]

Earlier observations[1,17] suggest that these hydrogen transfer reactions proceed from a triplet state. In

(3) Irradiations were carried out at concentrations of about 1 mg/ml in benzene solution unless otherwise indicated using a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well and a Corning No. 3320 uranium glass filter.

(4) Results with **3** and **4** have been described briefly: A. B. Smith, III, A. M. Foster, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 5100 (1972).

(5) All yields are based on converted starting material and were determined by calibrated vapor phase chromatography (vpc).

(6) The alternative possibility that **12** arises from a photochemical cleavage of the spiroketone **9** or **11** first formed was ruled out experimentally. Cyclobutanone **9** was unchanged under the appropriate conditions of irradiation.

(7) D. W. Goheen and W. R. Vaughan, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 594.

(8) For a discussion of the effect of radical stability on rate of abstraction in the Type II reaction, see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

(9) W. L. Schreiber and W. C. Agosta, *J. Amer. Chem. Soc.*, **93**, 3814 (1971).

(10) H. H. Wasserman and D. C. Clagett, *ibid.*, 88, 5368 (1966). We are grateful to Professor Harry H. Wasserman for supplying these data.

(11) W. D. Emmons and G. B. Lucas, *ibid.*, 77, 2287 (1955).

(12) P. B. Talukdar and P. Bagchi, *J. Org. Chem.*, 20, 25 (1955), and references cited therein.

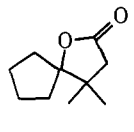
(13) W. E. Bachmann and W. S. Struve, *Org. React.*, 1, 38 (1942).

(14) R. L. Shriner, *ibid.*, **1**, 1 (1942).

(15) J. Crouzet, L. Giral, G. Cauquil, and J. Rouzaud, *Bull. Soc. Chim. Fr.*, 3722 (1967).

(16) A final proof of structures **9** and **10** lies in their independent synthesis from lactones **16** and **17**, respectively. This work, outlined briefly in our preliminary communication,[4] will be reported in detail elsewhere.

(17) D. Beluš, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969); R. Reinfried, D. Beluš, and K. Schaffner, *ibid.*, **54**, 1517 (1971); W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5474 (1967).



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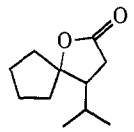

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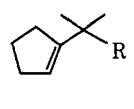
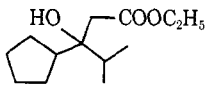


18, R = COOH
19, R = CH_2COOCH_3



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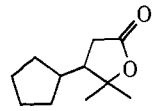
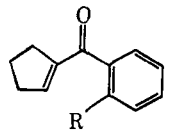


21

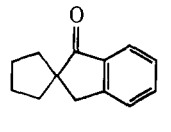
agreement with this expectation, we have found that formation of both **9** and **12** from unsaturated ketone **3** is quenched by low concentrations of 2,3-dimethylbuta-1,3-diene ($E_T \sim 60$ kcal/mol[18]) and may be efficiently sensitized by propiophenone ($E_T \sim 74.6$ kcal/mol[19]).

A similar abstraction and cyclization reaction occurred on irradiation of 1-cyclopentenyl *o*-tolyl ketone (**22**). This compound and the other aromatic ketones discussed below were also available *via* Friedel–Crafts acylation, this time using the appropriate benzoyl chloride. Photolysis of **22** gave a 94% yield of **23**, which was identical with an authentic sample.[20] Transfer of hydrogen here requires a seven-membered intermediate, but the array of sp^2 carbon atoms involved provides a favorable geometry without difficulty.

The effect of ring flexibility on the photochemical reactions of cycloalkenones and 1-acylcycloalkenes has been known[21] for some time, and it has been our previous experience with cyclohexenones that both intermolecular[1] and intramolecular[22] abstractions are much less successful than with cyclopentenones. A similar difference extends to abstraction processes in 1-acylcycloalkenes, for preliminary photochemical experiments with 1-cyclohexenyl isobutyl ketone (**24**) failed to give any isomerization products corresponding to those described above from cyclopentenes. The exceptionally high yield of **23** from **22** made it attractive, nonetheless, to examine the photochemistry of 1-cyclohexenyl *o*-tolyl ketone (**25**). The results underscore once again the controlling effect of ring size on photochemical behavior. Photolysis of **25** furnished none of the indanone **26**[23] corresponding to **23** but led to a 57% yield of the isomeric ketone **27**. The methyl group of **25** plays no obvious role in this reaction, and, as expected, the analogous transformation leading to **28** occurred on irradiation of the parent ketone **29**. Acid-catalyzed cyclization of **25** and **29** to yield **27**[24] and **28**,[25] respectively, is a known process, and authentic comparison samples of both compounds were prepared in this way. However, the possibility that the



22, R = CH_3
33, R = H



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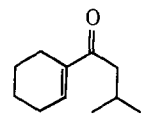

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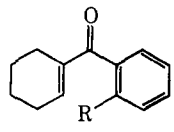
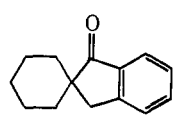


25, R = CH_3
29, R = H



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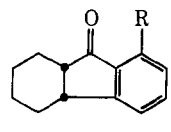
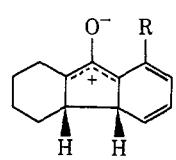


27, R = CH_3
28, R = H

photochemical cyclization involves adventitious protonation seems most unlikely, for the isomerization of **25** proceeded in essentially the same fashion in base-washed equipment using as solvent benzene containing suspended solid sodium bicarbonate. The simplest formulation of this ring closure is *via* **30**, in analogy with the known[26] photochemical cyclization of di-1-cyclohexenyl ketone (**31**) to **32**. The cis stereochemistry depicted in **30** and found[26] in **32** is expected from the requirement imposed by orbital symmetry considerations that the closure be disrotatory. The observed cis ring fusion in **27** and **28** is also consistent with these considerations, since the conversion of **30** to **27** or **28** should occur through intramolecular suprafacial migration of hydrogen.[26,27]

We attempted to force this electrocyclic reaction of **25** and **29** to occur in a cyclopentene, and conversely to force the abstraction reaction of **22** to take place in a cyclohexene. These efforts failed, however; irradiation of **33** and **34**, molecules suited for just these pur-



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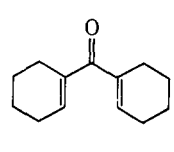

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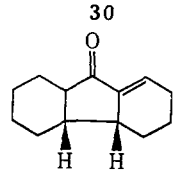

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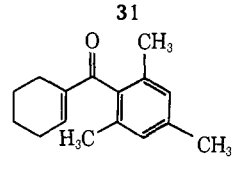

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poses, yielded no recognizable monomeric products. There is then a striking dependence of reaction pathway on ring size in these substrates. Using **22** and **29** as substrates, we have found that both the hydrogen transfer reaction and the electrocyclic process can be sensitized by propiophenone, but that only the former is quenched by 2,3-dimethyl-1,3-butadiene. We tentatively conclude that both transformations can occur from the lowest triplet state; further investigations, both photochemical and spectroscopic, are desirable here.

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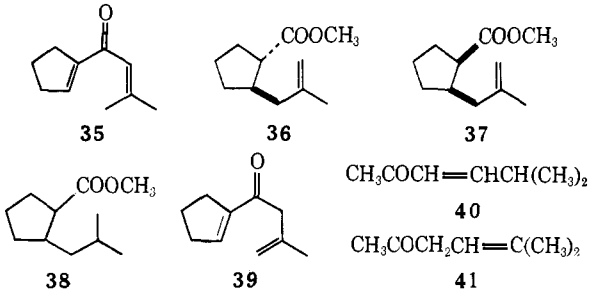
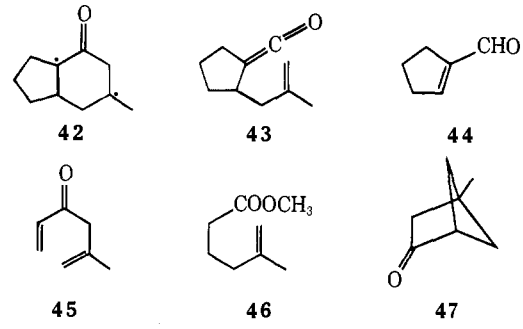
(19) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, 86, 4537 (1964).
(20) M. Mousseron, R. Jacquier, and H. Christol, *Bull. Soc. Chim. Fr.*, 346 (1957); R. T. Conley and L. J. Frainier, *J. Org. Chem.*, 27, 3844 (1962).
(21) See, for example, P. E. Eaton, *Accounts Chem. Res.*, 1, 50 (1968).
(22) A. B. Smith, III, and W. C. Agosta, *J. Org. Chem.*, 37, 1259 (1972).
(23) A sample of **26**, prepared by the method used for authentic **23**, was on hand.
(24) H. O. House, V. Paragamian, and D. J. Wluka, *J. Amer. Chem. Soc.*, 82, 2561 (1960).
(25) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *ibid.*, 82, 1457 (1960).
(26) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969), and references cited therein. See also L. M. Jackman, E. F. M. Stephenson, and H. C. Yick, *Tetrahedron Lett.*, 3325 (1970), for an example involving an aroylcyclohexene.
(27) O. L. Chapman, G. L. Eian, A. Bloom, and J. Clardy, *J. Amer. Chem. Soc.*, 93, 2918 (1971), discuss this last point in some detail for the mechanistically related, but conrotatory, photocyclization of *N*-aryl enamines.

A third type of photochemical isomerization occurs in dienone **35**, which was prepared using the appropriate acyl chloride and cyclopentene. On photolysis in methanol, neither transfer of hydrogen to the β carbon atom nor electrocyclic closure took place, but there was formed instead in 70% yield a 2:1 mixture of *trans*- and *cis*-2-methallylcyclopentanecarboxylic acid methyl ester (**36** and **37**). The structures of these esters were secured by hydrogenation of each to the corresponding *trans*- or *cis*-2-isobutylcyclopentanecarboxylate **38**, which was identical in each case with material independently prepared through conjugate addition of isobutylmagnesium bromide to methyl 1-cyclopentenecarboxylate[28] in the presence of the soluble cuprous iodide–tributylphosphine complex.[1,29] Cis and trans isomers in both the unsaturated and saturated series were separable by preparative vpc. The stereochemical assignment rests on methoxide-catalyzed epimerization[30] of **37** to **36**, as well as the relative chemical shift of the proton α to the carbonyl group. In the nmr spectra of both the methallyl and the isobutyl compounds, this proton is shifted upfield in the trans compound (hydrogen cis to alkyl group) relative to its position in the cis isomer.[31]

This transformation of **35** into **36** and **37** can be satisfactorily accounted for by the following suggested pathway. First **35** undergoes photoisomerization to β,γ isomer **39**. This has direct precedent in the efficient isomerization of 5-methyl-3-hexen-2-one (**40**) to its β,γ isomer **41** on irradiation[32] and is supported by the



observation that a very small amount of material having the same vpc retention time as authentic **39** is formed during photolysis of **35**. In a second photochemical step **39** closes to biradical intermediate **42**, which fragments to ketene **43**. Reaction with solvent methanol then gives **36** and **37**. Irradiation of **35** in benzene permitted direct observation of ketene **43**. Infrared monitoring of the reaction showed development of sharp absorption at 2110 cm^{-1}. Subsequent addition of methanol caused replacement of this band with absorption at 1735 cm^{-1}, and isolation led to esters **36** and **37**. In keeping with these ideas, photolysis of independently prepared **39** under the same conditions in methanol led to its rapid and quantitative conversion to esters **36** and **37**. The β,γ unsaturated ketone **39** was prepared by Grignard addition of methallylmagnesium chloride to 1-cyclopentenecarboxaldehyde (**44**)[33] followed by oxidation[34] of the secondary alcohol. During the course of this work with **35** and **39**, there appeared the report[35] of an investigation of the photochemistry of a variety of methyl-substituted 1,5-hexadien-3-ones, that is, open-chain analogs of **39**. Of the compounds examined, only 5-methyl-1,5-hexadien-3-one (**45**) underwent the reaction found here for **39**, giving ester **46** in 10% yield; an intermediate analogous to **42** was proposed. We have also irradiated **45** and have found that under our conditions it yields 27% of **46** along with 43% of the previously unobserved[35] cycloaddition product **47**. Several examples of intramolecular cycloadditions closely related to formation of **47** have been described,[35,36] and the structure of **47** could be assigned from comparison of its spectroscopic properties with those of these previously prepared bicyclo[2.1.1]hexan-2-ones.



It is noteworthy that this photochemical Cope rearrangement of **39** to **43** is quantitative. This transformation involving both double bonds in **39** occurs to the exclusion of various other[37] photochemical reactions of β,γ-unsaturated ketones, including both 1,2- and 1,3-acyl shifts as well as cyclobutanol formation. It appears that the transformation can occur from the triplet state, since formation of **36** and **37** was efficiently sensitized by propiophenone. The reaction was not quenched, however, by 2,3-dimethyl-1,3-butadiene, and it is therefore unclear at present whether the direct reaction occurs from the singlet or alternatively from a triplet too short lived to be quenched.

Experimental Section

Materials and Equipment. Solvents for photochemical experiments were Mallinckrodt benzene (analytical reagent) and Merck methanol (anhydrous reagent). All vpc was done using a Varian Aerograph Model 200 Autoprep or Model A-90-P3 with one of the following columns: (A) 30% SE-30, 10 ft × 3/8 in.; (B) 30% FFAP, 20 ft × 0.25 in.; (C) 15% QF-1, 15 ft × 3/8 in.; (D) 30% QF-1, 10 ft × 3/8 in.; (E) 25% Carbowax 20M, 20 ft × 3/8 in.; (F) 30% Carbowax 20M, 10 ft × 3/8 in.; (G) 30% SE-30, 20 ft × 0.25 in.; (H) 10% SE-30, 10 ft × 3/8 in.; (I) 25% Carbowax 1500, 10 ft × 3/8 in.; (J) 30% QF-1, 20 ft × 3/8 in.; (K) 15% Carbowax 20M, 40 ft × 0.25 in. The column oven was operated at 90–190°, and helium carrier gas flow rate was 100–120 ml/min. Unless otherwise

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(31) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 234–236, and references cited therein.
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(33) The procedure of E. D. Bergmann and A. Becker, *J. Amer. Chem. Soc.*, **81**, 221 (1959), was simplified by use of the osmium tetroxide catalyzed periodate method of R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956), for direct oxidation of cyclohexene to adipaldehyde.
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(35) T. W. Gibson and W. F. Erman, *ibid.*, **37**, 1148 (1972).
(36) F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Lett.*, 4865 (1965); J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968).
(37) Numerous references to these reactions are given by R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972); see also P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 4357 (1972).

noted, both ir and nmr spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 237B spectrophotometer and the latter on a Varian Model A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Ultraviolet spectra were obtained for solutions in 95% ethanol using a Cary Model 14 PM spectrophotometer. Melting points are corrected. Solutions were dried with either anhydrous Na_2SO_4 or $MgSO_4$. All photochemical experiments were carried out with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well using a uranium glass (Corning No. 3320) as filter. The reaction vessel was wrapped with aluminum foil.

General Procedure for Irradiations. A solution of the 1-acylcyclopentene (1 mg/ml) in benzene or methanol was flushed with dry nitrogen for 15–30 min and then irradiated for the stated time at about 15° under nitrogen with magnetic stirring. Benzene photolyses were monitored by ir using 1.0-mm cells. At the end of the irradiation period 1 ml of methanol was added, and the solution was stirred for several hours, after which the ir spectrum was redetermined. Photolyses in methanol were worked up by addition of water and extraction with pentane, which was then washed with brine and dried over sodium sulfate. Careful removal of the pentane through a long Vigreux column left the product as an oil, which was then analyzed and purified by vpc. Photolyses in benzene were worked up by distillation through a long Vigreux column to yield the product as an oil. All products were obtained as colorless oils unless otherwise indicated.

General Procedure for Synthesis of Acylcycloalkenes. The appropriate freshly distilled acid chloride (0.1 mol) was added to aluminum chloride (0.11 mol) suspended in 80 ml of methylene chloride. After 5 min the resulting complex was decanted from the excess aluminum chloride and cooled to 0°. The cycloalkene (0.1 mol) dissolved in 80 ml of methylene chloride was then added dropwise over a period of 0.5 hr. Upon completion of the addition, the mixture was added to crushed ice which was being vigorously stirred. After separation of the phases, the aqueous phase was extracted several times with methylene chloride. The combined methylene chloride fraction was washed with saturated aqueous $NaHCO_3$, water, and brine and dried. Removal of the solvent yielded an oil to which was immediately added 60 ml of triethylamine. The resultant mixture was then heated at reflux for 48–72 hr. Removal of the triethylamine yielded an oil which was diluted with ether and extracted with 10% HCl (v/v), saturated aqueous $NaHCO_3$, and brine. After drying, the solvent was removed to yield the 1-acylcycloalkene. Purification of the 1-acylcycloalkene was by distillation followed by vapor phase chromatography. In the case of the aromatic ketones, it was found convenient first to chromatograph the distillate on No. 2 neutral alumina. After elution with cyclohexane, elution with benzene yielded the 1-acylcycloalkene. All these ketones were obtained as colorless liquids unless otherwise indicated.

1-Cyclopentenyl Ethyl Ketone (1). Preparative vpc on column A gave pure **1**:[2] ir 3050 (w), 2950 (s), 2840 (m), 1650 (vs), 1618 (m), 1375 (m) cm^{-1}; nmr (220 MHz) δ 1.02 (t, J = 7 Hz, 3 H), 1.89 (quintet, J = 7 Hz, 2 H), 2.39–2.66, 2.58 (m, q, J = 7 Hz, 6 H), 6.56 (m, 1 H).

1-Cyclopentenyl *n*-Propyl Ketone (2). Preparative vpc on column A gave pure **2**:[2] ir 3050 (w), 2955 (s), 2865 (m), 1648 (vs), 1612 (m) cm^{-1}; nmr (220 MHz) δ 0.93 (t, J = 6 Hz, 3 H), 1.60 (sextet, J = 6 Hz, 2 H), 1.93 (quintet, J = 6 Hz, 2 H), 2.43–2.61, 2.54 (m, t, J = 6 Hz, 6 H), 6.59 (m, 1 H).

1-Cyclopentenyl Isobutyl Ketone (3). Preparative vpc on columns A and B gave pure **3**: ir 3050 (w), 2955 (s), 2860 (m), 1668 (vs), 1612 (m), 1462 (m), 1362 (m), 1290 (m), 1165 (m) cm^{-1}; nmr (220 MHz) δ 0.91 (d, J = 6 Hz, 6 H), 1.82–2.66 (m, 9 H), 6.59 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.94; H, 10.51.

1-Cyclopentenyl Isopentyl Ketone (4). Preparative vpc on column A gave pure **4**: ir 3050 (w), 2950 (s), 2860 (m), 1665 (vs), 1612 (m), 1460 (m), 1380 (m), 1362 (m) cm^{-1}; nmr (220 MHz) δ 0.92 (d, J = 6 Hz, 6 H), 1.38–1.65 (m, 3 H), 1.93 (quintet, 2 H), 2.44–2.62 (m, 6 H), 6.61 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.37; H, 11.13.

1-Cyclopentenyl Cyclopentylmethyl Ketone (5). Preparative vpc on column A gave pure **5**: ir 3055 (w), 2950 (s), 2860 (m), 1665 (vs), 1612 (m), 1370 (m), 1295 (m) cm^{-1}; nmr (220 MHz) δ 0.91–2.88 (m, 17 H), 6.50 (m, 1 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.71; H, 10.05.

1-Cyclopentenyl *o*-Tolyl Ketone (22). Preparative vpc on column D gave pure **22**: ir 3060 (w), 3012 (w), 2950 (s), 1655 (vs), 1612 (m), 1355 (m), 1395 (m), 1362 (m), 720 (m) cm^{-1}; nmr (60 MHz) δ 1.70–2.80, 2.20 (m, s, 9 H), 5.90–6.05 (m, 1 H), 6.65–7.20 (m, 4 H).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.11; H, 7.46.

1-Cyclohexenyl Isobutyl Ketone (24). Preparative vpc on column B gave pure **24**: ir 3050 (w), 2950 (s), 2860 (m), 1665 (vs), 1635 (m), 1190 (m) cm^{-1}; nmr (220 MHz) δ 0.88 (d, J = 7, 6 H), 1.56–1.66 (m, 4 H), 2.05–2.27 (m, 5 H), 2.40 (d, J = 7 Hz, 2 H), 6.72 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.42; H, 10.90.

1-Cyclopentenyl Phenyl Ketone (33). Preparative vpc on column C gave pure **33**:[38] ir 3075 (w), 3055 (w), 3020 (w), 1650 (vs), 1610 (m), 1595 (m), 1575 (w), 1440 (m), 1350 (m), 1305 (m), 1290 (m), 1265 (m), 700 (s), 685 (m), 660 (m) cm^{-1}; nmr (220 MHz) δ 1.94 (quintet, J = 6 Hz, 2 H), 2.48–2.70 (m, 4 H), 6.35 (m, 1 H), 7.21–7.44 (m, 3 H), 7.60 (dd, J = 7, 2 Hz, 2 H).

1-Cyclohexenyl *o*-Tolyl Ketone (25). Preparative vpc on column D gave pure **25**:[24] ir 3060 (w), 3010 (w), 2935 (m), 2855 (w), 1650 (vs), 1630 (m), 1265 (m), 1245 (m) cm^{-1}; nmr (220 MHz) δ 1.55–1.78 (m, 4 H), 2.12–2.26, 2.22 (m, s, 5 H), 2.29–2.41 (m, 2 H), 6.34–6.40 (m, 1 H), 7.07–7.26 (m, 4 H).

1-Cyclohexenyl Phenyl Ketone (29). Preparative vpc on column C gave pure **29**:[25] ir 3080 (w), 3055 (w), 3025 (w), 2940 (s), 2930 (m), 1650 (vs), 1635 (m), 1598 (w), 1575 (w), 1270 (s), 1250 (s), 685 (s) cm^{-1}; nmr (220 MHz) δ 1.59–1.82 (m, 4 H), 2.18–2.32 (m, 2 H), 2.32–2.43 (m, 2 H), 6.44 (m, 1 H), 7.25–7.48 (m, 3 H), 7.57 (dd, J = 7, 2 Hz, 2 H).

1-Cyclohexenyl 2,4,6-Trimethylphenyl Ketone (34). Preparative vpc on column A gave pure **34**: ir 3040 (w), 2940 (m), 2860 (w), 1655 (vs), 1637 (m), 1612 (m), 1270 (m), 1248 (m) cm^{-1}; nmr (220 MHz) δ 1.57–1.80 (m, 4 H), 2.02 (s, 6 H), 2.09–2.20 (m, 2 H), 2.25 (s, 3 H), 2.27–2.36 (m, 2 H), 6.23–6.32 (m, 1 H), 6.64 (s, 2 H).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.29; H, 8.73.

1-Cyclopentenyl 2-Methyl-1-propen-1-yl Ketone (35). Recrystallization from pentane followed by sublimation gave pure **35**: mp 47.5–48.5° (lit.[39] 51–51.5°); ir 3060 (w), 2960 (s), 2920 (s), 1660 (vs), 1610 (vs), 1440 (m), 1250 (m), 1155 (m) cm^{-1}; nmr (60 MHz) δ 1.68–2.32, 1.88, 2.08 (m, br s, br s, 8 H), 2.32–2.75 (m, 4 H), 6.26–6.68 (m, 2 H).

Photolysis of 1-Cyclopentenyl Ethyl Ketone (1). A solution of 617 mg of **1** in 2000 ml of benzene was irradiated for 6 days. Vpc on column D indicated destruction of 85% of **1** and formation of **7**[10] in 8% yield.

Photolysis of 1-Cyclopentenyl *n*-Propyl Ketone (2). A solution of 210 mg of **2** in 220 ml of benzene was irradiated for 17.5 hr. The ir spectrum of the photolysis solution showed no absorption in the 2100 cm^{-1} region. Work-up followed by vpc analysis on column D indicated the formation of **8** as the only product in 33% yield: ir 2960 (s), 2870 (m), 1775 (vs), 1445 (m), 1390 (m), 1370 (m), 1028 (m) cm^{-1}; nmr (220 MHz) δ 1.16 (d, J = 7 Hz, 3 H), 1.46–2.05 (m, 8 H), 2.12–2.31 (m, 1 H), 2.42 (d of d, J_1 = 17, J_2 = 6 Hz, 1 H), 3.12 (d of d, J_1 = 17, J_2 = 8 Hz, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.32; H, 10.12.

Photolysis of 1-Cyclopentenyl Isobutyl Ketone (3). A solution of 99 mg of **3** in 60 ml of benzene was irradiated for 4 hr, after which its ir spectrum showed absorption at 2110 cm^{-1}. Addition of methanol caused the replacement of the band by a new absorption at 1735 cm^{-1}. An aliquot of the resulting solution was examined by vpc on column E, and found to contain two products, with almost complete absence of **3**. Preparative vpc gave a pure sample of each product. The first (25%) was shown to be methyl cyclopentanecarboxylate by comparison with an authentic sample.[7] The second product (36%) was cyclobutanone **9**: ir 2960 (s), 2865 (m), 1775 (vs), 1460 (m), 1440 (m), 1390 (m), 1378 (m), 1365 (m), 1225 (m), 1085 (m), 1040 (m) cm^{-1}; nmr (220 MHz) δ 1.14 (s, 6 H), 1.36–1.81 (m, 8 H), 2.66 (s, 2 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.94; H, 10.67.

Photolysis of 1-Cyclopentenyl Isopentyl Ketone (4). A solution of 599 mg of **4** in 700 ml of benzene was irradiated for 50 hr, after which the ir spectrum of the photolysis solution showed no ab-

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(39) S. A. Vartanyan and G. A. Chukhadzhyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauki*, **15**, 53 (1962).

sorption in the ketene region. Work-up followed by vpc analysis on columns F and C indicated the formation of three products in the ratio of 27:5.8:1.0, with almost complete destruction of **4**. Preparative vpc gave a pure sample of each product and they are listed below in order of elution.

The first product (36%) was cyclobutanone **10**: ir 2960 (s), 2860 (m), 1775 (vs), 1470 (m), 1425 (m), 1405 (m), 1385 (m), 1370 (m) cm^{-1}; nmr (220 MHz) δ 0.927 (d, J = 5 Hz), 0.955 (d, J = 5 Hz) (6 H), 1.36–2.08 (m, 10 H), 2.60 (d of d, J_1 = 17, J_2 = 8 Hz, 1 H), 2.82 (d of d, J_1 = 17, J_2 = 8 Hz, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.63; H, 10.87.

A 2,4-dinitrophenylhydrazone was prepared: mp 128–128.5°, from ethanol; mass spectrum *m/e* 346.1634 (M^+) (calcd for $C_{17}H_{22}N_4O_4$: 346.1640).

The second product (~8%) was the unsaturated ketone **14**: ir 3075 (w), 2950 (s), 2870 (m), 1715 (vs), 1650 (m), 885 (m) cm^{-1}; nmr (220 MHz) δ 1.48–1.82, 1.70 (m, broad s, 11 H), 2.22 (t, J = 8 Hz, 2 H), 2.50 (t, J = 8 Hz, 2 H), 2.81 (quintet, J = 7 Hz, 1 H), 4.62 (broad s, 1 H), 4.66 (broad s, 1 H); mass spectrum *m/e* 166.1362 (M^+) (calcd for $C_{11}H_{18}O$, 166.1357).

The third product was presumed to be a ketone from its ir spectrum: 3060 (s), 3970 (m), 1740 (vs); it was not further characterized.

Photolysis of 1-Cyclopentenyl Cyclopentylmethyl Ketone (5). A solution of 153 mg of **5** in 200 ml of benzene was irradiated for 4.5 hr, after which its ir spectrum showed absorption at 2110 cm^{-1}. Addition of methanol caused the replacement of this band by a new absorption at 1735 cm^{-1}. An aliquot of the resulting solution was examined by vpc on column F, and found to contain predominately two products, with almost complete destruction of **5**. Preparative vpc gave a pure sample of each product.

The first product eluted (27%) was shown to be methyl cyclopentanecarboxylate as described above.

The second product (31%) was cyclobutanone **11**; ir 2950 (s), 2860 (m), 1775 (vs), 1448 (w), 1385 (w), 1035 (w) cm^{-1}; nmr (220 MHz) δ 1.45–1.92 (m, 16 H), 2.72 (s, 2 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.80; H, 10.18.

Hydrogenation of Cyclopentyl 3-Methyl-3-buten-1-yl Ketone (14). A solution of 20.7 mg of **14** in 2 ml of methanol was hydrogenated over 5.6 mg of 5% palladium on carbon. Work-up and isolation gave a quantitative yield of **15** which was purified by vpc on column D. Ketone **15**, as prepared here, had ir and nmr spectra identical with those of a sample prepared by hydrogenation of **4**.

Hydrogenation of 1-Cyclopentenyl Isopentyl Ketone (4). A solution of 59 mg of **4** in 2 ml of methanol was hydrogenated over 6.6 mg of 5% palladium on carbon. Work-up and isolation gave 57 mg of **15** which was purified by vpc on column F: ir 2950 (s), 2875 (m), 1715 (s), 1465 (w), 1445 (w), 1375 (w), 1360 (w) cm^{-1}; nmr (220 MHz) δ 0.89 (d, J = 7 Hz, 6 H), 1.36–1.82 (m, 11 H), 2.35 (t, J = 7 Hz, 2 H), 2.79 (quintet, J = 8 Hz, 1 H).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.47; H, 11.83.

Photolysis of Cyclobutanone 9. A solution of 31 mg of **9** in 20 ml of benzene was irradiated for 13 hr. Infrared analysis of the photolysis solution indicated no decrease in the amount of **9** present. Addition of 200 μl of methanol followed by work-up and vpc analysis, including coinjection of authentic material, indicated that no (≤1%) methyl cyclopentanecarboxylate was formed.

Oxidation of Cyclobutanone 9. To a solution of 500 μl of freshly prepared peroxytrifluoroacetic acid,[11] and 148 mg of Na_2HPO_4 in 1 ml of methylene chloride was added 16.6 mg of cyclobutanone **9**. This mixture was stirred over night at room temperature. Work-up with water and ether gave a quantitative yield of an oil. Vpc analysis and purification on column F indicated the presence of one major product, identical with authentic **16** by comparison of ir and nmr spectra and vpc retention time.

Synthesis of Lactone 16. A solution of 1.923 g (11.2 mmol) of the acid chloride derived from **18**[12] in 15 ml of ether was added dropwise to 350 ml of an ethereal solution of CH_2N_2 (~0.1 *N*). After the addition was complete, the excess CH_2N_2 was removed on a steam bath. Removal of the solvent yielded a yellow oil, which displayed a strong infrared absorption band at 2100 cm^{-1}. This oil was dissolved in 70 ml of methanol and irradiated through a Corex filter (No. 9700) for 1 hr. Work-up followed by calibrated vpc analysis indicated the formation of ester **19** in 42% yield. Preparative vpc on column D gave pure **19**: ir 3055 (w), 2950 (s), 2840 (m), 1740 (vs), 1200 (m), 1120 (m) cm^{-1}; nmr (220 MHz) δ 1.14 (s, 6 H), 1.84 (quintet, J = Hz, 2 H), 2.21–2.34, 2.38 (m, s, 6 H), 3.55 (s, 3 H), 5.29–5.34 (m, 1 H); mass spectrum *m/e* 182.1310 (M^+) (calcd for $C_{11}H_{18}O_2$, 182.1307).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.67; H, 9.84.

A solution of 138 mg of ester **19**, 1.5 ml of methanol, and 1.0 ml of 15% aqueous NaOH (w/v) was heated at reflux for 1.5 hr. Isolation of the acidic material yielded 112 mg of acid: ir 3400–2400 (broad), 1710 (vs) cm^{-1}; mass spectrum *m/e* 168.1150 (M^+) (calcd for $C_{10}H_{16}O_2$, 168.1141). A solution of 46 mg of this acid, 1 ml of methanol, and 1 ml of 1.0 *N* aqueous HCl was heated at reflux for 1.5 hr. Work-up followed by isolation gave 34.4 mg (75%) of lactone **16**. Preparative vpc on column F gave pure **16** as a solid: mp 31–32°; ir 2970 (s), 2870 (m), 1780 (vs), 1230 (m), 1155 (m), 975 (m), 925 (m) cm^{-1}; nmr (220 MHz) δ 1.09 (s, 6 H), 1.55–2.04 (m, 8 H), 2.26 (s, 2 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.58.

Oxidation of Cyclobutanone 10. A 54-mg sample of **10** was oxidized as described above for **9**. Preparative vpc on column A gave a pure product, identical with authentic **17** by comparison of ir and nmr spectra and vpc retention time.

Synthesis of Lactone 17. To a suspension of 658 mg of freshly activated zinc dust heated at reflux was added a solution of 1.41 g of cyclopentyl isopropyl ketone[13] and 1.67 g of ethyl bromoacetate in 10 ml of benzene.[14] After 6 hr at reflux, the mixture was cooled and added to ice and 10% (v/v) HCl. This mixture was extracted with ether and the ether solution dried. Isolation gave 2.01 g of an oil, which was purified by preparative vpc on column D to give pure hydroxy ester **20**: ir 3580 (sh), 3500 (m), 2960 (s), 2870 (s), 1735 (sh), 1720 (vs), 1185 (s) cm^{-1}; nmr (220 MHz) δ 0.865 (d, J = 6 Hz) and 0.895 (d, J = 6 Hz) (6 H), 1.28 (t, J = 7 Hz, 3 H), 1.36–2.09 (m, 10 H), 2.21 (d, J = 14 Hz, 1 H), 2.37 (d, J = 14 Hz, 1 H), 3.93 (br s, 1 H), 4.12 (q, J = 7 Hz, 2 H).

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.44; H, 10.64.

A solution of 1.74 g of **20** and 855 mg of KOH in 15 ml of ethanol was heated at reflux for 2 hr. Isolation of the acidic material gave 652 mg of hydroxy acid (ir). Treatment of 104 mg of this crude acid with 9 ml of 32% (v/v) aqueous H_2SO_4 for 2 hr at reflux followed by isolation of neutral material gave 59 mg of oil. Vpc analysis on column F indicated the presence of two products in equal amounts. Preparative vpc gave a pure sample of each in the order given below.

Lactone **17**: ir 2970 (s), 2875 (m), 1780 (vs), 1235 (m), 1165 (m), 1075 (m) cm^{-1}; nmr (220 MHz) δ 0.945 (d, J = 7 Hz) and 0.950 (d, J = 7 Hz) (6 H), 1.55–2.03 (m, 9 H), 2.03–2.27 (m, 2 H), 2.36–2.59 (m, 1 H); mass spectrum *m/e* 182.1299 (M^+) (calcd for $C_{11}H_{18}O_2$, 182.1306).

Lactone **21**: ir 2955 (s), 2860 (m), 1780 (vs), 1370 (m), 1340 (m), 1265 (s) cm^{-1}; nmr (220 MHz) δ 1.03–1.25 (m, 2 H), 1.27 (s, 3 H), 1.44 (s, 3 H), 1.48–2.09 (m, 8 H), 2.25 (d of d, J_1 = 17 Hz, J_2 = 12 Hz, 1 H), 2.44 (d of d, J_1 = 17 Hz, J_2 = 8 Hz, 1 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.39; H, 9.92.

Photolysis of 1-Cyclopentenyl *o*-Tolyl Ketone (22). A solution of 172 mg of **22** in 200 ml of benzene was irradiated for 0.5 hr. Work-up followed by vpc analysis on column G indicated formation of only one product (94%), with almost complete destruction of **22**. This product was shown to be **23** by comparison of ir and nmr spectra and vpc retention time with those of an authentic sample,[20] as well by comparison of 2,4-dinitrophenylhydrazones, mp 211–213°, mmp 212–213.5°, mp 212–213.5° for authentic sample (lit.[20] mp 208°).

Photolysis of 1-Cyclohexenyl *o*-Tolyl Ketone (25). A solution of 210 mg of **25** in 220 ml of benzene was irradiated for 4 hr. Work-up followed by vpc analysis on column H indicated formation of one major product (57%) and three minor components (<4% each), with almost complete destruction of **25**. The major product was shown to be **27** by comparison of ir, nmr, and vpc retention time with an authentic sample.[24] Coinjection of authentic **26**[20] with the photolysate indicated that it was not present (<1%).

Repetition of the photolysis in base-washed glassware and in the presence of suspended solid $NaHCO_3$ led to essentially unchanged results.

Photolysis of 1-Cyclohexenyl Phenyl Ketone (29). A solution of 80 mg of **29** in 70 ml of benzene was irradiated for 3.5 hr. Work-up followed by vpc analysis on column C indicated formation of one major product (65%) with almost complete destruction of **29**. This product was shown to be *cis*-hexahydrofluorenone (**28**) by comparison of ir and nmr spectra, vpc retention time, and melting point

with an authentic sample,[25] mp 38–40°, mmp 39.5–41° (lit.[25] mp 40–41°).

Photolysis of 1-Cyclopentenyl Phenyl Ketone (33). A solution of 59 mg of **33** in 70 ml of benzene was irradiated for 2.25 hr, during which time ~80% of **33** was destroyed. Work-up followed by vpc analysis on column C indicated formation of very little volatile material.

Photolysis of 1-Cyclohexenyl 2,4,6-Trimethylphenyl Ketone (34). A solution of 52 mg of **34** in 60 ml of benzene was irradiated for 4.25 hr, during which time ~80% of **34** was destroyed. Work-up followed by vpc analysis on column A indicated formation of very little volatile material.

1-Cyclopentenyl 2-Methyl-1-propen-1-yl Ketone (35). A solution of 197 mg of **35** in 75 ml of methanol was irradiated for 72 hr. Work-up followed by vpc analysis on column A indicated formation of two major products with almost complete destruction of **35**. Preparative vpc gave a pure sample of each in the order listed below.

The first product (45%) was **36**: ir 3065 (w), 2950 (s), 2870 (w), 1735 (vs), 1645 (w), 1445 (m), 1430 (m), 1188 (m), 1155 (s), 880 (m) cm^{-1}; nmr (220 MHz) δ 1.08–2.48, 1.71 (m, s, 13 H), 3.58 (s, 3 H), 4.61, 4.64 (br s, br s, 2 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.40; H, 9.78.

The second product (25%) was **37**: ir 3070 (w), 2950 (s), 2870 (w), 1735 (vs), 1640 (w), 1445 (m), 1430 (m), 1360 (m), 1185 (m), 1160 (s), 880 (m) cm^{-1}; nmr (220 MHz) δ 1.34–2.38, 1.68 (m, s, 12 H), 2.68–2.82 (m, 1 H), 3.10 (s, 3 H), 4.59, 4.63 (br s, br s, 2 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.56; H, 9.88.

In addition, vpc analysis (including coinjection of authentic **39**) indicated the presence of a component which corresponded in retention time to **39**, when **35** was irradiated to low conversion.

A solution of 252 mg of **35** in 200 ml of benzene was irradiated for 66 hr, after which its ir spectrum displayed an absorption at 2110 cm^{-1}. Addition of methanol caused the replacement of this band by a new absorption at 1735 cm^{-1}. Subsequent isolation gave **36** and **37**.

Epimerization of Ester 37. A solution of 26 mg of pure **37** and 52 mg of $NaOCH_3$ in 1 ml of methanol was allowed to stand at room temperature for 5 days. Work-up and isolation followed by vpc analysis on column A indicated a mixture of **36** and **37** in the ratio of ~5:1, respectively. The major component was isolated by preparative vpc and shown to be **36** by comparison of ir and nmr spectra as well as vpc retention time.

Synthesis of *cis*- and *trans*-2-Isobutylcyclopentanecarboxylic Acid Methyl Esters (38). To a mixture of 358 mg of magnesium turnings in 15 ml of ether was added dropwise 2.04g (14.9 mmol, 2.25 equiv) of isobutyl bromide at such a rate as to maintain a gentle reflux. Upon completion of the addition, 260 mg (0.663 mmol, 10 mol %) of tetrakisiodo(tri-*n*-butylphosphine)copper in 5 ml of ether was added, and stirred for 5 min. To this mixture was added 835 mg (6.63 mmol) of 1-carbomethoxycyclopentene.[28] The resultant mixture was stirred for 0.5 hr and then worked up by addition to a vigorously stirred solution of saturated aqueous NH_4Cl containing 2 ml of concentrated NH_4OH. Extraction with ether and isolation gave 1.046 g of oil, which upon vpc analysis on column K was shown to contain *trans*-**38** and *cis*-**38** in the ratio 1.8:1.0. Preparative vpc gave a pure sample of each ester in the order listed below.

The first was *trans*-**38**: ir 2955 (s), 2870 (m), 1735 (vs), 1188 (m), 1150 (m) cm^{-1}; nmr (220 MHz) δ 0.75–1.21, 0.90 (m, d, J = 6 Hz, 9 H), 1.21–2.02 (m, 6 H), 2.02–2.30 (m, 2 H), 3.61 (s, 3 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.68; H, 11.04.

The second was *cis*-**38**: ir 2960 (s), 2870 (m), 1735 (vs), 1190 (m), 1165 (m) cm^{-1}; nmr (220 MHz) δ 0.886 (d, J = 6 Hz) and 0.923 (d, J = 6 Hz) (6 H), 0.978–2.25 (m, 10 H), 2.63–2.77 (m, 1 H), 3.56 (s, 3 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.47; H, 11.02.

Hydrogenation of Ester 36. A solution of 12.4 mg of **36** in 2 ml of methanol was hydrogenated over 1 mg of 5% palladium on carbon. Work-up and isolation gave a pure compound which was shown to be *trans*-**38** by comparison of the nmr spectrum with that of authentic material prepared above.

1-Cyclopentenecarboxaldehyde (44). To a solution of 150 ml of H_2O, 150 ml of ether, 4.05 g of cyclohexene, and 92 mg of OsO_4 was added 23.3 g of $NaIO_4$ over a 1 hr period. After 18 hr, 3 g of KOH dissolved in 10 ml of H_2O was added and the resultant mixture stirred for 2 hr. Separation of the ether layer and work-up gave 1.385 g (31%) of **44**.[33] For small quantities this procedure is quite convenient.

1-Cyclopentenyl 2-Methyl-2-propen-1-yl Ketone (39). Over a period of 1 hr 10 g (111 mmol) of methallyl chloride was added to 2.66 g (111 g-atoms) of magnesium turnings in 80 ml of ether at 0°. After the addition, the solution was stirred at 0° for an additional 10 hr and then 3.55 g (37 mmol) of **44** was added. The mixture was warmed to room temperature and stirred overnight. Work-up gave 6.16 g of oil which was distilled; bp 110–114° (10 Torr). Preparative vpc on column H gave pure 1-(1-cyclopentenyl)-3-methyl-3-buten-1-ol: ir 3510–3400 (w), 3060 (w), 2940 (s), 2840 (s), 1645 (m), 885 (s) cm^{-1}; nmr (220 MHz) δ 1.64 (s, 1 H), 1.75 (broad s, 3 H), 1.86 (quintet, J = 7 Hz, 2 H), 2.07–2.41 (m, 6 H), 4.23 (dd, J_1 = 5 Hz, J_2 = 9 Hz, 1 H), 4.73 (broad s, 1 H), 4.80 (broad s, 1 H), 5.52 (broad s, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.73; H, 10.62.

A solution containing 656 mg of this alcohol was added in one portion to a solution of the chromic oxide–pyridine complex prepared by adding 3.89 ml of pyridine to 2.41 g of CrO_3 suspended in 60 ml of methylene chloride.[34] The resulting mixture was stirred at room temperature for 15 min and then added to water. The organic phase was washed with water, aqueous $CuSO_4$, and water and dried. Isolation gave 541 mg of a yellow oil which was flash-distilled and then purified on columns I and A to yield pure ketone **39**: ir 3090 (w), 2960 (m), 1665 (vs), 1610 (m), 1350 (m), 885 (m) cm^{-1}; nmr (220 MHz) δ 1.74 (s, 3 H), 1.84–2.04 (m, 2 H), 2.43–2.61 (m, 4 H), 3.25 (s, 2 H), 4.71 (s, 1 H), 4.82 (s, 1 H), 6.64 (br s, 1 H); mass spectrum m/e 150.1018 (M^+) (calcd for $C_{10}H_{14}O$, 150.1044).

Photolysis of 1-Cyclopentenyl 2-Methyl-2-propen-1-yl Ketone (39). A solution of 23.4 mg of **39** in 15 ml of methanol was irradiated for 1 hr. Work-up followed by vpc analysis on column A indicated the formation of **36** (61%) and **37** (39%) with complete destruction of **39**. Preparative vpc gave a pure sample of each ester, identified by comparison with material produced from **35**.

Photolysis of 5-Methyl-1,5-hexadien-3-one (45). A solution of 218 mg of **45**[35] in 220 ml of methanol was irradiated for 36 hr. Work-up followed by vpc analysis on column J indicated formation of two products, with almost complete destruction of **45**. Preparative vpc gave a pure sample of each product in the order listed below.

The first product (27%) was shown to be 5-methyl-5-hexenoic acid methyl ester (**46**) by comparison of ir and nmr spectra with values previously reported.[35]

The second product (43%) was 4-methylbicyclo[2.1.1]hexan-2-one: ir 3010 (w), 2960 (s), 2915 (m), 2885 (m), 1762 (vs), 1450 (m), 1370 (m), 1315 (m), 1120 (m), 1030 (m) cm^{-1}; nmr (220 MHz) δ 1.29 (s, 3 H), 1.60 (d of d, J_1 = 2 Hz, J_2 = 4 Hz, 2 H), 1.78–1.90 (m, 2 H), 1.93 (t, J = 2 Hz, 2 H), 2.67 (t, J = 2 Hz, 1 H).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.03

Sensitization and Quenching Experiments. Sensitization, quenching, and control samples for each ketone were irradiated simultaneously through uranium glass in a "merry-go-round" apparatus.

Ketone 3. Irradiation of a 0.0063 M solution of **3** in benzene for 2.25 hr followed by addition of methanol gave 32% conversion to **9** and methyl cyclopentanecarboxylate. A sample containing 7.82 mol equiv of propiophenone, which absorbs 82% of the light, gave 67% conversion. A sample 0.025 M in 2,3-dimethyl-1,3-butadiene gave 5% conversion.

Ketone 22. Irradiation of a 0.0050 M solution of **22** in benzene for 1.5 hr gave 80% conversion to **23**. A sample containing 56.5 mol equiv of propiophenone, which absorbs 81% of the light, gave 100% conversion. Samples containing 2,3-dimethyl-1,3-butadiene gave the following conversions: 0.024 M, 69%; 0.064 M, 54%.

Ketone 29. Irradiation of a 0.0053 M solution of **29** in benzene for 3 hr gave 31% conversion to **28**. A sample containing 37.8 mol equiv of propiophenone, which absorbs 78% of the light, gave 81% conversion to **28**. In a separate experiment, samples 0.125 and 0.382 M in 2,3-dimethyl-1,3-butadiene gave the same conversion as a simultaneously irradiated control.

Ketone 39. Irradiation of a 0.0052 M solution of **39** in methanol for 2.3 hr gave 84% conversion to esters **36** and **37**. A sample containing 65.5 mol equiv of propiophenone, which absorbs 80% of the light, gave 80% conversion to **36** and **37**. Samples 0.123 or 0.384 M in 2,3-dimethyl-1,3-butadiene gave 85% conversion to **36** and **37**.

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Lanthanide Shift Reagents. II.[1] (a) Photochemical Ring Expansion of a β-Lactam and Product Identification Using LSR Nmr Shifts and X-Ray Crystallography. (b) Probable Structure of an LSR–Substrate Complex in Solution. (c) Conformational Analysis Using LSR Nmr Data[2]

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Abstract: Irradiation of *exo*-3-aza-4-ketobenzotricyclo[4.2.1.$0^{2,5}$]non-7-ene (**6**) in methanol gave *exo*-2-methoxy-3-aza-4-keto-7,8-benzobicyclo[4.2.1]nonene (**7**) in 43% yield, a reaction which involved ring expansion of the β-lactam moiety in **6** plus the addition of the elements of methanol. The reaction mechanism is discussed. The structure of **7** was determined by nmr using the lanthanide shift reagents (LSR) Eu(dpm)$_3$ and Pr(dpm)$_3$, and by a single-crystal, X-ray diffraction analysis. A series of least-squares calculations was carried out to determine the "best" position of the Ln atom in the LSR–substrate complex, using the McConnell–Robertson pseudo-contact equation to provide a means of computing an nmr shift from an assumed LSR–substrate geometry. The procedure used the shift data for the 12 ring protons and minimized the function $\Sigma(R_{oi} - R_{ci})^2$, where the R's are ratios of the Lanthanide-induced nmr shifts. The conformational minima of the methoxy group in **7** and the ethoxy group in the *exo*-2-ethoxy homolog of **7** were also determined from the nmr shift data for these substituents.

In 1969, Hinckley reported[4] that the addition of the dipyridinate of tris(dipivaloylmethanato)europium-(III)[5] to a CCl_4 solution of cholesterol produced a substantial paramagnetic shift in the nmr spectrum of the compound with essentially no line broadening. This communication triggered an avalanche of scientific interest in the so-called "lanthanide shift reagents" (LSR), most of which has centered on the application of the reagents to the resolution of problems in molecular structure.[6] In this paper, we report (1) the photochemical ring expansion of a polycyclic β-lactam, (2) the use of lanthanide induced shifts (LIS) to produce a first-order nmr spectrum of the photoproduct and the identification of the material from these data, (3) a single-crystal X-ray diffraction determination of the structure of the photoproduct, (4) the determination of the probable structure of the lanthanide–photoproduct complex in solution, and (5) conformational analysis using the LIS nmr data.

Results and Discussion

Photochemical Ring Expansion. An investigation by Fisher[7] in 1968 of the photochemistry of β-lactams **1** revealed that ring cleavage occurred at essentially two points (dashed lines labeled A and B in structure **1**), and that the direction of cleavage depended on the degree of substitution at the 3 position. On the basis of these results plus an analysis of quantum yield data, Fisher suggested that the initial photochemical process involved cleavage of a C–N bond to a diradical intermediate (**2** or **3**) which subsequently underwent homolysis of the appropriate bond to form product.

The subsequent chemistry of these reactive fragments is of interest, but in the case of monocyclic β-lactams they tend to diffuse apart and the major products arise from reaction with solvent. However, if a polycyclic system were constructed, these fragments could be prevented from diffusing apart and their mutual reactions might be realized. We initiated a study of this

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(2) (a) The partial support of this work by the Center for Materials Science, University of Maryland, and the National Science Foundation (GP-15791) is gratefully acknowledged. Computer time was generously provided through the facilities of the Computer Science Center, University of Maryland. (b) Presented in part before the Organic Division, 162nd National Meeting of the American Chemical Society, Washington D. C., Sept 1971, and the American Crystallographic Association, Winter Meeting, Albuquerque, N. M., April 1972.

(3) (a) Department of Chemistry; (b) Department of Biophysics; (c) taken in part from the Ph.D. dissertation of W. J. Kopecky to be submitted to the Department of Biophysics, University of Maryland; (d) taken in part from the Ph.D. dissertation of H. J. Tamburin, University of Maryland, 1971.

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(5) Eu(dpm)$_3$(py)$_2$; Hdpm = 2,2,6,6-tetramethylheptane-3,5-dione; py = pyridine.

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