(16) (a) Wilson, T.; Landis, M. E.; Baumstark, A. L.; Bartlett, P. D. *J. Am. Chem. Soc.* **1973**, *95*, 4765. (b) Bartlett, P. D.; Barmstark, A. L.; Landis M. E. *J. Am. Chem. Soc.* **1974**, *96*, 5557.

(17) For methyl-1-adamantyldioxetanone, reported activation parameters are $\Delta H^{\ddagger}$ = 13.7 kcal/mol, and $\Delta S^{\ddagger} = 24.1$ eu.[4b] Trace impurity catalysis appears to dominate the decomposition in this case.

(18) Richardson, W. H.; O'Neal, H. E. *J. Am. Chem. Soc.* **1977**, *94*, 8665.

(19) (a) Turro, N. J.; Lechtken, P. *J. Am. Chem. Soc.* **1972**, *94*, 2886. (b) Adam, W.; Duran, N.; Simpson, G. A. *Ibid.* **1975**, *97*, 5464.

(20) (a) Wilson, T.; Golan, D. E.; Harris, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086. (b) Kopecky, K. R.; Filby, J. E. *Can. J. Chem.* **1979**, *57*, 283. (c) Adam, W.; Cheng; C.-C.; Cueto, O.; Sakaniski, K.; Zinner, K. *J. Am. Chem. Soc.* **1979**, *101*, 1324.

(21) Adam and co-workers[10] determined a 0.05% singlet acetone yield from **2a** at 23 °C by absolute fluorescence intensity. Recently, Adam and co-workers[20c] determined a (1.1 ± 0.1)% triplet acetone yield from **2**a by chemical titration.

(22) Lechtken, P. *Chem. Ber.* **1976**, *109*, 2862.

(23) The exceptions in the present series of activators are *N,N*-dimethyl-6-aminochrysene (DMACh) and 1,3-diphenylisobenzofuran which are consumed in the reaction with **2a.** In these cases the kinetics therefore were carried out with excess activator and first-order behavior was observed. The electrochemical oxidation of DMACh is irreversible.

(24) These values represent a composite activation energy for all steps leading to and including luminescence. For example, the temperature dependence of the rate of separation of the cage ion pairs (see below) is also included: Werner, H.-J.; Schulten, Z.; Schulten, K. *J. Chem. Phys.* **1977**, *67*, 646.

(25) Two examples of silica gel catalyzed chemiluminescence from aryldioxetanes have been reported recently but no activation parameters were given: Zaklika, K. A.; Burns, P. A.; Schaap, A. P. *J. Am. Chem. Soc.* **1978**, *100*, 318. McCapra F.; Beheshti, I.; Burford, A.; Hann, R. A.; Zaklika, K. A. *J. Chem. Soc., Chem. Commun.* **1977**, 944.

(26) (a) The fluorescence efficiency of 9,10-dibromoanthracene was taken to be 10% at 25 °C and the triplet–singlet energy transfer efficiency 25%.[20a,26b] (b) Bernefel'd, V. M.; Chumavskii, E. V.; Grinev, M. P.; Kuryatnikov, Y. I.; Artem'ev, E. T.; Dzhagatspanyan, R. V. *Bull. Acad. Sci. USSR, Phys. Ser.* (*Eng. Transl.*) **1970**, *3*, 597.

(27) Application of the steady-state approximation for [acetone*] leads to eq 11. Under the conditions of the experiment, [**2a**] is constant. Therefore when $k_L \ll k_D$, eq 11 reduces to eq 3.

$$\text{intensity} \propto k_A[\mathbf{2a}][k_L/(k_L + k_D)] \tag{11}$$

(28) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(29) (a) Calculated values of $\Delta H_f°$ are: dioxetanone **2a** −88 kcal mol^{-1};[17] dioxetane **1a**, −68.8 kcal mol^{-1}.[29b] (b) Richardson, W. H.; O'Neal, H. E. *J. Am. Chem. Soc.* **1970**, *92*, 6553.

(30) Horn, K. A.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 6649.

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(33) The electrochemical oxidation of alkyl carboxylates is irreversible. Use of this potential therefore provides only a lower limit to energy separation of the two states: Reichenbacher, P. H.; Morris, M. D.; Skell, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 3432.

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(40) This estimation was made by taking 0.001 for the fluorescence efficiency of acetone, 2×10^{10} M^{-1} s^{-1} for the energy transfer rate constant, and 2 ns for acetone singlet lifetime, and comparing the relative perylene and acetone emission intensities.

(41) (a) Turro, N. J.; Lechtken, P.; Schuster, G.; Orell, J.; Steinmetzer, H.-C.; Adam, W. *J. Am. Chem. Soc.* **1974**, *96*, 1627. (b) See ref 20a. The possibility of a kinetically indiscernible path accounting for a significant fraction of the total light generation in systems which have overall low (ca. 1%) quantum efficiencies was suggested by Dr. M. Rauhut in a discussion at the 2nd International Conference on Chemiluminescence: "Chemiluminescence and Bioluminescence"; Cormier, J. J., Hercules, D. M., Lee, J., Eds.; Plenum Press: New York, 1973; p 282.

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(54) NOTE ADDED IN PROOF. Subsequent to the submission of this manuscript, a report by Adam and Cueto on dimethyldioxetanone chemiluminescence appeared: Adam, W.; Cueto, C. *J. Am. Chem. Soc.* **1979**, *101*, 6511. Several of the observations reported in that paper are contrary to our experience and warrant further discussion. We have not been able to detect kinetically catalysis of the reaction of **2a** by high oxidation-potential activators such as DPA. In contrast, Adam and Cueto claim to have observed catalysis by DPA kinetically. However, their data indicate that the reaction of **2a** is actually *faster* in the absence of DPA (entry 37, Table I of Adam and Cueto) than in its presence (entries 31–33, Table I of Adam and Cueto). This incongruity indicates that Adam's reported rate constants in this case are not of sufficient precision to be used as evidence of catalysis. Moreover, Adam and Cueto's claim (footnote 19) that their k_{obsd} is dependent on the concentration of **2a** is internally inconsistent with their report (eq 2 and Table I) of first-order decay of the chemiluminescence intensity. As stated above, it is our experience that, for carefully purified solutions of **2a**, the observed rate constants are independent of concentration. Finally, our explanation for the observed slope of $-0.3/RT$ (Figure 3 and footnote 25 of Adam and Cueto) is incorrectly interpreted in Adam's report. The meaning of the magnitude of the slope is discussed fully above.

Absence of Stereoelectronic Control in the Photochemistry of Two Diastereomeric β,γ-Epoxy Ketones

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Received April 20, 1979

Abstract: The preparation and photolysis of ketones **5**, **8**, and **11** are described. Both diastereomeric spiro epoxy ketones **5** and **8** yield the same products, **12** and **13**, at the same rate (± ~3%); spiro cyclopropyl ketone **11** gives **16–18**, and a labeling experiment with **11D** showed that these products arise through stereospecific cleavage of the axial cyclopropyl bond of **11** (see **20D**). These results indicate that, while opening of the cyclopropane ring of **11** is under stereoelectronic control, as expected, there is no observable stereoelectronic effect in cleavage of the epoxide ring of **5** and **8**. An explanation for this behavior is offered.

There is strong evidence that an important set of photochemical reactions of β,γ-cyclopropyl ketones involves α cleavage, subsequent rearrangement of the initial cyclopropylmethyl radical to a homoallyl radical, and then product formation from the resulting radical pair or biradical.[1] This pathway, first suggested some 12 years ago,[2] is shown in eq 1, X = CH_2. More recently an analogous sequence has been put forward for related photochemical reactions of β,γ-epoxy ketones.[3] These steps are shown in eq 1, X = O, and they satisfactorily account for the behavior of a variety of substrates.[3-5]

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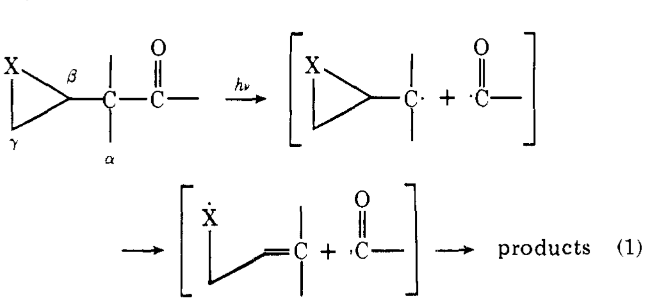
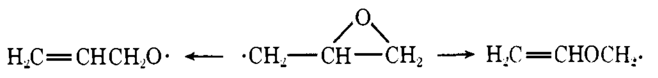
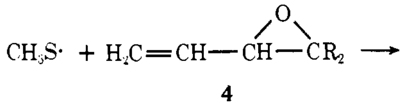


(1)



$$H_2C{=}CHCH_2O\cdot \longleftarrow \cdot CH_2{-}\overset{O}{CH{-}CH_2} \longrightarrow H_2C{=}CHOCH_2\cdot$$

1 2 3



$$CH_3S\cdot + H_2C{=}CH{-}\overset{O}{CH{-}CR_2} \longrightarrow$$

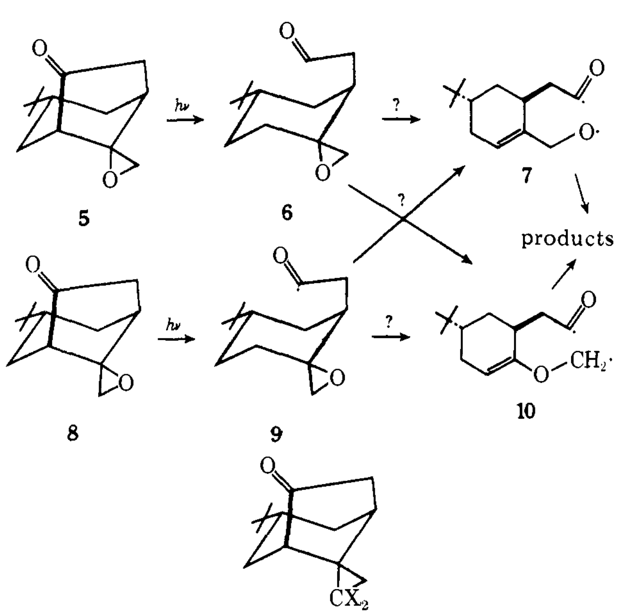
4

$$[CH_3SCH_2\dot{C}H{-}\overset{O}{CH{-}CR_2}] \longrightarrow$$

$$CH_3SCH_2CH{=}CHCR_2O\cdot \text{ and } CH_3SCH_2CH{=}CHOCR_2\cdot \qquad (2)$$

Since in β,γ-cyclopropyl ketones[1] opening of the three-membered ring is under stereoelectronic control,[6] it was natural to inquire whether such a stereoelectronic effect plays a role in the photolysis of β,γ-epoxy ketones. In a rigid system with no free rotation about the $C(\alpha)$-$C(\beta)$ bond in the presumed oxiranylmethyl radical intermediate,[7] this effect could manifest itself through an enhanced rate of $C(\beta)$-O cleavage with increasing overlap of this bond with the orbital on $C(\alpha)$ containing the unpaired electron. It is also possible that the site of fragmentation of the epoxide could depend on whether the $C(\beta)$-O or the $C(\beta)$-$C(\gamma)$ bond better overlaps this orbital on $C(\alpha)$. Rather little information is available concerning this second possibility. Thermochemical calculations based on group equivalents yield an energy difference of ~3.2 kcal/mol favoring homolysis of the carbon-oxygen bond (**1**) rather than the carbon-carbon bond (**3**) in the simple oxiranylmethyl radical (**2**).[8] In line with this relatively small difference, it has been shown that addition of methylthiyl radicals to various vinyloxiranes **4** leads to either carbon-carbon or carbon-oxygen scission, depending on the nature of the substituents in **4** (eq 2).[9] Since the stereoelectronic effect that operates in cyclopropylmethyl radical cleavage appears to provide several kcal/mol stabilization, frequently resulting in formation of the less stabilized of two possible radicals,[6] it seems plausible that such an effect in the oxiranylmethyl system might well be great enough to cause carbon-carbon rather than carbon-oxygen cleavage. In any case information concerning the presence or absence of a stereoelectronic effect in the photochemical behavior of β,γ-epoxy ketones would contribute to our predictive ability and knowledge of this system.

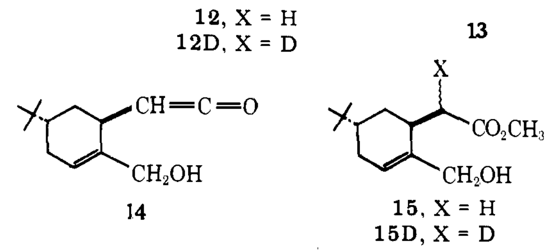
In order to assess the importance of stereoelectronic factors in the photochemistry of β,γ-epoxy ketones we have prepared and studied the photochemistry of the two spiro epoxy ketones **5** and **8**. Application of eq 1, X = O, to these substrates suggests that they should undergo α cleavage to **6** and **9**, respectively, and then rupture of the three-membered ring to **7**; simple spiro epoxy ketones do follow this path.[4] Alternatively, carbon-carbon cleavage in **6** or **9** would furnish **10**. Previous experience with the photolysis of bicyclo[3.2.1]octan-6-ones indicates that **6** and **9** should undergo further reaction in the chair geometry shown because of the anchoring effect of the equatorial *tert*-butyl group.[10,11] This pair of diastereomeric compounds then furnishes two different situations. In the first, ketone **5**, the $C(\beta)$-O bond of the epoxide is essentially coplanar with the carbonyl-$C(\alpha)$ bond in the ketone and with the orbital of the alkyl radical on $C(\alpha)$ in the derived biradical



11, X = H
11D, X = D

6, while the $C(\beta)$-$C(\gamma)$ bond of the epoxide is far removed from such coplanarity. In the second, ketone **8**, these relationships are reversed, and the photochemical behavior of the pair should provide a useful probe for a stereoelectronic effect. As a control on the expected consequences of a stereoelectronic effect in this ring system we have also prepared and examined the photolysis of the related spiro cyclopropyl ketone **11** and its isotopic isomer **11D**. Photochemical results with these various substrates are discussed first, followed by details of preparative experiments.

Irradiation of epoxy ketones **5** and **8** in dry benzene (~0.015 M; λ >2800 Å) led to lactone **12** and dialdehyde **13**. These products were separated and purified by preparative vapor phase chromatography (VPC), and these structures were assigned on the basis of spectroscopic data given in detail in the Experimental Section. Both **12** and **13** are products expected from biradical **7**. When the irradiation was conducted in benzene containing 4% methanol-*O*-*d* (v/v, 0.99 M), the lactone finally isolated contained ~84% of one deuterium atom α to the carbonyl group (**12D**), as indicated by NMR spectroscopy. This result suggests that lactone **12** arises largely, not by direct collapse of **7**, but through disproportionation of **7** to hydroxy ketene **14**, which then closes.[12] Incorporation of deuterium in **12D** then could involve either (or both) direct cyclization of **14**, with solvent methanol-*O*-*d* providing the hydrogen α to the carbonyl group, or capture of **14** by methanol-*O*-*d* to give the α-deuterated hydroxy ester **15D**, followed by lactonization with loss of methanol. Spectral examination of the crude photolysate from irradiations in benzene-methanol indeed suggested the presence of variable amounts of **15**,[13]

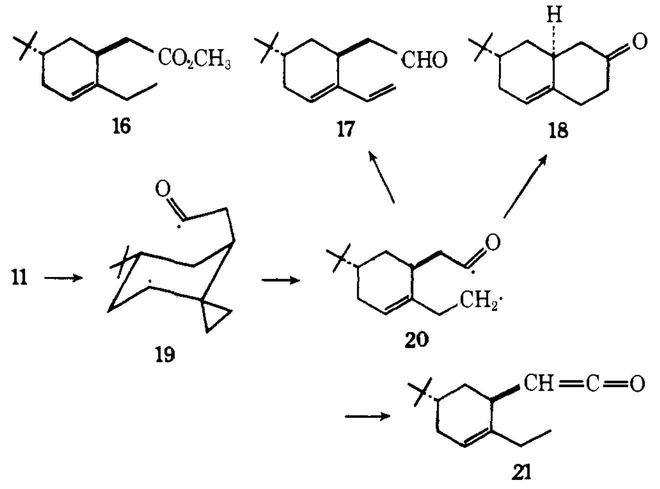


12, X = H
12D, X = D

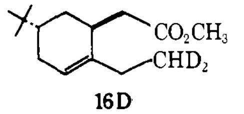
15, X = H
15D, X = D

although isolation by VPC always gave only lactone **12.** Disproportionation of **7** in the opposite direction leads directly to **13.** Under a variety of conditions in benzene or benzene-methanol at 95% conversion we obtained 70–75% of **12,** 10–15% of **13,** and 10–15% of **15,** as determined by NMR. Isolated yields from such a mixture were typically ∼50% of **12** and ∼12% of **13.** Photolysis in acetone at −76 °C or in refluxing *o*-xylene at 144 °C caused no significant change in the yield of lactone **12,** but aldehyde **13** was destroyed under these conditions. In no experiment with either **5** or **8** was any product isolated that could have arisen from biradical **10.** We next examined the relative rates of photolysis of **5** and **8.** The disappearance of ketone in simultaneous irradiations at both 30 and −76 °C was followed by VPC to 25–35% reaction. Within experimental error **5** and **8** disappeared at the same rate (± ca. 3%).[14] Thus neither the products nor the rates of reaction provide evidence of any effect of oxirane stereochemistry on the course of these photolyses of ketones **5** and **8.**

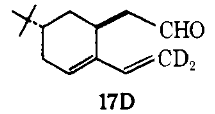
One possible explanation for these results is that, contrary to our expectation, the stereochemistry of **5** and **8** or of the derived biradicals **6** and **9** does not introduce a sufficient difference between the $C(\beta)-C(\gamma)$ and $C(\beta)-O$ bonds to permit stereoelectronic discrimination between them. If this were the case, we would expect cleavage of only the energetically favored carbon-oxygen bond. We investigated this possibility through photolysis of cyclopropyl ketone **11** and its dideuterated isomer **11D.** Irradiation of **11** in benzene-methanol as described above for **5** and **8** furnished a mixture of ester **16,** aldehyde **17,** and ketone **18.** From NMR measurements of the reaction mixture, yields at 85% conversion were **16** (55%) and **17** (15%); the yield of **18** could not be determined in this way, but 11% of **18** was obtained on isolation. In addition there were 5-6 minor products (≤5% yield). These structures are again assigned from spectroscopic data, and the products are those expected if photolysis of **11** proceeds according to eq 1, $X = CH_2$, to yield **19** and then **20.** Disproportionation of **20** furnishes **17** and ketene **21,** which gives **16** on addition of methanol; collapse of **20** gives **18.** Similar irradiation of **11D** led to deuterated isomers of these products, and examination of the ester and aldehyde by NMR indicated that each contained two deuterium atoms located as shown in structures **16D** and **17D.** This result requires that photolysis of **11D** proceed completely by way of **20D** to the exclusion of the isotopically isomeric biradical **20D′**, and thus that opening of the cyclopropane of **11D** (and **11**) occur stereospecifically by way of cleavage of the stereoelectronically favored axial carbon-carbon bond.[15] The behavior of **11** is in complete accord with earlier results on structurally quite different β,γ-cyclopropyl ketones,[1] and this finding provides good evidence that the ring system of **5** and **8** should be sensitive to any stereoelectronic effect operating in cleavage of the epoxide.



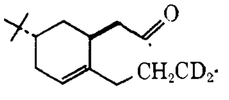
It seems unlikely that the behavior of ketones **5** and **8** reflects the general absence of a stereoelectronic effect in cleavage of a carbon-oxygen bond adjacent to a radical center, particularly since there is quite good evidence for operation of the effect in scission of carbon-carbon[6,16] and carbon-hydrogen[11,17a] bonds similarly situated, as well as in the β scission of oxygen-carbon bonds in dialkoxyalkyl radicals.[17b] We believe that the following explanation specifically applicable to β,γ-epoxy ketones is more attractive. Cleavage of the epoxide in **6** or **9** leads to a species that is more accurately represented as **7** ↔ **22,** if we expressly indicate the inherent zwitterionic character of biradical **7.**[18] We have previously observed photochemical behavior of a β,γ-epoxy ketone that appears to result from just such polar properties of a 1,4-alkoxy acyl biradical.[5] It may then be that the zwitterionic stabilization available to **7** ↔ **22** is sufficiently great and important at the time of bond fission to be controlling and to overwhelm whatever energetic gain is possible through stereoelectronic factors in **6** or **9.** Such an effect would of course play no role in rearrangement of simple oxiranylmethyl radicals.



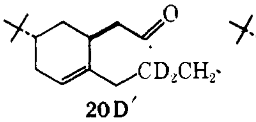
16D



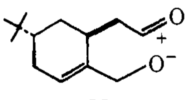
17D



20D



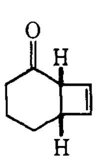
20D′



22

Preparative Experiments. Ketones **5** and **8** were prepared starting with 5-*tert*-butylcyclohex-2-en-1-one (**23**),[19] which was converted to the key intermediate **28** as shown in Scheme I. The steps to cyclobutenes **26** and **27** follow earlier synthesis of the parent *cis*-bicyclo[4.2.0]oct-7-en-2-one (**30**) from cyclohexenone.[11,20-22] In the substituted series, ketals **24** and **25** were obtained in a ratio of ∼4:7 and could be separated and purified with some difficulty by preparative VPC. On hydrolysis these furnished **26** and **27,** which were individually rearranged on chromatography as described below to the bicyclo[3.2.1]octenone isomers **28** and **29,** respectively. Subsequent structural assignment to **28** then permitted stereochemical assignments for **26** and **27.**

Previous studies have defined conditions both for transformation of ketone **30** to **31**[20,23] and also for the similar rearrangement of the related tosylates.[21] In the *tert*-butyl-substituted series we found no overall advantage in use of the tosylates, which of course requires several additional synthetic steps. The procedures that have been worked out for acid-catalyzed rearrangement of **30** to **31**[23] required some modification for **26** and **27.** Our best conditions were use of boron trifluoride etherate in refluxing *o*-xylene for 1 h, and these furnished **28** in an overall yield of 90% on a preparative scale,



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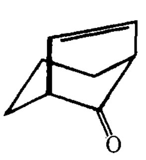

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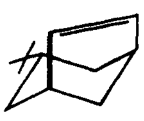

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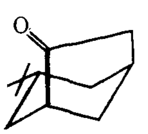

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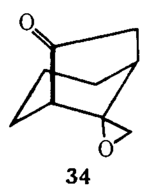

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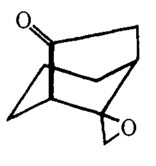

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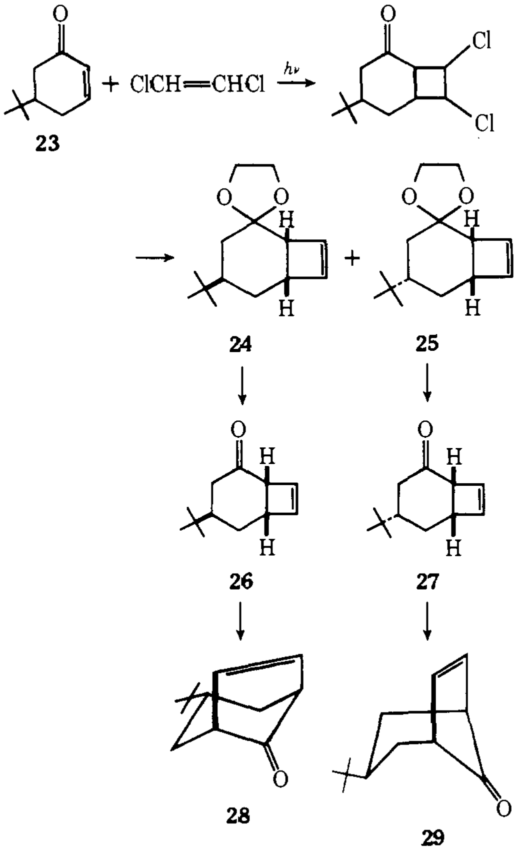
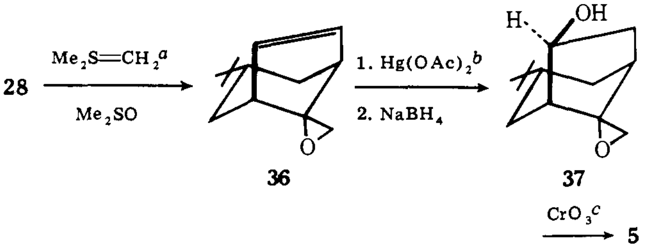
Scheme I

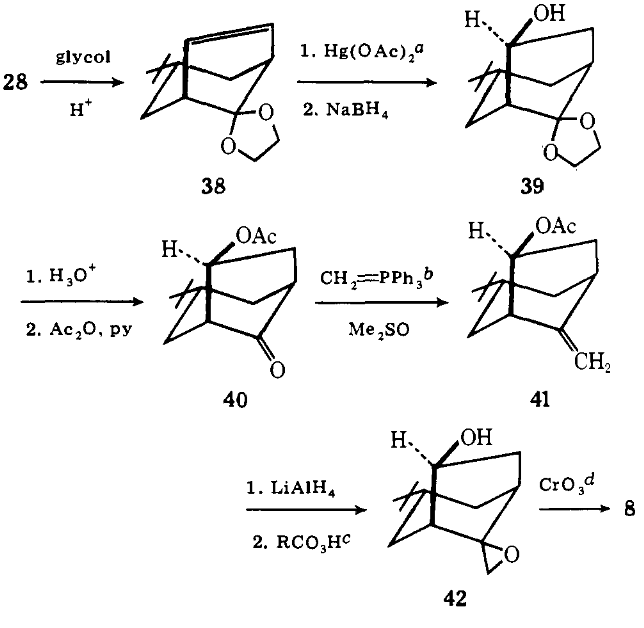


Scheme II



[a] Reference 26. [b] References 27 and 28. [c] Reference 29.

Scheme III



[a] References 27 and 28. [b] Reference 30. [c] R = *m*-ClC_6H_4; reference 31. [d] Reference 29.

starting with the mixture of ketals **24** and **25**. The yield of **29** obtained simultaneously was only 23%, indicating that in this system the course of reaction is a sensitive function of specific structure. Similar effects are on record for related rearrangements.[24] Comparable yields were obtained on rearrangement of the mixture of **26** and **27** by VPC over a QF-1 column at 170–175 °C.

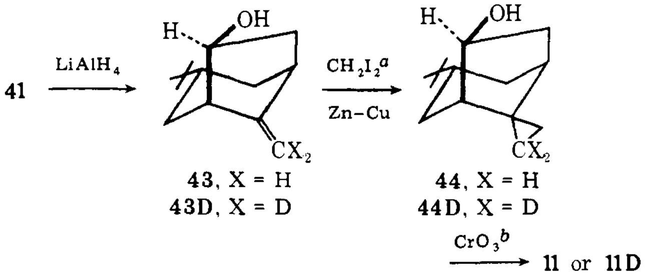
The structure of **28** was confirmed through Wolff-Kishner reduction to the corresponding olefin **32**, which was identical with an authentic sample prepared earlier from ketone **33**.[11] The structure of **29** was assigned on the basis of spectral characteristics very similar to those of **28**, including ^{13}C NMR spectra of only six lines in the range δ_{Me_4Si} 25–140 ppm, as required by the symmetry properties of both ketones. From studies in related bicyclic systems, it appears that there should be little energy difference between these two ketones, despite the conformational inversion necessary to accommodate the *tert*-butyl group in an equatorial position in each case.[25]

The routes for transformation of **28** into epoxy ketones **5** and **8** are shown in Schemes II and III, respectively. These were first worked out by using the more readily available parent enone **31**, providing the simpler epoxy ketones **34** and **35**, and were based on the observation that hydride reduction of the carbonyl group of **31** occurs stereospecifically from the side of the two-carbon olefinic bridge.[11,32] We expected that this selectivity could be used to advantage with **28**; this proved to be correct, and each route gave a single epoxy ketone, and the stereochemistry of these products is assigned on the basis of this selectivity. Only those steps in Schemes II and III requiring specific comment are discussed below.

Oxymercuration of epoxy olefin **36** was quite slow relative to substrates described earlier,[27] but more recently reported work has brought to light several examples of such unexpected variations in reactivity.[28] This low reactivity of **36**, together with its poor solubility in aqueous media required careful control of conditions for both oxymercuration and the subsequent hydride reduction. Oxymercuration in aqueous acetonitrile followed by reduction with basic sodium borohydride at 0 °C furnished hydroxy epoxide **37** in ~90% yield. The contact time in this reduction was controlled to permit hydrolysis of the acetate initially formed without concomitant opening of the epoxide ring. Ketal **38** was somewhat more soluble in aqueous solvents. In this series the reaction furnished mainly alcohol **39**. Reacetylation was conveniently postponed until after hydrolysis of the ketal. Only a single alcohol or acetate was obtained in each series, and the exo stereochemistry depicted for **37** and **39** follows from the known[27] stereospecific exo oxymercuration-demercuration of norbornene. In addition, various previously observed additions to the double bond of **32** and related bicyclo[3.2.1]oct-6-enes occur stereospecifically from the exo side.[11]

The spiro cyclopropyl ketone **11** was available as outlined in Scheme IV. Synthesis of the deuterated isomer **11D** required **43D**, which was prepared from **40** and the Wittig reagent formed on treatment of trideuteriomethyltriphenylphosphonium bromide with *tert*-butyllithium. This procedure minimizes the loss of deuterium through exchange under other conditions for deprotonation of the phosphonium salt,[34] and using it, we obtained **11D** containing ~95% of two deuterium atoms. In the NMR spectrum of alcohol **44D** the remaining cyclopropane protons appear as a clear AB quartet, indicating that the two deuterium atoms are uniquely located in one of the cyclopropane methylene groups. This is assigned as depicted in **44D** and **11D** on the basis of the expected direction of attack of the Simmons-Smith reagent on the exo methylene group of **43** and **43D**. As pointed out in the past,[11] from ex-

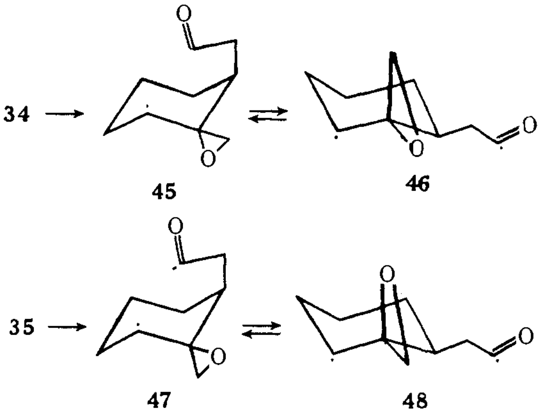
Scheme IV



[a] Reference 33. [b] Reference 29.

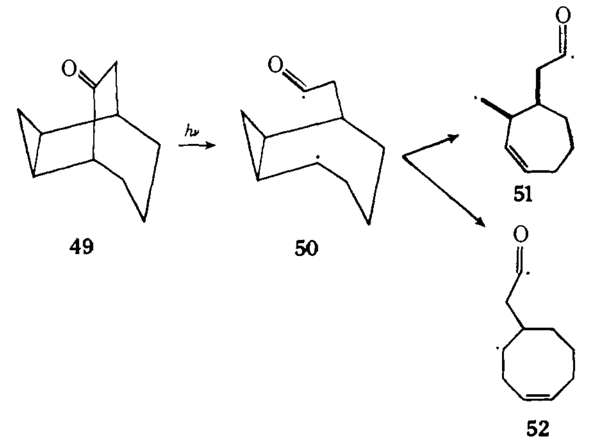
amination of molecular models the axial hydrogens at C(2) and C(4) appear to shield approach to C(8) from that side of the molecule. Furthermore, it is likely that the effect of the hydroxyl group of **43** is to direct attack of the reagent from its side of the double bond,[33,35] and thus to reinforce this stereospecificity.

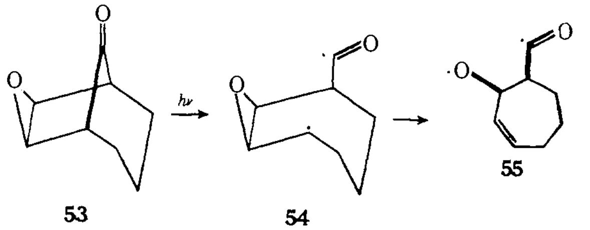
As we mentioned above, we prepared the parent ketones **34** and **35** from bicyclooctenone **31** in the course of working out reaction conditions for **5** and **8**. The simpler β,γ-epoxy ketones served as substrates for some preliminary photochemical work and gave results that appeared to be parallel to those described in detail above for the substituted series. These parent compounds were less suitable for our purposes, however, since there is necessarily some ambiguity in interpretation of their photochemical behavior. Without extensive physical data, it is impossible to ascertain whether the presumed biradicals **45** and **47** formed on α cleavage of **34** and **35** undergo scission of the epoxide before or after their expected conformational inversion to **46** and **48**. Details of some of the experiments with this parent series are given in the Experimental Section.



In summary our findings suggest that the photolysis of these β,γ-epoxy ketones is subject to different controlling factors from that of β,γ-cyclopropyl ketones, and this result should enhance our ability to predict the course of photochemical reactions in related compounds. At the present the only other example known to us that permits some comparison between opening of cyclopropane and oxirane comes from two studies completed in our laboratory during the course of the present investigation. Irradiation of the tricyclodecanone **49** leads to products derivable from rearrangement of the initial biradical **50** in both possible senses (see **51** and **52**), and examination of models suggests that **50** is sufficiently flexible to reach conformations permitting good overlap of either the external or internal cyclopropane bond with the alkyl radical center.[1] In contrast, all volatile products from the related epoxy ketone **53** can be accounted for by rearrangement of **54** uniquely to the alkoxy acyl biradical **55**.[5]

Experimental Section





General. All VPC was carried out on a Varian Aerograph Model 920, 700 Autoprep, or A-90-P gas chromatograph using columns prepared from aluminum tubing (0.25 in. diameter) and operating at a helium flow rate of 100-120 mL/min. The following columns (all 25% stationary phase on 40/60 Chromosorb W) were used: (A) QF-1, 5 ft; (B) QF-1, 7 ft; (C) QF-1, 8 ft; (D) EGA, 10 ft; and (E) QF-1, 20 ft.

Unless otherwise specified, 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 T-60A (60 MHz) spectrometer. Varian HR-220 (220 MHz, CW or FT mode) and Bruker HX-90 (22.63 MHz, for ^{13}C spectra) spectrometers were also used as indicated. All NMR signals (including ^{13}C) are reported relative to tetramethylsilane (~1% internal reference; 0 ppm). All UV spectra were recorded on a Cary Model 14 spectrophotometer. Samples for melting points and analyses were usually repurified by VPC before use. Melting points were obtained on Thomas-Hoover apparatus and are corrected. Unless otherwise noted, solutions were dried over $MgSO_4$, K_2CO_3, or Na_2SO_4, and solvents were removed in vacuo with a rotary evaporator. All pure compounds were obtained as colorless oils unless otherwise indicated.

General Procedure for Photolysis of Ketones. For preparative experiments a solution of the pure ketone (0.010-0.016 M) in anhydrous benzene (3-4% CH_3OH by volume) contained in a toroidal Pyrex glass vessel (capacity ~70 mL) was flushed with dry nitrogen for 30 min and irradiated with a Hanovia 450-W medium-pressure mercury lamp, cooled in a quartz well. The mixture was kept in a 30 °C water bath and under nitrogen atmosphere throughout the photolysis.

Relative rate studies at room temperature were accomplished by simultaneous irradiation of solutions in sealed Pyrex test tubes placed on a merry-go-round apparatus. An extra Pyrex filter was placed around the lamp when necessary to permit measurements at low conversion.

Photolysis of 5 and 8. A. Preparative Experiments. Irradiation of **5** (46 mg) in methanolic benzene for 45 min resulted in ~95% conversion to products. Analysis of the crude photolysate by NMR revealed the presence of **12** (~75%), **13** (~15%), and **15** (~6%). However, VPC showed only two of the products and a trace of starting material. The two compounds were isolated by VPC (column B, 170 °C) and characterized as **12** and **13** from the following data. For **12** (47% recovered yield, retention time 25-37 min): mp (recrystallized from pentane) 65.0-65.5 °C; IR 2952 and 2935 (s, merged), 2865 (m), 1740 (s, br), 1475 and 1465 (w), 1385 (w sh), 1377 (m), 1361 (m), 1224 (w), 1188 (m), 1160 (w, br), 1038 (w), 1015 (m), 980 (w), 880 (w), 855 (w) cm^{-1}; NMR δ 5.83 (br d, $J \sim 6$ Hz, 1 H), 4.76 and 4.51 (AB quartet, lower field doublet br, $J_{AB} \sim 12$ Hz, 2 H), 2.90-1.20 (m, 8 H), 0.90 (s, 9 H); mass spectrum, m/e 208.1466 (M^+, calcd for $C_{13}H_{20}O_2$, 208.1463). For **13** (12% recovered yield, retention time 12 min): IR 2960 (s), 2870 (w), 2810 (w), 2715 (w), 1730 (s), 1687 (s), 1646 (w), 1475 and 1468 (w), 1420 (w), 1392 (w), 1363 (m), 1242 (w), 1151 (m), 1025 (w) cm^{-1}; NMR δ 9.80 (m, 1 H), 9.45 (s, 1 H), 6.77 [m (probably dd, J ~3, 5 Hz, with further coupling), 1 H], 3.50–1.30 (m, 8 H), 0.90 (s, 9 H); mass spectrum, *m/e* 208.1483 (M^+, calcd for $C_{13}H_{20}O_2$, 208.1463).

Comparison of photolysates from different runs indicated **15** was usually ~10% of the mixture, but varied from 6 to 64% (**12** plus **15** ca. 80%), depending on conditions. A mixture containing 64% of **15** [characteristic NMR signals at 5.70 (br s, 1 H), 3.93 (br s, 2 H), 3.66 (s, 3 H) ppm] gave **12** as the major product on VPC.

Photolysis of ketone **8** gave the same product distribution. The two major products were isolated and shown to have VPC retention times and spectral properties identical with **12** and **13**. Photolysis of **8** in refluxing *o*-xylene also gave **12** and no new products.

B. Comparison of Photolysis of 5 and 8 in Benzene and in CH_3OD/Benzene. Four solutions [**5** and **8** in pure benzene (5 mL) and **5** and **8** in CH_3OD/benzene (4% v/v; 5 mL)] were prepared (0.017 M each) and irradiated simultaneously at room temperature. Aliquots taken from each sample throughout the photolysis indicated (VPC on column B) that **5** and **8** disappeared at about the same rate to give the same product distribution, with or without CH_3OD. The lactone (**12** or **12D**) from each sample was isolated by VPC (~60% yield). Comparison of NMR spectra (2.80–2.30 ppm region) revealed that deuterium was incorporated (~0.84 atom) in the α position of both lactone samples obtained from CH_3OD/benzene solutions.

C. Comparison of Photolysis Rates of 5 and 8. Solutions of **5** and **8** (each 0.019 M in benzene; 4 mL) were irradiated simultaneously at room temperature. The photolysis was followed by VPC (3–25% conversion), which showed that **5** and **8** disappeared at essentially the same rate: Time (min) (% **5** remaining, % **8** remaining) 7 (97.7, 96.9), 12 (96.2, 95.4), 32 (87.3, 82.3), 43 (84.6, 76.2), 63 (76.2, 73.8).

Two acetone solutions of **5** and **8** (each 0.019 M; 2 mL) were prepared in test tubes and immersed in a dry ice/acetone bath contained in a clear Pyrex Dewar flask. A mercury lamp was placed at an equal distance from the two tubes. The samples were kept at −76 °C during the photolysis. Aliquots were taken and analyzed by VPC. The positions of the two tubes were exchanged periodically for uniformity of irradiation. Essentially no difference in rate of disappearance of **5** and **8** could be observed at 3–30% conversion: Time (min) (% **5** remaining, % **8** remaining) 12 (96.8, ~100), 37 (92.5, 95.8), 72 (83.0, 90.0), 150 (80.6, 77.5), 220 (73.1, 67.5). Both samples gave about the same yield of **12**; most of **13** was destroyed under the photolysis conditions.

Photolysis of 11 and 11D. A solution of **11** (0.01 M, 50-mg sample) in methanolic benzene was irradiated for 1.25 h (85% conversion). Analysis of the crude photolysate by VPC (column C, 155 °C) revealed approximately nine new products. NMR of the crude mixture indicated the presence of a methyl ester (55%) and an aldehyde (15%). The major three products were isolated by VPC (40, 8, and 12% recovered yields, in order of increasing VPC retention time) and identified as **16**, **17**, and **18**, respectively. For **16**: IR 2970 (s), 2888 (sh), 2842 (w), 1738 (s), 1462 (w, br), 1430 (m), 1362 (m), 1242 (w, br), 1185 (w), 1155 (m, br), 1008 (m, br), 922 (w), 855 (w) cm^{-1}; NMR (220 MHz) δ 5.34 (m, 1 H), 3.62 (s, 3 H), 2.53 (br dd, J = 3.7, 10.8 Hz, 1 H), 2.38 (dd, J = 3.7, 14.8 Hz, 1 H), 2.15 (dd, J = 10.8, 14.8 Hz, 1 H), 2.05–1.82 (m, 3 H), 1.82–1.55 (m, 2 H), 1.41–1.09 (m, 2 H), 1.01 (t, J = 7.4 Hz, 3 H), 0.86 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 173.6 (s, C=O), 140.6 (s, >C=), 121.6 (d, -CH=), 51.4, 38.3, 37.8, 35.0, 31.9, 28.5, 27.4, 27.1, 26.5, and 12.6.

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.67; H, 10.89.

For **17**: IR 3088 (w), 2960 (s), 2872 (sh), 2830 and 2810 (w), 2710 (w), 1726 (s), 1642 (w), 1608 (w), 1475 and 1465 (w), 1362 (m), 1237 (w), 985 (m), 891 (m) cm^{-1}; NMR (220 MHz) δ 9.73 (d, J = 2.3 Hz, 1 H), 6.14 (dd, J = 10.9, 17.7 Hz, 1 H), 5.70 (br dd, J = 2.8, 5.0 Hz, 1 H), 4.99 (d, J = 17.7 Hz, 1 H), 4.89 (d, J = 10.9 Hz, 1 H), 3.14 (br dd, J ~3, 10 Hz, 1 H), 2.59 (dd, J = 2.7, 17.5 Hz, 1 H), 2.42 (ddd, J = 2.3, 10.1, 17.5 Hz, 1 H), 2.28–1.18 (m, 5 H), 0.87 (s, 9 H); UV λ_{max} (cyclohexane) 231 nm (ϵ ~13 000); mass spectrum, *m/e* 206.1655 (M^+, calcd for $C_{14}H_{22}O$, 206.1670).

For **18**: IR 2953 (s), 2852 (m), 1712 (s), 1475 and 1465 (w), 1390 (w), 1362 (m), 1308 (w), 1250 (w), 1230 (w), 1163 (w), 945 (w), 905 (w) cm^{-1}; NMR δ 5.63 (d, with fine structure, J ~6 Hz, 1 H), 2.62–1.72 (m, 9 H), 1.72–1.20 (m, 3 H), 0.91 (s, 9 H): characterized as 2,4-dinitrophenylhydrazone (mp 209–211 °C from ethyl acetate).

Anal. Calcd for $C_{20}H_{26}N_4O_4$: C, 62.16; H, 6.78; N, 14.50. Found: C, 62.60; H, 6.90; N, 14.58.

Irradiation of a solution of **11D** (40 mg) in methanolic benzene for 2.25 h (83% conversion) gave approximately the same ratios of products (VPC, column C, 155 °C) as **11**. **16D** and **17D** were identified from the following data.

For **16D**: IR same as **16** except for additional weak bands at 2215 and 2120 cm^{-1}; NMR (220 MHz) same as for **16** except 2.05–1.82 (m, 3 H) sharper and 1.05–0.92 (br m, 1 H). For **17D**: IR same as for **17**, except 3088, 1608, 985, and 891 cm^{-1} missing, and new bands at 1565 and 935 cm^{-1}; NMR (220 MHz) same as for **17**, except that 6.14 (dd, 1 H) collapsed to 6.12 (br s, 1 H), 4.99 (d, 1 H), and 4.89 (d, 1 H) missing; UV same as **17**.

Solutions of **11** and **11D** (0.015 M) were irradiated simultaneously (each 6.3 mg in 5% CH_3OH/benzene) at 30 °C and the photolyses followed by VPC. The value of the secondary isotope effect was calculated from the rates of disappearance of **11** and **11D**: k_H/k_D ~1.2.

Photolysis of 34 and 35. Irradiation of **34** (125 mg, 0.82 mmol) in methanolic benzene (50 mL) for 2 h 40 min (>95% conversion) gave two new products which were isolated by VPC on column A at 165 °C. The major product (68% recovered yield; retention time, 22 min) was characterized as 2-hydroxymethyl-2-cyclohexene-1-acetic acid δ-lactone: IR 2925 (m), 2850 (w), 1750 (s, br), 1460 (w), 1440 (w), 1427 (w), 1370 (w, br), 1245 (w), 1220 (m), 1208 (w), 1170 (w), 1118 (w), 1082 (w), 1032 (m), 950 (w), 850 (w) cm^{-1}; NMR (220 MHz) δ 5.67 (br s, fine structure, 1 H), 4.70 and 4.57 (m, AB q, fine splitting, J_{AB} = 13.3 Hz, 2 H), 2.77–2.34 (m, 2 H), 2.34–1.10 (m, 7 H); ^{13}C NMR (C_6F_6) δ 171.4, 125.1, 124.7, 72.6, 38.0, ca. 34 and 31, 26.3, 22.6.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.05; H, 7.98.

The minor product (8.5% recovered yield; retention time 11 min) was 2-formyl-2-cyclohexene-1-acetaldehyde: IR 2930 (m), 2860 (w), 2813 (w), 2713 (w), 1730 (m), 1688 (s), 1638 (w), 1445 (w), 1418 (w), 1160 (m), 1120 (w), 1062 (w), 855 (w) cm^{-1}; NMR (220 MHz) δ 9.68 (d, J = 2.6 Hz, 1 H), 9.31 (s, 1 H), 6.79 (apparent t, J = 3.8 Hz, 1 H), 3.40–1.40 (m, ~9 H); mass spectrum, *m/e* 134.0756 ($M^+ - H_2O$, calcd for $C_9H_{10}O$, 134.0731), 124.0904 ($M^+ - CO$, calcd for $C_8H_{12}O$, 124.0888).

Irradiation of a small sample of **35** (8.5 mg) according to the above procedure gave the same two products as evidenced by VPC retention times and spectra of the isolated products.

***exo-* and *endo*-4-*tert*-Butylbicyclo[4.2.0]oct-7-en-2-one Ethylene Ketals (24 and 25).** A solution of 5-*tert*-butylcyclohex-2-en-1-one (17.5 g, 0.115 mol)[19] and 1,2-dichloroethylene (65.5 g, 0.675 mol; mixture of isomers, MCB) in purified pentane (425 mL) was flushed with dry nitrogen for 30 min and irradiated at room temperature with a Hanovia 450-W medium-pressure mercury lamp surrounded by a Pyrex filter.[22] The cycloaddition was complete (followed by disappearance of IR band at 1686 cm^{-1} and appearance of new band at 1711 cm^{-1}) in 19 h. Removal of solvent gave a mixture of bicyclic ketones as a brown oil (26.0 g, 0.104 mol; 91%): IR 2960 (s), 2862 (w), 1711 (s), 1470 and 1460 (m, merged), 1388 (w), 1360 (m), 1287 (w), 1250 (w), 1225 (w), 1185 (w), 835 (w) cm^{-1}. The crude product was treated with ethylene glycol (~12 g, 0.2 mol) and a few milligrams of *p*-toluenesulfonic acid in refluxing benzene (180 mL) with continuous separation of water (followed by disappearance of 1711-cm^{-1} band). After 3 h the solution was cooled, washed with 5% aqueous $NaHCO_3$ and brine, and dried. Removal of solvent gave the crude saturated ketal mixture (~30 g, 99%).

A solution of the ketal mixture (41.5 g, 0.142 mol; from combined reactions) in anhydrous ether (250 mL) was added to liquid ammonia (600 mL) contained in a three-necked flask, fitted with a dry ice condenser. The greenish yellow solution was stirred vigorously under nitrogen while sodium metal (8 g, 0.35 g-atom) was added portionwise over a period of 30 min.[22] The resulting dark blue mixture was stirred at −30 °C for an additional 2 h and then treated with excess NH_4Cl (18.6 g). The ammonia was allowed to evaporate overnight. Water was added and the organic products were extracted into ether. The combined solution was washed with brine and dried. Removal of the ether gave a golden mixture of the unsaturated ketals (29.6 g). Analysis by VPC (column C, 125 °C) and NMR indicated the presence of two isomeric alkenes (60% of the crude mixture) in ca. 4:7 ratio. Subsequent preparative reactions were carried out on the crude mixture. A small portion was distilled (67–74 °C, 0.08 mm) to yield a colorless liquid (59%; 53% based on 5-*tert*-butyl-2-cyclohex-1-one) which was chromatographed on column C (120 °C) to separate the two ketals. Best results were obtained by injection directly onto a clean column. These ketals were repurified under the same VPC conditions and characterized as follows. For **24:** IR 3120 (w), 3040 (w), 2960 (s), 2870 (m), 1465 (m, split), 1388 (w), 1361 (m), 1340 (w), 1277 (w), 1102 (s), 1019 (m), 970 (w), 930 (w, split), 882 (w), 854 (w), 826 (vw), 701 (w) cm^{-1}; NMR δ 6.22 and 6.09 (two d, *J* ∼2.8 Hz, further unresolved coupling, 2 H), 3.87 (m, 4 H), 3.30–2.97 (m, 1 H), 2.87–2.63 (m, 1 H), 1.93–1.16 (m, 5 H), 0.82 (s, 9 H).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.83; H, 10.00.

For **25:** IR region 3200–1200 same as for **24**, 1110 (m, br), 1019 (m), 988 (w), 937 (w), 878 (w), 854 (w), 830 (vw), 700 (w) cm^{-1}; NMR δ 6.22 and 5.96 (two d, *J* ∼2.8 Hz, further unresolved coupling, 2 H), 3.88 (s, 4 H), 3.20–2.73 (m, 2 H), 2.00–1.10 (m, 5 H), 0.83 (s, 9 H).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.75; H, 9.93.

***exo*- and *endo*-4-*tert*-Butylbicyclo[4.2.0]oct-7-en-2-one (26 and 27).** The crude ketal mixture from above (5.0 g, 22.5 mmol) was dissolved in acetone (180 mL) and treated with *p*-toluenesulfonic acid (156 mg). The deketalization was followed by VPC (column A, 135 °C). After 5 h at room temperature, 5% aqueous $NaHCO_3$ was added and most of the acetone removed in vacuo. The mixture was extracted with ether. The combined organic phase was washed with brine and dried, and the ether removed to give a quantitative yield of crude brown mixture of enones. Distillation (80–87 °C, 0.4–0.5 mm) gave a colorless oil (45%; ca. 90% pure mixture by NMR). Attempts to separate the two isomers by VPC resulted in partial to complete rearrangement to the [3.2.1] enones (see below) and/or in decomposition. The mixture was used without further purification. With careful monitoring of time and control of acid concentration, this deketalization could be scaled up to 33 g of **24** and **25.** Samples of pure **26** and **27** were obtained from the corresponding pure ketals **24** and **25** under these conditions.

For **26:** IR 3120 (w), 3045 (w), 2960 (s), 2935 and 2915 (w, sh), 2865 (w), 1696 (s), 1471 and 1462 (w, merged), 1389 (w), 1361 (m), 1276 (w), 1229 (w), 1146 (w), 917 (w), 712 (w) cm^{-1}; NMR δ 6.20 and 6.03 (d with fine structure and m, respectively, 2 H), 3.60–3.17 (m, 2 H), 2.67–1.40 (m, 5 H), 0.92 (s, 9 H); mass spectrum, *m/e* 178.1365 (M^+, calcd for $C_{12}H_{18}O$, 178.1313). For **27:** IR region 3200–1300 same as for **26** except for carbonyl band at 1703 (s), 1268 (w), 1231 (w), 1179 (w), 950 (w), 712 (w) cm^{-1}; NMR δ 6.20 and 6.07 (2 m, 2 H), 3.57–2.93 (m, 2 H), 2.67–1.40 (m, 5 H), 0.90 (s, 9 H); mass spectrum, *m/e* 178.1360 (M^+, calcd for $C_{12}H_{18}O$, 178.1313).

***exo*- and *endo*-3-*tert*-Butylbicyclo[3.2.1]oct-6-en-8-one (28 and 29). A. From Rearrangement of 26 and 27 in Solution.** A solution of the distilled mixture of **26** and **27** (4.45 g, 25 mmol) in anhydrous *o*-xylene (250 mL) was heated to reflux temperature, under nitrogen atmosphere, and boron trifluoride etherate (100 μL, 0.8 mmol; Aldrich) was injected directly into the solution over <1 min. The color turned golden brown. Stirring at reflux temperature was continued for 1 h, at which time NMR revealed two new products in ca. 9:4 ratio (representing 100 and 25% rearrangement of **26** and **27**, respectively) and no starting material. Once formed, **28** and **29** appeared to be more stable to reaction and VPC conditions than **26** and **27.** The mixture was cooled, washed with 5% aqueous $NaHCO_3$ and brine, and dried. Removal of solvent followed by distillation (73–75 °C, 0.2–0.3 Torr) gave a yellowish liquid containing ca. 80% of the desired enones. Repeated recrystallizations from pentane gave about half of **28** in pure form. Then VPC of the combined supernatant liquid on column D (175 °C) afforded both **28** and **29** as white solids (a total of 31.5 and 12.5% yield, respectively, based on **26** and **27**). For **28** (retention time, 30 min): mp 67.5–68.0 °C; IR 3056 (w), 2960 (s), 2860 (m), 1917 (vw), 1812 (w), 1764 (s), 1720 (vw sh), 1642 (vw), 1575 (vw), 1467 (m, split), 1387 (w), 1361 (m), 1303 (w), 1267 (w), 1240 (w), 1219 (w), 1167 (w), 1111 (w), 1094 (vw), 1058 (w), 890 (w), 850 (w, split), 709 (m) cm^{-1}; NMR (220 MHz) δ 6.19 (t, *J* = 1.5 Hz, 2 H), 2.65 (br s, fine structure, 2 H), 1.93–1.68 (m, 2 H), 1.68–1.36 (m, 3 H), 0.85 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 27.8 (q), 30.4 (t), 31.8 (s), 39.1 (d), 48.7 (d), 129.7 (d), carbonyl carbon not observed.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.95; H, 10.11.

Wolff-Kishner reduction[36] of **28** (55 mg) followed by VPC purification gave the corresponding hydrocarbon, *exo*-3-*tert*-butylbicyclo[3.2.1]oct-6-ene (**32**), which had IR and NMR spectra identical with those of the authentic compound.[11]

For **29** (retention time, 33 min): mp 35–40 °C; IR 3056 (w), 2960 (s), 2860 (m), 1871 (w), 1764 (s), 1718 (vw), 1585 (vw), 1472 and 1465 (m, merged), 1387 (w), 1361 (m), 1238 (w), 1221 (w), 1160 (vw), 1135 (w), 1097 (vw), 1072 (w), 918 (w), 863 (w), 826 (w), 708 (m) cm^{-1}; NMR (220 MHz) δ 6.36 (t, *J* = 1.6 Hz, 2 H), 2.48 (br d, *J* = 8.7 Hz, 2 H), 2.22–1.88 (m, 2 H), 1.86–1.39 (m, 3 H), 0.83 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 26.7 (q), 29.8 (t), 32.7 (s), 42.1 (d), 44.2 (d), 135.5 (d), carbonyl carbon not observed.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.65; H, 10.17.

B. From Rearrangement of 26 and 27 by VPC. The mixture of enones **26** and **27** was injected onto column E (170 °C, 20–25-mg injections), and the major peak (retention time 16.5–21.5 min) was collected (40% by weight). VPC and NMR inspection of this material indicated a mixture of **28** and **29** (2.4:1, respectively). The two products, separated on column D (175 °C), had IR and NMR spectra identical with those of samples obtained in A (% rearrangement: ≥80 for **26** and ≥20 for **27**).

Similar separate rearrangement for purified samples of **26** and **27** revealed that the minor enone **26** gives **28** and the major enone **27** gives **29.**

(1*R,3*S**,5*S**,8*R**)-3-*tert*-Butylspiro[bicyclo[3.2.1]oct-6-en-8,2′-oxirane] (36).** Dimethylsulfonium methylide was prepared[26] from trimethylsulfonium iodide (1.22 g; 5.98 mmol) and methylsulfinyl carbanion. A solution of enone **28** (421 mg, 2.37 mmol) in dimethyl sulfoxide (1.6 ml) was added to the cold reagent. Stirring was continued for 15 min at 5 °C and 3.75 h at room temperature. Workup with pentane afforded a white solid in quantitative yield. The product was characterized as **36** from the following data: mp 46–48 °C; IR 3050 (w), 2950 (s, split), 2860 (w), 1485 (w), 1470 (w), 1458 (w), 1358 (m), 1245 (vw), 1230 (w), 1215 (w), 1060 (w), 1000 (w), 965 (m), 907 (m), 838 (m), 712 (w) cm^{-1}; NMR δ 5.97 (t, *J* ∼2 Hz, 2 H), 2.73 (s, 2 H), 2.16–1.87 (m, 2 H), 1.63–1.30 (m, 5 H), 0.87 (s, 9 H); mass spectrum, *m/e* 192.1507 (M^+, calcd for $C_{13}H_{20}O$, 192.1514).

(1*R,3*S**,5*R**,8*R**)-3-*tert*-Butylspiro[bicyclo[3.2.1]octane-8,2′-oxiran]-6-one (5).** Epoxide **36** (192 mg, 1.0 mmol) was added directly to a vigorously stirred suspension of mercuric acetate (320 mg, 1.0 mmol; Mallinckrodt) in water and acetonitrile (1.0 mL each).[27] Stirring was continued for 32 h at room temperature. During this period the thick orange suspension changed into a pale yellow and then colorless solution, and a white precipitate started forming (5 h). After 1 day a milky suspension had formed and was diluted with CH_3CN (∼0.4 mL). At the end of the indicated reaction period, the mixture was cooled in a 0 °C bath for 5 min and treated with cold (0–5 °C) 3 N NaOH solution (1.0 mL). After stirring for 5 min at room temperature, a cold solution of $NaBH_4$ (1.0 mL; 0.5 M in 3 N NaOH) was added, with brief external cooling. The resulting gray mixture was stirred at room temperature for 10 min. More CH_3CN (0.6 mL) and an excess of NaCl were added, followed by ether (∼2 mL) after 5 min. The mixture was stirred for 5 min longer to allow the solids to coagulate, and the ether layer was separated (∼30 min total time after the addition of 3 N NaOH). The aqueous phase was extracted with ether. The combined organic solution was washed with brine and dried. Removal of solvent gave a white solid (∼80% desired alcohol **37**). Chromatography on column A (140 °C) gave a purer sample for spectra: IR 3610 (w), 3500–3200 (m), 2995 (w), 2910 (s), 2820 (w), 1475 and 1465 (w), 1440 (w), 1362 (m), 1134 (w), 1012 and 1000 (m), 930 (m) cm^{-1}; NMR δ 4.10 (dd, further coupling, *J* ∼3, 7 Hz, 1 H), 2.82 (s, 2 H), 2.60 (br s, variable, 1 H), 2.40–1.10 (m, ∼9 H), 0.88 (s, ∼9 H). Ratcliffe oxidation[29] of crude **37** gave ketone **5.** Sublimation (60–70 °C, 0.1 mm) afforded a white solid (90% pure; overall yield from **36**, 60–70%). A sample was chromatographed on column A (140 °C): mp 88–91 °C; IR 3038 (w), 2960 (s), 2862 (w), 1750 (s), 1474 and 1464 (w), 1413 (w), 1398 and 1388 (w), 1363 (m), 1238 (w), 1137 (w), 1112 (w), 970 (w), 925 (w), 845 (w) cm^{-1}; NMR δ 2.81 (s, 2 H), 2.43–2.20 (m, 2 H), 2.20–1.20 (m, 7 H), 0.90 (s, 9 H); mass spectrum, *m/e* 208.1463 (M^+, calcd for $C_{13}H_{20}O_2$, 208.1463).

***exo,exo*-3-*tert*-Butyl-8-oxobicyclo[3.2.1]oct-6-yl Acetate (40).** Enone **28** (2.28 g, 12.8 mmol) was treated with excess ethylene glycol in the usual fashion to yield ketal **38** (98%). A sample purified on column B (130 °C) had the following properties: mp 50–52 °C; IR, 3050 (w), 2950 (s), 2870 (m), 1475 and 1462 (w), 1158 (m), 1142 (m), 1120 (s, br), 1092 (m), 1075 (w), 1030 (w), 1012 (w), 980 (w), 945 (w), 920 (w), 855 (vw), 712 (vw) cm^{-1}; NMR δ 5.83 (t, *J* ∼2 Hz, 2 H), 3.85 (m, 4 H), 2.28 (br s, 2 H), 2.00–1.00 (m, 5 H), 0.83 (s, 9

H). Ketal **38** (2.76 g; 12.5 mmol) was added to a suspension of mercuric acetate[27] (3.99 g; 12.5 mmol) in a 1:1 mixture of water and acetonitrile (12.5 mL each) and the mixture was stirred vigorously at room temperature for 30.5 h. The thick orange solids disappeared within the first 1.5 h, giving a clear golden solution. After 30.5 h, the solution was cooled in an ice bath and treated with cold 3 N NaOH (12.5 mL), quickly followed by cold $NaBH_4$ (12.5 mL, 0.5 M solution in 3 N NaOH). Ether workup gave a quantitative yield of a mixture of **39** and the corresponding acetate. (Rapid workup gave more of the acetate.) Samples of the two compounds were isolated by VPC (column B, 150 °C) for spectra. For **39**: IR 3565 (m), 2955 (s), 2870 (m), 1472 and 1465 (w), 1445 (w), 1412 (w), 1370 and 1360 (m), 1262 (w), 1220 (m), 1110 (s, br), 1025 and 1015 (s), 1000 (w), 940 (m) cm^{-1}; NMR δ 3.93 and 3.90–3.50 (s, m, 5 H), 2.40–1.10 (m, 10 H), 0.83 (s, 9 H). For acetate: IR 2950 (s), 1735 (s), 1362 (m), 1240 (s, br), 1112 (m), 1025 (m) cm^{-1}; NMR δ 4.75 (m, 1 H), 3.90 (s, 4 H), 2.10–1.10 (m, s at 2.00, 12 H), 0.87 (s, 9 H). Crude ketal **39** (968 mg, 4.0 mmol) was dissolved in ether (5 mL) and treated with 3 N HCl (20 mL) and stirred vigorously at room temperature for 22.5 h. Ether workup gave the crude keto alcohol in 98% yield. A small sample of the white solid was recrystallized from pentane: mp 83–84 °C; IR 3600–3150 (m), 2960 (s), 2870 (w), 1750 (s, br), 1475 and 1466 (w), 1445 (w), 1365 (m), 1190 (w), 1120 (m), 1035 (m, br), 940 (w) cm^{-1}; NMR δ 4.20 (m, 1 H), 3.50 (br s, variable, 1 H), 2.60–1.20 (m, $\sim$9 H), 0.87 (s, 9 H). The crude alcohol (780 mg; 4.0 mmol) was treated with acetic anhydride (1.3 mL) and pyridine (0.8 mL) for 10 h. Usual workup with pentane gave a yellow oil (90%). A sample was purified on column B (150 °C) and characterized as **40**: IR 2955 (m), 2865 (w), 1754 and 1738 (s), 1475 and 1465 (w), 1440 (w), 1365 (m), 1230 (s, br), 1188 (w), 1120 (w), 1025 (m), 975 (w), 890 (w) cm^{-1}; NMR δ 5.05 (dd, J $\sim$3, 8 Hz, 1 H), 2.62–1.40 (m, s at 2.00 ppm, 12 H), 0.91 (s, 9 H).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.76; H, 9.28.

***exo,exo*-3-*tert*-Butyl-8-methylenebicyclo[3.2.1]oct-6-yl Acetate (41).** Methylenetriphenylphosphorane (15.0 mmol) was prepared from methylsulfinyl carbanion and (methyl)triphenylphosphonium bromide in dry dimethyl sulfoxide (total, 18 mL).[30] A solution of ketone **40** (779 mg, 3.28 mmol) in dimethyl sulfoxide (3 mL) was added to the Wittig reagent and the mixture was stirred for 23.5 h at room temperature under nitrogen. The resulting product was poured over a mixture of ice and brine. Workup with pentane and removal of solvent gave a viscous oil, which was taken up in pentane ($\sim$2 mL). The solids were filtered and washed. The combined pentane solution was then dried and the solvent removed to yield the crude alkene (>95%). The product was used without further purification. A sample was purified on column B (134 °C) and identified as **41**: IR 3065 (w), 2960 and 2935 (s), 2862 (w), 1735 (s), 1678 (w), 1475 and 1465 (w), 1440 (w), 1360 (m), 1235 (s, br), 1188 (w), 1137 (w), 1030 (m), 1020 (w sh), 935 (w), 880 (m), 688 (w) cm^{-1}; NMR δ 5.83 and 5.67 (dd, J $\sim$3, 7 Hz, and m, respectively, 3 H), 2.80–1.20 (m, with s at 1.93 ppm, 12 H), 0.83 (s, 9 H).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.32; H, 10.26.

(1*R,3*S**,5*R**,8*S**)-3-*tert*-Butylspiro[bicyclo[3.2.1]octane-8,2′-oxiran]-6-one (8).** Crude **41** (3.3 mmol) in anhydrous ether (20 mL) was added to a cold slurry of $LiAlH_4$ (300 mg, 7.9 mmol) in ether over 10 min. The mixture was stirred for 5 min at 0 °C and for 1 h at room temperature under nitrogen. The resulting product was cooled in an ice bath and hydrolyzed with saturated aqueous Na_2SO_4 (3 mL). Standard workup gave the crude alcohol. Bulb-to-bulb distillation (90–150 °C, 0.03 mm) afforded a white solid (561 mg, 2.9 mmol; 87% yield of $\sim$90% pure **43**). A sample was purified further on column B: IR 3610 (w), 3550–3150 (m), 3065 (w), 2950 and 2932 (s), 2865 (w), 1675 (w), 1475 and 1465 (w), 1440 (w), 1388 (w), 1361 (m), 1130 (w), 1030 (m), 878 (m), 685 (w) cm^{-1}; NMR δ 4.73 (m, 2 H), 4.00 (dd, J $\sim$2, 7 Hz, 1 H), 2.80–1.10 (m, 10 H), 0.83 (s, 9 H). The unsaturated alcohol was treated with *m*-chloroperoxybenzoic acid (85%; Aldrich) in methylene chloride (10 min at 5 °C and 6 h at room temperature). Workup[5] gave a quantitative yield of white solid (75% desired epoxy alcohol **42**, by NMR). A sample was purified by sublimation (90–100 °C, 1 mm): IR 3570 (w), 3450 (br), 3035 (w), 2955 and 2935 (s), 2860 (w), 1475 and 1465 (w), 1362 (m), 1238 (w), 1130 (w), 1035 (w), 1014 (w), 945 (m), 875 (w), 835 (w) cm^{-1}; NMR δ 4.00 (m, 1 H), 2.74 (s, 2 H), 2.40–1.20 (m, 10 H), 0.83 (s, 9 H).

Oxidation of the crude alcohol according to the method of Ratcliffe and Rodehorst[29] gave the crude ketoepoxide, which was purified on column B (155 °C, recovered yield $\sim$50%). The white solid had a longer retention time (column B) than ketone **5** and was characterized as **8**: mp 84.5–87.5 °C; IR 2950 (s), 2855 (w), 1753 (s), 1475 and 1465 (w), 1395 (w), 1361 (m), 1135 (w), 1105 (w), 940 (w), 880 (vw) cm^{-1}; NMR δ 2.83 (s, with some overlap of adjacent m, total $\sim$2.2 H), 2.60–1.20 (m, $\sim$9 H), 0.88 (s, 9 H); mass spectrum, *m/e* 208.1466 (M^+, calcd for $C_{13}H_{20}O_2$, 208.1463).

***exo*-3-*tert*-Butylspiro[bicyclo[3.2.1]octane-8,1′-cyclopropan]-6-one (11).** A mixture of zinc-copper couple (260 mg, $\sim$3.6 mg-atom Zn; Ventron-Alfa) and iodine (2–3 tiny crystals) in anhydrous ether (3.6 mL) was stirred under nitrogen and warmed to reflux temperature. As soon as the brown color of iodine disappeared, a portion of CH_2I_2 (20 μL; Aldrich) was syringed into the mixture. After 20 min at the same temperature, another crystal of iodine was added, followed immediately by a solution of CH_2I_2 (160 μL; total of $\sim$600 mg, 2.23 mmol) and alcohol **43** (100 mg, 0.52 mmol; sublimed at 0.04 mm) in ether (1.4 mL), and then another crystal of iodine. The reaction mixture was heated for 2.5 h longer, cooled in an ice bath, and quenched with saturated aqueous NH_4Cl (5 mL). Workup[33] followed by sublimation ($\sim$50 °C, 0.04 mm) gave **44** (78 mg; 72%): mp (VPC) 101–102 °C; IR 3615 (w), 3400 (w, br), 3065 (w), 2955 (sh), 2930 (s), 2870 (w), 1465 (w), 1435 (w), 1370 (w), 1362 (m), 1135 (w), 1032 (w), 1012 (m, br) cm^{-1}; NMR (220 MHz) δ 4.04 (dd, J = 2.6, 7.0 Hz, 1 H), 2.02 (dd, J = 7.0, 13.7 Hz, 1 H), 1.81 (br s, variable, 1 H), 1.80–1.04 (m, 8 H), 0.83 (s, 9 H), 0.57–0.27 (m, 4 H).

Oxidation of **44** with chromium trioxide-pyridine complex[29] gave a soft white solid which was purified by VPC (column B, 155 °C; 65% recovered yield) and identified as ketone **11**: mp 41–43 °C; IR 3065 (w), 2950 (s, split), 2870 (w), 1747 (s), 1480 and 1465 (w), 1402 (w), 1364 (m), 1175 (vw), 1138 (w), 1120 (w), 1005 (w) cm^{-1}; NMR (220 MHz) δ 2.40 (dd, J = 6.3, 17.8 Hz, 1 H) 2.06 (d, J = 17.8 Hz, 1 H), 1.95–1.20 (m, 7 H), 0.86 (s, 9 H), 0.66–0.32 (m, 4 H); mass spectrum, *m/e* 206.1694 (M^+, calcd for $C_{14}H_{22}O$, 206.1670).

The deuterated ketone **11D** was prepared from deuterated **41** (see below) by the same procedure. Spectroscopic properties confirmed the assigned structures. For **43D**: IR missing bands of **43** at 3065, 878, and 685 cm^{-1} NMR δ 4.73 (m, $\leq$5% of 2 H). For **44D**: NMR (220 MHz) δ 0.52 (d, J = 3.9 Hz, 1 H) and 0.37 (d, J = 3.9 Hz, 1 H) in place of 0.57–0.27 (m, 4 H) of **44**. For **11D**: NMR (220 MHz) δ 0.42 (br s, 2 H) in place of 0.66–0.32 (m, 4 H) of **11**.

***exo,exo*-3-*tert*-Butyl-8-methylene-d_2-bicyclo[3.2.1]oct-6-yl Acetate (41-d_2).** Methylene-d_2-triphenylphosphorane was prepared from methyl-d_3-triphenylphosphonium bromide (1.00 mmol; 99+ atom % D, Aldrich) and *tert*-butyllithium (1.6 M solution in *n*-pentane; Ventron-Alfa).[34] A solution of ketone **40** (0.95 mmol) in ether (1.3 mL) was added all at once to the cold ($\sim$5 °C) reagent. The resulting heavy suspension was stirred at room temperature for 40 min, cooled in an ice bath, and treated with D_2O (2 mL). Ether workup gave a crude product containing the desired alkene and triphenylphosphine oxide. The oil was taken up in pentane ($\sim$1.5 mL) to allow precipitation of the impurities, and the product was isolated by VPC on column B ($\sim$40% recovered yield of soft white solid). Comparison of the spectra with those obtained for **41** indicated that the new product was **41**-d_2 ($\geq$95% $=CD_2$; IR bands at 3065, 880, and 688 cm^{-1} absent; 1678-cm^{-1} band moved to 1640 cm^{-1}; NMR δ 5.67 (m) diminished to $\leq$5% of 2 H).

(1*R,5*S**,8*R**)-Spiro[bicyclo[3.2.1]oct-6-en-8,2′-oxirane].** By using the same procedure as described above for preparation of **36**, the parent enone **31** was converted to this epoxide in 90% yield. Purification on column A (130 °C) gave an analytical sample: mp 35–38 °C; IR 3050 (w), 2930 (s), 2850 (m), 1490 (w), 1442 (w), 1400 (w), 1278 (w), 1240 (w), 1060 (w), 988 (w), 917 (w, sh), 908 (m), 853 (w), 720 (m) cm^{-1}; NMR δ 5.93 (t, J $\sim$2 Hz, 2 H), 2.72 (s, 2 H), 2.10–1.87 (m, 2 H), 1.87–1.10 (m, 6 H); mass spectrum, *m/e* 136.0882 (M^+, calcd for $C_9H_{12}O$, 136.0888).

(1*R,5*R**,8*R**)-Spiro[bicyclo[3.2.1]octane-8,2′-oxiran]-6-one (34).** The epoxyalkene obtained in the previous reaction was converted to the epoxy alcohol, following Brown's oxymercuration-demercuration procedure.[27] The oxymercuration step (2.2 mmol scale) was allowed 29 h at room temperature before cooling and addition of the basic solutions. Ether workup gave a viscous oil (80% desired compound, <10% corresponding acetate, and <10% unidentified byproduct, by NMR). A sample (white solid) purified on column A (140 °C) had the following spectral properties: IR 3608 (w), 3200–3550 (m), 3035 (w), 2990 (w), 2935 (s), 2855 (w), 1485 (w), 1445 and 1440 (w, merged), 1240 (w), 1025 (w), 1005 (m), 960 (w), 918 (m), 858 (m) cm^{-1}; NMR δ 4.10 (dd with fine structure, $J \sim 3$ and 7 Hz, 1 H), 2.74 (s, 2 H), 2.30–1.20 (m, 11 H). Ratcliffe oxidation[29] (2.0 mmol scale) gave the corresponding ketone (**34**; 75% yield, 90% pure). **34** was collected by VPC (column A, 140 °C): mp 65–69 °C; IR 3035 (w), 2990 (w), 2938 (m), 2858 (w), 1750 (s), 1485 (w), 1440 and 1435 (w, merged), 1415 (w), 1238 (w), 1225 (w), 1150 (m), 1130 (w). 1115 (w), 1003 (w), 975 (w), 958 (w), 908 (w), 850 (w) cm^{-1}; NMR δ 2.75 (s, 2 H), 2.43–2.20 (m, 2 H), 2.20–1.30 (m. 8 H); mass spectrum, *m/e* 152.0822 (M$^+$, calcd for $C_9H_{12}O_2$, 152.0837).

***exo*-8-Oxobicyclo[3.2.1]octan-6-yl Acetate.** Enone **31** (1.17 g; 9.6 mmol) was converted to the ethylene ketal with ethylene glycol (1.06 mL) and *p*-toluenesulfonic acid in the usual fashion. Oxymercuration of the crude ketal (27.5 h at room temperature) and demercuration,[27] followed by ether workup, gave a cloudy oil (1.72 g; mixture of ketal alcohol and the corresponding acetate; 95% yield). A portion of the crude mixture (1.5 g) was dissolved in ether (9 mL) and treated with 5% aqueous HCl with vigorous stirring for 16.5 h at room temperature. At the end of this period, the aqueous layer was saturated with NaCl and extracted with ether (three times manually, then 16 h continuously). The combined extracts were washed with saturated $NaHCO_3$ and brine, and dried. The solvent was removed to yield a yellowish soft solid (1.19 g, 100%). VPC and NMR of the crude mixture revealed no more ketal or acetate. The crude keto alcohol was acetylated with acetic anhydride ($\sim$3 mL) and pyridine ($\sim$2 mL) in the usual fashion to furnish a crude oil ($\sim$70%, based on **31**). VPC on column B (150 °C) afforded a colorless liquid identified as *exo*-8-oxobicyclo[3.2.1]-octan-6-yl acetate: IR 2942 (m), 2858 (w), 1782 (w sh), 1755 and 1735 (s, merged), 1442 (w), 1370 and 1355 (w, merged), 1232 (s), 1172 (w), 1151 (w), 1071 (w), 1025 (m) cm^{-1}; NMR δ 5.05 (dd, $J \sim 3$, 8 Hz, 1 H), 2.62–1.40 (m, with s at 1.98 ppm, 13 H).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.87; H, 7.66.

(1*R,5*R**,8*S**)-Spiro[bicyclo[3.2.1]octane-8,2′-oxiran]-6-one (35).** The above ketoacetate underwent Wittig reaction with methylenetriphenylphosphorane[30] as described for conversion of **40** to **41** to furnish a mixture of *exo*-8-methylenebicyclo[3.2.1]octan-6-ol and the corresponding acetate. A sample of the acetate purified on column A (160 °C) had the following properties: IR 3070 (w), 2935 (m), 2855 (w), 1738 (s), 1680 (w), 1440 (w), 1375 (w), 1358 (w), 1235 (s), 1158 (m), 1025 (m), 882 (m), 685 (w) cm^{-1}; NMR δ 4.83 (dd, $J \sim 3$, 8 Hz, 1 H), 4.61 (m, 2 H), 2.80–2.00 (m, 3 H), 2.00–1.38 (m, with s at 1.93 ppm, 9 H).

The crude mixture of alcohol and acetate was treated with $LiAlH_4$ in ether (see reduction of **41**). After the usual workup the unsaturated alcohol was purified by VPC [column A, 150 °C, 52% recovered yield; IR 3608 and 3580 (w), 3550–3200 (w), 3065 (w), 2935 (m), 2850 (w), 1670 (w), 1440 (w), 1240 (w), 1125 (w), 1030 (w sh), 1023 (m), 878 (m), 850 (w), 685 (w) cm^{-1}; NMR δ 4.66 (m, 2 H). 3.98 (dd, $J \sim 3$, 7 Hz, 1 H), 2.77–2.40 (m, 1 H), 2.40–1.30 (m, 10 H)] and treated with *m*-chloroperoxybenzoic acid[5] in CH_2Cl_2 solution (30 min at 0 °C and 2.5 h at room temperature). The resulting epoxy alcohol appeared nearly pure and had properties different from the epimeric epoxide [longer retention time on column A; NMR δ 3.97 (dd, 1 H). 2.72 (s, 2 H), 2.33 (br s, 1 H), 2.20–1.20 (m, 10 H)]. Oxidation of the alcohol with chromium trioxide–pyridine complex[29] gave nearly pure **35** (66%). This epoxy ketone was purified on column A (retention time longer than that of **34**; recovered yield $\sim$35%) before photolysis: IR 3035 (w), 2945 (m), 2850 (w), 1752 (s), 1490 (w), 1445 and 1440 (w, merged), 1412 (w), 1395 (w), 1238 (w), 1150 (w), 1130 (m). 1112 (w), 1005 (w). 970 (w), 910 (m), 855 (w). 832 (w), 822 (w) cm^{-1}; NMR δ 2.80 (s. 2 H, with overlap of adjacent m, total 2.3 H), 2.60–1.20 (m. 9.7 H).

Acknowledgments. We thank Professor Steven Wolff for his counsel and significant contributions, Dr. Kurt L. Loening (Chemical Abstracts Service) for advice on nomenclature, Mr. William Rosenstein for technical assistance, Mr. S. T. Bella for microanalyses, and Mr. William Wittbold for ^{13}C and 220-MHz ^1H NMR spectra. The latter were obtained on an instrument at The Rockefeller University and operated by a consortium supported in part by National Science Foundation Grant PCM77-07671. This research was supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(14) Kinetic data are given in the Experimental Section.
(15) Simultaneous irradiation of **11** and **11D** in a merry-go-round apparatus at 30 °C was followed by VPC and yielded a relative rate $k_{11}/k_{11D} \sim 1.2$. This corresponds to a secondary α-deuterium isotope effect $k_H/k_D \sim 1.1$ per atom, a result that is in good agreement with earlier values in the range 1.09–1.15 for a variety of unimolecular cleavages. See Seltzer. S. *J. Am. Chem. Soc.* **1961**, *83*, 2625; Taagepera, M.; Thornton, E. R. *Ibid.* **1972**, *94*, 1168, and references cited therein. Values of k_H/k_D reported were corrected to 30 °C as described in these papers.
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Solid-State Photooligomerization of an Extended Chiral Bifunctional Monomer, (+)-2,4:3,5-Di-*O*-methylene-D-mannitol 1,6-Di-*trans*-cinnamate

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Abstract: Irradiation of crystalline (+)-2,4:3,5-di-*O*-methylene-D-mannitol 1,6-di-*trans*-cinnamate (**1**) induces intermolecular cyclobutane formation leading to chiral oligomers of increasing length. The dimer, trimer, tetramer, and pentamer have been isolated and characterized. The intramolecular distance between the olefinic residues within the molecules of **1** is larger than in any previous examples of solid-state photodimerization or oligomerization and, in spite of the large, bulky tetraoxa-*cis*-decalin group separating the reaction centers, the cinnamate groups of the monomer are properly aligned for intermolecular photocycloaddition. Crystals of **1** are monoclinic, a = 15.218 (6) Å, b = 13.217 (7) Å, c = 5.882 (3) Å, β = 76.95 (3)°; the space group is $P2_1$, with two molecules in the cell. The structure has been solved by direct methods and refined to an R factor of 0.043 on 2270 nonzero reflections. The crystal structure analysis establishes the correct molecular structure of the sugar alcohol derivative, previously in doubt, and elucidates the molecular packing which is responsible for the observed products. The chemical consequences of solid-state irradiation of compound **12**, a monothiophene analogue of **1**, have been considered; **12**, however, shows an unexpected reluctance to crystallize in the same structure as **1**.

Introduction

Solid state produced polymers are unique in their potential for specificity in directional properties compared to polymers prepared in fluid phases, and hence have been a subject of continuing interest.[2a-c] In recent developments it has been shown that optically active photodimer and photopolymers can be prepared in the medium of a chiral crystalline environment and that optical yields may approach 100%.[2d,e]

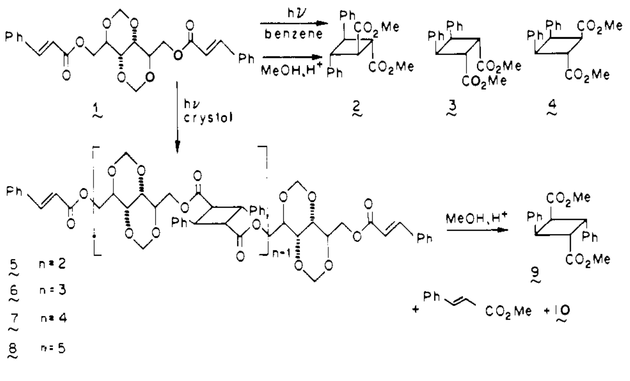
We describe here a solid-state photooligomerization reaction with several interesting features: an inexpensive, readily available starting material, D-mannitol, provides a source of chirality which is manifested by crystallization in a chiral crystallographic space group; the products contain alternating blocks of hydrophobic and hydrophilic regions (the latter may be accentuated by chemical modification); the low molecular weight oligomers can be isolated in pure form and provide potential starting materials for new syntheses; the two halves of the monomer are related by a molecular twofold axis which is very nearly retained in the crystal; finally it is the unique nature of the crystal structure which leads to the product specificity.

Results and Discussion

When the sugar alcohol dicinnamate derivative (+)-2,3:4,5-di-*O*-methylene-D-mannitol 1,6-di-*trans*-cinnamate (**1**) is irradiated in solution, photocycloaddition takes place to yield cyclobutane isomers, which, on ester exchange with methanol, yield the truxinic esters **2**, **3**, and traces of **4**. The optical yield in the synthesis of (−)-**2** is 48%.[3]

When the same D-mannitol dicinnamate **1** is irradiated in the *solid state* only intermolecular cycloaddition is observed and the products are the dimer, trimer, tetramer, pentamer, and higher oligomers of **1** where, in each case, the cyclobutane link has the α-truxillate (**9**) stereochemistry.

Prior to the work reported here solid-state photodimerization and oligomerization have been observed only in molecules where the two reacting olefins are separated by planar or nearly planar aromatic, ester, or amide groups, or short, unsubstituted aliphatic chains.[2b,e,4] Bulky groups such as the tetraoxa-*cis*-decalin have not been previously reported as "spacers" between the reaction centers in solid-state oligomerizations nor are there any examples where the two reacting groups are separated, as in **1**, by 11 covalent bonds. In addition, the molecular structure of **1** was open to question,[5] and it was therefore important to perform a crystal structure analysis in order to elucidate both the molecular structure of **1** and the nature of the intermolecular packing which leads to the formation of the observed photoproducts **5–8**.



Structure Description. The crystal structure analysis of **1** establishes the correct molecular structure of the diol, from

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