min at room temperature and then irradiated for 30 min under a slow stream of O_2 bubbling. The solvent was removed in vacuo to leave a yellow oil, which was separated on a Florisil column with ether/hexane as the eluant, giving 3-acetyl-3-acetoxyphthalide (16; 249 mg, 43%) and 3-acetoxy-3-methylisochroman-1,4-dione (17); 75 mg, 13%).[2c]

16: mp 97–99 °C; mass spectrum, m/e (relative intensity) 218 (M^+ – 18, 1), 192 (30), 191 (20), 176 (5), 175 (7), 148 (100). Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.23; H, 4.65.

17: mp 101–102 °C; mass spectrum, m/e (relative intensity) 218 (M^+ - 18, 3), 191 (25), 148 (100). Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.28; H, 4.71.

To a benzene solution of 3a (500 mg, in 600 mL) was added a solution of Rose Bengal (30 mg) in 10 mL of methanol. The solution was bubbled with O_2 for 30 min and then irradiated for 30 min under a slow stream of O_2 bubbling. Separation of the products on a Florisil column gave 16 (394 mg, 68%) and 17 (93 mg, 16%).

A solution of 3a (500 mg) and β-carotene (30 mg) in 600 mL of benzene was similarly irradiated for 1 h. The starting epoxynaphthoquinone 3a was recovered (260 mg), and the products were the dimers 6a (60 mg, 25%) and 6b (20 mg, 8.3%).

Acknowledgment. I am most grateful to Professor K. Maruyama for first attracting my interest to the photochemistry of epoxynaphthoquinones and for regularly reinforcing that interest and to Professor H. Suzuki for his discussions and valuable comments on the manuscript. This work was supported by the Saneyoshi Scientific Foundation.

Registry No. **3a**, 53948-58-6; **3b**, 63688-80-2; **3c**, 74954-87-3; **3d**, 85304-73-0; **3e**, 54328-51-7; **6a**, 73198-12-6; **6b**, 73245-74-6; **7a**, 75-07-0; **7b**, 123-38-6; **7c**, 123-72-8; **7d**, 78-84-2; **7e**, 97-96-1; **7f**, 122-78-1; **7g**, 947-91-1; **7h**, 112-54-9; **7i**, 555-16-8; **7j**, 123-11-5; **7k**, 104-87-0; **7l**, 100-52-7; **7m**, 104-88-1; **8a**, 69979-43-7; **8b**, 69918-94-1; **8c**, 69918-95-2; **8d**, 69918-96-3; **8e**, 85304-74-1; **8f**, 85304-75-2; **8g**, 85304-76-3; **8h**, 85304-77-4; **8i**, 69918-97-4; **8j**, 73624-01-8; **8k**, 73624-02-9; **8l**, 73624-03-0; **8m**, 73624-04-1; **9a**, 69918-98-5; **9b**, 69979-39-1; **9c**, 69979-40-4; **9d**, 69979-41-5; **9e**, 85353-58-8; **9f**, 85353-59-9; **9g**, 85353-60-2; **9i**, 69979-42-6; **9j**, 73678-76-9; **9k**, 73678-77-0; **9l**, 73678-78-1; **9m**, 73678-79-2; **14a**, 69918-99-6; **14b**, 69919-00-2; **14c**, 69919-01-3; **14d**, 69919-02-4; **14e**, 82279-21-8; **16**, 75761-78-3; **17**, 75761-79-4; **25**, 85304-78-5; **26**, 85353-61-3; **28**, 85304-79-6; **29**, 85353-62-4; **30**, 85304-80-9; **31**, 85353-63-5; **32**, 85304-81-0; **33**, 74954-88-4; **34**, 74954-89-5; **35**, 85304-82-1; **36**, 85304-83-2; **42**, 77455-25-5; **43**, 85304-84-3; O_2, 7782-44-7; acetone, 67-64-1; 2-pentanone, 107-87-9; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; acetophenone, 98-86-2.

Photochemical Rearrangements of β,γ-Cyclopropyl-β′,γ′-epoxy Ketones

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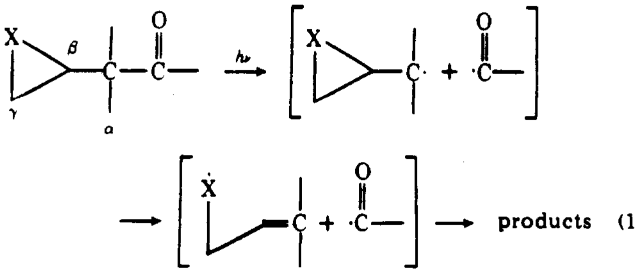
Received December 3, 1982

Ketones 1–5 have been prepared and photolyzed in benzene and in benzene–methanol (λ > 280 nm). Major volatile products were isolated by gas chromatography and their structures determined by a combination of spectroscopic and chemical methods. The products from 1–4 can be explained by way of α cleavage and selective fission of the carbon–oxygen bond of the epoxide, according to eq 1 (X = O). No effective competition from cleavage of the cyclopropane ring (eq 1, X = CH_2) is observed. Reaction of 2 is slow because of steric crowding, and there is evidence for a small amount of competitive photoisomerization of 2 to 1. In contrast with 1–4, ketone 5 decarbonylates with formation of 5a.

Previous investigations have provided good evidence that a major pathway in the photolysis of β,γ-cyclopropyl ketones is α cleavage, opening of the resultant cyclopropylmethyl radical to homoallyl under stereoelectronic control, and then product formation from the radical pair or biradical, as depicted in eq 1 (X = CH_2).[1,2] The photochemistry of β,γ-epoxy ketones follows an analogous path,[3,4] except that here opening of the oxirane ring occurs through preferred carbon–oxygen bond cleavage, with no evidence for the influence of stereoelectronic factors;[5-7] this is shown in eq 1 (X = O). These conclusions led us to inquire what pathways would be favored in the photochemistry of ketones incorporating both a cyclopropyl and



(1)

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(1) Smith, A. B., III; Brodsky, L.; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1975**, 509. Hess, L. D.; Jacobson, J. L.; Schaffner, K.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 3684.

(2) Takakis, I. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2383.

(3) Carlson, R. G.; Huber, J. H.-A.; Henton, D. E. *J. Chem. Soc., Chem. Commun.* **1973**, 223. Murray, R. K., Jr.; Goff, D. L. *Ibid.* **1973**, 881. Murray, R. K., Jr.; Morgan, T. K., Jr.; Polley, J. A. S.; Andruskiewicz, C. A., Jr.; Goff, D. L. *J. Am. Chem. Soc.* **1975**, *97*, 938.

(4) Ayral-Kaloustian, S.; Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1978**, *43*, 3314.

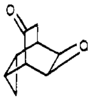
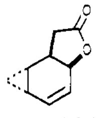
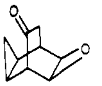
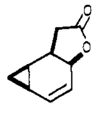
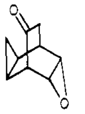
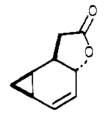
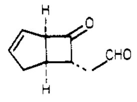
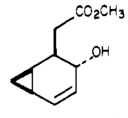
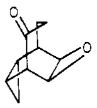
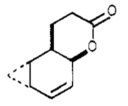
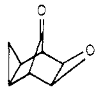
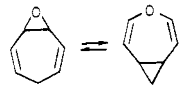
(5) Ayral-Kaloustian, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 314.

(6) For recent evidence suggesting the absence of stereoelectronic control also in the opening of epoxymethyl radicals generated thermally, see: Barton, D. H. R.; Motherwell, R. S. H.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2363.

(7) Recently reported observations suggest that stereoelectronic effects are important, however, in directing the photochemistry of two isomeric β,γ-epoxy α-diketones: Liao, C. C.; Lin, H. S.; Hseu, T. H.; Tang, C. P.; Wang, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 292. One difference between the two classes of compounds is the lower energy of the first excited states of α-diketones ($E_S \approx 65$, $E_T \approx 56$ kcal/mol) in comparison with those of alkanones ($E_S \approx 88$, $E_T \approx 80$ kcal/mol). The manifestation of stereoelectronic effects may well be associated with this lower energy, as well as with the availability in these α-diketones of several competitive pathways for reaction.

0022-3263/83/1948-1718$01.50/0

Table I. Products of Photolysis of Cyclopropyl Epoxy Ketones

ketone	quantum yield for disappearance	product (yield), %
 1		 1a (70%)
 2	0.38	 + 1a (12%)[a] 2a (23%)
 3	0.80	 3a (40%)  3b (15%)  3c (13%)[b]
 4	0.30	 4a (80%)
 5	0.72	 5a (≥50%)

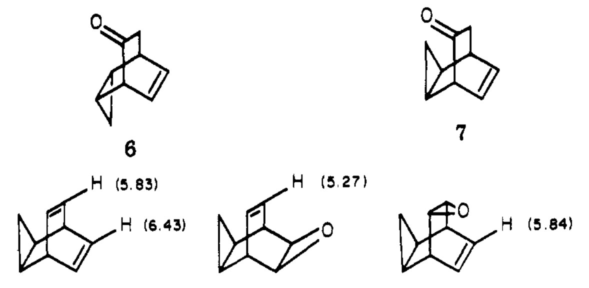
[a] See text. [b] Formed only in benzene-methanol as the solvent.

an epoxy ring, each β,γ to the carbonyl group, and in particular whether carbon-oxygen cleavage would also dominate these reactions. We have explored this question through preparation and photolysis of several novel β,γ-cyclopropyl-β',γ'-epoxy ketones. The results not only clarify the photochemistry of these specific compounds but more importantly they also contribute to our understanding of the relative importance of different possible courses of reaction for acyl alkyl biradicals that incorporate these structural features.

Results

The compounds studied, ketones **1**–**5**, were photolyzed in solution (0.01–0.04 M) in benzene and in benzene containing ~4% methanol (v/v, ~1 M) through Pyrex ($\lambda > 280$ nm) at ~25 °C. Irradiations were typically carried to 80–100% conversion, although photolysis of **4** ceased after 60–75% reaction. The results presented in Table I include all volatile products formed in yields of greater than ~3%. Since both the starting ketones and several of the products are relatively unstable, the yields reported are estimated from proton nuclear magnetic resonance (NMR) spectra before purification and are based on unrecovered starting material. In general the presence of methanol in the solvent did not materially affect the results. Formation of **3c** is an exception, and the yield of **3a** was essentially unaltered by the added methanol. Apart from **4a**, all products were isolated by preparative vapor-phase chromatography (VPC). Structures of these products, preparation of the starting ketones, and the treatment of **4a** are discussed below. We have determined quantum yields for four of these photolyses. The data, which are included in Table I, were obtained for benzene solutions irradiated in a merry-go-round apparatus at ~313 nm (potassium chromate filter,[8] medium-pressure mercury arc) by using as a chemical actinometer the concurrent photolysis of valerophenone.[8] The values recorded are for disappearance of substrate at ~10% conversion. Because of difficulties in quantitative separations of rather unstable compounds the results are only approximate (±~12%). Appropriate conditions could not be found for **1**, but qualitative observations suggested that its rate of disappearance lies between those of **2** and **3**.

Chart I



Preparative Experiments. Ketones **1**–**5** were rather sensitive to heat and traces of acid but were fully characterized after purification by preparative VPC under relatively mild conditions. These substrates were available from the corresponding unsaturated tricyclic ketones, which were prepared as previously described. Thus oxidation of **6**[9,10] (Chart I) with *m*-chloroperbenzoic acid yielded epoxy ketone **1** in good yield. The assigned stereochemistry is consistent with several earlier observations in structurally related systems, indicating that attack on the double bond occurs highly selectively from the side away from the cyclopropane ring.[11-13] Oxidation of the isomeric unsaturated ketone **7**[14,15] with *m*-chloroperbenzoic acid gave both possible products, epoxy ketones **2** and **3**, in similar amounts. A tentative stereochemical assignment for these isomers was possible on the basis of NMR spectra, particularly the shielding of cyclopropyl methine hydrogens by the oxirane ring[16] in **3** ($\Delta\delta \approx 0.2$ ppm) relative to their position in **2**. Also supporting this assignment is the similarity of chemical shifts in **2** and its lower homologue **5**, the stereochemistry of which (see below) is secure from its mode of preparation. More rigorous evidence for the stereochemistry of **2** and **3** came from an alternative synthesis of **2** starting with the known tricyclic diene **8**, which is available on treatment of the tosylhydrazone of **6** with methyllithium.[9,17] Epoxidation of **8** gave a mixture

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(8) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

(9) de Meijere, A.; Weitmeyer, C.; Schallner, O. *Chem. Ber.* **1977**, *110*, 1504.

(10) Freeman, P. K.; Balls, D. M.; Brown, D. J. *J. Org. Chem.* **1968**, *33*, 2211.

(11) Fray, G. I.; Hilton, R. J.; Teire, J. M. *J. Chem. Soc. C* **1966**, 592.

(12) Prinzbach, H.; Klaus, M.; Mayer, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 883. Prinzbach, H.; Kagabu, S.; Fritz, H. *Ibid.* **1974**, *13*, 482.

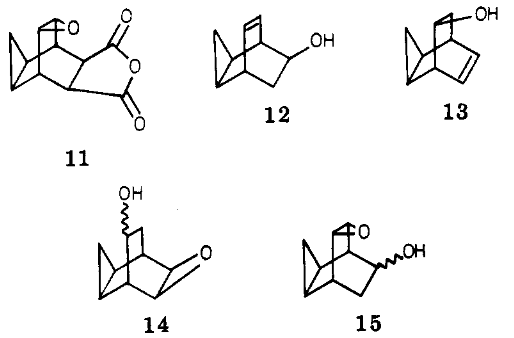
(13) In this regard note also the selective exo attack on the double bond of bicyclo[3.2.1]oct-6-enes discussed in ref 5.

(14) Prinzbach, H.; Schal, H.-P.; Hunkler, D. *Tetrahedron Lett.* **1978**, 2195.

(15) Schal, H.-P. Dissertation, Albert-Ludwigs-Universität, Freiburg im Breisgau, Germany, 1978. We are indebted to Prof. Horst Prinzbach for the generous provision of experimental details and spectroscopic data from this dissertation.

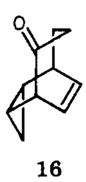
(16) Jefferies, P. R.; Rosich, R. S.; White, D. E. *Tetrahedron Lett.* **1963**, 1853. Tori, K.; Kitahonoki, K.; Takano, Y.; Tanida, H.; Tsuji, T. *Ibid.* **1964**, 559. Franz, J. E.; Osuch, C.; Dietrich, M. W. *J. Org. Chem.* **1964**, *29*, 2922. Huisgen, R.; Moebius, L; Mueller, G.; Stangl, H.; Szeimies, G.; Vernon, J. M. *Chem. Ber.* **1965**, *98*, 3992. Agosta, W. C.; Wolff, S. *J. Am. Chem. Soc.* **1977**, *99*, 3355.

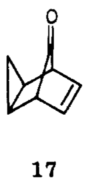
Chart II

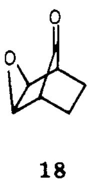


of ethers that, from its spectroscopic properties and subsequent reactions, is largely a ~2:1 mixture of epoxy cyclopropanes **9** and **10**. Attempted purification of this mixture by VPC or adsorption chromatography under a variety of conditions led either to no separation or else to destruction of major component **9**. The minor product **10**, however, could be purified by VPC; its properties agreed with those on record for this substance synthesized[14,15] by degradation of the related anhydride **11**[11] (Chart II). Reaction of the mixture **9** and **10** with lithium aluminum hydride led to reduction of **9** to alcohol **12**, which was directly oxidized[18] to ketone **6**; the more hindered epoxide **10** was recovered unchanged under these conditions. Upon more vigorous reduction of the mixture with sodium in liquid ammonia,[14,15] both **9** and **10** were attacked, and the resulting alcohols **12** and **13** were directly oxidized[18] to ketones **6** and **7**. These transformations require that the major product of epoxidation of **8** be either **9** or else the isomeric endo epoxide. NMR data presented with structures **8**–**10** indicate that **9** is correct. These measurements show that olefinic protons in **8** and **10** are shielded ~0.6 ppm by either a cyclopropane[19] or an oxirane[16] ring syn to the double bond. The even farther upfield position of the corresponding signal for **9** is understandable only as the additive effect of shielding by two such rings, and this requires the stereochemistry shown. Treatment[5,20] of the mixture of **9** and **10** with mercuric acetate in aqueous acetonitrile followed by borohydride reduction furnished epoxy alcohols **14** and **15**, and these were oxidized[18] without purification to **2** and **1**, respectively. Formation of **1** from **10** is expected, and this independent preparation of **2** from **9** provides the desired evidence concerning the stereochemistry of **2** and **3**.

Epoxy cyclopropyl ketone **4** was prepared from the related unsaturated ketone **16**.[21] Although **16** itself failed to undergo epoxidation, the alcohol formed on hydride reduction reacted smoothly with peracid. Reoxidation[18] of the hydroxy group then furnished **4**. Selective epoxidation on the unshielded side of the double bond is expected,[11,12] as noted above.


16


17


18

Scheme I

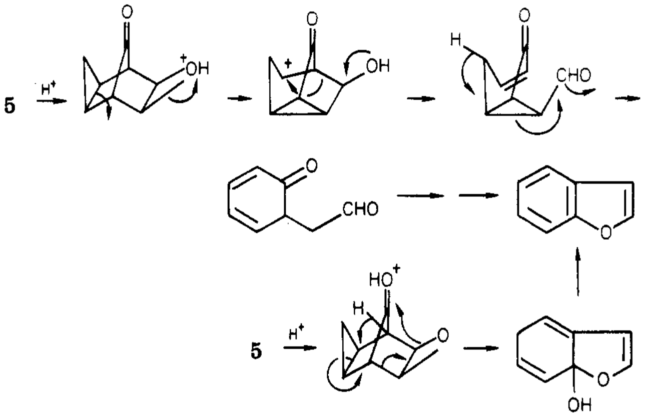
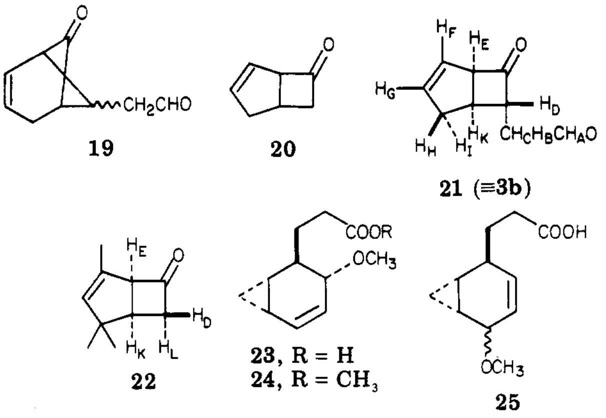


Chart III



In the remaining series, oxidation of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-one (**17**)[22] proceeded without difficulty to give a single product, **5**. Here, specific exo attack by the oxidant has good precedent in the stereoselective formation of **18** on epoxidation of norbornen-7-one.[23] Incidental to preparation of **5**, we observed an interesting acid-catalyzed reaction. Treatment of this ketone with *p*-toluenesulfonic acid in benzene leads to rearrangement with loss of water and formation of benzofuran. Two possible rationalizations for this aromatization are shown in Scheme I. This process apparently also occurs in the isobutane chemical-ionization mass spectrum of **5**, which has only two sizeable ions, *m/z* 137 [$(M + 1)^+$, 100%] and 119 [$(M - H_2O + 1)^+$, 50%]. In contrast, the electron-impact spectrum lacks significant ions appropriate to benzofuran but does have *m/z* 107 and 108 [$(M - HCO)^+$, $(M - CO)^{+\cdot}$] that may correspond to the photochemical decarbonylation product to be discussed below.

Structures of Products. Of the products in Table I, **2a**[15] and **5a**[24] are previously described compounds, and our samples gave infrared (IR) and NMR spectra in agreement with those reported. The remaining substances, other than **4a**, have been fully characterized and show spectroscopic

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[17] de Meijere, A.; Schallner, O.; Weitemeyer, C. *Tetrahedron Lett.* **1973**, 3483.

[18] Ratcliffe, R., Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000 and references cited therein.

[19] Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 98 and references cited therein.

[20] Brown, H. C.; Hammar, W. J. *Tetrahedron* **1978**, *34*, 3405 and references cited therein.

[21] Takakis, I. M.; Agosta, W. C. *J. Org. Chem.* **1978**, *43*, 1952.

[22] Halton, B.; Battiste, M. A.; Rehberg, R.; Deyrup, C. L.; Brennan, M. E. *J. Am. Chem. Soc.* **1967**, *89*, 5964. Clarke, S. C.; Frayne, K. J.; Johnson, B. L. *Tetrahedron* **1969**, *25*, 1265.

[23] Gassman, P. G.; Pape, P. G. *J. Org. Chem.* **1964**, *29*, 160.

[24] (a) Klein, H.; Kursawa, W.; Grimme, W. *Angew. Chem.* **1973**, *85*, 624; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 580. (b) Attempted VPC of **5a** at 145 °C led to formation of benzaldehyde. Related reactions have been described by: Miyamoto, R.; Tezuka, T.; Mukai, T. *Tetrahedron Lett.* **1975**, 891. Schiess, P. W.; Wisson, M. *Helv. Chim. Acta* **1974**, *57*, 1692.

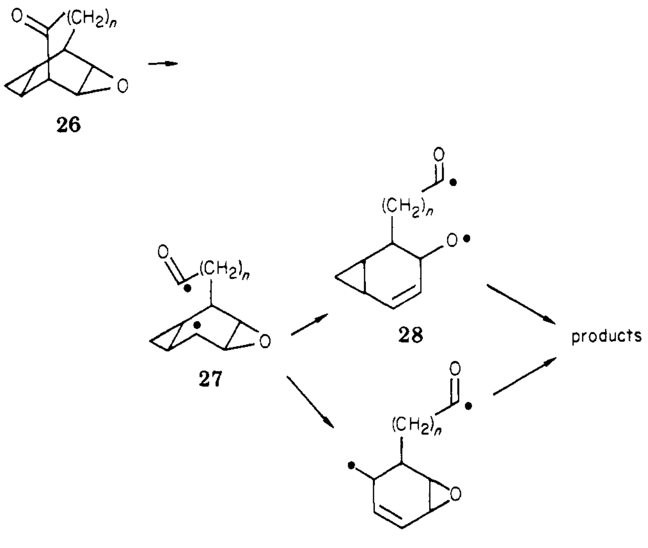
properties compatible with their assigned structures. Detailed analyses of these spectra are given in the Experimental Section. For reasons discussed later, in the case of **3b** it was important to decide between this structure and the isomeric bicyclo[3.1.1]heptenone **19** (Chart III). Strong support for **3b** came from comparison of IR, proton NMR, and mass spectra for our compound with those reported for the parent ketone **20**[25] and two methyl-substituted derivatives.[26] In **3b**, **20**,[25] **22**,[26] and a related isomer[26] of **22** the signal for H_E (see **21**) appears at $\delta \geq 4.0$ ppm. For **3b** and **20** this signal and those for H_F and H_G are complex multiplets having nearly identical spin-spin couplings and chemical shifts in the two compounds. Also, the base peak in the mass spectrum of both **3b** and **20** is at *m/z* 66 ($C_5H_6^+$). In contrast to these relationships, the reported NMR spectra of various bicyclo[3.1.1]hept-2-en-6-ones[27,28] suggest that neither bridgehead proton in **19** would resonate below 3 ppm. Furthermore, formation of *m/z* 66 from **19** would imply a relative complex rearrangement, whereas for **3b** and **20** it can result merely from a [2 + 2] cycloreversion of the cyclobutanone. In addition to these arguments the ^{13}C NMR and the ultraviolet (UV) spectra of the photoproduct are in much better accord with structure **3b** than **19**. The assignment of stereochemistry to the side chain in **3b** is tentative and based on the observation that $J_{KD} \approx 6.6$ Hz. Earlier analysis of the spectrum of **22**[26] yielded values of 6.0 Hz for J_{KD} and 8.1 Hz for J_{KL}.

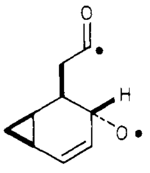
In the crude product from photolysis of **4** there appeared characteristic signals attributable to **4a**, but this δ-lactone proved to be unusually sensitive to heat and traces of acid. Attempted purification by preparative VPC under a variety of conditions led to loss of both lactone and cyclopropane functionalities; no lactone was recoverable. We finally found that in refluxing methanol **4a** slowly reacted to give largely **23**, accompanied by a minor amount of another methoxy acid. Esterification with diazomethane furnished **24**, which could be purified by VPC and fully characterized. Previous experience[29] indicates that displacement reactions on 2-cyclohexen-1-yl esters under nonacidic conditions are complex and, depending on the nucleophile, leaving group, and solvent, can lead to S_N2 reactions with inversion, as well as S_N2' reactions with syn or anti stereochemistry. From these observations and from the spectroscopic properties of **23** and **24**, we deduce the indicated structures and stereochemistry for these compounds. That is, **23** is the product of direct displacement on **4a** with inversion. We consider that these results, together with the general pattern of photochemical behavior of **1**–**3**, establish the structure of **4a** as shown. The minor product (~20%) formed in the reaction of **4a** with hot methanol appears to be one of the S_N2' ethers **25**.

Discussion

Aside from the surprising formation of a small amount of **1a** from **2**, which we discuss later, all the products formed on photolysis of **1**–**4** can be accounted for through application of the sequence of eq 1 (X = O) (via **26** → **27** → **28**, Scheme II). The structural differences in **1**–**4** influence the fate of **28** but introduce only a minor effect on the efficiency of its formation. It is interesting that for **1**, **2**, and **4**, the presence of methanol in the solvent does not divert the essential course of reaction. It is only in **3** that some hydroxy methyl ester is formed, perhaps because here cyclization of acyl alkoxy biradical **30** to a trans-fused γ-lactone is slower.[30] This stereochemistry can also account for formation of the keto aldehyde **3b** through the following sequence of events. Competitive disproportionation of **30** to **31**, followed by fragmentation (presumably photochemical and via α cleavage),[31] can lead to the unsaturated ketene **32**. Intermediate formation of a ketene is indeed confirmed by IR measurements during the course of irradiation. Intramolecular thermal [2 + 2] cyclization of unsaturated ketenes at room temperature is known,[32] so that self-addition in **32** to yield **3b** is credible. Crossed, rather than straight, [2 + 2] cyclization would have given **19**. There is published evidence[27] for just such crossed closure of a similar unsaturated ketene to form a bicyclo[3.1.1]hept-2-en-6-one under conditions that leave unclear whether the reaction is thermal or photochemical, and there is also a report[33] suggesting that both straight and crossed thermal cycloaddition occur in a closely related system. For these reasons we felt obliged to distinguish between **3b** and its alternative **19** with some care. The arguments favoring **3b** given above were adduced with this issue in mind.

Scheme II





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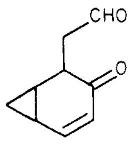

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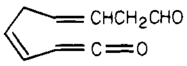

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[25] Schuster, D. I.; Axelrod, M.; Auerbach, J. *Tetrahedron Lett.* **1963**, 1911. Fleming, I.; Au-Yeung, B.-W. *Tetrahedron Suppl.* **1981**, *No. 1*, 13. We are grateful to Prof. David I. Schuster, New York University, for providing the 60-MHz NMR spectrum of **20**.

[26] Beereboom, J. J. *J. Am. Chem. Soc.* **1963**, *85*, 3525.

[27] Erman, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 3828.

[28] Schaffer, G. W.; Pesaro, M. *J. Org. Chem.* **1974**, *39*, 2489.

[29] Stork, G.; Kreft, A. F., III *J. Am. Chem. Soc.* **1977**, *99*, 3850. Dobbie, A. A.; Overton, K. H. *J. Chem. Soc., Chem. Commun.* **1977**, 722.

(30) Lactone **3a** is stable to the reaction conditions, a fact indicating that **3c** arises through capture of an intermediate by methanol. It is known that hydroxy esters such as **3c** can form both from direct capture of an alkoxy acyl biradical and from capture of the hydroxy ketene formed on disproportionation of the biradical. Likewise, there are precedents for lactone formation both by collapse of the biradical and by way of the hydroxy ketene. Details are given in ref 4 and 5.

(31) Baldwin, J. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1969**, *91*, 2396. Bellamy, A. J.; Crilly, W. *J. Chem. Soc., Perkin Trans. 2* **1973**, 122.

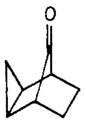
(32) Masamune, S.; Fukumoto, K. *Tetrahedron Lett.* **1965**, 4647. Yates, P.; Fallis, A. G. *Ibid.* **1968**, 2493. Baldwin, S. W.; Page, E. H., Jr. *J. Chem. Soc., Chem. Commun.* **1972**, 1337.

(33) Smit, A.; Kok, J. G. J.; Geluk, H. W. *J. Chem. Soc., Chem. Commun.* **1975**, 513.

The isomerization of **2** to a mixture of **2a** and **1a** was unexpected. Ketone **2** was prepared by two independent routes, and we satisfied ourselves that contamination of **2** by **1** prior to irradiation was not the explanation for formation of **1a**. We take the formation of **1a** to reflect a small amount of rearrangement of **2** to **1** during irradiation. In comparison with **1**, **3**, and **4**, the photolysis of **2** is inefficient, and recovery of volatile products is low. This behavior is attributable to the steric hindrance introduced by the two three-membered rings flanking the carbonyl group. In **2** α cleavage leads to a biradical (see **27**, $n = 1$) that has little mobility and must reclose readily. It is well-known that under such circumstances unfavorable and otherwise unobservable photochemical transformations may take place.[34] In this situation permitting minor processes, irradiation of **2** presumably leads to a small amount of cleavage of the internal bond of the cyclopropane, inversion of the 1,3 biradical with relief of steric congestion, and collapse to **1**.[35] Relatively efficient photoisomerization of **1** then could furnish **1a**.

Apart from this abnormal behavior of **2**, the isolated products from **1–4** arise through carbon–oxygen cleavage of the oxirane ring. Material recoveries of 68–80% indicate that opening of the β,γ-cyclopropyl group (see **29**) cannot be very important, even on the extreme assumption that all such cleavage of the cyclopropane leads to unrecovered products. This latter seems to be an unrealistic assumption, since irradiation of the simple β,γ-cyclopropyl ketones related to **1–4** causes just such cleavage of the cyclopropane with recoveries of 60–78% of volatile products.[2] Thus, the cyclopropyl group appears to offer no effective competition, and the carbon–oxygen scission previously seen in simple β,γ-epoxy ketones[3-5] dominates the photochemical behavior of these more complex substrates. The simplest explanation for this selectivity is that less energy is required for homolysis of oxiranes than cyclopropanes; for the parent three-membered rings this amounts to some 6–9 kcal/mol,[36] and a similar difference between opening oxiranylmethyl and cyclopropylmethyl radicals to the corresponding homoallylic species (see **28** and **29**) seems reasonable. The difference in energy between the two processes in these biradicals (see **27**) may be even greater if zwitterionic stabilization[5] of the acyl alkoxy biradical formed on rupture of the epoxide (as **28**) significantly decreases the activation energy for carbon–oxygen bond fission.

In contrast with the behavior of **1–4**, ketone **5** undergoes decarbonylation on photolysis, yielding the known fluxional ether **5a**, which exists largely as the oxirane isomer at room temperature.[24] It is instructive to compare decarbonylation of **5** with the photochemical behavior of the two model compounds **18** and **33**. Cyclopropyl ketone **33** decarbonylates and furnishes 1,4-cycloheptadiene (**34**) as the only monomeric product.[37] Epoxy ketone **18**, on the other hand, gives some 25–30% of diverse monomeric products that arise not from decarbonylation but rather from carbon–oxygen bond cleavage in the epoxide.[4] There is good evidence that systems related to **33** suffer decarbonylation in a stepwise fashion by way of initial α cleavage,[38] suggesting that reaction of **5** proceeds in the same way (see **27**, $n = 0$). The fluxional nature of **5a** prevents us from deducing directly from the product whether decarbonylation occurs with concomitant rupture of the internal bond of the cyclopropane or the oxirane ring (or both). The limited available information, however, implies most simply that in the decarbonylation reaction cleavage of a cyclopropane is faster than that of an oxirane and thus that in **27** ($n = 0$) it is the cyclopropane that opens as carbon monoxide is lost. This implied preference for internal scission of a cyclopropane has an interesting parallel in the difference in rates of thermal Cope rearrangement of *cis*-1,2-divinylcyclopropane (**35**) and the corresponding epoxide **36**. While **35** reacts rapidly at room temperature,[39] rearrangement of **36** requires several hours at 98 °C.[40,41]



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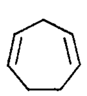

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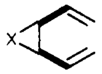

35, X = CH_2
36, X = O

With the carbonyl group in a one-carbon bridge, then, decarbonylation is the preferred pathway. Otherwise, these representative β,γ-cyclopropyl-β′,γ′-epoxy ketones behave photochemically like simpler β,γ-epoxy ketones, without serious competition from cleavage of the cyclopropane ring. If this behavior proves to be general, it should provide a useful supplement to the mechanistic scheme of eq 1.

Experimental Section

General Methods. All VPC was carried out on a Varian Aerograph Model 920 or A-90-P gas chromatograph by using columns prepared from aluminum tubing (0.25 in. diameter) packed with 25% QF-1 on 40/60 Chromosorb W (columns A–D were 2, 4, 8, and 10 ft, respectively) and operating at a helium flow rate of 90–110 mL/min. Unless otherwise specified, IR spectra were obtained for CCl_4 solutions on a Perkin-Elmer Model 237B spectrophotometer, and NMR spectra were obtained for $CDCl_3$ solutions on a Nicolet/Oxford NT-300 (300 MHz for ^1H and 75.46 MHz for ^{13}C) spectrometer. A Varian T-60A (60 MHz) spectrometer was also used as indicated. All NMR signals are reported relative to tetramethylsilane (~1% internal reference; 0 ppm). UV spectra were recorded for benzene solutions on a Cary Model 14 spectrophotometer. Samples for melting points and analyses were usually repurified by recrystallization before use. Melting points were obtained on a Thomas-Hoover apparatus in sealed capillaries and are corrected. Solutions were dried over $MgSO_4$, K_2CO_3, or Na_2SO_4, and solvents were removed in vacuo with a rotary evaporator.

(1α,2α,4α,5α,6β,8β)-3-Oxatetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]decan-9-one (1). Method A. *exo*-Tricyclo[3.2.2.$0^{2,4}$]non-8-en-6-one (**6**; 392 mg, 2.92 mmol)[9,10] in CH_2Cl_2 (19 mL) was treated with *m*-chloroperbenzoic acid (Aldrich, 85% pure; 651 mg, 3.20 mmol), and the solution stirred for 4 days at room temperature. The resulting mixture was diluted with ether and washed with 5% NaOH, 10% Na_2SO_3, 5% NaOH, water, and brine and dried. Removal of solvent gave a soft solid (406 mg) which contained

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[34] Such circumstances, for example, favor formation of alkoxycarbenes from saturated ketones, a point discussed by: Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* **1975**, *8*, 209. For examples of related effects of steric hindrance on α-cleavage reactions see: Agosta, W. C.; Wolff, S. *J. Am. Chem. Soc.* **1976**, *98*, 4182 and also ref 2.

[35] There is good evidence[2] that this process does not occur under comparable conditions in the photochemistry of the β,γ-cyclopropyl ketone related to **2**, *endo*-tricyclo[3.2.2.$0^{2,4}$]nonan-6-one.

[36] See in this regard: Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279. Gray, P.; Williams, A. *Trans. Faraday Soc.* **1959**, *55*, 760 and references cited therein.

[37] Clarke, S. C.; Johnson, B. L. *Tetrahedron* **1971**, *27*, 3555. This result is reported for photolysis in pentane solution, in a quartz apparatus, and with a medium-pressure mercury lamp.

[38] Cooke, R. S.; Lyon, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 7312 and references cited therein.

[39] Brown, J. M.; Golding, B. T.; Stofko, J. J., Jr. *J. Chem. Soc., Chem. Commun.* **1973**, 319. Schneider, M. *Angew. Chem.* **1975**, *87*, 717; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 707.

[40] Pommelet, J. C.; Manisse, N.; Chuche, J. *Tetrahedron* **1972**, *28*, 3929.

[41] For a discussion of theoretical explanations of this difference see: Mollere, P. D.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 3226.

ca. 30% starting material. VPC separation (column C, 170 °C) gave **6** (20%) and a white solid (t_r = 12.5 min) identified as **1**: 41%; mp 154.0–155.0 °C (from *n*-hexane); IR 3078 (vw), 3020 (w), 2944 (w), 1736 (s), 1395 (w), 1259 (vw), 1156 (m), 1062 (m), 1032 (s, br), 945 (m), 879 (w), 817 (w) cm^{-1}; ^{1}H NMR δ 3.30–3.21 (m, 2 H), 3.04 (dd, J = 4.8, 4.8 Hz, 1 H), 2.86 (m, 1 H), 2.24 (dd, J = 17.8, 2.5 Hz, 1 H), 2.07 (dd, J = 17.8, 3.1 Hz, 1 H), 1.30–1.15 (m, 2 H), 1.08 (dddd, $J \simeq$ 7.8, 7.5, 4.5, 4.0 Hz, 1 H), 0.64 (ddd, $J \simeq$ 7.5, 7.0, 6.5 Hz, 1 H); UV λ_{max} 289 nm (ϵ 63.5), ϵ_{313} = 25.5; mass spectrum, m/z 150.0702 (M$^+$ calcd for $C_9H_{10}O_2$, 150.0680).

Method B. Ratcliffe[18] oxidation of alcohol **15** gave **1** as described below for the preparation of **2** (method B).

(1α,2α,4α,5α,6α,8α)-3-Oxatetracyclo[3.3.2.0^{2,4}.0^{6,8}]decan-9-one (2). Method A. *endo*-Tricyclo[3.2.2.0^{2,4}]non-8-en-6-one[14,15] (**7**; 1.08 g, 8.1 mmol) in CH_2Cl_2 (67 mL) was epoxidized with *m*-chloroperbenzoic acid (12.70 mmol, added in portions) in 2 days. A workup as above afforded a mixture of starting material (~10%) and two isomeric epoxides. The latter were separated by VPC [column B, 135 °C; t_r = 15–22 (20%) and 27–40 min (33%)]. The latter was characterized as **2**: mp (sublimed and recrystallized from *n*-hexane) 169–174 °C (with decomposition and sublimation); IR 3095 (vw), 3044 (m), 2978 (m), 1739 (s), 1412 (w), 1395 (m), 1317 (m), 1173 (m), 1139 (w), 1029 (m), 939 (m), 878 (m), 826 (w) cm^{-1}; ^{1}H NMR δ 3.69 (m, 5 lines, 2 H), 3.14 (m, 1 H), 2.83 (m, 1 H), 2.08 (dd, J = 18.8, 3.2 Hz, 1 H), 1.72 (dd, J = 18.8, 3.0 Hz, 1 H), 1.41 (m, 2 H), 0.86 (ddd, $J \simeq$ 7.5, 7.5, 7.9 Hz, 1 H), 0.68 (ddd, $J \simeq$ 7.5, 3.8, 3.8 Hz, 1 H); UV λ_{max} 281 nm (ϵ 47.0), ϵ_{313} = 15.6. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.95; H, 6.73. The second solid product was identified as **3** (see data below).

Oxidation of **7** with *p*-nitroperbenzoic gave approximately the same ratio of products.

Method B. Tricyclo[3.2.2.0^{2,4}]nona-6,8-diene[9,17] (**8**; 1.11 g, 9.36 mmol) was epoxidized with *m*-chloroperbenzoic acid (ca. 10 mmol, 3.5 h) according to the above procedure. Spectral analysis of the resulting mixture revealed the presence of epoxides **9** and **10**[14,15] (ca. 2:1 from NMR) as the main products. Attempts to separate the two epoxides by VPC, TLC, sublimation, or distillation resulted either in the decomposition of **9** or no separation. The mixture was distilled bulb-to-bulb (aspirator) to yield a colorless oil (74%). A portion of this (240 mg, 1.79 mmol) was added to a freshly prepared suspension of mercuric acetate[5] (643 mg, 2.02 mmol) in water (2 mL) and acetonitrile (2 mL). The mixture was stirred at room temperature for 4 days (more mercuric acetate was added at intervals, 1.0 mmol total) and treated with cold 3 N aqueous NaOH (3 mL). After 5 min a cold solution (3 mL) of 0.5 M $NaBH_4$ in 3 N NaOH was added, and the mixture stirred for 10 min. A workup[5] afforded an oily solid (75%), mainly alcohols **14** and **15** (as evidenced by IR and NMR spectra). Ratcliffe oxidation[18] of the crude mixture gave a partial solid (70%). The two major products were separated by VPC on column B (135 °C) and identified as ketones **1** (12%; t_r = 38–43 min; spectra identical with those of ketone **1** prepared above) and **2** (26%; t_r = 30–38 min; spectra identical with those of ketone **2** prepared above).

(1α,2β,4β,5α,6α,8α)-3-Oxatetracyclo[3.3.2.0^{2,4}.0^{6,8}]decan-9-one (3). Epoxidation of **7**[14,15] gave **3** (20% t_r = 15–22 min; see preparation of **2**, method A, for details) which was characterized by the following data: mp (*n*-hexane) 150.5–152.0 °C; IR 3096 (w), 3025 (m), 2986 (m), 1737 (s), 1460 (w), 1415 (m), 1317 (w), 1257 (w, br), 1194 (w), 1164 (m), 1139 (m), 1032 (m), 944 (m), 898 (w), 848 (m) cm^{-1}; ^{1}H NMR δ 3.42 (dd, $J \simeq$ 4.5, 4.4 Hz, 1 H), 3.22 (dd, $J \simeq$ 4.4, 4.3 Hz, 1 H), 3.07 (dd, $J \simeq$ 4.7, 4.5 Hz, 1 H), 2.81 (m, 1 H), 2.06 (dd, J = 19.0, 3.1 Hz, 1 H), 2.00 (dd, J = 19.0, 2.8 Hz, 1 H), 1.24 (dddd, $J \simeq$ 8.5, 8.3, 4.4, 4.0 Hz, 1 H), 1.13 (dddd, $J \simeq$ 8.5, 8.3, 4.6, 4.2 Hz, 1 H), 0.44 (ddd, $J \simeq$ 7.7, 7.7, 7.7 Hz, 1 H), 0.15 (ddd, J = 7.5, 4.2, 4.2 Hz, 1 H); UV λ_{max} 296 nm (ϵ 44.4), ϵ_{313} = 23.6. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.79, H, 6.63.

Preparation of 6 and 7 from 9 and 10. Reduction of a mixture of **9** and **10** (see preparation of **2**, method B) with $LiAlH_4$ (6 h, room temperature) gave a mixture of unreacted **10** and alcohol **12** which were separated on column C (110 °C, t_r = 22, 15 min).

Oxidation of **12** with $CrO_3{\cdot}pyr_2$ complex[18] gave ketone **6** which was characterized by its properties (t_r, IR, NMR) that were identical with those of an authentic sample.[9,10]

A mixture of **9** and **10** was reduced with sodium in liquid ammonia.[14,15] Spectra of the crude product (92%) revealed nearly complete reduction to alcohols **12** and **13**. The mixture was oxidized with $CrO_3{\cdot}pyr_2$.[18] The resulting ketones were separated on column D (125 °C) and identified as **6** (51%; t_r = 51–58 min) and **7** (16%; t_r = 43–50 min) by comparison of their spectra with those of authentic **6**[9,10] and **7**.[15]

(1α,2α,4α,5α,6β,8β)-3-Oxatetracyclo[3.3.3.0^{2,4}.0^{6,8}]undecan-9-one (4). A solution of *exo*-tricyclo[3.3.2.0^{2,4}]dec-9-en-6-one[21] (**16**; 65 mg, 0.44 mmol) in ether (2.5 mL) was added to a slurry of $LiAlH_4$ (58 mg, 1.52 mmol) in ether (4.5 mL). The mixture was stirred for 2.8 h at room temperature. A standard workup[5] (saturated Na_2SO_4/ether) gave an oil (64 mg, 97%) which appeared to be the desired enol: VPC (column A, 125 °C) t_r = 2.5 min; IR 3650 (w), 3575–3150 (m), 3055 (w), 3023 (w), 2934 (s), 2875 (w), 1450 (w), 1438 (w), 1025 (w), 1010 (m), 959 (w), 930 (w), 870 (w), 703 (m) cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 5.57 (m, 2 H), 3.53 (m, 1 H), 2.90 (br s, variable, 1 H), 2.80–2.30 (m, 2 H), 2.30–1.00 (m, 4 H), 1.10–0.60 (m, 2 H), 0.60–0.00 (m, 2 H). The crude product was epoxidized with *m*-chloroperbenzoic acid (0.50 mmol; see procedure for **1**). The reaction was only ca. 65% complete in 3.3 days (epoxidation was also incomplete with *p*-nitroperbenzoic acid). A sample of the epoxy alcohol was isolated by VPC (column A 125 °C; t_r = 12–15 min): IR 3600 (w), 3575–3100 (m), 3044 (w), 2978 (m), 2894 (s), 1448 (w), 1414 (w), 1402 (w), 1182 (w, split), 1162 (w), 1077 (m), 1048 (m), 1025 (w), 987 (w), 963 (w), 920 (w), 890 (w), 852 (w), 838 (w) cm^{-1}; NMR (60 MHz, CCl_4) δ 3.85 (m, 1 H), 3.20–2.20 (m, 4 H), 2.20–1.30 (m, 3 H), 1.30–0.06 (m, 4 H). Oxidation of the crude mixture with $CrO_3{\cdot}pyr_2$ complex[18] gave a mixture of **16** and the desired epoxy ketone **4**, which were separated by VPC on column A (150 °C). Ketone **4** (t_r = 11 min, 32% overall yield based on reacted **16**) was identified from the following data: mp 145–148 °C (*n*-hexane); IR 3100 (w), 3030 (s), 2949 (s), 1712 (s, br), 1449 (w), 1415 (m), 1312 (w), 1285 (w), 1248 (w), 1225 (w), 1124 (w), 1100 (w), 1073 (w), 1035 (m), 970 (w), 939 (w), 888 (w), 874 (w) cm^{-1}; ^{1}H NMR δ 3.27 (dd, $J \simeq$ 7.1, 3.8, 1 H), 3.18 (m, 2 H), 2.88 (m, 1 H), 2.72 (ddd, $J \simeq$ 15.1, 11.0, 10.5 Hz, 1 H), 2.18 (ddd, $J \simeq$ 15.1, 5.1, 2.6 Hz, 1 H), 1.92–1.84 (m, 2 H), 1.19 (dddd, $J \simeq$ 8.1, 7.6, 4.2, 3.8 Hz, 1 H), 1.09 (dddd, $J \simeq$ 8.1, 7.8, 4.1, 3.9 Hz, 1 H), 0.72 (ddd, J = 5.8, 4.4, 4.4 Hz, 1 H), 0.60 (ddd, J = 8.2, 8.2, 5.9 Hz, 1 H); UV λ_{max} 285 nm (ϵ 41.8), ϵ_{313} = 13.0; mass spectrum, m/z 164.0827 (M$^+$ calcd for $C_{10}H_{12}O_2$, 164.0837).

(1α,2α,3α,4α,5α,6α)-3-Oxatetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonan-9-one (5). Oxidation of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-one (**17**, 8.3 mmol)[22] with *m*-chloroperbenzoic acid (12.8 mmol total) over a period of 21 h (see procedure for **1**) gave a yellowish solid. Recrystallization from CCl_4 or VPC (column B, 150 °C; t_r = 9.5 min) gave a white solid, **5**: 52%; mp (*n*-hexane) 94.0–95.0 °C; IR 3061 (w), 3024 (w), 1863 (w), 1799 (s, br), 1450 (w), 1373 (w, split), 1308 (w), 1231 (w), 1188 (m), 1122 (w), 1042 (m), 911 (w), 879 (m), 827 (w) cm^{-1}; ^{1}H NMR δ 3.92 (s, with fine structure, 2 H), 2.63 (s, with fine structure, 2 H), 1.58 (ddd, J = 7.1, 3.4, $\leq$1 Hz, 2 H), 0.93 (dt, J = 7.1, 7.1 Hz, 1 H), 0.66 (dt, J = 7.1, 3.4 Hz, 1 H); UV λ_{max} 284 nm (ϵ 25.0), ϵ_{313} = 5.8. Anal. Calcd for $C_8H_8O_2$: C, 70.57, H, 5.92. Found: C, 70.37; H, 5.84.

General Procedure for Photolysis. For preparative experiments a solution of purified ketone (0.01–0.04 M) in anhydrous benzene (0–4% methanol by volume, as specified) contained in a toroidal Pyrex glass vessel (capacity ~70 mL) was flushed with dry nitrogen for 30 min and irradiated at ca. 30 °C with a Hanovia 450-W medium-pressure mercury lamp, cooled in a quartz well.

Quantum Yield Measurements. Solutions of ketones **2**–**5** were prepared in benzene, and 2.6 mL of each was placed in a separate 13 × 100 mm test tube. These were irradiated at 313 nm simultaneously with 0.1 M solutions (2.6 mL) of valerophenone in benzene by following previously reported procedures.[8,42] Disappearance of valerophenone was used as the actinometer in all cases, and formation of acetophenone was used as an additional actinometer with ketones **3** and **5**. All determinations were carried out by VPC on column A. The percents reactions (5–15%) of epoxy ketone and valerophenone were measured by direct com-

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(42) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1292.

parison of VPC areas before and after irradiation. Yields of acetophenone were determined by calibration. Quantum yields for disappearance of ketones **2–5** are shown in Table I.

Photolysis of 1. Irradiation of **1** (93 mg, 0.62 mmol) in benzene for 1.8 h resulted in ~95% conversion. The crude photolysate (92 mg) was taken up in CH_2Cl_2, and the solids were filtered (~20% insoluble material). NMR and VPC (column A, 125 °C) analysis revealed the presence of one major (70%) product and six or more minor products. The major component of the mixture (**1a**) was isolated by VPC (t_r = 16 min; 60%) as a waxy solid: mp 50–58 °C; IR 3098 (w), 3066 (w), 2950 (w), 1786 (s), 1640 (w), 1448 (w), 1412 (w), 1401 (w), 1333 (w), 1318 (w), 1234 (w), 1161 (m), 1140 (m), 1039 (w), 1011 (m), 996 (m), 935 (m, with sh), 868 (w), 794 (w) cm^{-1}; ^{1}H NMR δ 6.29 (ddd, *J* = 10.2, 5.3, 1.8 Hz, 1 H), 5.31 (dd, *J* = 10.2, 1.5 Hz, 1 H), 4.74 (ddd, *J* = 8.8, ~1.8, ~1.5 Hz, 1 H), 3.20 (ddd, *J* ≈ 12.4, 8.8, 8.2 Hz, 1 H), 2.59 (dd, *J* = 17.0, 8.2 Hz, 1 H), 2.35 (dd, *J* = 17.0, 12.6 Hz, 1 H), 1.37 (m, 2 H), 1.06 (ddd, *J* = 8.4, 8.4, 4.5 Hz, 1 H), 0.28 (ddd, *J* = 5.9, 4.5, 4.5 Hz, 1 H); mass spectrum, *m/z* 150.0685 (M^+, calcd for $C_9H_{10}O_2$, 150.0681).

Photolysis in the presence of methanol gave the same yield of **1a**, a ≤5% yield of methyl esters, and several minor volatile products which were not isolated.

Photolysis of 2. Irradiation of **2** (58 mg, 0.39 mmol) in benzene for 9.5 h resulted in ca. 80% conversion. The crude photolysate (53 mg) was taken up in CH_2Cl_2, and the solids (~37%) were filtered. VPC chromatography of the photolysate on column A (125 °C) gave several minor products (≤10% total), ketone **2**, and a mixture of **1a** and **2a** (ca. 1:2 ratio; 35% corrected yield), identified by comparison of its NMR spectrum with those of pure **1a** and **2a**.[15] A sample of **2a** obtained by VPC had IR and NMR spectra identical with those of authentic **2a**. Reinjection of this material on column A (145 °C) resulted in ca. 30% rearrangement to a new γ-lactone (IR 1789 cm^{-1}) with no cyclopropyl hydrogen signals in the NMR spectrum.

Photolysis in benzene/methanol gave the same results, with only a trace amount of methyl esters.

Photolysis of 3. Irradiation of **3** (56 mg, 0.37 mmol) for 2 h resulted in >95% conversion. VPC (column A, 125 °C) and NMR after filtration of the solids (~14%) revealed the presence of four or more products, two of which were isolated and characterized (~8% minor products not isolated) as follows. **3a**: t_r = 13–17 min (~40% of crude mixture); IR 3050 (w, split), 2903 (w), 1800 (s), 1613 (w), 1421 (w), 1396 (w), 1350 (w), 1216 (w), 1196 (w, sh), 1187 (m), 1106 (w), 1095 (w), 1039 (m), 1025 (m), 956 (m), 945 (m), 854 (w), 706 (w) cm^{-1}; ^{1}H NMR δ 6.08 (ddd, *J* = 10.1, 5.2, 2.6 Hz, 1 H), 5.97 (br d, *J* = 10.1 Hz, 1 H), 4.14 (d m, *J* = 11.4 Hz, 1 H), 2.74 (ddd, *J* = 15.8, 5.9, 0.7 Hz, 1 H), 2.43 (dd, *J* = 15.8, 13.7 Ha, 1 H), 2.19 (dddd, *J* = 13(?), 11.3, 5.9, 2.5 Hz, 1 H), 1.59–1.45 (m, 2 H), 0.93 (ddd, *J* ≈ 8.2, 5.9, 5.8 Hz, 1 H), 0.85 (ddd, *J* ≈ 5.4, 5.7, 5.7 Hz, 1 H); mass spectrum, *m/z* 150.0677 (M^+ calcd for $C_9H_{10}O_2$, 150.0680). **3b**: t_r = 6.5 min, ~5.2% of crude mixture; IR 3088 (w), 2928 (m), 2867 (w), 2839 (w), 2734 (w), 1778 (s), 1728 (s), 1598 (w), 1433 (w), 1398 (w), 1377 (w), 1274 (w), 1200 (w), 1066 (w), 1035 (w), 919 (w) cm^{-1}; ^{1}H NMR (see **21**) δ 9.77 (br s, with fine structure,[43] H_A), 5.93 and 5.68 (both m, H_F, H_G) 4.28 (m, H_E), 3.35 (m, H_D), 2.95 (dd, *J* = 4.8, 18.9 Hz, H_B) 2.84 (d m, *J* = 17.7 Hz, H_H or H_I), 2.77 (dd, with fine structure, *J* = 8.5, 18.9, ≤1 Hz, H_C), 2.66 (d m, *J* = 17.7 Hz, H_I or H_H) 2.53 (ddd, *J* ≃ 6.5, 6.6, 6.8 Hz, H_K), signal assignments and the following coupling constants were derived from spin-decoupled spectra (J_{BC} = 18.8 Hz; J_{HI} = 17.7 Hz; J_{CD} = 8.5 Hz; $J_{DK} \approx J_{EK} \approx J_{IK} \approx$ 6.6 Hz; J_{BD} = 4.7 Hz; $J_{FG} \approx$ 5.2 Hz; $J_{EF} \approx$ 2.4 Hz; $J_{HK} \leq$ 1 Hz; J_{AB}, J_{AC} = 0–0.6 Hz); ^{13}C NMR δ 208.46 (s), 198.91 (d, *J* = 174 Hz), 133.65 (d, *J* = 162 Hz), 125.83 (d, *J* = 166 Hz), 72.06 (d, *J* = 147 Hz), 58.62 (d, *J* = 131 Hz), 43.07 (td, *J* ≈ 127, 26 Hz), 40.29 (t, *J* ≈ 130 Hz), 33.72 (d, *J* = 143 Hz); UV λ_{max} (*n*-hexane) 304 nm (ε 230); mass spectrum, *m/z* 150.0699 (M^+ calcd for $C_9H_{10}O_2$, 150.0681), 66.0448 (base peak, calcd for C_5H_6, 66.0470). A higher yield (~15%) of **3b** was obtained when the photolysis was stopped at ~80% conversion (15–20 min). When the progress of the photolysis was followed by IR (benzene), the formation and disappearance (with or without light) of a ketene band (2072 cm^{-1}) was observed. Addition of methanol to aliquots containing ketene, **3a**, and **3b**, in the dark, did not affect the distribution of products observed by VPC.

Photolysis of **3** in the presence of methanol gave a new product in addition to **3a** (~40%) and ca. eight minor volatile products (~30% total yield of compounds with CHO, CO_2CH_3, and OCH_3 groups as evidence by IR and NMR spectra, including some **3b**). The crude photolysate contained <10% insoluble material. The new product was isolated by VPC on column A (~125 °C; t_r = 7.5–12.5 min; ~13%) and identified as **3c**: IR 3685–3290 (m, br), 3090 (w), 3055 (m), 2968 (m), 2922 (w), 1738 (s), 1642 (w), 1433 (m), 1247 (m, br), 1150 (m, br), 1017 (m), 945 (w), 901 (w), 848 (w) cm^{-1}; ^{1}H NMR δ 6.09 (ddd, *J* = 10.0, 5.3, 2.5 Hz, 1 H), 5.41 (dd, *J* = 10.0, 1.5 Hz, 1 H), 3.72 (s, 3 H), 3.70–3.63 (m, 1 H), 2.82 (dd, *J* = 15.3, 5.6 Hz, 1 H), 2.55 (dd, *J* = 15.3, 7.5 Hz, 1 H), 2.25 (br s, 1 H), ~2.03 (m, 1 H), 1.42–1.27 (m, 2 H), 0.77 (ddd, *J* ≈ 8.4, 8.3, 4.6 Hz, 1 H), 0.21 (ddd, 4.7, 4.6, 4.5 Hz, 1 H); mass spectrum (CI) *m/z* 183.1023 [$(M + 1)^+$, calcd for $C_{10}H_{15}O_3$, 183.1021], 183.0936 (M^+; calcd for $C_{10}H_{14}O_3$, 182.0943). When an aliquot of the photolysate containing **3a**, **3c**, and methanol was stored in the dark, no change was observed in the VPC ratios of the two products; **3a** stored in methanolic benzene for 1 day did not form **3c**.

Photolysis of 4. Irradiation of **4** (29.9 mg, 0.18 mmol) for 6.5 h resulted in 60–75% conversion. The crude photolysate contained ~20% insoluble material and one major product (**4a**, 50–60% of mixture, ~80% based on reacted starting material), as evidence by the following spectral data: IR 3026 (w), 2950 (m, br), 1744 (s), 1370 (w), 1344 (w), 1236 (w), 1170 (w), 1059 (m), 1023 (w), 911 (w) cm^{-1}; ^{1}H NMR δ (ddd, *J* = 10.1, 5.3, 2.6 Hz, 1 H), 5.41 (ddd, *J* ≈ 10.2, 1.3, 1.2 Hz, 1 H), 4.82 (dm, *J* ≈ 7.1 Hz, 1 H), 3.16 (m, 1 H), 2.8–2.4 (m, 2 H?), 1.76 (m, 2 H?) 1.33 (m, 1 H), 1.22 (m, 1 H), 0.95 (ddd, *J* ≈ 8.4, 8.4, 5.0 Hz, 1 H), 0.45 (m, 1 H). Attempted separation of **4a** by VPC gave <25% of a rearranged product and no **4a**. Treatment of the crude photolysate with refluxing methanol for ca. 2 days afforded a mixture containing **23** and its isomers (~60%). Esterification with CH_2N_2 furnished **24** and **25** (~4:1 by NMR and VPC), isolated by VPC on column A (135 °C). **24** (t_r = 7–10 min, 27%) was characterized as follows: IR 3099 (w), 2975 (w), 2830 (w), 1741 (s), 1430 (w, with sh), 1311 (w), 1245 (w), 1188 (w), 1158 (w), 1089 (m), 967 (w), 856 (m) cm^{-1}; NMR δ 5.51 (m, 2 H), 4.12 (br dd, *J* = 5.4, 1.4 Hz, 1 H), 3.67 (s, 3 H), 3.44 (s, 3 H), 2.48 (ddd, *J* ≈ 4.7, 5.3, 5.6 Hz, 1 H), 2.34 (m, 2 H), 1.79 (m, 2 H), 1.48 (m, 1 H), 1.01 (m, 1 H), 0.59 (ddd, *J* = 8.4, 8.3, 4.6 Hz, 1 H), 0.43 (ddd, *J* ≈ 5.1, 5.0, 4.6 Hz, 1 H); mass spectrum, *m/z* 210.1257 (M^+ calcd for $C_{12}H_{18}O_3$, 210.1256). **25** (t_r = 5.5–7 min, 12–20%) has the following characteristics: IR, same as for **24**, except 1076 cm^{-1} instead of 1089 cm^{-1}; ^{1}H NMR δ 5.66 (m, 2 H), 4.02 (br d, *J* ≈ 2.0 Hz, 1 H), 3.67 (s, 3 H), 3.39 (s, 3 H), 2.46 (m, 3 H), 1.91 (d, *J* ≈ 7 Hz, 1 H), 1.87 (dd, *J* ≈ 7.7, 1.5 Hz, 1 H), 1.24 (m, 1 H), 0.96 (m, 1 H), 0.56 (ddd, *J* = 8.8, 8.7, 4.5 Hz, 1 H), 0.15 (ddd, *J* ≈ 4.8, 5.0, 5.1 Hz, 1 H).

Photolysis of **4** in the presence of methanol gave **4a** (~50%) and <10% methyl ester(s).

Photolysis of 5. Irradiation of **5** (26 mg, 0.19 mmol) for 5.5 h gave a bright yellow photolysate. Analysis of the crude mixture indicated ca. 90% conversion and >40% yield of a new product. Attempts to isolate this product on column D (145 °C) resulted in its total rearrangement to benzaldehyde (identified by comparison with the IR and NMR spectra of authentic material) and a less stable aldehyde. For minimization of loss or decomposition of the product, a fresh photolysate solution in benzene was injected directly on column B (90–95 °C), and the volatile material (t_r = 2.5 min) was collected (~25% isolated yield based on converted **5**) and characterized as **5a**.[24] During a separate run the progress of the reaction was followed by IR and NMR ($CDCl_3$). No ketene was observed in the photolysate, and **5a** appeared to be the major (≥80%) product forming from **5** at low or high conversion. **5a** gradually decomposed at room temperature.

The presence of methanol during the photolysis gave ~10% of material containing CO_2CH_3 (by NMR) in addition to a ≥50% yield of **5a**.

Acid-Catalyzed Rearrangement of 5. A solution of **5** (12 mg, 0.09 mmol) in benzene (1.5 mL) was treated with *p*-toluenesulfonic acid (~2 mg) for 3 h at 80 °C. After a standard

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[43] In the structurally related example of 2-(2-oxocyclohexyl)ethanal the aldehydic proton appears as a singlet: Larchevêque, M.; Valette, G.; Cuvigny, T. *Tetrahedron* **1979**, *35*, 1745.

workup, VPC on column B (90–95 °C) afforded a colorless oil (4 mg, 33%; t_r = 5.5 min) which was identified as benzofuran by comparison of its IR and NMR spectra and VPC retention time with those of authentic benzofuran (Aldrich). Treatment of **5** with *p*-toluenesulfonic acid at 30 °C (2.5 days in benzene) or heating in toluene at 120 °C (1.7 days) in the absence of an acid catalyst resulted in very little decomposition and no benzofuran.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Mr. Eric Orava for technical assistance, Mr. Francis Picart for 300-MHz spectra, and Mr. S. T. Bella for microanalyses. The 300-MHz NMR spectrometer was purchased with assistance from the National Science Foundation and from the Camille and Henry Dreyfus Foundation. Low-resolution mass spectra were obtained on facilities supported by National Institutes of Health Grant RR-862.

Registry No. **1**, 85267-47-6; **1a**, 85267-48-7; **2**, 85316-99-0; **2a**, 85317-00-6; **3**, 85317-01-7; **3a**, 85317-02-8; **3b**, 85267-49-8; **3c**, 85267-50-1; **4**, 85267-51-2; **4a**, 85267-52-3; **5**, 85267-53-4; **5a** (isomer 1), 50356-49-5; **5a** (isomer 2), 50356-50-8; **6**, 50744-35-9; **7**, 68297-49-4; **8**, 7092-05-9; **9**, 85317-03-9; **10**, 85317-04-0; **12**, 50898-31-2; **13**, 85317-05-1; **14**, 85267-54-5; **16**, 65311-34-4; **16** (hydroxy derivative), 85267-55-6; **16** (hydroxyepoxy derivative), 85267-56-7; **17**, 17876-06-1; **24**, 85267-57-8; **25**, 85267-58-9.

Photochemical Cycloadditions of 2,3-Dihalobenzo[*b*]thiophenes: Stereochemical and Mechanistic Results

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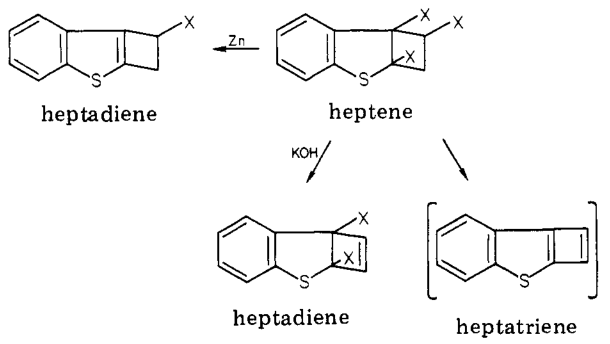
Received August 27, 1982

Synthetic approaches to 2-thia-3,4-benzobicyclo[3.2.0]-1,3,6-heptatriene and to 2-thia-3,4-benzobicyclo-[3.2.0]-1,3-heptadiene required halogenated cyclobutanes derived from $[_\pi 2_s + {}_\pi 2_s]$ photocycloadditions of 2,3-dichlorobenzo[*b*]thiophene and either vinyl bromide or 1,2-dichloroethylene. Addition reactions of vinyl bromide and dichloroethylene with 2,3-dichlorobenzo[*b*]thiophene and with 2,3-dibromobenzo[*b*]thiophene are reported. X-ray crystal structures of the two adducts derived from vinyl bromide and 2,3-dichlorobenzo[*b*]thiophene specify their stereochemistry. The adducts to 2,3-dibromobenzo[*b*]thiophene are linear, and structure determinations for these compounds are also reported.

The photocycloaddition of halo olefins to benzo[*b*]thiophene was first reported by Neckers and Dopper in 1970.[1] These authors reported that such cycloadditions were best carried out as triplet-sensitized processes, with sensitizers with triplet energies above 68 kcal/mol sufficing to catalyze the reaction. In early studies,[1] it was shown that the stereochemistry of the cyclic adducts reflected the stereochemistry of the starting olefins, though the reactions were not 100% stereospecific.

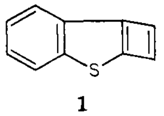
Photochemical $[_\pi 2_s + {}_\pi 2_s]$ cycloaddition reactions of electron-deficient olefins and benzo[*b*]thiophene derivatives generally provide high-yield routes to fused-ring systems, and 2-thia-3,4-benzobicyclo[3.2.0]-1,3-heptadiene and 2-thia-3,4-benzobicyclo[3.2.0]-3,6-heptadiene were both originally synthesized by this route.[2] Recent reports from our laboratories have applied similar processes to other fused-ring heterocyclic systems,[3-12] and the scope of such cycloadditions is now such that many heterocyclic derivatives can be produced by this general pathway. Some of the known photoreactions for monoheteroatom fused systems with alkynes and alkenes are outlined in Scheme I.

The 2-thia-3,4-benzobicyclo[3.2.0]heptene, -heptadiene, and -heptatriene ring skeletons are readily approached by such a photochemical process which builds a cyclobutane ring between a benzo[*b*]thiophene and a partner addend. If either or both possess a readily dissociable pair of functional groups, stereochemically positioned so that they are readily eliminated, the desired ring systems can be derived (eq 1).

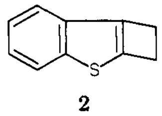


(1)

As part of a program seeking the highly strained heterocycles 2-thia-3,4-benzobicyclo[3.2.0]-1,3,6-heptatriene (**1**) and 2-thia-3,4-benzobicyclo[3.2.0]-1,3-heptadiene[2] (**2**)



1



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