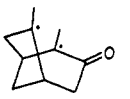
value of 61.8 kcal/mol which we find for the carvone triplet is, in all probability, indicative of a $\pi \rightarrow \pi^*$ configuration of the triplet state and is in excellent agreement with the value of 61 ± 1 kcal/mol estimated by Hammond[10] for the cyclohexenone ($\pi \rightarrow \pi^*$). Sensitization and quenching studies have shown that the photocycloaddition of cyclopentenones and cyclohexenones to olefins[10-12] involves triplet excited states. The initial interaction between the excited state and the olefins leads to the formation of a complex (exciplex) which then collapses to a 1,4 biradical[13,14] and ultimately gives the photoproduct. Attempts by laser flash photolysis to identify this biradical, i.e.



were unsuccessful.

Acknowledgment. Thanks are due to Dr. J. C. Scaiano for allowing us to use the laser flash photolysis facilities and for his helpful suggestions.

Registry No. *l*-I, 6485-40-1; *d*-I, 2244-16-8; II, 39196-52-6; III, 4638-90-8.

(10) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967). See also D. R. Kearns and G. Marsh, *J. Chem. Phys.*, **49**, 3316 (1968).
(11) P. de Mayo, J. P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968).
(12) R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, 1, 301 (1969).
(13) P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **91**, 5090 (1969).
(14) E. J. Corey, J. Dolf Bass, L. Le Mortieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1966).

Cytochalasin Support Studies.[1] The C_{14}-C_{19} Subunit of Cytochalasin C. Intramolecular 2 + 2 Photochemical Cycloaddition of Vinyl Sulfones[2]

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Received February 5, 1982

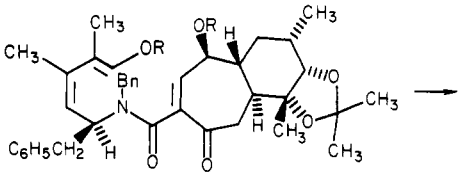
An intramolecular $2\pi + 2\pi$ photochemical cycloaddition between a six-membered ring vinyl sulfone and a five-membered ring vinylogous ester is described. The process occurs with moderate regiospecificity, the direction being controlled by a *cis*-acetonide moiety on the six-membered ring. Attempts to fragment the β-alkoxy sulfone adduct to trigger a DeMayo ring expansion were unsuccessful.

Introduction

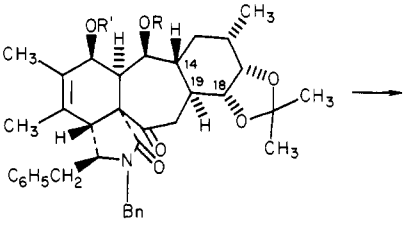
One conceptual approach to the synthesis of the cytotoxic mold metabolite Cytochalasin C (**3**) involves the union of two strategies that we have established in simpler model systems,[4,5] namely, intramolecular Diels–Alder cyclization of the chiral (*Z*)-dienyl amide **1** to lactam **2**[6] followed by an enolate-promoted intraannular fragmentation to generate the eleven-membered ring diene moiety of Cytochalasin (**3**)[7] (Scheme I).

The plan for synthesis of the cyclization substrate **1** was based upon the union of the previously available chiral dienyl amine **4**[5] and the cycloheptenone carboxylic acid **5**. Synthesis of **5** was envisaged to arise (in several steps) via a DeMayo-type retroaldol strategy[8] with the polycyclic sulfone **34**. Construction of vinyl sulfone photochemical precursor **33** was projected to be possible from sulfinic acid elimination of either sulfoxide **18** or **19**, which in turn, could be prepared from olefin **13** (see Scheme II).

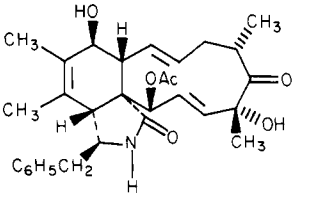
Scheme I



1, R′ = $CH_2CH_2Si(CH_3)_3$



2, R′ = $CH_2CH_2Si(CH_3)_3$



3

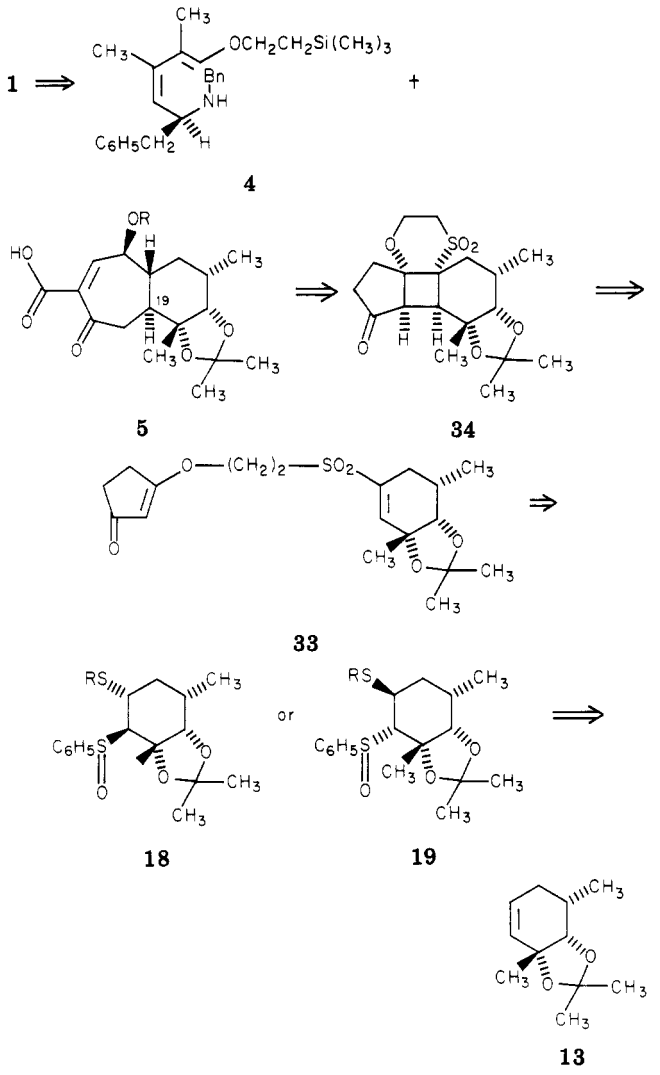
Results and Discussion

Conversion of 5-methyl-1,3-cyclohexanedione **6** to vinylogous ester **7** followed by lithium aluminum hydride reduction affords 5-methylcyclohex-2-en-1-one (**8**) in 78%

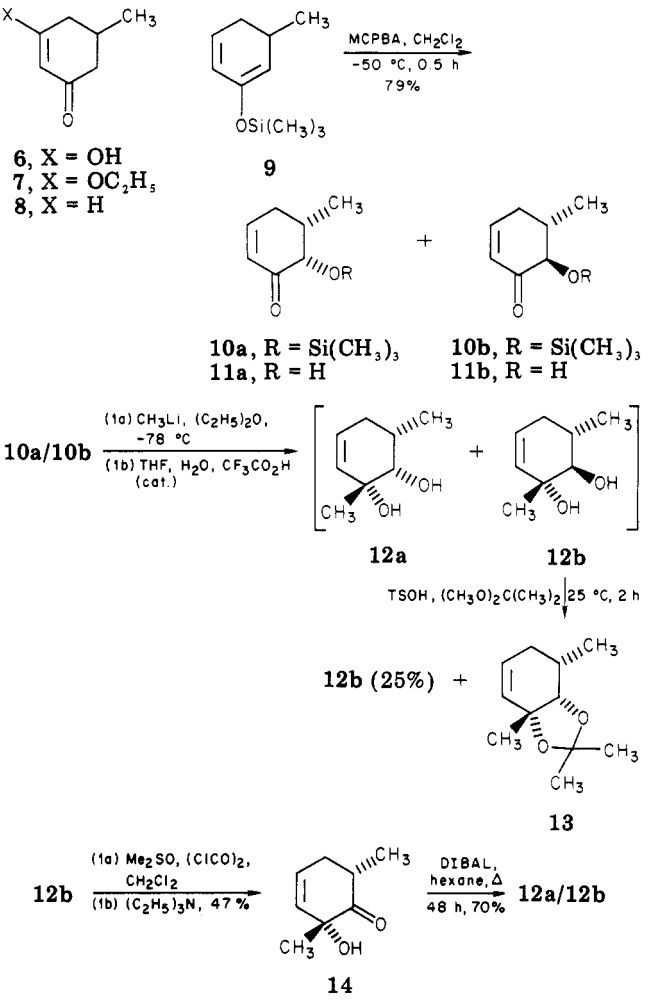
(1) Cytochalasin Support Studies. 3. For paper 2 see S. G. Pyne, M. J. Hensel, S. R. Byrn, A. T. McKenzie, and P. L. Fuchs, *J. Am. Chem. Soc.*, **102**, 5962 (1980).
(2) Synthesis Via Vinyl Sulfones. 8. For paper 7 in this series see J. C. Saddler, and P. L. Fuchs, *J. Am. Chem. Soc.*, **103**, 2112 (1981).
(3) Postdoctoral Research Associate.
(4) D. A. Clark and P. L. Fuchs, *J. Am. Chem. Soc.*, **101**, 3567 (1979).
(5) S. G. Pyne, M. J. Hensel, and P. L. Fuchs, *J. Am. Chem. Soc.*, **104**, in press.
(6) For a successful realization of this goal see S. G. Pyne, D. C. Spellmeyer, S. Chen, and P. L. Fuchs, *J. Am. Chem. Soc.*, **104**, *0000* (1982).
(7) Although there are two diastereomeric trans-fused bicyclo[5.4.0] systems that could fragment to the *trans,trans*-undecadienone moiety of **3**, models suggest that the C-19 β-isomer **2** is the more desirable target molecule.
(8) (a) P. DeMayo, *Acc. Chem. Res.*, **4**, 41 (1970); (b) J. Kossanyi, *Pure Appl. Chem.*, **51**, 181 (1979); and references contained therein.

0022-3263/82/1947-3121$01.25/0

Scheme II



Scheme III



overall yield on a multimole scale[9,10] (Scheme III).

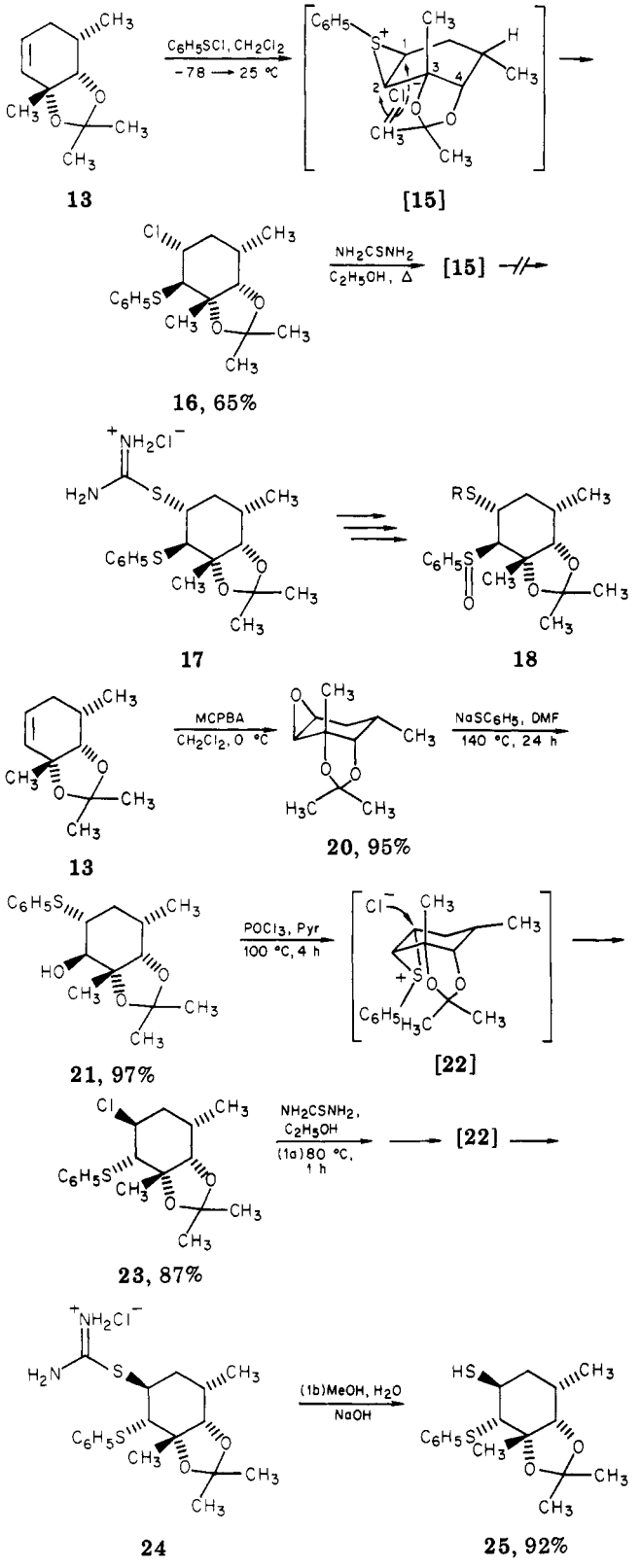
Treatment of the kinetic enolate[11] of **8** with trimethylchlorosilane affords silyloxy diene **9** in 82% yield after distillation. Oxidation of **9** with *m*-chloroperoxybenzoic acid by the method of Rubottom[12] at −50 °C in methylene chloride produces a 3:2 mixture of α-silyloxy enones *cis*-**10a** and *trans*-**10b**, which were separated and characterized as the less labile, desilylated α-hydroxy enones **11a**/**11b**. The mixture of α-silyloxy enones **10a**/**10b** was not routinely separated but rather treated directly in ether with methyllithium at −78 °C. Deprotection of the resulting β-silyloxy alcohols with catalytic trifluoroacetic acid in aqueous tetrahydrofuran affords a 3:2 mixture of diols **12a**/**12b**. Although these diols were separated for characterization purposes (see Experimental Section), it was found to be much more convenient to simply treat the crude **12a**/**12b** diol mixture with neat 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-toluenesulfonic acid for 2 h at room temperature to generate an easily separable mixture of acetonide **13** (45% overall) as well as returned diol **12b** (25%). The "undesired" isomer **12b** could be partially recycled by a two-step Swern oxidation[13]/diisobutylaluminum hydride reduction sequence (Scheme III).

With a ready source of acetonide **13** available, we next turned our attention to the development of a means for the regiocontrolled disulfurization of the olefin moiety. Synthesis of β-thiol sulfoxide **18** was first attempted via a simple chlorosulfenylation sequence (Scheme IV). Namely, treatment of acetonide **13** with phenylsulfenyl chloride (generated in situ from the reaction of NCS and thiophenol[14]) in methylene chloride afforded chloro sulfide **16** as a single isomer. It is interesting to note that the C-3,C-4 acetonide control element has directed both episulfonium ion formation from the less hindered β face (**13** → **15**) as well as promoting trans-diequatorial opening of the episulfonium ion at the less hindered C-1 site. (The electronically "preferred" trans-diaxial opening of episulfonium ion **15** would require chloride attack at the very hindered neopentyl C-2 center.) Although mechanistically interesting, chloro sulfide **16** proved to be a dead end synthetically. Attempts to react **16** with thiourea[15] provided no useful precursors for sulfoxide **18**. Presumably this unreactivity is a consequence of the hindered nature of the α face of the requisite episulfonium ion intermediate (**15**) toward the mild sulfur nucleophile.

Based upon the premise that an α-face episulfonium ion intermediate (**22**) would provide a reasonable entry to the

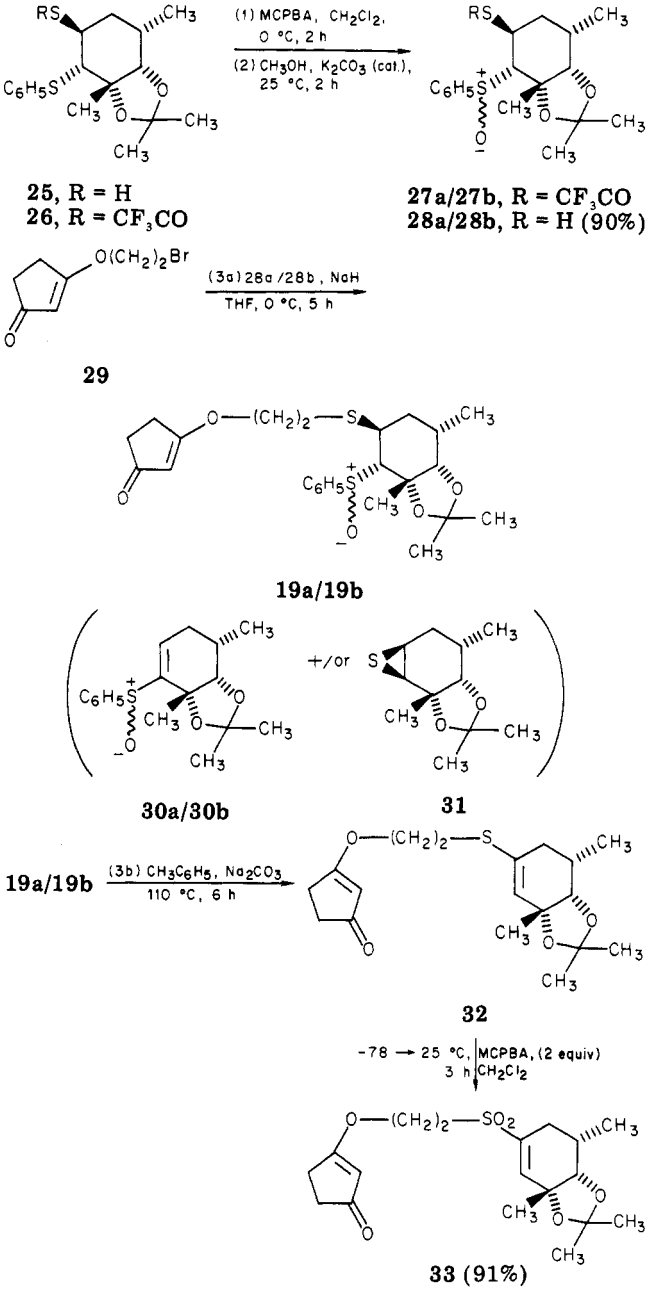
(9) (a) A. W. Crossley and N. Renouf, *J. Chem. Soc.*, 602 (1915). (b) J. P. Blanchard and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 5863 (1951).
(10) K. Conrow, *J. Org. Chem.*, **31**, 1050 (1966).
(11) (a) C. Girard and J. M. Conia, *Tetrahedron Lett.*, 3327 (1974). (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
(12) G. M. Rubottom and J. M. Gruber, *J. Org. Chem.*, **43**, 1599 (1978).
(13) A. J. Mancuso, S. L. Huang, and D. Swern, *J. Org. Chem.*, **43**, 2480 (1978).
(14) P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, **43**, 1208 (1978).
(15) G. G. Urquhart, J. W. Gates, Jr., and R. Connor, *Org. Synth., Coll. Vol. 3*, 363 (1955).

Scheme IV



opposite trans-substituted sulfoxide **19**, we returned to olefin **13** (Scheme IV). Epoxidation of **13** occurred specifically from the β face to provide **20**; the control presumably again resulting from steric shielding by the acetonide moiety. Nucleophilic opening of epoxide **20** with thiolate anion from the hindered α face required extremely harsh conditions but proceeded in excellent yield to afford β-hydroxy sulfide **21**. Treatment of sulfide **21** with phosphorus oxychloride in hot pyridine afforded the rearranged *trans*-β-chloro sulfide **23**.[16] This reaction occurs

Scheme V

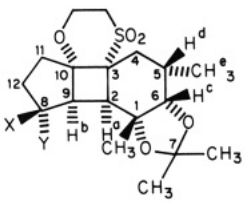


via trans-diaxial opening of episulfonium ion **22** at the less hindered C-1 center. Chloro sulfide **23** is a far more rewarding substrate in the thiourea reaction than is isomer **16**. Heating a solution of thiourea and chloro sulfide **23** in ethanol produces thiouronium salt **24**, which was not characterized but was treated further with aqueous methanolic sodium hydroxide to afford *trans*-β-mercapto sulfide **25** in excellent yield.

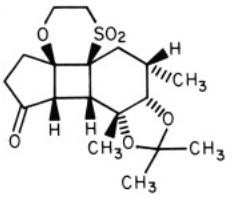
Conversion of **25** to **19** requires chemospecific oxidation of the phenylthio moiety in the presence of a more electron-rich sulfur group (mercaptan or alkylthio). This was easily accomplished by reaction of thiol **25** with trifluoroacetic anhydride in pyridine to afford thiol ester **26** in 89% yield (Scheme V). MCPBA oxidation of **26** produces an inseparable mixture of sulfoxide thiol ester diastereomers **27a/27b**, which were readily converted to the corresponding diastereomeric mixture of thiol sulfoxides

(16) (a) P. J. Kocienski and B. Lythogoe, *J. Chem. Soc., Perkin Trans. 1*, 1290 (1979). (b) J. F. King and K. Abikar, *Can. J. Chem.*, **46**, 1, 9, (1968).

Table I. Partial 470-MHz ^{1}H NMR Data



34, X = Y = O
36, X = OH; Y = Hf



35

compd	proton					
	H^a	H^b	H^c	H^d	CH^e_3	other
34	δ 3.76 (d) J_{ab} = 12.0 Hz	δ 2.91 (dd) J_{ab} = 12.0 Hz J_{bx} = 1.3 Hz[a]	δ 3.85 (d) J_{cd} = 2.1 Hz	δ 1.35 (m) J_{cd} = 2.1 Hz J_{de} = 6.5 Hz	δ 1.08 (d) J_{de} = 6.5 Hz	
35	δ 2.76 (d) J_{ab} = 9.1 Hz	δ 2.89 (dd) J_{ab} = 9.1 Hz J_{bx} = 1.5 Hz	δ 3.85 (d) J_{cd} = 0.8 Hz	δ = 2.02 (m) J_{cd} = 0.8 Hz J_{de} = 6.6 Hz	δ 1.17 (d) J_{de} = 6.6 Hz	
36	δ 3.82 (d) J_{ab} = 13.1 Hz	δ 2.85 (dd) J_{ab} = 13.1 Hz J_{af} = 7.5 Hz	δ 3.95 (d) J_{cd} = 3.0 Hz	δ 2.91 (m) J_{cd} = 3.0 Hz J_{de} = 6.9 Hz J_{dy} = 13.8 Hz[b]	δ 1.02 (d) J_{de} = 6.9 Hz	H^f: δ 4.61 (m) J_{af} = 7.5 Hz

[a] Long-range coupling to CH_x of C-12. [b] Trans-diaxial coupling to CH_x of C-4.

28a/28b by treatment with methanolic potassium carbonate (90% overall from **26**). Although sulfoxides **28a** and **28b** could be chromatographically separated for purposes of characterization (see Experimental Section), they were used as the mixture in all subsequent synthetic operations.

Treatment of mercaptan sulfoxides **28a/28b** with 1 equiv of sodium hydride *in the presence of bromide* ***29*** (prepared from cyclopentane-1,3-dione and bromoethanol) in tetrahydrofuran at 0 °C affords the desired sulfur-alkylated sulfoxides **19a/19b**. Considerable experimental care must be exercised with the stoichiometry of this reaction. Excess base, particularly in the presence of excess alkylating agent **29**, fosters β elimination of the sulfide moiety to produce vinyl sulfoxides **30a/30b** (identical with an authentic sample prepared from chloro sulfide **23** by oxidation/β elimination); while a deficiency of the alkylating agent **29** promotes cyclization of **28a/28b** to episulfide **31**. Although sulfoxides **19a** and **19b** can be separated for characterization, this is unnecessary since a toluene solution of both sulfoxides smoothly undergoes sulfenic acid elimination at 110 °C in the presence of solid sodium carbonate to afford vinyl sulfide **32**. MCPBA oxidation of "crude" vinyl sulfide **32** yields the requisite vinyl sulfone **33** (91% overall from **28a/28b** (Scheme V).

Although the 2 + 2 photochemistry of cyclic vinyl sulfones has been shown to include both dimerization and intermolecular additions to olefins,[17] we are unaware of any intramolecular examples similar to that required in the **33** → **34** transformation[18] (Scheme VI). In the event, photolysis of **33** in acetonitrile at room temperature rapidly produced two products (**34**, 74%; **35**, 20%) in a combined yield of 94%.

Examination of the 470-MHz proton NMR of **34** and **35** revealed that both products exhibited a pair of isolated doublets with large vicinal coupling constants, consistent

Scheme VI

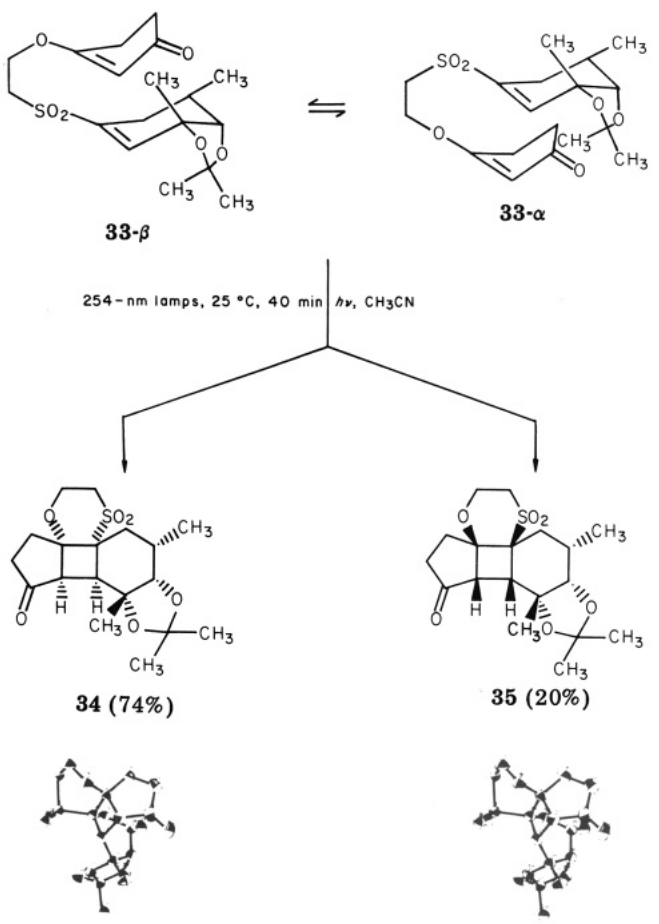


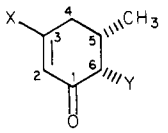
Figure 1. Stereoview of **34**.

with the presence of a *cis*-cyclobutane structure.[19] This observation indicated that the correct connectivity had been achieved but that a noncontrolled addition of the vinylogous ester to both faces of the olefin moiety of **33** had occurred. Assignment of **34** as the major photoproduct was based strongly on the abnormally high field chemical shift of the C-5 methine proton. Borohydride reduction

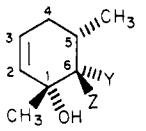
(17) (a) M. A. A. M. El Talbei, N. V. Kirby, and S. T. Reid, *Tetrahedron Lett.* 565 (1980); (b) M. J. Hopkinson, W. W. Schloman, Jr., B. F. Plummer, E. Wenkert, and M. Raju, *J. Am. Chem. Soc.*, **101**, 2157 (1979); (c) E. Block, *Q. Rep. Sulfur Chem.*, **4**, 321 (1969); and references contained therein.

(18) Sulfide **32**, as well as the mixture of sulfoxide diastereomers derived from it by monooxidation with MCPBA, when subjected to the successful photochemical conditions employed for **33**, afforded a plethora of photoproducts that were not further characterized.

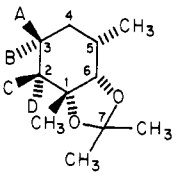
Table II. ^{13}C NMR Data



6, X = OH; Y = H
7, X = OCH_2CH_3; Y = H
8, X = H; Y = H
11a, X = H; Y = OH



12a, Y = OH; Z = H
12b, Y = H; Z = OH
14, X = Y = O



13, AB,CD = CH=CH
16, A = D = H; B = Cl; C = SC_6H_5
20, A = C = O; B = D = H
21, A = D = H; B = C_6H_5S; C = OH
23, A = Cl; B = C = H; C = SC_6H_5
25, A = SH; B = C = H; D = SC_6H_5
26, A = CF_3COS; B = C = H; D = SC_6H_5
27a/27b, A = CF_3COS; B = C = H; D = C_6H_5SO
28a/28b, A = SH; B = C = H; D = C_6H_5SO
31, A = C = S; B = D = H

compd	carbon							
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	CH_3's
6	192.5	103.8	≡C(1)	40.6	28.9	≡C(4)		20.8
7	177.16	102.2	173.7	37.3	28.8	45.1		20.9
				(45.1)		(37.3)		20.9
8	199.4	129.5	149.7	34.0	30.4	46.3		21.1
				(46.3)		(34.0)		
11a	200.0	127.0	149.1	33.0	35.3	78.1		11.4
12a	71.7	127.0	131.8	28.5	31.1	77.0		27.1
		(131.8)	(127.0)					18.4
12b	74.3	125.8	133.7	32.7	34.5	80.6		22.7
		(133.7)	(125.8)					18.1
14	74.5	125.9	133.9	37.4	38.9	214.1		29.0, 13.7
		(133.9)	(125.9)					
13	78.5	126.3	130.9	28.0	30.4	82.8	107.5	27.8, 27.6, 24.9, 18.9
		(130.9)	(126.3)					
16[a]	82.6	65.5	62.5	40.4	30.3	83.3	108.3	28.2, 26.8, 19.8, 17.5
		(62.5)	(65.5)					
20	76.8	53.5	55.7	26.9	28.2	81.9	108.1	26.5, 23.3, 21.8, 18.4
		(55.7)	(53.5)					
21	83.3	75.8	51.6	35.2	31.5	84.1	108.0	28.5, 27.0, 17.6, 16.7
23	83.2	63.1	60.3	37.5	27.1	84.0	108.4	27.8, 27.1, 25.8, 18.4
		(60.3)	(63.1)					
25	83.3	64.8	37.8	36.0	27.7	84.8	108.3	27.3, 27.1, 25.9, 18.7
26	83.2	59.2	45.4	34.3	28.1	84.4	108.8	27.2, 26.8, 25.7, 18.7
27a[a,b,c]	80.8	69.3	32.6	36.7	28.1	83.7	109.5	28.7, 26.9, 26.7, 26.1, 18.2, 18.0
27b	81.1	72.1	35.2	37.9	28.9	85.2	109.8	
28a	80.5	76.4	30.3	34.5	27.3	83.9	109.3	29.2, 26.6, 26.2, 18.4
			(27.3)		(30.3)			
28b	81.4	77.8	31.7	27.6	27.6	85.7	109.5	28.6, 27.0, 26.4, 18.0
31	78.2	37.8	42.8	28.0	27.1	82.5	108.0	27.5, 26.7, 22.6, 18.1

[a] Aryl carbons not tabulated, see Experimental Section. [b] (Trifluoroacetyl)thio carbonyl and methyl carbons not observed. [c] Assignment of lower field resonance positions to diasteromer b is arbitrary. [d] OCH_2CH_3 (64.2, 14.1 ppm).

of **34** afforded a single alcohol (**36**), which exhibited a "normal" chemical shift for the C-5 methine, suggesting that the upfield shift was a consequence of shielding by the carbonyl group. Consistent with this assignment is the observation that in **34** the pseudoequatorial C-2 hydrogen is further downfield than in **35**, where the C-2 hydrogen is pseudoaxial[19] (see Table I).

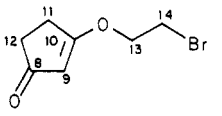
In order that the aforementioned structural assignment could be unambiguously secured, an X-ray analysis was undertaken with the major photoproduct, **34**. As can be readily seen in Figure 1, the major photoadduct (**34**) is the product that results from addition of the vinylogous ester moiety to the olefin face away from the acetonide protecting group. The bond angles and distances for adduct **34** can be found in Tables IV and V in the Supplementary Material.

Attempts at synthesis of dione **41** (precursor of **5**) by metalation (KO-*t*-Bu, DBU, LDA, etc.) of photoproduct **34** were completely unrewarding (Scheme VII). Numerous products were produced but no trace of any vinyl sulfone containing species (**40**, **41**) were detected. On the premise that the cyclopentanone carbonyl was responsible for the unwanted chemistry observed, metalation of alcohol **36** was also explored. Once again, no trace of the desired alcohol resulting from intermediate **40** was obtained.

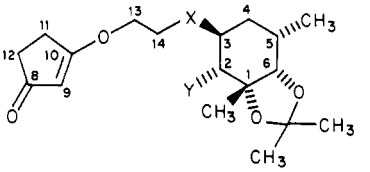
In an alternative approach, sulfones **34** and **36** were separately subjected to reductive desulfonylation with lithium and methylamine[23] (Scheme VII). Under these conditions only overreduced cyclobutanes **37** and **38** were

(19) "Stereochemistry", Vol. 1, H. B. Kagan, Ed., Thieme: Stuttgart, 1977.
(20) P. Main, "MULTAN, a Direct Method Solution Program to Crystal Structure", Department of Physics, University of York, York, England 1978.
(21) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
(22) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(23) W. E. Truce, D. P. Lute, and D. N. Burdge, *J. Am. Chem. Soc.*, 2872, **82** (1960).

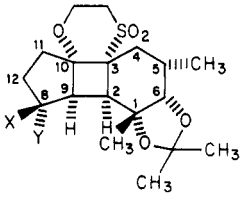
Table III. ^{13}C NMR Data



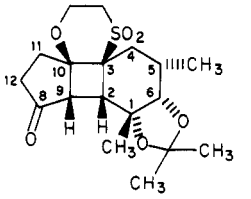
29



19a/19b, X = S; Y = C_6H_5SO
32, X = S; Y = H; Δ2,3-unsaturated
33, X = SO_2; Y = H; Δ2,3-unsaturated



34, X = Y = O
36, X = OH; Y = H



35

compd	carbon														
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	CH_3's
29								205.2	105.2	189.1	28.3	34.1	71.0	27.9	
19a[a]	79.1	74.1	38.9	30.2	31.0	82.5	109.0	205.5	105.1	189.3	28.4	34.1	70.6	30.2	27.0, 26.3 25.8, 18.0
19b[a]	84.1	75.8	39.4	33.4	29.4	84.8	109.3	205.5	105.1	189.3	27.6	34.1	70.5	29.4	28.4, 26.8, 26.2, 18.1
32	79.5	124.6	132.1	32.5	30.9	81.9	107.7	205.3	105.0	189.3	28.4	34.1	69.9	28.6	27.8, 27.6, 25.0, 18.4
33	78.4	140.7	137.6	30.7	28.3	81.4	108.6	205.1	105.7	188.6	26.0	34.2	64.3	51.6	28.0, 27.1, 23.5, 18.4
34	79.8	43.5	65.4	27.2	29.4	80.2	108.0	214.8	51.8	86.6	24.7	37.8	59.9	46.8	27.0, 26.1, 23.8, 18.1
35	77.8	48.4	66.7	28.2	28.5	80.6	108.4	212.9	58.8	84.1	25.6	37.1	61.8	49.7	27.5, 26.8, 24.1, 19.5
36	81.4	37.6	64.0	b	b	81.7	106.9	73.2	51.6	89.2	b	36.5	58.9	44.3	27.7, 27.0, 26.3, 18.0

[a] Aryl carbons not tabulated; see Experimental Section. [b] (Trifluoroacetyl)thio carbonyl and methyl carbons not observed.

produced, respectively. Conditions using a stoichiometric amount of lithium afforded mixtures of starting material and product, but no olefin **39** could be isolated; apparently the strained intermediate **39** undergoes reduction more easily than sulfones **34** and **36**.

In view of this difficulty for refunctionalization of **34** and with an efficient alternative synthesis of **5** from **13** available,[6] this avenue of investigation was terminated.

Experimental Section

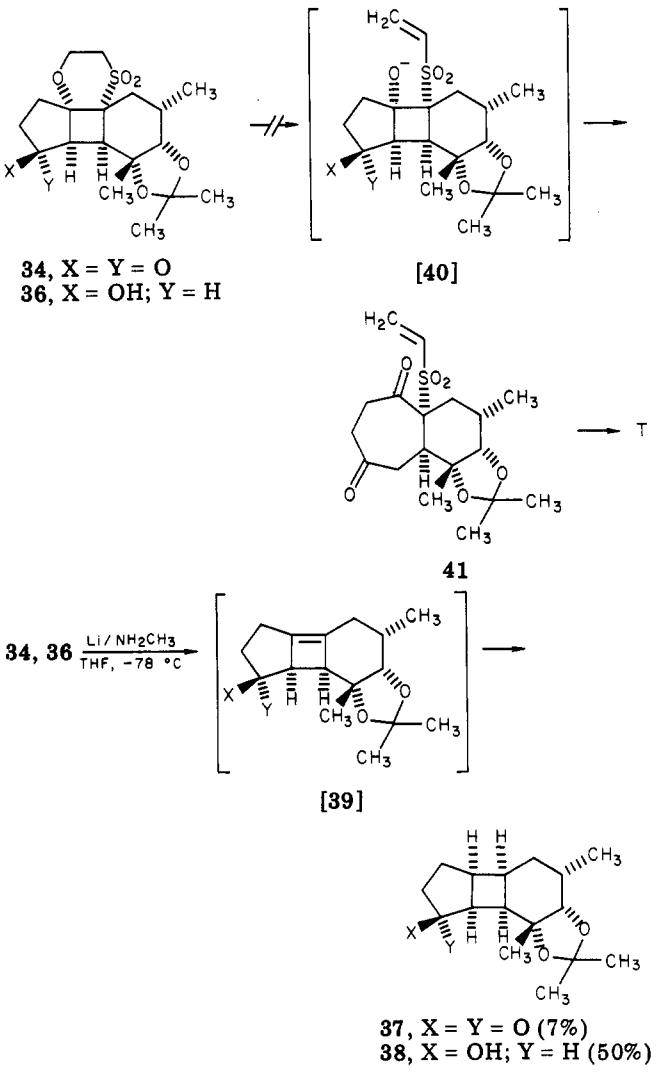
General Procedures. Melting points were determined on a Fisher-Johns melting-point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer in chloroform solution, unless otherwise stated. ^1H NMR spectra were recorded on either a Perkin-Elmer R-32, a Nicolet 360, or a Nicolet instrument at 90, 360, and 470 MHz, respectively. The spectra were measured in deuteriochloroform, unless otherwise stated, relative to tetramethylsilane (δ 0.00). Each signal is described in terms of chemical shift in ppm from tetramethylsilane, multiplicity, intensity, and coupling constant (Hz) in that order with the use of the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; and $W_{1/2}$, width of peak at half height. ^{13}C NMR spectra were recorded on a Varian CFT-20 instrument operating at 20 MHz or on a Varian XL 200 operating at 50 MHz. The spectra were measured in deuterochloroform solution, unless otherwise stated, relative to tetramethylsilane (δ 0.00). Both ^1H-decoupled and off-resonance spectra were recorded. Mass spectra were recorded on a CEC-21-110-B high-resolution mass spectrometer at an ionizing voltage of 70 eV and an ionizing current of 100 A. Exact mass determinations were obtained on the CEC-21-110-B instrument. Microanalysis were performed by C. S. Yeh and M. Lam, Department of Chemistry, Purdue University.

All reactions were run under a positive pressure of nitrogen. All organic extracts were dried over anhydrous sodium sulfate, filtered, and then evaporated on a Buchi Rotavapor. Tetrahydrofuran (THF) and ether were distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride, toluene, triethylamine, and pyridine were distilled from calcium hydride. Thin-layer chromatography (TLC) was performed on 0.25-mm Merck precoated silica gel plates (60 F-254). Preparative thick-layer chromatography (preparative TLC) was performed on 2 mm × 20 cm × 20 cm Merck precoated silica gel plates (60 F-254). Column chromatography was performed on silica gel 60–200 mesh obtained from Sargent-Welch.

5-Methyl-1,3-cyclohexanedione (6). Sodium metal (520.9 g, 22.6 mol) was added to 11 L of absolute ethanol in a three-neck 22-L reaction flask equipped with a mechanical stirrer, dropping funnel, and high-capacity reflux condenser. The sodium was added at a rate sufficient to maintain a gentle reflux (7 h). After all the sodium reacted, ethyl acetoacetate (3000 g, 25 mol) was added over a 5-h period via a dropping funnel. Ethyl crotonate (2679 g, 96% pure, 22.6 mol) was then added more rapidly over a 2-h period. The yellow solution was very carefully heated to a gentle reflux. When precipitation of the product began, the reaction became extremely exothermic, and external heat was removed. Once the reaction returned to a gentle reflux, external heat was then applied in order to maintain a gentle reflux overnight. The white precipitate was then filtered. Due to dimerization of the final product in acid, the next two steps were conducted on a smaller scale.

Potassium hydroxide (560 g, 10 mol) was added to a stirred solution of the above dione salt (1100 g, 5 mol) in 2.7 L of water. The dark orange solution was heated to reflux and allowed to remain at that temperature for 4 h. The ethanol and most of the water was removed by distillation under reduced pressure. The residue was diluted with 3 L of water and concentrated HCl was

Scheme VII



added dropwise to a pH of 6. Concentrated HCl was then added at a rate equal to the reflux rate. Note: CO_2 should evolve at this point. The HCl was added until the color of the solution turned to yellow and the pH changed to 1 or 2. The yellow solution was kept at reflux until no more CO_2 was given off. The solution was then quickly cooled to 0 °C in order to precipitate the product out of the acidic solution, so dimerization can be kept to a minimum. The precipitate was filtered and the mother liquor extracted with methylene chloride. The organic layer was then dried over $MgSO_4$ and the solvent removed in vacuo. This procedure was repeated until all of the dione salt was converted to the dione **6**. The crude dione was recrystallized from ethyl acetate, affording 1663.8 g (58%) of colorless prisms: mp 129.5–130 °C (lit. mp 128 °C);[9] ^{1}H NMR ($CDCl_3$, 90MHz) δ 1.08 (d, J = 4 Hz), 1.80–2.90 (m, 5 H) 3.40 (s, 1 H), 5.49 (s, 1 H); ^{13}C NMR ($CDCl_3$) 192.52 (s), 103.85 (d), 40.56 (t), 28.90 (d), 20.83 (q); IR ($CHCl_3$) 3–4.5 (s), 5.85 (s) μm. Examination of the residues from the crystallization of dione **6** reveals the dimer 2-(3-hydroxy-5-methyl-2-cyclohexenyl)-3-oxo-5-methyl-1-cyclohexene (**6D**):[10] mp sublimes 70 °C (recrystallized from methanol); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.08 (d, 6 H), 2.0–2.8 (m, 10 H), 5.92 (s, 1 H), 6.08 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 159.86 (s), 149.9 (s), 129.16 (d), 116.65 (s), 45.36 (t), 41.56 (t), 38.23 (t), 30.32 (d), 27.96 (d), 21.09 (q), 20.85 (q); IR ($CHCl_3$) 6.05 (s), 6.22(s) μm; mass spectrum, m/z $C_{14}H_{18}O_3$ 234 (M^+), 219 ($M - CH_3$).

3-Ethoxy-5-methylcyclohex-2-en-1-one (7). In a 12-L round-bottom flask equipped with a fractionating column and a heavier than water extractor were combined 5-methyl-1,3-cyclohexanedione (**6**) (1 kg, 7.9 mol), p-toluenesulfonic acid (1 g, 5.3 mmol), 4 L of absolute ethanol, and 4 L of chloroform. The solution was heated at reflux until no more water was given off (10 days). The solvents were removed under reduced pressure. Distillation of the crude liquid afforded 1136.7 g (93%) of **7**: bp 78–80 °C (0.1 mmHg) (lit. bp 83 °C);[10] ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.1 (d, J = 2 Hz, 3 H), 1.36 (t, J = 7 Hz, 3 H), 1.9–2.7 (m, 5 H), 3.94 (q, J = 7 Hz, 2 H), 5.31 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 177.16 (s), 173.69 (s), 102.19 (d), 64.22 (t), 45.12 (t), 37.25 (t), 28.83 (d), 20.87 (q), 14.12 (q); IR (neat) 6.05 (s), 6.20 (s) μm; mass spectrum, m/z $C_9H_{14}O_2$ (154 M^+).

5-Methylcyclohex-2-en-1-one (8). A solution of 3-ethoxy-5-methylcyclohex-2-en-1-one (**7**) (500 g, 3.25 mol) in 1.5 L of anhydrous ethyl ether was added dropwise to a suspension of lithium aluminum hydride (35 g, 0.897 mol) in 2 L of anhydrous ethyl ether at a rate sufficient to maintain a gentle reflex. Due to the formation of a heavy white precipitate during the addition, additional ether may be required in order to allow the reaction mixture to stir efficiently. The white suspension was allowed to stir overnight before careful quenching with 35 mL of water followed by 105 mL of 10% sodium hydroxide and finally another 35 mL of water. A fine filterable precipitate was formed after stirring at room temperature for 2 h. The precipitate was filtered, and 1 L of 10% sulfuric acid was added to the mother liquor. After stirring overnight, the organic layer was separated and washed with a saturated carbonate solution. The dried and evaporated reaction mixture gave after distillation 301.1 g (84% yield) of the desired enone **8**: bp 38–41 °C (1 mmHg) (lit. bp 60 °C (8 mmHg));[9] ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.07 (d, J = 3 Hz, 3 H), 1.8–2.7 (m, 5 H), 6.0 (d, J = 9 Hz, 1 H), 6.85–7.08 (ddd, J = 9, 5, 2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 173.14 (s), 149.71 (d), 129.54 (d), 46.28 (t), 34.00 (t), 30.35 (d), 21.15 (q); IR (neat) 5.95 (s) μm.

1-Methyl-3-(trimethylsilyloxy)-2,4-cyclohexadiene (9). n-Butyllithium in hexane (548 mL, 1.15 mol) was added via a syringe to a solution of diisopropylamine (154 mL, 1.10 mol) in 2.5 L of tetrahydrofuran under N_2 cooled to −78 °C in an acetone/dry ice bath.[11] After 30 min, a solution of 5-methylcyclohex-2-en-1-one (110 g, 1.00 mol) in 500 mL of THF was added dropwise over 2 h. The clear solution was allowed to stir at −78 °C for an additional hour before rapidly adding chlorotrimethylsilane (150 mL, 1.2 mol). The reaction mixture was slowly warmed to room temperature. Most of the THF was then removed in vacuo, and hexane was added. The white suspension was washed with ice-cold aqueous bicarbonate solution, ice-cold 1% HCl solution, and another portion of ice-cold bicarbonate solution. The clear yellow solution was dried over magnesium sulfate and the solvent removed in vacuo. Fractional distillation at reduced pressure gave 149 g (82% yield) of the desired silyloxy diene **9**: bp 59–62 °C (2 mmHg); ^{1}H NMR ($CDCl_3$, 90 MHz internal Me_3Si group as reference) δ 0.0 (s, 9 H), 0.85 (d, J = 6.6 Hz, 3 H), 1.6–2.6 (m, 3 H), 4.6 (m, 1 H), 5.5–5.75 (m, 2 H); ^{13}C NMR δ 147.64 (s), 127.57 (d), 125.99 (d), 109.33 (d), 31.23 (t), 28.15 (d), 20.59 (q), 0.0 (q); IR (neat) 6.09 (s), 6.28 (s) μm; mass spectrum m/z $C_{10}H_{18}OSi$ 182 (M^+).

***cis*- and *trans*-5-Methyl-6-(trimethylsiloxy)cyclohex-2-en-1-one (10a and 10b).** Solid m-chloroperbenzoic acid (71 g (81.7% pure), 1.1 equiv) was added to a solution of 1-methyl-3-(trimethylsiloxy)-2,4-cyclohexadiene (**9**) (55.5 g, 0.30 mol) in 3 L of methylene chloride cooled to an internal temperature of −50 °C. After 30 min, the reaction had gone to completion. It is very important for the reaction to go to completion as fast as possible. If the reaction was not complete in 30 min, more MCPBA was added. The white suspension was filtered cold and the solution washed with cold sodium bisulfite solution followed by several cold saturated potassium carbonate solutions. The clear colorless organic layer was dried over magnesium sulfate and the solvent removed in vacuo. The pale yellow liquid was distilled under high vacuum (1 mmHg), collecting 47.5 g (79%) of the desired product (a mixture of two diastereomers) with some hydroxy ketone and aromatic impurity in a cold receiver, in the range of 40–65 °C. The pot residue contained a solid aromatic impurity that codistills with the product at higher temperatures. The following spectral data are for the corresponding hydroxy ketones due to the lability of the Me_3Si group: (**11a**) ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.92 (d, J = 7 Hz, 3 H), 2.20–3.02 (m, 3 H), 3.72 (br s, 1 H, exchanges with D_2O), 4.40 (d, J = 5 Hz, 1 H), 6.13 (dd, J = 10, 3 Hz, 1 H), 6.80–7.05 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 99.96 (s), 149.07 (d), 126.95 (d), 76.08 (d), 35.28 (d), 33.02 (t), 11.37 (q); IR (neat) 2.6–3.2 (s), 5.95 (s) μm. **11b**: mp 34–35 °C (sublimes); ^{1}H NMR ($CDCl_3$, 90MHz) δ 1.24 (d, J = 6 Hz, 3 H), 2.0–2.8 (m, 3 H), 3.72 (br s, 1 H,

exchanges with D_2O), 3.86 (d, J = 12 Hz, 1 H), 6.14 (dd, J = 9, 3 Hz, 1 H), 6.9–7.2 (m, 1 H).

***cis*-3,4-Dihydroxy-*trans*-3,5-dimethylcyclohexene 3,4-Acetonide (13).** Methyllithium (1.0 equiv) was added via a dropping funnel to an acetone/dry ice cooled solution of 5-methyl-6-(trimethylsiloxy)cyclohex-2-en-1-one (61.5 g, 0.31 mol) in 1.5 L of anhydrous ether under nitrogen. The yellow solution was quenched with ice and washed with water. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo. The yellow oil was dissolved in 500 mL of THF and 25 mL of water, and 1 mL of trifluoroacetic acid was added. The pale yellow solution was allowed to stir at room temperature until the reaction was complete (approximately 2 h). The reaction mixture was quenched with potassium carbonate and filtered. The THF was removed in vacuo. The colorless oil was picked up in ether and washed with water. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo. The colorless oil, consisting of a mixture of *cis*-**12a** and *trans*-**12b** diols, was dissolved in 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid was added. The solution was allowed to stir at room temperature until the reaction was complete (approximately 2 h). The mixture was quenched with potassium carbonate and filtered, and the solvent was removed in vacuo. The pale yellow oil was then plugged through 500 g of silica gel with hexane, giving 25 g (45%) of the desired acetonide (**13**). The *trans*-diol (**12b**, 25%) can then be obtained by washing the column with ether. **12a** (oil): ^1H NMR ($CDCl_3$, 90MHz) δ 1.04 (d, J = 5 Hz, 3 H), 1.25 (s, 3 H), 1.8–2.1 (m, 3 H), 3.5–3.6 (m, 1 H), 3.65 (br s, 2 H, exchanges with D_2O), 5.34–5.80 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 131.82 (d), 127.04 (d), 77.00 (d), 71.66 (s), 31.10 (d), 28.53 (t), 27.12 (q), 18.38 (q); IR (neat) 2.7–3.2 (s), 6.06 (w) μm; exact mass calcd for $C_8H_{14}O_2$, 142.099; found; 142.098. **12b**: mp 57–58 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.05 (d, J = 6 Hz, 3 H), 1.23 (s, 3 H), 1.50–2.35 (m, 3 H), 3.00–3.30 (m, 2 H), 3.45 (br s, 2 H, exchanges with D_2O), 5.50–5.65 (m, 2 H); ^{1C} NMR ($CDCl_3$) δ 133.75 (d), 125.79 (d), 80.59 (d), 74.32 (s), 34.47 (t), 32.67 (d), 22.68 (q), 18.10 (q); IR ($CHCl_3$) 2.8–3.2 (s), 6.04-μm; (w) exact mass calcd. for $C_8H_{14}O_2$: 142.099; found 142.097. *13*: bp 90 °C (1.5 mmHg); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.13 (d, J = 7 Hz, 3 H), 1.31 (s, 3 H), 1.36 (s, 3 H), 1.38 (s, 3 H), 1.45–2.20 (m, 3 H), 3.77 (br s, 1 H), 5.32–5.80 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 130.87 (d), 126.27 (d), 107.51 (s), 82.79 (d), 78.47 (s), 30.36 (d), 28.02 (t), 27.76 (q), 27.63 (q), 24.86 (q), 18.86 (q); IR (neat) 6.03 (w), 7.28 (s), 7.33 (s) μm; exact mass calcd for $C_{11}H_{18}O_2$ (M – CH_3), 167.017; found, 167.015.

***trans*-3,5-Dimethyl-3-hydroxycyclohex-1-en-4-one (14).** A solution of dimethyl sulfoxide (4.7 mL, 0.066 mol) in 10 mL of methylene chloride was added dropwise to a solution of oxalyl chloride (2.8 mL, 0.033 mol) in 75 mL of methylene chloride.[13] The internal temperature was kept below –50 °C during the addition. The colorless solution was allowed to stir an additional 5 min before the dropwise addition of **12b** (4.27 g, 0.030 mol) over a half-hour period. The white suspension was allowed to stir an additional half hour before slowly adding triethylamine (21 mL, 0.15 mol). The reaction mixture was stirred 10 min after addition and then allowed to warm to room temperature. The methylene chloride solution was washed sequentially with water, aqueous 10% HCl, saturated aqueous K_2CO_3, and water. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo. Distillation at 150 °C (12 mmHg) afforded 1.98 g (47%) of **14**: ^1H NMR ($CDCl_3$, 90 MHz) δ 1.12 (d, J = 6 Hz, 3 H), 1.43 (s, 3 H), 1.87–3.33 (m 3 H), 3.85 (br s, 1 H), 5.70–5.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 214.06 (s), 133.91 (d), 125.93 (d), 74.47 (s), 38.89 (d), 37.42 (t), 29.02 (q), 13.70 (q); IR (neat) 2.73–3.18 (s), 5.87 (s) μm; mass spectrum, m/y $C_8H_{12}O_2$ 140 (M^+).

DIBAL Reduction of 14. Hydroxy ketone **14** (1.62 g, 11.6 mmol) in 10 mL of hexane was slowly added to a solution of DIBAL (60 mL, 60.0 mmol) in 100 mL of hexane at –78 °C under a nitrogen atmosphere. The colorless solution was allowed to slowly warm to room temperature and allowed to remain at that temperature for 20 h. The solution was very carefully quenched with 20 mL of 10% NaOH solution. The precipitate was filtered and the hexane solution was washed with water. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo. Chromatography on 100 g of SiO_2 with 20% ethyl acetate in methylene chloride afforded 0.655 g (40%) of **12a** and 0.494 g (30%) of **12b**.

1-Chloro-*trans*,cis-dimethyl-*cis*,*cis*-3,4-dihydroxy-*trans*-2-(phenylthio)cyclohexane 3,4-Acetonide (16). Thiophenol (0.64 g, 5.85 mmol) was slowly added to a suspension of *N*-chlorosuccinimide (0.81 g, 6.10 mmol) in methylene chloride (25 mL) over 10 min to produce an orange-red solution of phenylsulfenyl chloride.[14] This solution was cooled to –78 °C, and acetonide (1.01 g, 5.5 mmol) in methylene chloride (5 mL) was added and the solution allowed to warm to room temperature over 1 h. During the course of the reaction the color of the solution faded to a light yellow. TLC analysis of the reaction mixture (10% THF–hexane) showed chloro sulfide **16** and diphenyl disulfide. Carbon tetrachloride (3 volumes) was added to the reaction mixture to precipitate the succinimide, which was removed by filtration,[14] the mixed halocarbon solution was washed with sodium thiosulfate and sodium carbonate and dried over magnesium sulfate, and the solvent was removed in vacuo to afford 2.16 g of a yellowish oil. The chlorosulfide was separated from diphenyl disulfide by plug filtration on silica gel with hexane and an increasing gradient of methylene chloride. Elution with 2:3 hexane–CH_2Cl_2 afforded 1.16 g of chloro sulfide **16** (65%), which was recrystallized from hexane (–78 °C) to provide an analytical sample: mp 68–69 °C; ^{13}C NMR ($CDCl_3$) δ 137.3 (s), 133.1 (d), 128.6 (d), 127.1 (d), 108.3 (s), 83.3 (d), 82.6 (s), 65.5 (d), 62.5 (d), 40.4 (t), 30.3 (d), 28.2 (q), 26.8 (q), 19.8 (q), 17.5 (q); exact mass calcd for $C_{17}H_{23}ClO_2S$, 326.111; found 326.111.

β-1,2-Epoxy-α-*cis*-3,4-dihydroxy-*trans*-3,5-dimethylcyclohexane 3,4-Acetonide (20). Solid *m*-chloroperbenzoic acid (1.0 equiv) was added to an ice-water-cooled solution of acetonide **13** (25 g, 0.137 mol) in 300 mL of methylene chloride. The colorless solution was allowed to slowly warm to room temperature. The white suspension was washed with a 10% aqueous sodium bisulfite solution followed by several aqueous saturated carbonate solutions. The colorless solution was dried over magnesium sulfate and the solvent removed in vacuo, giving 25.5 g (95%) of the desired epoxide **20** as a colorless liquid: ^1H NMR ($CDCl_3$, 90 MHz) δ 1.03 (d, J = 6 Hz, 3 H), 1.36 (s, 9 H), 1.64–1.88 (m, 3 H), 2.82–2.95 (m, 1 H), 3.20–3.35 (m, 1 H), 3.59 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 108.05 (s), 81.90 (d), 76.78 (s), 55.66 (d), 53.49 (d), 28.16 (d), 26.87 (t), 26.47 (q), 23.27 (q), 21.84 (q), 18.35 (q); IR (neat) 7.25 (s), 7.30 (s), 8.1–8.3 (s), 11.1 (s) μm; mass spectrum, 183 (M – CH_3).

***trans*,*cis*-3,5-Dimethyl-1-(phenylthio)-*trans*,*cis*,*cis*-2,3,4-trihydroxycyclohexane 3,4-Acetonide (21).** Thiophenol (3.3 g, 30 mmol) was carefully added via a syringe to a suspension of sodium hydride (0.3 g, 12.5 mmol) and epoxide **13** (2.0 g, 10 mmol) in 25 mL of DMF under nitrogen. The cloudly solution was then heated to 140 °C and allowed to remain at that temperature for 24 h. The reaction mixture was cooled and hexane added. The light yellow solution was washed with several 10% aqueous sodium hydroxide solutions. The pale yellow solution was then dried over magnesium sulfate and the solvent removed in vacuo. The yellow solid was recrystallized from hexane–ether, giving 3.0 g (97%) of the desired sulfide alcohol **21**: mp 97–98 °C; ^1H NMR ($CDCl_3$, 470 MHz) δ 1.04 (d, J = 6.7 Hz, 3 H), 1.30 (s, 3 H), 1.34 (s, 3 H), 1.42 (s, 3 H), 1.55 (ddd, J = 12.7, 12.7, 12.7 Hz, 1 H), 1.81 (ddd, J = 12.7, 3.7, 3.7 Hz, 1 H), 1.84 (m, 1 H), 2.74 (d, J = 2.0 Hz, 1 H, exchanges with D_2O), 2.80 (ddd, J = 12.5, 11.5, 3.1 Hz, 1 H), 3.74 (d, J = 2.9 Hz, 1 H), 7.30 (m, 3 H), 7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 133.92 (d), 132.47 (s), 128.95 (d), 127.89 (d), 108.04 (s), 84.05 (d), 83.30 (s), 75.82 (d), 51.56 (d), 35.24 (t), 31.54 (d), 28.50 (q), 27.00 (q), 17.60 (q), 16.66 (q); IR ($CHCl_3$) 2.75–3.00 (m) μm; exact mass calcd for $C_{17}H_{24}O_2S_2$, 308.145; found, 308.148.

1-Chloro-*cis*,*trans*-3,5-dimethyl-*trans*,*trans*-3,4-dihydroxy-*trans*-2-(phenylthio)cyclohexane 3,4-Acetonide (23). Phosphorus oxychloride (13 mL, 0.14 mmol) was slowly added via a syringe to a solution of sulfide alcohol **21** (8.6 g, 0.028 mmol) in 150 mL of pyridine under a nitrogen atmosphere. The pale yellow solution was heated to 100 °C and allowed to remain at that temperature for 4 h. After cooling to room temperature, the solution was carefully poured onto ice. The aqueous suspension was washed several times with ether. The ether extracts were washed several times with saturated cupric sulfate solutions until all of the pyridine was removed. The ether solution was dried over $MgSO_4$ and the solvent removed in vacuo, affording 7.9 g (87%) of the desired chloro sulfide **23**: mp 86.5–88 °C (recrystallized from hexane); ^1H NMR ($CDCl_3$, 470 MHz) δ 1.09 (d, J

= 6.4 Hz, 3 H), 1.41 (s, 3 H), 1.50 (s, 3 H), 1.65 (s, 3 H), 2.00–2.08 (m, 2 H), 2.24–2.29 (m, 1 H), 3.03 (d, J = 11.4 Hz, 1 H), 3.95 (s, 1 H), 4.39 (ddd, J = 11.4, 7.5, 5.8 Hz, 1 H), 7.19–7.30 (m, 3 H), 7.55 (d, J = 7.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 137.79 (s), 131.42 (d), 128.81 (d), 126.64 (d), 108.35 (s), 84.00 (d), 83.15 (s), 63.08 (d), 60.29 (d), 37.54 (t), 27.79 (q), 27.09 (q), 27.09 (d), 25.76 (q), 18.43 (q); IR ($CHCl_3$) 7.25 (s), 7.29 (m) μm; exact mass calcd for $C_{17}H_{23}ClO_2S$, 326.111; found, 326.108.

***cis,trans*-3,5-Dimethyl-*trans,trans*-3,4-dihydroxy-1-mercapto-*trans*-2-(phenylthio)cyclohexane 3,4-Acetonide (25).** A solution of chlorosulfide **23** (7.9 g, 0.024 mol) and thiourea (1.88 g, 24.6 mmol) in 50 mL of absolute ethanol was stirred at 80 °C under nitrogen for 1 h.[15] The solution was then allowed to stir at room temperature overnight. The ethanol was removed in vacuo. The residue was dissolved in 100 mL of methanol, and 5 mL of water was added. The solution was degassed and put under an argon atmosphere before the addition of sodium hydroxide (2.2 g, 0.055 mol). The solution was stirred at room temperature for 3 h. The methanol was removed in vacuo and the residue picked up in 300 mL of hexane. The hexane was washed with water and then dried over magnesium sulfate. Removal of the solvent in vacuo afforded 7.2 g (92%) of **25** as a white powder: mp 82–83.5 °C; ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.07 (d, J = 6.9 Hz, 3 H), 1.41 (s, 3 H), 1.49 (s, 3 H), 1.57 (s, 3 H), 1.67 (ddd, J = 13.5, 8.1, 7.9 Hz, 1 H), 1.90 (m, 1 H), 2.08 (ddd, J = 13.5, 12.0, 11.3 Hz, 1 H), 2.55 (dd, J = 3.5 Hz, 1 H, exchanges slowly with D_2O), 2.90 (d, J = 12.2 Hz, 1 H), 3.52 (dddd, J = 12.2, 12.0, 8.1, 3.5 Hz, 1 H), 3.96 (s, 1 H), 7.18–7.29 (m, 3 H), 7.60 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 138.59 (s), 130.75 (d), 128.85 (d), 126.36 (d), 108.29 (s), 84.83 (d), 83.33 (s), 64.78 (d), 37.85 (d), 36.02 (t), 27.69 (d), 27.26 (q), 27.09 (q), 25.87 (q), 18.68 (q); exact mass calcd for $C_{17}H_{19}O_2S_2$, 324.122; found, 324.126.

***cis,trans*-3,5-Dimethyl-*trans,trans*-3,4-dihydroxy-*trans*-2-(phenylthio)-1-[(trifluoroacetyl)thio]cyclohexane 3,4-Acetonide (26).** Trifluoroacetic anhydride (1.5 mL, 10.7 mmol) was added via a syringe to an ice-water-cooled solution of thiol sulfide **25** (1.2 g, 3.7 mmol) in 10 mL of pyridine under an argon atmosphere. The bright yellow solution was allowed to slowly warm to room temperature. The reaction mixture was allowed to stir at that temperature for an additional hour. The solution was diluted with 200 mL of hexane and then washed with water followed by several saturated cupric sulfate solutions. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo, affording 1.34 g (89%) of white crystalline **26**: mp 114–116.5 °C (recrystallized from hexane); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.12 (d, J = 5 Hz, 3 H), 1.47 (s, 3 H), 1.62 (s, 3 H), 1.71 (s, 3 H), 1.60–2.55 (m, 3 H), 3.15 (d, J = 13 Hz, 1 H), 4.03 (s, 1 H), 4.04.55 (m, 1 H), 7.20–7.68 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 137.26 (s), 131.44 (d), 129.09 (d), 127.00 (d), 108.81 (s), 84.36 (d), 83.18 (s), 59.20 (d), 45.36 (d), 34.30 (t), 28.07 (d), 27.15 (q), 26.80 (q), 25.73 (q), 18.66 (q); IR ($CHCl_3$) 5.58 (m), 5.85 (s) μm; exact mass calcd for $C_{19}H_{23}F_3O_3S_2$, 420.104; found, 420.108.

***cis,trans*-3,5-Dimethyl-*trans,trans*-3,4-dihydroxy-1-mercapto-*trans*-2-(phenylsulfinyl)cyclohexane 3,4-Acetonide (28a and 28b).** *m*-Chloroperbenzoic acid (0.68 g, 1 equiv) was added to a methanol–ice-cooled solution of (trifluoroacetyl)thio sulfide **26** (1.4 g, 3.3 mmol) in 50 mL of methylene chloride. The white suspension was allowed to warm to 0 °C over a 2-h period. The mixture was washed with several saturated potassium carbonate solutions. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo, affording a white crystalline mixture of diastereomers **27a** and **27b**. The mixture was dissolved in 50 mL of methanol, and a catalytic amount of potassium carbonate was added. The solution was allowed to stir at room temperature under argon until the reaction was complete (2 h). The methanol was removed in vacuo and the residue dissolved in 100 mL of methylene chloride. The solution was washed with water and the organic layer dried over sodium sulfate, and the solvent was removed in vacuo, affording 1.08 g (98%) of a white crystalline mixture of diastereomers **28a** and **28b**. These diastereomers can be separated on prep TLC plates by using methylene chloride as the eluent. Spectral data for **27a** and **27b** (inseparable diastereomers) are as follows: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.03 (d, J = 6 Hz, 3 H), 1.10 (d, 6 Hz, 3 H), 1.48 (s, 6 H), 1.56 (s, 3 H), 1.61 (s, 3 H), 1.64 (s, 3 H), 1.88 (s, 3 H), 1.9–2.5 (m, 6 H), 3.11 (d, J = 12 Hz, 1 H), 3.33 (d, J = 9 Hz, 1 H) 3.45–3.85 (m, 1 H), 3.85–4.40 (m, 1 H), 4.02 (s, 2 H), 7.38–7.78 (m, 8 H), 7.8–8.1 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 145.22 (s), 139.89 (s) 131.36 (d), 128.94 (d), 128.38 (d), 127.46 (d), 124.40 (d), 109.75 (s), 109.50 (s), 85.22 (d), 83.67 (d), 81.13 (s), 80.83 (s), 72.06 (d), 69.28 (d), 37.86 (t), 36.69 (t), 35.20 (d), 32.59 (d), 28.89 (d), 28.68 (q), 28.10 (d), 26.93 (q), 26.70 (q), 26.09 (q), 18.20 (q), 17.96 (q); IR ($CHCl_3$) 5.60 (m), 5.85 (s) μm; exact mass calcd for $C_{19}H_{23}F_3O_4S_2$, 436.099; found, 436.101. *28a*: mp 120–122 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.06 (d, J = 6 Hz, 3 H), 1.41 (s, 3 H), 1.43 (s, 3 H), 1.70 (s, 3 H), 1.5–2.2 (m, 4 H), 2.75–3.10 (m, 2 H), 3.91 (s, 1 H), 7.30–7.80 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 146.54 (s), 129.87 (d), 129.01 (d), 124.56 (d), 109.25 (s), 83.90 (d), 80.54 (s), 76.40 (d), 34.53 (t), 30.28 (d), 29.16 (q), 27.34 (d), 26.59 (q), 26.18 (q), 18.36 (q). **28b**: mp 121–124 °C (recrystallized from ether–hexane; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.00 (d, J = 6.5 Hz, 3 H), 1.40 (s, 3 H), 1.42 (s, 3 H), 1.81 (s, 3 H), 1.7–2.3 (m, 3 H), 2.42 (d, J = 4 Hz, 1 H slowly exchanges with D_2O), 3.02 (s, 1 H), 2.9–3.22 (m, 1 H), 3.98 (s, 1 H), 7.4–7.7 (m, 3 H), 7.9–8.1 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 141.60 (s), 131.10 (d), 128.47 (d), 127.37 (d), 109.47 (s), 85.77 (d), 81.39 (s), 77.84 (d), 36.76 (t), 31.68 (d), 28.64 (q), 27.63 (d), 26.99 (q), 26.42 (q), 18.02 (q).

3-(2-Bromoethoxy)cyclopent-2-en-1-one (29). A suspension of 1,3-cyclopentanedione (2.75 g, 28.1 mmol), 2-bromoethanol (10 mL, 140 mmol), and a catalytic amount of toluenesulfonic acid in 150 mL of ethanol was heated at reflux with a Dean–Stark trap for 6 h. After cooling to room temperature, the dark red solution was added to 200 mL of ether and washed several times with a saturated sodium carbonate solution. The yellow organic layer was dried over magnesium sulfate and the solvent removed in vacuo. Excess bromoethanol was removed under high vacuum. Recrystallization of the crude crystalline residue from hexane afforded 4.95 g (86%) of **29** as yellow platelets: mp 61–63 °C; 1H NMR ($CDCl_3$, 90 MHz) δ 2.40–2.58 (m, 2 H), 2.60–2.80 (m, 2 H), 3.61 (dd, J = 6 Hz, 2 H), 4.30 (dd, J = 6 Hz, 2 H), 5.32 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 205.23 (s), 189.10 (s), 105.19 (d), 71.00 (t), 34.14 (t), 28.33 (t), 27.86 (t); IR ($CHCl_3$) 5.86 (s), 5.95 (s), and 6.30 (s) μm; mass spectrum, m/z 204 (M^+), 206).

Vinyl Sulfone 33. Sodium hydride (0.05 g, 2.1 mmol) was added to a methanol–ice-cooled solution of thiol sulfoxides **28a** and **28b** (0.693 g, 2.04 mmol) and bromo enone **29** (0.420 g, 2.05 mmol) in THF under an argon atmosphere. The grey suspension was allowed to slowly warm to 0 °C over a 2.5-h period. Methylene chloride was then added and the pale yellow solution washed with water. The aqueous layer was back-extracted with ethyl ether. The organic layers were combined and dried over magnesium sulfate. Removal of the solvent in vacuo afforded a colorless oil, which contained a mixture of diastereomers **19a** and **19b**. The oil was dissolved in toluene, and a large excess of sodium carbonate was added. The white suspension was heated at reflux for 6 h. The sodium carbonate was removed by filtration and the toluene removed in vacuo, affording **32** as a pale yellow oil. *m*-Chloroperbenzoic acid (2 equiv) was added to an acetone–dry ice cooled solution of crude **32** in 10 mL of methylene chloride. The white suspension was allowed to slowly warm to room temperature over a 3-h period. The cloudy solution was then extracted with a 10% sodium bisulfite solution followed by several saturated carbonate solutions. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo. The crude crystalline material was then recrystallized from ether–hexane, affording 0.687 g (91%) of **(33)**.

19a: ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.14 (d, J = 6.3 Hz, 3 H), 1.44 (s, 3 H), 1.53 (s, 3 H), 1.68 (s, 3 H), 2.10–1.16 (m, 3 H), 2.44 (t, J = 5.2 Hz, 2 H), 2.61 (t, J = 5.2 Hz, 2 H), 2.58–2.62 (m, 1 H), 2.71 (ddd, J = 14, 7, 7 Hz, 1 H), 2.93 (d, J = 2.6 Hz, 1 H), 3.74 (m, J = 2.6 Hz, 1 H), 3.89–3.93 (m, 2 H), 3.98 (d, J = 2.7 Hz, 1 H), 7.27 (s, 1 H), 7.45–7.52 (m, 3 H), 7.74 (dd, J = 7.4, 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.50 (s), 189.39 (s), 146.55 (s), 130.31 (d), 129.02 (d), 124.95 (d), 109.02 (s), 105.08 (d), 82.54 (d), 79.12 (s), 74.06 (d), 70.55 (t), 38.85 (d), 34.07 (t), 30.99 (d), 30.22 (t), 30.22 (t), 28.38 (t), 27.00 (q), 26.25 (q), 25.84 (q), 17.96 (q); IR ($CHCl_3$) 5.87 (s), 5.98 (s), 6.29 (s) μm; mass spectrum for $C_{24}H_{32}O_5S_2$ 449 (M – CH_3), 338 (M – C_6H_5SOH), 323 (M– CH_3 – C_6H_5SOH).

19b: ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.07 (d, J = 6.2 Hz, 3 H), 1.48 (s, 3 H), 1.53–1.58 (m, 1 H), 1.59 (s, 3 H), 1.80 (s, 3 H), 1.90–1.96 (m, 2 H), 2.43–2.53 (m, 3 H), 2.56–2.62 (m, 3 H), 2.75–2.77

(m, 1 H), 2.80 (d, J = 8.4 Hz, 1 H), 3.68–3.76 (m, 2 H), 3.92 (s, 1 H), 5.16 (s, 1 H), 7.49–7.57 (m, 3 H), 7.88–7.89 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.50 (s), 189.28 (s), 142.72 (s), 131.16 (d), 128.54 (d), 127.22 (d), 109.26 (s), 105.14 (d), 84.84 (d), 81.14 (s), 75.76 (d), 70.49 (t), 39.40 (d), 34.10 (t), 33.35 (t), 29.35 (t), 29.39 (t, d), 28.40 (q), 27.57 (t), 26.75 (q), 26.20 (q), 18.09 (q); IR 5.87 (s), 5.98 (s), 6.30 (s) μm; mass spectrum for $C_{24}H_{32}O_5S_2$ 449 (M – CH_3), 338 (M – C_6H_5SOH), 323 (M – CH_3 – C_6H_5SOH).

30a/30b (oil): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.60 (br s, 3 H), 1.10 (d, J = 6.5 Hz, 3 H), 1.20 (s, 3 H), 1.64 (s, 3 H), 1.8–2.3 (m, 3 H), 3.80 (br s, 1 H), 6.65 (m, 1 H), 7.42 (m, 3 M), 7.70 (m, 2 H).

31 (liquid): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.00 (d, J = 6.5 Hz, 3 H), 1.32 (s, 3 H), 1.40 (s, 3 H), 1.47 (s, 3 H), 1.70–2.20 (m, 3 H), 3.04 (d, J = 6 Hz, 1 H), 3.20–3.40 (m, 1 H), 3.60 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 107.97 (s), 82.45 (d), 78.18 (s), 42.83 (d), 37.81 (d), 28.00 (t), 27.48 (q), 27.11 (d), 26.65 (q), 22.62 (q), 18.07 (q); mass spectrum for $C_{11}H_{18}O_2S$ 214 199 (M^+) (M – CH_3).

32: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.16 (d, J = 6 Hz, 3 H), 1.31 (s, 3 H), 1.33 (s, 3 H), 1.38 (s, 3 H), 1.96–2.17 (m, 2 H), 2.18–2.35 (m, 1 H), 2.38–2.58 (m, 2 H), 2.58–2.80 (m, 2 H), 3.10 (t, J = 7 Hz, 2 H), 3.79 (s, 1 H), 4.14 (t, J = 7 Hz, 2 H), 5.30 (s, 1 H), 5.35 (s, 1 H); ^{13}C NMR δ 205.28 (s), 189.33 (s), 132.11 (s), 124.62 (d), 107.69 (s), 105.01 (d), 81.90 (d), 79.45 (s), 69.85 (t), 34.05 (t), 32.44 (t), 30.92 (d), 28.60 (t), 28.37 (t), 27.81 (q), 27.58 (q), 25.00 (q), 18.38 (q); IR ($CHCl_3$) 5.88 (s), 5.96 (s), 6.03 (s) μm mass spectrum for $C_{18}H_{26}O_4S$ 338 (M^+), 323 (M – CH_3).

33: mp 103–104 °C (recrystallized from ether); ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.22 (d, J = 6.8 Hz, 3 H), 1.28 (s, 3 H), 1.39 (s, 3 H), 1.97 (m, 1 H), 2.20 (ddd, J = 17.0, 11.2, 2.8 Hz, 1 H), 2.41 (dd, J = 17.0, 5.2 Hz, 1 H), 2.46–2.48 (m, 2 H), 2.61–2.64 (m, 2 H), 3.36 (ddd, J = 14.5, 6.2, 6.2 Hz, 1 H), 3.45 (ddd, J = 14.5, 6.2, 6.2 Hz, 1 H), 3.82 (s, 1 H), 4.36 (eight-line pattern, 2 H), 5.33 (s, 1 H), 6.60 (d, J = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 205.14 (s), 188.60 (s), 140.65 (d), 137.59 (s), 108.59 (s), 105.66 (d), 81.37 (d), 78.38 (s), 64.33 (t), 51.46 (t), 34.19 (t), 30.70 (t), 28.33 (d), 28.06 (q), 27.05 (q), 26.02 (t), 23.49 (q), 18.39 (q); IR ($CHCl_3$) 5.86 (s), 5.98 (s), 6.30 (s) μm; exact mass calcd for $C_{18}H_{26}O_6S$, 370.145; found, 370.145.

Photolysis of 33. Preparation of Photoadducts 34 and 35. A solution of vinyl sulfone **33** (0.254, 0.69 mmol) in 30 mL of acetonitrile (distilled from CaH_2) was degassed by bubbling argon through the solution for 0.5 h. The solution was then irradiated in a Rayonet instrument with 254-nm lamps through a Vycor filter for 40 min. The residue after the removal of the solvent in vacuo contained a mixture of two diastereomers. Chromatography on a Lobar liquid chromatograph, SiO_2, size B column, with a 10% ethyl acetate in chloroform solution, afforded the less polar photoadduct **35** (50 mg, 20%) and the more polar photoadduct **35** (187 mg 74%).

34: mp 188 °C (sublimes); ^{1}H NMR ($CDCl_3$, 470MHz) δ 1.08 (d, J = 6.5 Hz, 3 H), 1.22–1.38 (m, 1 H), 1.40 (s, 3 H), 1.49 (s, 3 H), 1.59 (dd, J = 15.0, 3.0 Hz, 1 H), 1.67 (s, 3 H), 2.02–2.17 (m, 1 H), 2.38–2.51 (m, 3 H), 2.69–2.79 (m, 1 H), 2.91 (d, J = 12.0 Hz, 1 H), 3.07 (ddd, J = 14.3, 7.0, 7.0 Hz, 1 H), 3.34 (ddd, J = 14.3, 5.8, 5.8 Hz, 1 H), 3.76 (d, J = 12.0 Hz, 1 H), 3.85 (d, J = 2.1 Hz, 1 H), 4.19 (ddd, J = 12.3, 6.0, 6.0 Hz, 1 H), 4.28 (ddd, J = 12.3, 6.3, 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 214.84 (s), 107.97 (s), 86.60 (s), 80.20 (d), 79.77 (s), 65.43 (s), 59.90 (t), 51.81 (d), 46.82 (t), 43.49 (d), 39.84 (t), 29.42 (d), 27.22 (t), 27.02 (q), 26.08 (q), 24.13 (t), 23.84 (q), 18.07 (q); IR ($CHCl_3$) 5.74 (s) μm; mass spectrum for $C_{17}H_{23}O_6S$, 357 (M – CH_3).

35: mp 190 °C (sublimes) (recrystallized from chloroform–ether); ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.17 (d, J = 6.6 Hz, 3 H), 1.24 (s, 3 H), 1.28 (s, 3 H), 1.45 (s, 3 H), 1.99–2.04 (m, 1 H), 2.28 (dd, J = 14.4, 6.0 Hz, 1 H), 2.37–2.44 (m, 3 H), 2.48–2.54 (m, 1 H), 2.76 (d, J = 9.1 Hz, 1 H), 2.75–2.77 (m, 1 H), 2.89 (d, J = 9.1 Hz, 1 H), 3.17 (ddd, J = 14.9, 10.5, 10.5 Hz, 1 H), 3.37 (ddd, J = 15.1, 11.2, 6.2 Hz, 1 H), 3.85 (s, 1 H), 4.20 (ddd, J = 13.0, 6.3, 3.1 Hz, 1 H), 4.35 (ddd, J = 12.6, 12.6, 4.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 212.89 (s), 108.42 (s), 84.05 (s), 80.63 (d), 77.83 (s), 66.71 (s), 61.84 (t), 58.81 (d), 49.74 (t), 48.43 (d), 37.05 (t), 28.83 (t), 28.57 (d), 27.54 (q), 26.82 (q), 25.64 (t), 24.11 (q), 19.50 (q); IR ($CHCl_3$) 5.74 (s) μm; exact mass calcd for $C_{18}H_{26}O_6S$, 370.145, found, 370.151.

Sodium Borohydride Reduction of 34 and Synthesis of Alcohol 36. Sodium borohydride (0.056 g, 1.48 mmol) was added to a solution of **34** (0.250 g, 0.676 mmol) in 10 mL of absolute ethanol. The ethanol was removed in vacuo after the solution had stirred at room temperature for 3 h. The residue was dissolved in chloroform and washed carefully with a saturated aqueous ammonium chloride solution. The chloroform layer was dried over magnesium sulfate and the solvent removed in vacuo. Recrystallization from ether afforded 0.21 g (84%) of **36**: mp 190–192 °C; ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.02 (d, J = 6.9 Hz, 3 H), 1.40 (s, 3 H), 1.46 (s, 3 H), 1.50 (dd, J = 14.5, 3.5 Hz, 1 H), 1.61 (s, 3 H), 1.77–1.86 (m, 3 H), 2.16 (ddd, J = 15.5, 15.5, 7.0 Hz, 1 H), 2.38 (dd, J = 14.5, 14.5 hz, 1 H), 2.85 (dd, J = 13.1, 7.5 Hz, 1 H), 2.88–2.94 (m, 1 H), 3.06 (ddd, J = 14.5, 8.0, 8.0 Hz, 1 H), 3.25 (ddd, J = 14.5, 8.7, 3.0 Hz, 1 H), 3.82 (d, J = 13.1 Hz, 1 H), 3.95 (d, J= 3.0 Hz, 1 H), 4.06 (ddd, J = 12.0, 8.7, 3.0 Hz, 1 H), 4.24 (ddd, J = 1.20, 8.4, 8.4 Hz, 1 H), 4.61 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 106.86 (s) 89.28 (s), 81.72 (d), 81.54 (s), 73.23 (d), 63.96 (s), 58.89 (t), 51.66 (d), 44.29 (t), 37.60 (d), 36.54 (t), 27.69 (q), 26.96 (q), 26.29 (q), 17.99 (q); IR ($CHCl_3$) 2.78–3.08 (m) μm.

***cis*-10,11-Dihydroxy-*trans*-9,11-dimethyltricyclo-[5.4.0.0^{2,6}]undecan-3-one 10,11-Acetonide (37).** A blue solution of lithium dissolved in methylamine was added dropwise via a dropping funnel to an acetone–dry ice cooled solution of **34** (0.20 g, 0.54 mmol) in 20 mL of methylamine. When the blue color persisted the solution was immediately quenched with methanol. After evaporation of the methylamine, the residue was dissolved in ether and washed with a 10% HCl solution. The ether solution was dried over magnesium sulfate and the solvent removed in vacuo. Chromatography on 50 g of SiO_2 with 20% ethyl acetate in chloroform afforded 11.1 mg (7%) of **37**: mp 58–59 °C; ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.09 (d, J = 7.0 Hz, 3 H), 1.22 (s, 3 H), 1.31 (s, 3 H), 1.34 (ddd, J = 1.18, 11.8, 11.8 Hz, 1 H), 1.48 (s, 3 H), 1.62 (ddd, J = 11.9, 3.8, 3.8 Hz, 1 H), 1.75–1.84 (m, 2 H), 1.87–1.95 (m, 2 H), 2.24 (dd, J = 13.4, 8.8, 1 H), 2.39 (ddd, J = 19.4, 8.8, 2.2 Hz, 1 H), 2.53 (ddd, J = 19.4, 9.7, 9.7 Hz, 1 H), 2.78 (ddd, J = 6.4, 6.4 Hz, 1 H), 2.90 (dd, J = 8.4, 7.2 Hz, 1 H), 3.54 (d, J = 3.6 Hz); ^{13}C NMR ($CDCl_3$) δ 212.85, 107.15, 85.31, 80.79, 49.04, 47.28, 41.53, 39.54, 34.76, 29.06, 29.96, 25.58, 18.34, 18.25, 16.08; IR ($CHCl_3$) 5.80 (s) μm; mass spectrum for $C_{16}H_{24}O_3$ 264 (M^+), 249 (M – CH_3).

***trans,trans*-10,11-Dihydroxy-*cis,trans*-9,11-dimethyltricyclo[5.4.0.0.^{2,6}]undecan-3-ol 10,11-Acetonide (38).** A blue solution of lithium dissolved in methylamine was added dropwise via a dropping funnel, equipped with a dry ice condenser, to a solution of **36** (47.8 mg, 0.128 mmol) in 10 mL of methylamine at –78 °C. The solution was immediately quenched with methanol when the blue color persisted. After evaporation of the methylamine, the residue was chromatographed on 50 g of SiO_2 with 20% ethyl acetate in chloroform. Chromatography afforded 18.1 mg (50%) of **38** as an oil: ^{1}H NMR ($CDCl_3$, 470 MHz) δ 1.08 (d, J = 7.3 Hz, 3 H), 1.20–1.27 (m, 2 H), 1.32 (s, 3 H), 1.49 (s, 3 H), 1.51 (s, 3 H), 1.53–1.58 (m, 2 H), 1.67–1.71 (m, 1 H), 1.72–1.79 (m, 1 H), 1.88–1.93 (m, 2 H), 2.35 (dd, J = 13.6, 8.5 Hz, 1 H), 2.47 (ddd, J = 6.0, 6.0, 6.0 Hz, 1 H), 2.95 (ddd, J = 8.0, 8.0, 8.0 Hz, 1 H), 3.60 (d, J = 4.1 Hz, 1 H), 4.32 (ddd, J = 8.0, 8.0, 8.0 Hz, 1 H); mass spectrum, m/z 266, 251.

X-ray Study of 34. Crystals suitable for an X-ray analysis were grown from a chloroform–ether solution. The crystal used approximated a cube with an edge length of 0.3 mm. Oscillation and Wissenberg photographs indicated monoclinic symmetry with the space group P_2/n. Unit cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles of 15 three-dimensional reflections measured on a Syntex P3 automated diffractometer equipped with a graphite monochromator. Crystallographic data are as follows: a = 12.958 (4) Å, b = 10.064 (3) Å, c = 15.388 (4) Å, β = 116.26 (2)°, V = 1799.6 Å^3, Z = 4, ρ_{calcd} = 1.37, ρ_{expt} ≥1.0, $F(000)$ = 792, μ = 17.6 cm^{-1}, λ (Cu Kα) = 1.5418 Å.

Intensity data were collected using θ–2θ scanning mode with a variable scan rate of 2–29° min^{-1}, depending on the reflection intensity. Background counting time was equal to the scan time. Three standard reflections were monitored for every fifty reflections and although they showed no systematic variations, they did decrease by 5% over the entire data collection time interval. A total of 2442 reflections were collected, of which 2237 with $F_o > 3\rho(F_o)$ were used in the solution and refinement of the structure. The data set was corrected for Lorentz and polarization effects

and for the decay in intensity but not for absorption effects.

The direct method program MULTAN[20] served to locate the sulfur, oxygen, and the majority of carbon atoms. Several cycles of least-squares refinement followed by the calculation of difference Fourier maps revealed the remaining atoms. Block refinement of the positional and anisotropic thermal parameters of the heavy atoms followed by the positional and isotropic thermal parameters of the hydrogen atoms produced convergence with $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ both equal to 0.051. Anomalous dispersion effects of all non-hydrogen atoms were included in the calculation of F_c using $\Delta F'$ and $\Delta F''$ calculated by Doyle and Turner.[21] The atomic scattering factors were taken from Cromer and Liberman.[22] A list of all interatomic distances and angles are available as supplementary material.

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Registry No. **6**, 4341-24-6; **7**, 35023-83-7; **8**, 7214-50-8; **9**, 81939-74-4; **10a**, 81939-75-5; **10b**, 81939-76-6; **11a**, 81939-77-7; **11b**, 81939-78-8; **12a**, 81939-79-9; **12b**, 81969-75-7; **13**, 81939-80-2; **14**, 81939-81-3; **16**, 81939-82-4; **19** (isomer 1), 81939-83-5; **19** (isomer 2), 81939-84-6; **20**, 81939-85-7; **21**, 81939-86-8; **23**, 81939-87-9; **25**, 81939-88-0; **26**, 81939-89-1; **27** (isomer 1), 81939-90-4; **27** (isomer 2), 81939-91-5; **28** (isomer 1), 81939-92-6; **28** (isomer 2), 81939-93-7; **30a** (β-sulfoxide isomer), 81940-00-3; **30b** (α-sulfoxide isomer), 81940-01-4; **29**, 42858-97-9; **31**, 81939-94-8; **32**, 81939-95-9; **33**, 81939-96-0; **34**, 81939-97-1; **35**, 81969-76-8; **36**, 81956-23-2; **37**, 81939-98-2; **38**, 81939-99-3; ethyl acetoacetate, 141-97-9; ethyl crotonate, 10544-63-5; thiophenol, 108-98-5; trifluoroacetic anhydride, 407-25-0; 1,3-cyclopentanedione, 3008-40-0; 2-bromoethanol, 540-51-2.

Supplementary Material Available: Tables of interatomic distances and angles (6 pages). Ordering information is given on any current masthead page.

Photochemistry of Epoxyquinones. 6.[1] Norrish Type II Photoreaction of 2,3-Dihydro-2,3-epoxy-1,4-naphthoquinone

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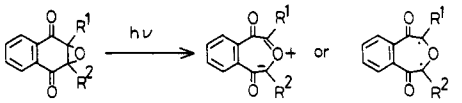
Photochemical reactions of 2,3-dialkyl-substituted or 2-alkyl-substituted 2,3-dihydro-2,3-epoxy-1,4-naphthoquinones in which the carbonyl group has intramolecularly abstractable γ-hydrogen atoms have been studied. On irradiation, epoxynaphthoquinones **11a–h** initially afforded cyclobutanols **12a–h** and phthiocols **13a,b**. The former are Norrish type II cyclization products, while the latter may be formed via an allene oxide intermediate which is a direct Norrish type II elimination product. The cyclobutanols **12a–h** underwent secondary photorearrangement to β-diketones **14a–h** and β-alkoxy enones **15a–d,g**, but **14g** and **14h** were readily dehydrated on chromatographic separation over silica gel to give indenone derivatives **15g** and **15h**. Preference for the Norrish type II photoreaction over the generation of the carbonyl ylide or 1,3-diradical is discussed in terms of the rate constants for each process. A tentative mechanism for the novel photochemical reactions of the cyclobutanols is proposed.

Considerable attention has been focused in recent years on the photochemistry of small-ring heterocyclic compounds.[2] Among these, investigations of a number of α,β-epoxy ketones **1** have demonstrated that these compounds are photochemically labile, and most can be classified into two groups according to their reaction modes: (a) C_α–O bond cleavage leading to the formation of a 1,3-diradical **2** which would give a β-diketone **3** by 1,2-alkyl migration of either the R^2 or R^3 group and (b) C_α–C_β bond fission leading to the formation of a carbonyl ylide **4a** or 1,3-diradical **4b** which would give a tetrahydrofuran **5** by 1,3-cycloaddition to olefin (Scheme I). Recently, photochemical generation of the carbonyl ylide **6** or 1,3-diradical **7** from several epoxynaphthoquinones (eq 1) was reported.[3]

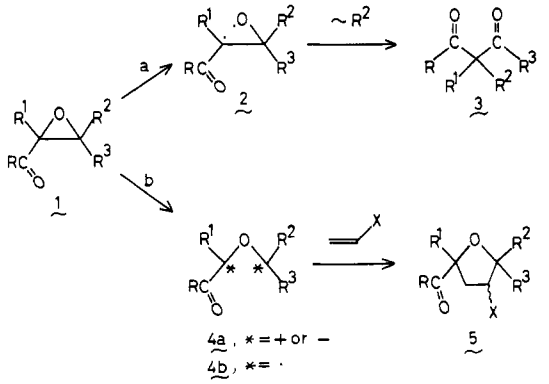


(1)

11i, $R^1 = R^2 =$ Me
j, $R^1 =$ Me; $R^2 = CH_2C(Me)_3$

6 **7**

Scheme I



These reactive intermediates were successfully trapped by olefins,[3a] ketones,[3b] and aldehydes.[3b] However, irradiation of dimethylacrylophenone oxide (**8a**) and *trans*-dypnone oxide (**8b**) were reported to give the unsaturated keto alcohols, **9a** and **9b**, respectively, as the major products[4]. (Scheme II). The absence of detectable amounts of β-diketo products in those cases is noteworthy. The authors

(1) Part 5: Osuka, A., *J. Org. Chem.*, in press.

(2) For reviews, see: (a) Padwa, A. *Org. Photochem.* **1967**, *1*, 91. (b) Bertoniere, N. R.; Griffin, G. W. *Ibid.* **1973**, *3*, 138. (c) Griffin, G. W.; Padwa, A. In "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; Wiley: New York, 1976; p 41. (d) Nastasi, M.; Streith, J. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. III, p 381.

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