on silica gel (elution with 9% ethyl acetate in petroleum ether) to give a mixture of **48a** and **49a** (85%). Recrystallization from ethyl acetate–petroleum ether and subsequently from ether furnished the more polar isomer in analytically pure form: colorless crystals; mp 181–182 °C; ^{1}H NMR ($CDCl_3$) δ 8.0–7.0 (m, 13 H), 4.51 (d, J = 1.8 Hz, 1 H), 4.41 (s, 1 H), 2.21 (d, J = 1.8 Hz, 1 H), 1.50 (s, 3 H), 0.09 (s, 9 H); MS, m/e (M^+) calcd 432.1579, obsd 432.1590. Anal. Calcd for $C_{26}H_{28}O_2SSi$: C, 72.18; H, 6.52. Found: C, 71.97; H, 6.51.

The less polar isomer exhibited the following ^{1}H NMR spectral data ($CDCl_3$): δ 7.95–7.01 (m, 13 H), 4.41 (d, J = 1.6 Hz, 1 H), 4.36 (s, 1 H), 2.13 (d, J = 1.6 Hz, 1 H), 1.28 (s, 3 H), −0.14 (s, 9 H).

7-Methyldibenzobarrelene (50a). A magnetically stirred solution of the more polar isomer **48a** or **49a** (33.4 mg, 0.077 mmol) and tetra-*n*-butylammonium fluoride (1 mL of 1 M solution in THF) in dry tetrahydrofuran was heated at the reflux temperature under nitrogen for 30 min. The usual workup afforded 16.2 mg (71%) of **50a** after silica gel chromatography (elution with petroleum ether). The analytical sample (mp 107–108 °C) was obtained by preparative VPC (12 ft × 0.25 in. 5% SE-30, 180 °C): ^{1}H NMR ($CDCl_3$) δ 7.31–6.92 (m, 8 H), 6.51 (ddq, 1 H), 5.02 (d, J = 6 Hz, 1 H), 4.80 (d, J = 1.8 Hz, 1 H), 1.96 (d, J = 1.7 Hz, 3 H). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.50; H, 6.47.

When the less polar isomer was treated analogously, **50a** was produced with equal efficiency. Hydrocarbon **50a** can be conveniently prepared in 58% overall yield from **43** if intermediates are not purified.

Prenylation of 43. From 0.50 g (1.2 mmol) of **43**, excess prenyl bromide (1 mL), and *n*-butyllithium (2.55 mL of 1.5 M solution in hexane) there was isolated after reaction as above an 80% yield of a crude **48b**/**49b** mixture. Because attempts at chromatographic purification caused decomposition, this material was subjected to elimination without further handling.

7-Prenyldibenzobarrelene (50b). The preceding material (96.3 mg, 0.198 mmol) dissolved in dry tetrahydrofuran (2 mL) was heated under nitrogen for 1 h with tetra-*n*-butylammonium fluoride. The usual workup gave **50b** (44 mg, 82%) as a colorless oil which decomposed slowly upon standing: ^{1}H NMR ($CDCl_3$) δ 7.28–6.91 (m, 8 H), 6.45 (m, 1 H) 5.11–5.0 (m, 2 H), 4.80 (d, J = 1.5 Hz, 1 H), 2.95 (d, J = 7 Hz, 2 H), 1.69 (s, 3 H), 1.58 (s, 3 H); MS, m/e (M^+) calcd 272.1467, obsd 272.1516.

The direct conversion of **43** to **50b** proceeds in 63% overall yield.

Acknowledgment. We thank the National Science Foundation for the financial support which made this research possible.

Registry No. **1**, 5535-48-8; **2**, 64489-06-1; **3**, 64489-07-2; **4**, 4837-01-8; **5**, 1822-73-7; **6**, 64489-03-8; **7**, 32501-93-2; **8**, 87568-19-2; *exo*-**9**, 19242-75-2; *endo*-**9**, 19285-87-1; *exo*-**10**, 73301-13-0; *endo*-**10**, 73346-62-0; **11**, 73301-14-1; **12**, 73301-18-5; **13**, 498-66-8; **14**, 931-64-6; **15**, 1674-10-8; **16**, 5675-64-9; **17**, 73301-15-2; **18**, 640-57-3; **19**, 87637-85-2; **20**, 87568-20-5; **21**, 87637-86-3; **22**, 73301-16-3; **23**, 73301-20-9; *exo*-**24**, 73301-17-4; *endo*-**24**, 87637-87-4; **25**, 25489-02-5; **26a**, 73301-21-0; **26b**, 73301-29-8; **27a**, 87568-21-6; **27b**, 87568-22-7; **28a**, 73301-23-2; **28b**, 73301-31-2; *exo*-**29a**, 87637-88-5; *endo*-**29a**, 87637-90-9; *exo*-**29b**, 87637-89-6; *endo*-**29b**, 87637-91-0; *exo*-**30a**, 87638-49-1; *endo*-**30a**, 87637-93-2; *exo*-**30b**, 87637-92-1; *endo*-**30b**, 87637-94-3; *exo*-**31a**, 87637-95-4; *endo*-**31a**, 87637-97-6; *exo*-**31b**, 87637-96-5; *endo*-**31b**, 87638-50-4; **32a**, 73301-26-5; **32b**, 39178-72-8; **33a**, 73301-27-6; **33b**, 73301-36-7; **34a**, 73301-25-4; **34b**, 73301-35-6; **35a**, 73301-28-7; **35b**, 73301-37-8; **36**, 82201-44-3; **37**, 82262-88-2; **38**, 82262-89-3; **39**, 82209-55-0; **40**, 82263-28-3; **41**, 82263-29-4; **42**, 10211-14-0; **43**, 82201-45-4; **44**, 82201-47-6; **45a**, 2734-13-6; **45b**, 82201-50-1; **46**, 87585-84-0; **47**, 82209-56-1; **48a**, 82201-48-7; **48b**, 82201-49-8; **49a**, 87568-23-8; **49b**, 87568-24-9; **50a**, 82201-51-2; **50b**, 82201-52-3; PhSNa, 930-69-8; $BrCH_2CH_2Br$, 106-93-4; $BrCH_2CH_2CH_2Br$, 109-64-8; $Me_3SiCH{=}CH_2$, 754-05-2; $PhSO_2Cl$, 98-09-9; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}CHC(CH_3){=}CH_2$, 106-95-6; $CH_2{=}CHCH_2Br$, 106-95-6; Me_3SiCH_2OH, 3219-63-4; Me_3SiCH_2OTf, 64035-64-9; $I(CH_2)_4COOC_2H_5$, 41302-32-3; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; anthracene, 120-12-7; nopadiene, 473-00-7; myrcene, 123-35-3; 2,3-dihydroanisole, 2161-90-2; 1-(phenylthio)-3-bromopropane, 3238-98-0; 4-*p*-tolylpentanoic acid, 26232-97-3; 4-*p*-tolylpentanol, 19876-64-3; 4-*p*-tolylpentanol THP ether, 87568-25-0; 4-*p*-tolylpentyl bromide, 19872-53-8; geranyl bromide, 6138-90-5; bromoacetaldehyde diethyl acetal, 2032-35-1; 2-(iodomethyl)tetrahydrofuran, 5831-70-9; 1,3-diphenylisobenzofuran, 5471-63-6.

Regiocontrolled Synthesis of Mono-, Di-, and Trisubstituted Cyclohexenones by Cycloaddition of Vinyl Sulfones to 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadienes. Conversion of Alkenes into Effective Dienophilic Reagents

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Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

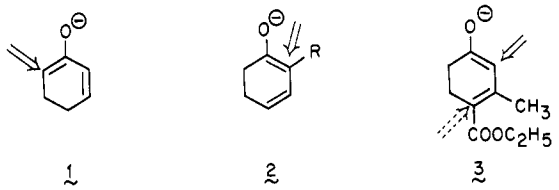
Received May 17, 1983

Cycloaddition of phenyl vinyl sulfone to Danishefsky's diene followed by direct ketalization provided **7**, a synthon for the 4-(2-cyclohexenyl) anion. Thus, **7** readily undergoes regiospecific γ-alkylation. Ensuing reductive desulfonylation and hydrolysis provides 2-(and 3-)cyclohexenones efficiently. Zingiberenol, a monocyclic sesquiterpene, was prepared by means of this methodology. Terminal alkenes and cyclic olefins enter into comparable regiocontrolled Diels–Alder addition if they are first subjected to selenosulfonation and oxidation to the vinyl sulfone. Removal of the phenylsulfonyl substituent after condensation provides the adducts which are formally derived from alkylation of the hypothetical C_5 anion of 2-cyclohexenone. The scheme can be expanded to include γ-alkylation prior to desulfonylation. By this means, one is able to prepare 4,5-disubstituted 2-(and 3-)cyclohexenones where the nature of the pendant side chains can be widely varied.

As a group, 2-cyclohexenones comprise an important class of starting materials for the synthetic chemist. Although their utilization in a myriad of contexts has evolved systematically over the years, complications continue to persist during attempts to functionalize such α,β-unsaturated ketones at specific sites. While their kinetic enolates, generalized by **1**, commonly allow for clean α'-alkylation,[1] thermodynamic enolates, e.g., **2**, have proven more difficult

(1) (a) House, H. O. "Modern Synthetic Reactions", 2nd ed; W. A. Benjamin: New York, 1972; pp 492–628. (b) d'Angelo, J. *Tetrahedron* **1976**, *32*, 2979.

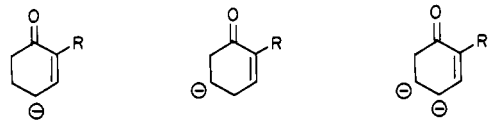
0022-3263/83/1948-4986$01.50/0



1 2 3

to generate[2] and suffer from strong tendency to undergo irreversible C-alkylation at their α position, even when this site is substituted.[3] The presence of an activating group as in Hagemann's ester (**3**) is not sufficient to bypass this difficulty.[4] Consequently, one has had to rely upon indirect methods to achieve net γ-alkylation. Functionalization at the δ position has not previously been accorded meaningful attention.

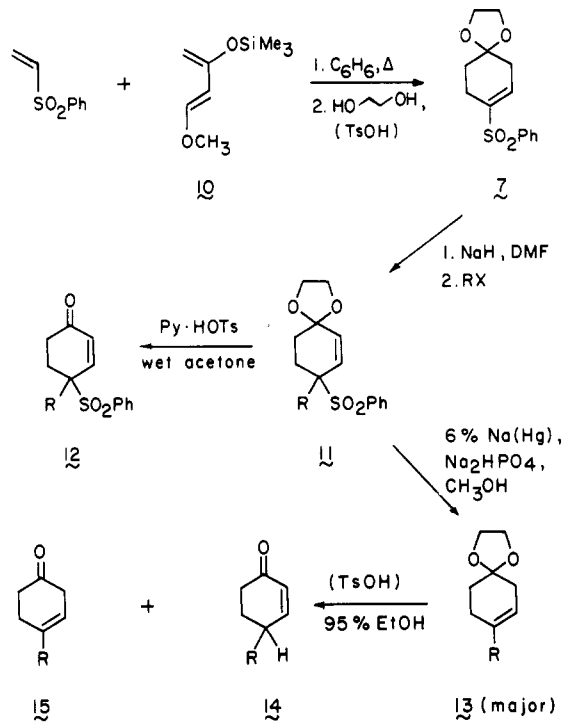
In considering a general approach that would provide synthons for monoanions **4** and **5** as well as dianion **6**, we



4 5 6

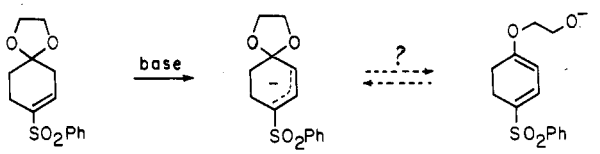
were attracted to a solution which has its foundations in the knowledge that (a) phenyl vinyl sulfone can serve as a convenient ethylene and terminal olefin equivalent in [4 + 2] cycloadditions,[5] (b) α,β-unsaturated sulfones are captured by unsymmetrical dienes with high regioselectivity,[5] and (c) sulfonyl substituents undergo alkylation with good regiochemical control.[6,7] Thus, Diels–Alder cycloaddition of a vinyl sulfone to suitably activated dienes, particularly those developed by Danishefsky,[8] followed by appropriate hydrolysis, was expected to lead efficiently to 4-sulfonyl-substituted cyclohexenones or their ketals. For completion of the sequence, the sulfonyl group must ultimately be removed reductively. Also possible was the option to effect alkylation α to the sulfone group prior to this final step. The breadth of this newly devised methodology, which is described herein,[9] is wide-ranging and offers several synthetic advantages, not previously available.

Scheme I



10 7 12 11 15 14 13 (major)

Regiospecific γ-Alkylation of 2-(and 3-)Cyclohexenones. Our strategy for achieving efficient γ-alkylation was based upon the expectation that the anion derivable from **7**, i.e., **8**, would exhibit heightened nucleo-



7 8 9

philicity at the carbon atom directly bonded to the phenylsulfonyl substituent.[10] This regiospecificity should be fostered additionally by the steric congestion provided by the ketal group. Not reliably determinable from the outset was the extent to which **8** might react via its ring-opened form **9**, especially when more hindered electrophilic agents were involved.

Consequently, benzene solutions of phenyl vinyl sulfone and **10**[8] were heated at the reflux temperature for 28 h, and the unpurified adduct was directly ketalized. In this manner, **7** could be routinely isolated as a colorless crystalline solid in 85% yield (Scheme I). It proved expedient to deprotonate **7** with sodium hydride in dimethylformamide and to treat **8** in situ with the desired alkylating agent. Examination of Table I reveals this conversion to proceed efficiently and with highly acceptable regiocontrol. At least with the primary halides listed therein, no competitive O-alkylation via **9** was observed.

In general, the alkylation products were characterized via their enones **12** after deketalization with pyridinium *p*-toluenesulfonate (PPTS)[11] in wet acetone. When preliminary examination of the direct desulfonylation of **12** with various reagents did not proceed as well as desired, we turned to the reduction of **11** with 6% sodium amalgam in Na_2HPO_4-buffered methanol.[12] These reactions were

(2) (a) Negishi, E.; Chatterjee, S. *Tetrahedron Lett.* **1983**, 1341. (b) Krafft, M. E., Holton, R. A. *Ibid.* **1983**, 1345.

(3) See, for example: (a) Gompper, R.; Wagner, H.-U. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 321. (b) Ando, M.; Büchi, G.; Ohmuna, T. *J. Am. Chem. Soc.* **1975**, *97*, 6880. (c) Schroepfer, G. J., Jr.; Parish, E. J.; Kandutsch, A. A. *Ibid.* **1977**, *99*, 5494. Exceptions can be found among intramolecular examples where the structural features of the substrate are particularly conducive to γ alkylation. Consult: (d) Piers, E.; Zbozny, M.; Wigfield, D. C. *Can. J. Chem.* **1979**, *57*, 1064. (e) Piers, E.; Zbozny, M. *Ibid.* **1979**, *57*, 2249. (f) Johnson, A. P.; Vajs, V. *J. Chem. Soc., Chem. Commun.* **1979**, 817.

(4) (a) White, J. D.; Snug, W. L. *J. Org. Chem.* **1974**, *39*, 2323. (b) Johnson, W. S.; Dawson, M. I.; Ratcliffe, B. E. *Ibid.* **1977**, *42*, 153.

(5) (a) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.*, preceding paper in this issue. (b) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853.

(6) (a) Lansbury, P. T.; Erwin, R. W. *Tetrahedron Lett.* **1978**, 2675. (b) Lansbury, P. T.; Erwin, R. W.; Jeffrey, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1602.

(7) Julia, M.; Arnouid, D. *Bull. Soc. Chim. Fr.* **1973**, 743.

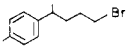
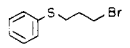
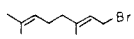
(8) (a) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. (b) Danishefsky, S.; Yan, C. F.; McCurry, P. M., Jr. *J. Org. Chem.* **1977**, *42*, 1819. (c) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996. (d) Danishefsky, S.; Yan, C. F.; Singh, R. K.; Gammill, R. B., McCurry, P. M., Jr.; Fritsch, N.; Clardy, J. *Ibid.* **1979**, *101*, 7001.

(9) Preliminary accounts of portions of this work have appeared previously: (a) Paquette, L. A.; Kinney, W. A. *Tetrahedron Lett.* **1982**, *23*, 131. (b) Paquette, L. A.; Kinney, W. A. *Ibid.* **1982**, 5127. (c) Paquette, L. A.; Crouse, G. D. *J. Org. Chem.* **1983**, *48*, 141.

(10) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

(11) Sterzycki, R. *Synthesis* **1979**, 724.

Table I. Regiospecific γ-Alkylation of 2-Cyclohexenones

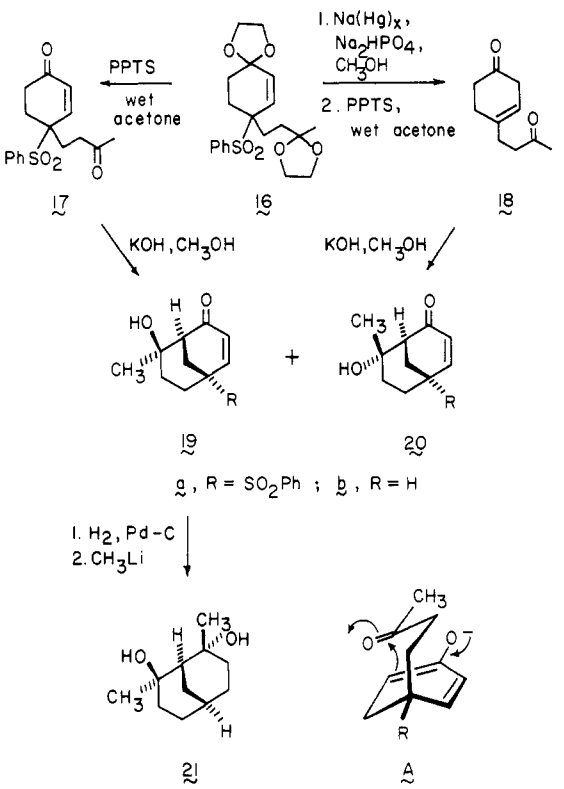
electrophile	alkylation yield, % of 11	desulfonylation yield, %	desulfonylation β,γ:α,β ratio	hydrolysis yield, %	hydrolysis α,β:β,γ ratio
a, CH_3I	83	89	59:41	74	80:20
b, 	77	98	69:31	73	61:39
c, 	91	100	66:34	87	62:38
d, 	81	100	68:32	83	68:32
e, 	89	90	63:37	82	70:30
f, 	92	92	67:33	87	47:53
g, 	76	95	64:36	72	69:31
h, 	94	100	62:38	93	69:31
i,	92	71	56:44	76	69:31

usually complete within 30 min at room temperature, the pendant functional groups were not chemically altered, and yields of the pure products generally bordered on quantitative. A preponderance of the more thermodynamically favored β,γ-unsaturated ketals **13** was routinely observed (^{1}H NMR analysis, Table I). Acid hydrolysis of these mixtures delivered the target cyclohexenones **14** ⇄ **15**. In most instances, ^{1}H NMR spectroscopy and/or chromatographic separation indicated the α,β isomer (**14**) to predominate, as expected. Little effort was made to determine the precise positions of equilibrium for these product pairs since this issue has been previously examined by others[13] and is reasonably well understood.

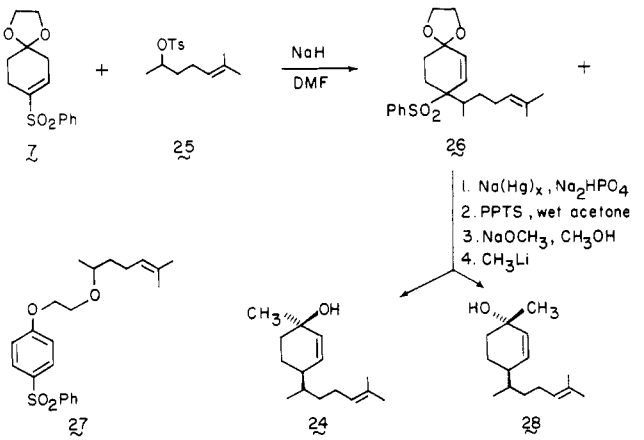
It should be recognized that no difficulties were encountered in separating **14** and **15** by medium-pressure liquid chromatography on silica gel. Accordingly, either double bond isomer is available in a pure state for further synthetic manipulation. Since the overall yields from **7** to the individual cyclohexenones are very good, this sulfonyl ketal is viewed as a useful, readily accessible, stable synthon for **4**.

When **7** was condensed with 4-bromo-2-butanone ethylene ketal[14] as before, **16** resulted (85%). Following independent conversion to **17** and **18** (Scheme II), these diketones were exposed to alcoholic potassium hydroxide. In the first instance, a pair of highly crystalline bicyclic keto alcohols was formed and isolated in yields of 72% and 11%, respectively. Preliminary structural assignment to these obviously epimeric (^{1}H NMR comparison) products was based on the premise that intramolecular aldol cyclization might well occur more rapidly from that conformation in which the carbonyl dipoles are opposed (see **A**). Some support for this conclusion was provided by the more highly shielded nature of the methyl singlet in **19a** (δ 1.20) relative to that in **20a** (δ 1.39), but these data are hardly conclusive. Consequently, **18** was comparably cyclized, and the exclusive aldol product (**19b**) having a methyl singlet at δ 1.21 was sequentially hydrogenated and exposed to methyllithium. The diol so produced (**21**) was seen by ^{13}C NMR analysis to be devoid of a plane of symmetry. Since the second methyl group in **21** is certain to have entered from the exo direction, the original alkyl substituent is required to be endo, in confirmation of the original structural hypothesis.

Scheme II



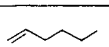
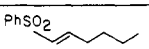
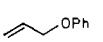
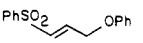
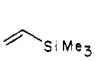
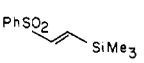
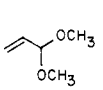
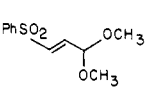
Scheme III



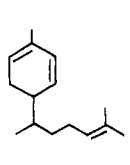
Short Synthesis of Zingiberenol. In an effort to delineate somewhat more fully the scope and limitations of the present methodology, application to the synthesis

(12) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.
(13) (a) Soffer, M. D.; Williston, A. C. *J. Org. Chem.* **1957**, *22*, 1254. (b) Lewis, K. G.; Williams, G. J. *Tetrahedron Lett.* **1965**, 4573. (c) Heap, N.; Whitham, G. *J. Chem. Soc.* **1966**, 164.
(14) Brown, F.; Dahl, R. *Bull. Soc. Chim. Fr.* **1972**, 4292.

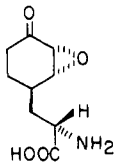
Table II. Preparation of 5-Substituted 2-Methyl-2-cyclohexenones

	olefin	selenosulfonation product	yield, %	cycloaddition-hydrolysis yield of 32, %	cycloaddition-hydrolysis α,β:β,γ ratio	desulfonylation yield of 33, %	desulfonylation α,β:β,γ ratio
a,			62	68	100:0	78	100:0
b,			89	79	67:33	63	100:0
c,			84				
d,			73	77	100:0	85	60:40

of a monocyclic natural product was viewed as desirable. Among the candidates which suggested themselves were zingiberene (**22**),[15] anticapsin (**23**),[16,17] and zingiberenol



22



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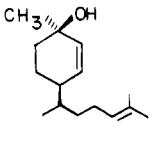
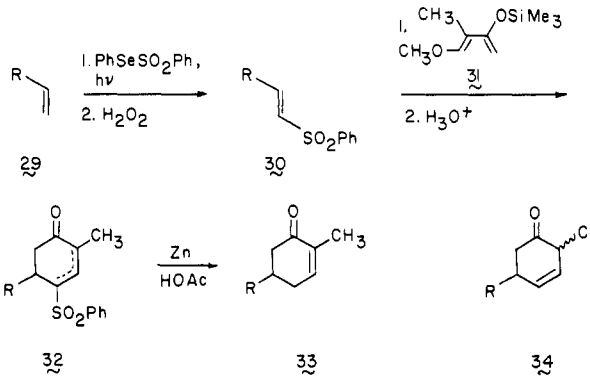


24

(**24**).[18] Because a directed synthesis of **24**, a sesquiterpene alcohol recently isolated from the essential oil of *Zingiber officinale* Rosc, had not yet been reported, it became the target. An additional attraction was the need to effect the alkylation of **7** with a secondary tosylate, viz. **25**.[19] By use of those conditions previously outlined, **26** was obtained (Scheme III) as a mixture of diastereomers (47%) whose separation into two pure components could be accomplished readily by MPLC. Accompanying **26** was the aromatic sulfone **27** (15%), evidently the oxidized end product of a sequence initiated by O-alkylation of **9**. Following desulfonylation of **26** and hydrolysis to the conjugated enone, reaction with methyllithium expectedly furnished both **24** and **28**. The desired trans isomer predominated (2.4:1) and was easily isolated in a pure state following chromatography. Although the sample of **24** prepared in this manner consisted of a mixture of two diastereomers, its infrared spectrum was superimposable upon that published for the naturally occurring substance. The infrared spectrum of **28** differed significantly, in agreement with the stereochemical assignments.

From Alkenes to 5-Substituted 2-(and 3-)Cyclohexenones. Guided by the preceding developments, the utility of uniting terminal vinyl sulfones (**30**) with **10** or **31**[8] via the Diels–Alder reaction was next pursued. Despite somewhat enhanced steric levels, strong orientational dominance by the sulfonyl group was expected to persist. Indeed, the protocol has proven successful and serves as a useful synthon for **5**.

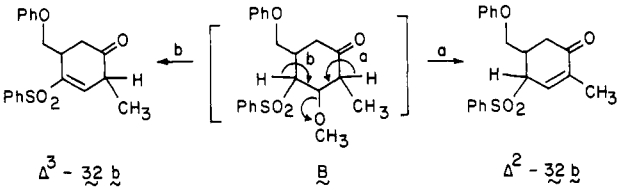
In order to arrive cleanly and rapidly at **30**, recourse was made to selenosulfonation of terminal alkenes. The thermal[20] and photochemical versions[21] of *Se*-phenyl benzeneselenosulfonate addition to **29** were initially examined. Although both procedures provided the desired



29 **30** **31** **32** **33** **34**

regioselectivity, the photochemical conditions proved substantially cleaner, more efficient, and easier to execute. Also, tolerance to a wide range of functional groups was seen, as evidenced by the suitability of such terminal alkenes as phenyl allyl ether, trimethylvinylsilane, acrolein dimethyl acetal (Table II), the prostaglandin intermediate **35**, and additional examples to follow.

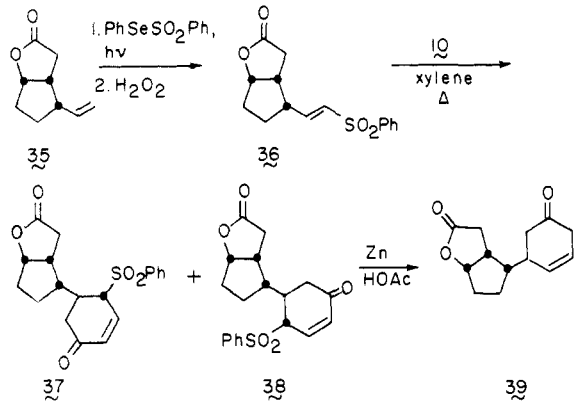
The cycloadditions of **30a,b,d** to **31** were carried out under nitrogen in refluxing xylene, generally for 20–80 h. The reaction mixtures were then cooled and hydrolyzed with 1% hydrochloric acid. Whereas the α,β-unsaturated isomers of **32a** and **32d** were formed exclusively, some 3-cyclohexenone was isolated in the phenoxymethyl example. Under equilibrating conditions (*p*-toluenesulfonic acid in ethanol), Δ^3-**32b** was converted to Δ^2-**32b**, thus suggesting that its original formation may be due to competing elimination within intermediate methoxy sulfone B.



Δ^3-**32b** **B** Δ^2-**32b**

When **36** was allowed to react with **10** and the reaction mixture was subjected directly to mild hydrolysis, the diastereomeric conjugated enones **37** and **38** were obtained

(15) Mukharji, S. M.; Bhattacharrya, N. K. *J. Am. Chem. Soc.* **1953**, *75*, 4698.
(16) Isolation: Shah, R.; Neuss, N.; Gorman, M.; Boeck, L. D. *J. Antibiot.* **1970**, *23*, 613. Walker, J. E.; Abraham, E. P. *Biochem. J.* **1970**, *118*, 563. Neuss, N.; Molloy, B. B.; Shah, R.; DeLattiguera, N. *Ibid.* **1970**, *118*, 571.
(17) Synthesis: Rickards, R. W.; Rodwell, J. L.; Schmalzl, K. J. *J. Chem. Soc., Chem. Commun.* **1977**, 849.
(18) Terhune, S. J.; Hogg, J. W.; Bromstein, A. C.; Lawrence, B. M. *Can. J. Chem.* **1975**, *53*, 3285.
(19) Breitholle, E. G.; Fallis, A. G. *Can. J. Chem.* **1976**, *54*, 1981.
(20) (a) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, 2213, 2215; **1981**, 5111. (b) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. (c) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.
(21) (a) Gancarz, R.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155; *J. Org. Chem.* **1981**, *46*, 4899. (b) Kang, Y.-H.; Kice, J. L. *Tetrahedron Lett.* **1982**, *23*, 5373.

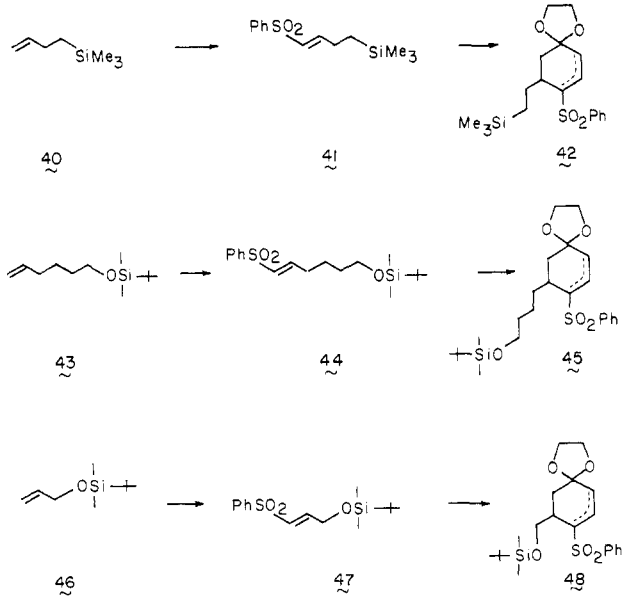


in a ratio of 2.8:1. Because the ^1H NMR spectra of these isomers are nearly identical, the individual assignments have been made on the basis of steric considerations. Molecular models indicate that less encumbered approach of the diene should favor the formation of **37**.

Reductions of the resultant γ-sulfonyl enones were achieved with zinc dust in glacial acetic acid. The relevant yield data are compiled in Table II. The formation of 3-cyclohexenones is noted to be particularly evident in those cases where the double bond would be more highly substituted in the β,γ position and when a 2-methyl group is absent.

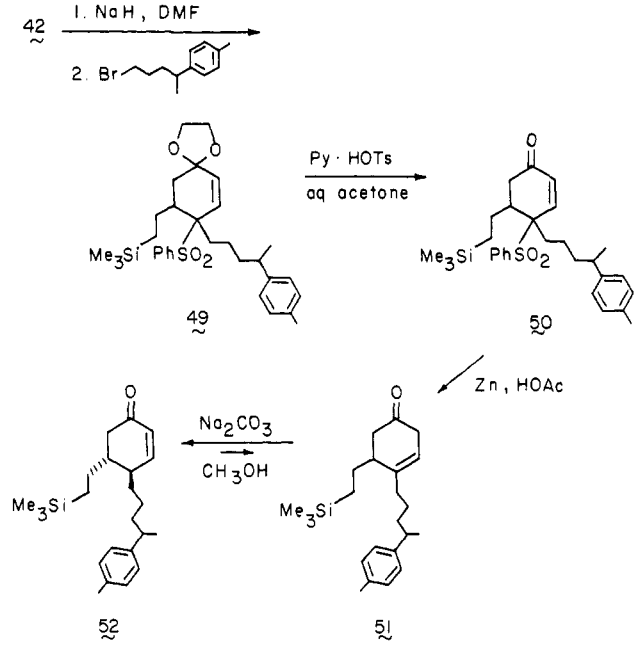
The chemistry surrounding **30d** is noteworthy in that it provides an indication that a potentially powerful method for achieving regiochemical reversal in Diels–Alder reactions is at hand. Thus, customary electronic influences would serve to transform acrolein into 4-formylcyclohex-2(or 3)-enone. However, acrolein dimethyl acetal gives, following conversion to **30d**, the 5-substituted isomer exclusively. As expected, the cyclohexenone moiety in **32d** could be unmasked under hydrolysis conditions which did not affect the acetal group. The two incipient carbonyl functionalities were thereby easily distinguished.

Alkylative Approach to 4,5-Disubstituted 2-(and 3-)Cyclohexenones. Attention was next turned to the development of a synthetic equivalent for **6**. Vinyl sulfones **41**, **44**, and **47**, which proved readily accessible by appro-



priate selenosulfonation of **40**, **43**, and **46**, respectively, in the predescribed manner, were heated with diene **10** and subsequently ketalized directly. Due to the acid lability of the *tert*-butyldimethylsilyloxy substituent in two of these substrates, the use of *p*-toluenesulfonic acid as the ketalization catalyst necessitated resilylation prior to product isolation. Under these conditions, the β,γ-unsaturated ketals are formed as the predominant products. Since the subsequent step involves deprotonation and alkylation, the isomeric ketals are directly usable without purification.

That the generation and trapping of these unsymmetrical anions is reasonably regioselective can be clearly seen in the conversion of **42** to **49**. Notwithstanding the rather



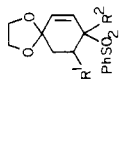
sterically congested environment about the α-sulfonyl carbon in this allylic intermediate, the charge affinity of the sulfonyl group dominates, delivering **49** rather cleanly (62% yield). Deketalization proceeded smoothly to give **50** (97%), the reductive desulfonylation of which with zinc in acetic acid efficiently (80%) delivered β,γ-enone **51**. Independent equilibration with sodium carbonate in methanol was required to arrive at **52**.

For the remaining syntheses summarized in Table III, the phenylsulfonyl group was cleaved with sodium amalgam prior to ketal hydrolysis. This particular sequence was followed to deter possible unwanted double bond migration from allylic C_4 substituents to an intra-ring position during conversions of the **50** → **51** type, e.g., with **54a**, **54b**, and **55c**. In actuality, no possible complications of this type were encountered.

It should be noted that somewhat reduced alkylation yields were realized when more bulky electrophiles such as the 3-(trimethylsilyl)-2-butenyl and geranyl bromides were utilized (Table III). These observations are attributed to reasonably competitive α-alkylation arising because of steric interaction with R^1. Small quantities of dialkylated product are therefore formed. The yield data which are cited refer to the amounts of pure γ-alkylated product obtained subsequent to MPLC purification. The trans stereochemical assignments to enones such as **52** follow from the usual thermodynamic factors operating during equilibration.

In those equilibration studies involving the 3-cyclohexenones **56a** and **56b** which carry a methylol side chain at C_5, intramolecular cyclization to the oxabicyclo[3.2.1]-octanones **58** occurs partially during base treatment. This phenomenon is understandably not observed when the hydroxyl group is held more remotely as in **55b**. As direct consequence of their large polarity differences, the chro-

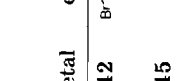
Table III. Sequential Alkylation, Reduction, Hydrolysis, and Equilibration of 42, 45, and 48

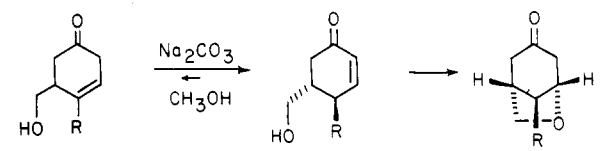


53

54

55

ketal	electrophile		yield, %		yield, %		yield, %
42		a, $R^1 = CH_2CH_2SiMe_3$; $R^2 = CH_3$ $R^2 = CH_2CH{=}CH_2$	71	a, $R^1 = CH_2CH_2SiMe_3$; $R^2 = CH_2CH{=}CH_2$	72	a, $R^1 = CH_2CH_2SiMe$; $R^2 = CH_2CH{=}CH_2$	51
45		b, 	35	b, $R^1 = (CH_2)_4OH$; $R^2 = CH_2CH{=}C(CH_3)SMe_3$	69	b, $R^1 = (CH_2)_4OH$; $R^2 = CH_2CH{=}C(CH_3)SiMe_3$	67
48		c, 	41	c, $R^1 = CH_2OH$; R^2 = geranyl	71	see text	
48		d, 	29	d, $R^1 = CH_2OH$; $R^2 = (CH_2)_2OCH_2C_6H_5$	75	see text	



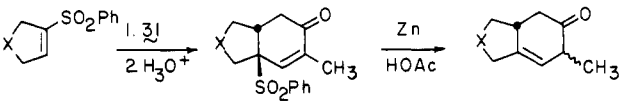
56 57 58

g, R = geranyl ; h, $R = (CH_2)_2OCH_2C_6H_5$

matographic separation of **57** and **58** can be readily accomplished.

Bicyclic Enones by Cycloaddition. Having established that 4,5-disubstituted cyclohexenones carrying widely different pendant groups can be prepared by an alkylative sequence, it remained to demonstrate that this class of compounds is also accessible by direct cycloaddition. The cyclic vinyl sulfones **59a** and **59b** were selected because their conversion to **61** would typify a cycloannulation process.

Following the selenosulfonation of cyclopentene and 2,5-dihydrofuran, the phenylsulfonyl derivatives were heated with **31** in xylene, and the adducts were subjected



59 60 61

g, X = CH_2 ; h, X = O

to mild acid hydrolysis. Smooth conversion to **60a** (44%) and **60b** (69%) was seen. Subsequent zinc-mediated reduction led straightforwardly to the annulated 3-cyclohexenones **61**.

Discussion. A general methodology has been developed that results in regiospecific γ- or δ-alkylation of 2-(and 3-)cycloalkenones, as well as 4,5-disubstitution of these versatile synthetic intermediates. Using the procedures outlined herein, it is clearly feasible to proceed readily from phenyl vinyl sulfone, terminal olefins, or cyclic alkenes to many desired end products of this class. Although there are many decided advantages to our procedures, it is important that these developments be placed in proper perspective.

The classical methods for accessing 4-substituted cyclohexenones appear to revolve around Birch reduction–hydrolysis of para-substituted phenols[22] and enamine condensations with methyl vinyl ketone.[23] More recently, a number of imaginative new advances have been made on this front. Among the useful new techniques can be found the copper-catalyzed addition of ethyl diazoacetate to 1-methoxy-1,3-cyclohexadienes,[24] zinc bromide catalyzed alkylation of O-silylated dienolates,[25] Baeyer–Villiger fragmentation of 1-methoxybicyclo[2.2.2]oct-5-enones,[26] and the addition of nucleophiles to (tricarbonyl)methoxycyclohexadienyl)iron cations followed by Jones oxidation.[27] Still more powerful is the regiocontrol achieved

(22) For example: Lewis, K. G.; Williams, G. J. *Tetrahedron Lett.* **1965**, 4573.

(23) For example: Joshi, G. D.; Kulkarni, S. N. *Ind. J. Chem.* **1965**, *3*, 1965; **1968**, *6*, 127.

(24) Wenkert, E.; Goodwin, T. E.; Rann, B. C. *J. Org. Chem.* **1977**, *42*, 2137.

(25) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, 3205, 3209.

(26) Madge, N. C.; Holmes, A. B. *J. Chem. Soc., Chem. Commun.* **1980**, 956.

(27) (a) Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1980**, *21*, 2455. (b) Birch, A. J.; Dahler, P.; Narula, A. S.; Stephenson, G. R. *Ibid.* **1980**, *21*, 3817. Kelly, L. F.; Dahler, P.; Narula, A. S.; Birch, A. J. *Ibid.* **1981**, *22*, 1433.

during the alkylation of 1,3-cyclohexanedione enol ethers[28] and β-enamino ketones derivable from secondary amines.[29,30]

The key difference between this diverse array of reactions and the present approach is one of molecular construction. Whereas vinyl sulfone cycloaddition reactions result in de novo fabrication of the six-membered ring, the others are dependent upon the availability of the preformed functionalized cyclohexane or arene substrate. Obviously, both schemes have important assets which are necessarily interlinked with other strategy considerations.

Finally, the vinyl sulfone intermediates pivotal to this study were prepared by selenosulfonation. Despite the mildness of this procedure, drawbacks such as cost and proper waste handling are relevant. At least two suitable alternatives are available for deployment in the majority of contexts. The first, due to Hopkins and Fuchs,[31] involves direct in situ chlorosulfenylation of olefins with an aryl thiol and *N*-chlorosuccinimide, followed by oxidation and dehydrochlorination with DBU. A somewhat more direct route is based upon the free-radical-initiated 1,2-addition of arenesulfonyl bromides to olefins and subsequent dehydrobromination.[32,33]

Experimental Section

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian EM-390 and EM-360 and Bruker WP-200 spectrometers. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

4,4-(Ethylenedioxy)-1-(phenylsulfonyl)cyclohexene (7). A solution of phenyl vinyl sulfone (3.91 g, 23.2 mmol) and 1-methoxy-3-[(trimethylsilyl)oxy]butadiene (4.98 g, 85% purity, 24.5 mmol) in benzene (10 mL) was heated at reflux for 28 h. After the mixture cooled, ethylene glycol (3.5 g), *p*-toluenesulfonic acid (300 mg), and benzene (15 mL) were added, and the reaction mixture was heated with removal of water for an additional 23 h, cooled, diluted with more solvent (40 mL), and extracted successively with saturated sodium bicaronate solution (20 mL), water (20 mL), and brine (20 mL). The organic phase was dried and concentrated, and the residue was chromatographed on silica gel (40 g, elution with 30% ethyl acetate in hexane). Crystallization of the product from ether afforded 5.53 g (85%) of pure **7** as colorless crystals: mp 77–78 °C; IR ($CHCl_3$) 3010, 2880, 1647, 1444, 1368, 1300, 1200, 1150, 1118, 1088 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.3 (m, 5 H), 6.92–6.72 (m, 1 H), 3.86 (s, 4 H), 2.5–2.2 (m, 4 H), 1.68 (t, J = 6 Hz, 2 H); MS, m/e (M^+) calcd 280.0769, obsd 280.0776.

6,6-(Ethylenedioxy)-3-(phenylsulfonyl)cyclohexene (11a). A cold (0 °C), magnetically stirred suspension of sodium hydride (101 mg of 50%, 2.1 mmol) in dry dimethylformamide (25 mL) was treated under argon with a solution of **7** (400 mg, 1.43 mmol) in 25 mL of the same solvent. Immediately thereafter, methyl iodide (0.28 combined organic layers were washed with water (75 mL) and brine (75 mL) prior to drying and solvent evaporation. Crystallization of the residue from ether furnished 350 mg (83%) of **11a** as colorless crystals: mp 94–96 °C; IR ($CHCl_3$) 3010, 2880, 1445, 1302, 1205, 1145, 1073 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–7.3 (m, 5 H), 5.88 d, J = 10 Hz, 1 H), 5.78 (d, J = 10 Hz, 1 H), 3.77 (m, 4 H), 2.4–2.0 (m, 1 H), 1.9–1.5 (m, 3 H), 1.35 (s, 3 H). Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.09; H, 6.13.

The ketal group in **11a** (317 mg, 1.08 mmol) was cleanly removed by heating at reflux with PPTS (73 m%) in wet acetone (11 mL) for 3 h. Following solvent evaporation, the residue was dissolved in ether (150 mL), and this solution was shaken in turn with 5% sodium bicarbonate solution (50 mL), 1 M hydrochloric acid (30 mL), and brine (30 mL) prior to drying. Concentration in vacuo and crystallization from ether gave **12a** as colorless crystals: mp 91.5–93.0 °C; 255 mg (94%); IR ($CHCl_3$) 3020, 1688, 1445, 1308, 1205, 1148, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.73 (d, J = 11 Hz, 1 H), 6.07 (d, J = 11 Hz, 1 H), 2.8–1.9 (series of m, 4 H), 1.53 (s, 3 H); MS, m/e (M^+) calcd 250.0663, obsd 250.0671. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.36; H, 5.65.

4-Methyl-2-cyclohexenone (14a) and 4-Methyl-3-cyclohexenone (15a). Dry methanol (18 mL, distilled from magnesium methoxide) was introduced via syringe into a nitrogen-blanketed solution of **11a** (530 mg, 1.80 mmol). Following the addition of disodium hydrogen phosphate (1.0 g) and pulverized 6% sodium amalgam (3.2 g), the reaction mixture was stirred until TLC analysis indicated the disappearance of starting material (2.5 h). Insoluble material was separated by filtration, and the product was partitioned between ether (150 mL) and water (25 mL). The organic phase was washed with brine (25 mL), dried, and evaporated to give 248 mg (89%) of a liquid consisting predominantly of **13a** (41:59 ratio, NMR analysis): IR (neat) 3010–2800, 1515, 1400, 1250, 1170, 1120, 1060, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.54 (br d, 0.4 H), 5.29 (m, 0.6 H), 4.86 (d, J = 5 Hz, 0.4 H), 3.98 (s, 2.4 H), 3.80 (br s, 1.6 H), 2.4–1.6 (m, 8.6 H).

The mixture of isomeric ketals (94 mg, 0.61 mmol) dissolved in 95% ethanol (15 mL) containing *p*-toluenesulfonic acid (300 mg) was heated at reflux for 20.5 h. The majority of the solvent was removed on a rotary evaporator, and the product was partitoned between ether (25 mL) and 5% sodium bicarbonate solution (15 mL). The organic phase was washed with brine, dried, and evaporated. ^1H NMR analysis indicated the ratio of **14a** to **15a** to be 80:20. Chromatography on silica gel (5 g, dichloromethane elution) gave **15a** (15 mg, 22%) and **14a** (35 mg, 52%) in pure form.

For **14a**: IR (neat) 3000–2800, 1690, 1460, 1395, 1380, 1255, 830, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.77 (br d, J = 11 Hz, 1 H), 5.92 (dd, J = 11 and 3 Hz, 1 eh), 2.7–1.6 (series of m, 5 H), 1.17 (d, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 110.0732, obsd 110.0735.

For **15a**: ^1H NMR ($CDCl_3$) δ 5.40 (br s, 1 H), 2.82 (br s, 2 H), 2.46 (m, 4 H), 1.79 (br s, 3 H). This substance has been reported previously on many occasions.

6,6-(Ethylenedioxy)-3-allyl-3-(phenylsulfonyl)cyclohexene (11b). Alkylation of **7** (1.00 g, 3.57 mmol) with 50% sodium hydride (258 mg, 5.38 mmol) and allyl bromide (0.62 mL, 7.16 mmol) in 50 mL of dimethylformamide was accomplished with 3.5 h of stirring. Workup as before and chromatography of the resulting oil on silica gel (60 g, elution with 25% ethyl acetate in hexane) afforded a colorless oil which crystallized from ether to give 877 mg (77%) of **11b** as a white powder: mp 81–83 °C; IR ($CHCl_3$) 3090–2840, 1448, 1305, 1210, 1144, 1083, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.88 (d, J = 10 Hz, 1 H), 5.75 (d, J = 10 Hz, 1 H), 5.7–5.4 (m, 1 H), 5.2–4.9 (m, 2 H), 3.84 (s, 4 H), 2.7–1.5 (series of m, 6 H).

Hydrolysis of **11b** (800 mg, 250 mmol) was carried out in wet acetone (20 mL) containing PPTS (150 mg) at the reflux temperature for 3 h. Subsequent workup and concentration in vacuo afforded 656 mg (95%) of 4-allyl-4-(phenylsulfonyl)-2-cyclohexenone as a colorless oil: IR ($CHCl_3$) 3100–2850, 1690, 1448, 1307, 1225, 1143, 1082, 924; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 6.64 (d, J = 11 Hz, 1 H), 6.18 (d, J = 11 Hz, 1 H), 5.8–5.4 (m, 1 H), 5.2–5.0 (m, 2 H), 2.8–2.2 (m, 6 H); MS, m/e (M^+) calcd 276.0820, obsd 276.0827.

4-Allyl-2-cyclohexenone (14b) and 4-Allyl-3-cyclohexenone (15b). Rapid (30 min), clean reduction of **11b** (557 mg, 1.74 mmol) with 1.10 g of Na_2HPO_4 and 5.5 g of 6% Na(Hg) was seen. Workup and solvent removal yielded 307 mg (98%) of a 31:69 mixture of α,β/β,γ isomers: IR (neat) 3070, 3000–2800, 1655, 1635, 1605, 1430, 1240, 1205, 1150, 1110, 1050, 905, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.0–4.8 (m, 4.3 H), 3.99 (s, 2.8 H), 3.83 (br s, 1.2 H), 2.9–1.6 (series of m, 7.7 H).

Deketalization and equilibration was achieved by heating this mixture (275 mg, 1.52 mmol) with 59 mg of *p*-toluenesulfonic acid

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in 15 mL of 95% ethanol for 11 h. Subsequent workup and silica gel chromatography (20 g, elution with 10% ether in pentane) afforded 50 mg (28%) of **15b** followed by 93 mg (45%) of **14b** (73% combined yield).

For **14b**: IR (neat) 3100–2800, 1680, 1385, 1280, 1200, 985, 910 cm^{-1} ^1H NMR ($CDCl_3$) δ 6.85 (br d, J = 11 Hz, 1 H), 5.96 (dd, J = 11, 3 Hz, 1 H), 6.0–5.5 (m, 1 H), 5.3–4.9 (m, 2 H), 2.6–1.5 (series of m, 7 H); MS, m/e (M^+) calcd 136.0888, obsd 136.0884.

For **15b**: IR (neat) 3100–2800, 1720, 1640, 1510, 1430, 1340, 1180, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.0–5.5 (m, 1 H), 5.47 (br s, 1 H), 5.2–4.9 (m, 2 H), 2.9–2.7 (m, 4 H), 2.45 (br s, 4 H); MS, m/e (M^+) calcd 136.0888, obsd 136.0884.

6,6-(Ethylenedioxy)-3-prenyl-3-(phenylsulfonyl)cyclohexene (11c). Comparable alkylation of **7** (1.00 g, 3.57 mmol) with 50% sodium hydride (258 mg, 5.38 mmol) and prenyl bromide (898 mg, 6.02 mmol) in dimethylformamide (50 mL) afforded 1.13 g (91%) of **11c** as a white powder (mp 91–92.5 °C) after silica gel chromatography (70 g, elution with 15% ethyl acetate in hexane): IR ($CHCl_3$) 3080–2820, 1445, 1300, 1200, 1140, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.86 (d, J = 10 Hz, 1 H), 5.72 (d, J = 10 Hz, 1 H), 5.07 (m, 1 H), 3.83 (br s, 4 H), 2.7–1.8 (series of m, 6 H), 1.69 (s, 3 H), 1.62 (s, 3 H).

When **11c** (343 mg, 0.98 mmol) was heated with pyridinium toxylate (77 mg) in wet acetone (20 mL) under reflux for 4 h, conversion to ketone **12c** occurred: 260 mg (87%); colorless needles; mp 90–91 °C (from ether); IR ($CHCl_3$) 3080–2840, 1690, 1450, 1310, 1230, 1148, 1088 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.3 (m, 5 H), 6.60 (d, J = 10 Hz, 1 H), 6.19 (d, J = 10 Hz, 1 H), 4.96 (m, 1 H), 2.7–1.8 (series of m, 6 H), 1.64 (2 s, 6 H). Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62. Found: C, 66.86; H, 6.69.

4-Prenyl-2-cyclohexenone (14c) and 4-Prenyl-3-cyclohexenone (15c). Desulfonylation of **11c** (458 mg, 1.32 mmol) was performed as before with 830 mg of Na_2HPO_4 and 4.1 g of 6% Na(Hg) in 20 mL of dry methanol over a period of 40 min. Workup and concentration afforded 275 mg (100%e of ketal consisting of β,γ- (66%) and α,β-unsaturated isomers (34%): IR (neat) 3000–2800, 1660, 1610, 1440, 1370, 1240, 1210, 1110, 1050, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.55 (br d, J = 5 Hz, 0.3 H), 5.30 (br s, 0.7 H), 5.14 (br t, J = 7 Hz, 1 H), 4.88 (d, J = 5 Hz, 0.3 H), 3.98 (s, 2.8 H), 3.83 (s, 1.2 H), 2.8–2.5 (m, 2 H), 2.3–2.0 (m, 5.7 H), 1.74 (s, 3 H), 1.64 (s, 3 H).

Hydrolysis of this material (234 mg, 1.12 mmol) with p-toluenesulfonic acid (50 mg) in 95% ethanol (reflux, 11 h) afforded a 62:38 mixture of α,β- and β,γ-unsaturated ketones. Chromatography on silica gel (20 g, elution with 5% ether in pentane) gave 58 mg of crude **15c** and 112 mg (61%) of pure **14c**. Preparative TLC chromatography of **15c** (silica gel, elution with 30% ether in pentane) afforded 48 mg of pure enone (87% combined yield).

For **14c**: IR (neat) 3050–2800, 1680, 1450, 1380, 1240, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (br d, J = 11 Hz, 1 H), 5.95 (dd, J = 11, 2 Hz, 1 H), 5.15 (br t, J = 7 Hz, 1 H), 2.6–2.0 (m, 7 H), 1.77 (s, 3 H), 1.67 (s, 3 H); MS, m/e (M^+) calcd 164.1201, obsd 164.1199.

For **15c**: IR (neat) 3050–2800, 1725, 1445, 1375, 1335, 1190, 840, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.43 (br s, 1 H), 5.13 (br t, J = 7 Hz, 1 H), 2.9–2.6 (m, 4 H), 2.5–2.3 (m, 4 H), 1.76 (s, 3 H), 1.66 (s, 3 H); MS, m/e (M^+) calcd 164.1201, obsd 164.1198.

6,6-(Ethylenedioxy)-3-benzyl-3-(phenylsulfonyl)cyclohexene (11d). From 1.00 g (3.57 mmol) of **7**, 258 mg (5.38 mmol) of 50% sodium hydride, and 1.02 g (6.0 mmol) of benzyl bromide in dimethyl formamide (50 mL) (room temperature, 4 h) there was obtained 1.07 g (81%) of **11d** as a colorless solid: mp 106–107 °C (from ether); IR ($CHCl_3$) 3100–2860, 1450, 1310, 1230, 1150, 1125, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1–7.4 (m, 5 H), 7.16 (br s, 5 H), 5.94 (d, J = 10 Hz, 1 H), 5.80 (d, J = 10 Hz, 1 H), 3.63 (br s, 4 H), 3.22 (br s, 2 H), 2.3–1.1 (series of m, 4 H).

Hydrolysis of this material (704 mg, 1.90 mmol) in wet acetone (20 mL) containing pyridinium tosylate (153 mg) (reflux, 4 h) yielded 486 mg (78%) of ketone **12d** as colorless needles: mp 108–110 °C (after recrystallization from ether); IR ($CHCl_3$) 3100–2840, 1685, 1450, 1310, 1250, 1148, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 7.3–7.0 (m, 5 H), 6.83 (d, J = 11 Hz, 1 H), 6.13 (d, J = 11 Hz, 1 H), 3.37 (d, J = 15 Hz, 1 H), 3.16 (d, J = 15 Hz, 1 H), 2.6–1.6 (series of m, 4 H); MS, m/e (M^+) calcd 326.0977, obsd 326.0982. Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 69.90; H, 5.60.

4-Benzyl-2-cyclohexenone (14d) and 4-Benzyl-3-cyclohexenone (15d). Application of the general desulfonylation procedure to **11d** (404 mg, 1.09 mmol) through the agency of Na_2HPO_4 (700 mg) and 6% Na(Hg) (3.5 g) in dry methanol (18 mL) for 1.5 h afforded 250 mg (100%) of a mixture of β,γ- (68%) and α,β-unsaturated ketals (32%): IR (neat) 3100–2800, 1660, 1605, 1490, 1450, 1240, 1210, 1105, 1050, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23 (br s, 5 H), 5.62 (br d, 0.3 H), 5.34 (br m, 0.7 H), 4.90 (d, J = 6 Hz, 0.3 H), 3.97 (s, 2.8 H), 3.83 (s, 1.2 H), 3.4–3.2 (m, 2 H), 2.4–1.6 (series of m, 5.7 H).

Deketalization and equilibration was achieved by refluxing 217 mg (0.94 mmol) of this mixture in 95% ethanol (12 mL) containing p-toluenesulfonic acid (50 mg) for 24 h. ^1H NMR analysis of the crude product indicated **14d** and **15d** to be present in a 68:32 ratio. Silica gel chromatography (20 g, elution with 5% ether in pentane) yielded 56 mg of impure **15d** followed by 114 mg (65%) of pure **14d**. Preparative TLC of **15d** (silica gel, 30% ether in pentane) afforded 31 mg of pure enone (83% combined yield).

For **14d**: IR (neat) 3100–2800, 1685, 1500, 1460, 1390, 1255, 1210, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 6.81 (br d, J = 11 Hz, 1 H), 5.96 (d, J = 11 Hz, 1 H), 2.78 (AB, J = 2 Hz, 2 H), 2.9–1.5 (series of m, 5 H); MS, m/e (M^+) calcd 186.1044, obsd 186.1050.

For **15d**: IR (neat) 3100–2800, 1715, 1490, 1450, 1335, 1190, 1070, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5 H), 5.50 (br m, 1 H), 3.38 (br, s, 2 H), 3.0–2.7 (m, 2 H), 2.5–2.2 (m, 4 H); MS, m/e (M^+) calcd 186.1044, obsd 186.1048.

6,6-(Ethylenedioxy)-3-(4-*p*-tolylpentyl)-3-(phenylsulfonyl)cyclohexene (11e). Alkylation of **7** (803 mg, 2.86 mmol) with 1.17 g (4.85 mmol) of 4-(4-methyl-p-tolyl)butyl bromide (DMF, room temperature, 6 h) afforded a dark yellow oil which was purified by silica gel chromatography (60 g, elution with 10% ethyl acetate in hexane). There was isolated 1.13 g (89%) of **11e** as a colorless oil: IR ($CHCl_3$) 3080–2840, 1514, 1450, 1303, 1220, 1145, 1087 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.3 (m, 5 H), 7.03 (s, 4 H), 5.9–5.6 (7, 2 H), 3.81 (br s, 4 H), 2.29 (s, 3 H), 2.8–1.1 (series of m, 11 H), 1.18 (d, J = 7 Hz, 3 H).

Hydrolysis of this product (1.01 g, 2.29 mmol) in the predescribed manner (PPTS, wet acetone) afforded 844 mg (93%) of ketone **12e** as a colorless immobile oil: IR ($CHCl_3$) 3080–2840, 1687, 1450, 1310, 1240, 1143, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.01 (br s, 4 H), 6.51 (dd, J = 11, 3 Hz, 1 H), 6.12 (d, J = 11 Hz, 1 H), 2.29 (s, 3 H), 2.7–1.1 (m, 11 H), 1.17 (d, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 396.1759, obsd 296.1770.

4-(4-*p*-Tolylpentyl)-2-cyclohexenone (14e) and 4-(4-*p*-Tolylpentyl)-3-cyclohexenone (15e). Reductive desulfonylation of **11e** (470 mg) with 700 mg of Na_2HPO_4 and 3.5 g of 6% Na(Hg) cleanly afforded 288 mg (90%) of ketal isomers (63% of β,γ and 37% α,β): IR (neat) 3000–2800, 1655, 1610, 1510, 1240, 1210, 1110, 1050, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.07 (s, 4 H), 5.51 (br d, J = 5 Hz, 0.4 H), 5.24 (br m, 0.6 H), 4.85 (br d, J = 5 Hz, 0.4 H), 3.96 (s, 2.4 H), 3.81 (br s, 1.6 H), 2.65 (q, J = 7 Hz, 1 H), 2.33 (s, 3 H), 2.4–1.2 (series of m, 11.6 H), 1.22 (d, J = 7 Hz, 3 H).

Heating of this mixture (254 mg, 0.84 mmol) for 16 h in 95% ethanol (12 mL) containing 60 mg of p-toluenesulfonic acid gave a 70:30 mixture of **14e** and **15e** (^1H NMR analysis). Chromatography on silica gel (20 g, elution with 5% ether in pentane) gave 64 mg of impure **15e** and 124 mg (57%) of pure **14e**. Preparative TLC chromatography (silica gel, elution with 30% ether in pentane) of the crude **15e** afforded 54 mg (25%) of pure enone.

For **14e**: IR (neat) 3050–2800, 1680, 1510, 1450, 1390, 1250, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.06 (s, 4 H), 6.74 (br d, J = 10 Hz, 1 H), 5.90 (dd, J = 10, 3 Hz, 1 H), 2.67 (q, J = 7 Hz, 1 H), 2.32 (s, 3 H), 2.5–1.1 (series of m, 11 H), 1.23 (d, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 256.1827, obsd 256.1821.

For **15e**: IR (neat) 3060–2800, 1720, 1510, 1450, 1185, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.06 (s, 4 H), 5.37 (br m, 1 H), 2.32 (s, 3 H), 2.9–1.1 (series of m, 13 H), 1.24 (d, J = 6 Hz, 3 H); MS, m/e (M^+) calcd 256.1827, obsd 256.1821.

6,6-(Ethylenedioxy)-3-[3-(phenylthio)propyl]-3-(phenylsulfonyl)cyclohexene (11f). Alkylation of **7** (446 mg, 1.59 mmol) with 50% sodium hydride (115 mg, 2.40 mmol) and 3-(phenylthio)-1-bromopropane (637 mg, 2.75 mmol) in dimethylformamide (30 mL) followed by silica gel chromatography (30 g, elution with 20% ethyl acetate in hexane) afforded **11f** (627 mg, 92%) as a

clear immobile oil: IR ($CHCl_3$) 3100–2840, 1590, 1485, 1450, 1443, 1305, 1230, 1143, 1083, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.24 (m, 5 H), 5.88 (d, J = 10 Hz, 1 H), 5.72 (d, J = 10 Hz, 1 H), 3.82 (br s, 4 H), 2.88 (t, J = 6 Hz, 2 H), 2.4–1.0 (series of m, 8 H).

Hydrolysis of this product (573 mg, 1.33 mmol) as previously described (PPTS, wet acetone) furnished 471 mg (92%) of ketone **12f** as colorless crystals: mp 61–62.5 °C (from ether); IR ($CHCl_3$) 3090–2840, 1690, 1587, 1480, 1450, 1440, 1308, 1225, 1142, 1082 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.23 (s, 5 H), 6.54 (d, J = 11 Hz, 1 H), 6.11 (d, J = 11 Hz, 1 H), 2.87 (t, J = 6 Hz, 2 H), 2.7–1.5 (series of m, 8 H). Anal. Calcd for $C_{21}H_{22}O_3S_2$: C, 65.25; H, 5.74. Found: C, 65.26; H, 5.74.

4-[3-(Phenylthio)propyl]-2-cyclohexenone (14f) and 4-[3-(Phenylthio)propyl]-3-cyclohexenone (15f). Reductive desulfonylation of **11f** (475 mg, 1.10 mmol) with 708 mg of Na_2HPO_4 and 3.5 g of 6% Na(Hg) during 1.5 h led to the isolation of 295 mg (92%) of ketal isomers (67% β,γ and 33% α,β): IR (neat) 3100–2800, 1655, 1605, 1580, 1480, 1435, 1240, 1210, 1100, 1050, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m, 5 H), 5.58 (br d, 0.3 H), 5.32 (br m, 0.7 H), 4.88 (br d, J = 6 Hz, 0.3 H), 3.98 (s, 2.8 H), 3.82 (br s, 1.2 H), 2.92 (t, J = 6 Hz, 2 H), 2.3–1.6 (series of m, 9.7 H).

The isomeric ketals (269 mg, 0.93 mmol) were stirred under reflux in 95% ethanol with *p*-toluenesulfonic acid for 19 h to give a 47:53 mixture of **14f** and **15f** (^1H NMR analysis). Chromatography on silica gel (15 g, 10% ether in pentane) afforded 101 mg (44%) of **15f** and 99 mg (43%) of **14f** (combined yield of 87%) as colorless oils.

For **14f**: IR (neat) 3000–2800, 1650, 1585, 1480, 1440, 1385, 1245, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 6.76 (br d, J = 11 Hz, 1 H), 5.94 (dd, J = 10, 2 Hz, 1 H), 3.1–1.4 (series of m, 11 H); MS, m/e (M^+) calcd 246.1078, obsd 246.1070.

For **15f**: IR (neat) 3000–2800, 1720, 1585, 1480, 1440, 1190, 1020, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.0 (m, 5 H), 5.44 (br m, 1 H), 3.0–2.7 (m, 4 H), 2.5–1.6 (series of m, 8 H); MS, m/e (M^+) calcd 246.1078, obsd 246.1085.

6,6-(Ethylenedioxy)-3-[(2-tetrahydrofuranyl)methyl]-3-(phenylsulfonyl)cyclohexene (11g). Reaction of **7** (1.00 g, 3.57 mmol) with 50% sodium hydride in oil (269 mg, 5.60 mmol) and 2-(iodomethyl)tetrahydrofuran (1.37 g, 6.46 mmol) in dimethylformamide (50 mL) as previously described (9 h) and silica gel chromatography of the product (elution with 20% ethyl acetate in hexane) gave 103 mg of unreacted **7** and 888 mg (76%, corrected for recovery) of **11g** as a white crystalline powder: mp 94–100 °C (from ether); IR ($CHCl_3$) 3100–2800, 1450, 1305, 1145, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.3 (m, 5 H), 6.0–5.7 (m, 2 H), 3.81 (s, 4 H), 4.1–3.5 (m, 3 H), 2.4–1.4 (series of m, 10 H).

Hydrolysis of this product (831 mg, 2.28 mmol) in wet acetone (25 mL) containing pyridinium tosylate (300 mg) in the predescribed manner gave enone **12g** as a thick colorless oil: 730 mg (100%); IR ($CHCl_3$) 3080–2840, 1690, 1450, 1310, 1230, 1150, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 6.73 (d, J = 11 Hz, 1 H), 6.21 (d, J = 11 Hz, 0.5 H), 6.09 (d, J = 11 Hz, 0.5 H), 6.09 (d, J =v 11 Hz, 0.5 H), 4.2–3.6 (m, 3 H), 2.8–1.3 (series of m, 10 H).

Preparative TLC on silica gel (elution with 50% ethyl acetate in hexane) served to separate the two diastereomers, the first being a crystalline solid (mp 87.5–89.5 °C) and the second a colorless oil. Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29. Found: C, 63.54; H, 6.33.

4-[(2-Tetrahydrofuranyl)methyl]-2-cyclohexenone (14g) and 4-[(2-Tetrahydrofuranyl)methyl]-3-cyclohexenone (15g). Reductive desulfonylation of **11g** (322 mg, 0.88 mmol) with 550 mg of Na_2HPO_4 and 2.8 g of 6% Na(Hg) was complete in 1 h and afforded 187 mg (95%) of ketal isomers (64% β,γ and 36% α,β): IR (neat) 3000–2800, 1655, 1605, 1430, 1360, 1240, 1210, 1110, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.64 (br d, J = 6 Hz, 0.4 H), 5.38 (br s, 0.6 H), 4.90 (d, J = 6 Hz, 0.4 H), 3.96 (s, 2.4 H), 3.83 (s, 1.6 H), 4.1–3.6 (m, 3 H), 2.4–1.3 (series of m, 11.6 H).

Acid hydrolysis of this product (157 mg, 0.70 mmol) in the manner described above furnished **14g** and **15g** in a 69:31 ratio (^1H NMR analysis). Preparative TLC chromatography on silica gel (elution with 40% ether in pentane) gave 91 mg (72%) of the same mixture. No success was realized in attempts to separate the isomers; IR (neat) 3000–2800, 1720, 1680, 1445, 1385, 1245, 1210, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (br d, J = 10 Hz, 0.7 H), 5.97 (dd, J = 10 and 3 Hz, 0.7 H), 5.55 (br s, 0.3 H), 4.1–3.6 (m, 3 H), 2.9–1.4 (series of m, 11.3 H); MS, m/e (M^+) calcd 180.1150, obs 180.1142.

6,6-(Ethylenedioxy)-3-geranyl-3-(phenylsulfonyl)cyclohexene (11h). Reaction of **7** (400 mg, 1.43 mmol) with 110 mg (2.29 mmol) of 50% sodium hydride and 0.54 mL (2.72 mmol) of geranyl bromide in 30 mL of dimethylformamide followed by silica gel chromatography (gradient elution with 10–20% ethyl acetate in hexane) afforded 564 mg (94%) of an oil which later crystallized from ether–hexane: mp 77.5–79 °C; IR ($CHCl_3$) 3080–2810, 1450, 1305, 1145, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.84 (d, J = 11 Hz, 1 H), 5.73 (d, J = 11 Hz, 1 H), 5.04 (br t, 2 H), 3.82 (s, 4 H), 2.59 (d, J = 7 Hz, 2 H), 2.3–1.5 (series of m, 17 H).

Hydrolysis of this product (493 mg, 1.18 mmol) in wet acetone (25 mL) containing PPTS (150 mg) as before, followed by filtration through silica gel (20 g, elution with 20% ethyl acetate in hexane), yielded 420 mg (96%) of enone **12 h** as a colorless oil: IR ($CHCl_3$) 3080–2840, 1690, 1450, 1390, 1310, 1145, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 6.58 (d, J = 11 Hz, 1 H), 6.17 (d, J = 11 Hz, 1 H), 4.86 (br t, 2 H), 2.62 (AB, J = 7 Hz, 2 H), 2.8–1.4 (series of m, 17 H); MS, m/e (M^+) calcd 372.1759, obsd 372.1751. Anal. Calcd for $C_{22}H_{28}O_3S$: C, 70.93; H, 7.58. Found: C, 70.92; H, 7.57.

4-Geranyl-2-cyclohexenone (14h) and 4-Geranyl-3-cyclohexenone (15h). Reductive desulfonylation of **7** (432 mg, 1.04 mmol) was achieved during 17 h with 700 mg of Na_2HPO_4 and 3.6 g of 6% Na(Hg). Workup and solvent removal furnished 288 mg (100%) of ketal isomers (62% β,γ and 38% α,β) as a colorless oil: IR (neat) 3000–2800, 1650, 1600, 1435, 1370, 1235, 1200, 1105, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.6–4.8 (m, 3.4 H), 3.99 (s, 2.4 H), 3.83 (br s, 1.6 H), 2.8–1.5 (series of m, 20.6 H).

Acid hydrolysis of this product (257 mg, 0.93 mmol) in 95% ethanol (12 mL) containing *p*-toluenesulfonic acid (50 mg) for 4 h delivered a 64:36 mixture of **15h** and **14h**. Silica gel chromatography (elution with 10% ether in pentane) afforded 124 mg (57%) of **15h** and 79 mg (36%) of **14** h (93% combined yield).

Heating for 24 h gave a 69:31 distribution of the same enones.

For **14h**: IR (neat) 3000–2800, 1680, 1440, 1380, 1245, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.82 (br d, J = 11 Hz, 1 H), 5.96 (br d, J = 11 Hz, 1 H), 5.3–4.9 (m, 2 H), 2.6–1.5 (series of m, 20 H); MS, m/e (M^+) calcd 232.1827, obsd 232.1834.

For **15h**: IR (neat) 3000–2800, 1720, 1440, 1375, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.44 (br m, 1 H), 5.3–5.0 (m, 2 H), 3.0–1.5 (series of m, 21 H); MS, m/e (M^+) calcd 232.1827, obsd 232.1834.

6,6-(Ethylenedioxy)-3-(4-carbethoxybutyl)-3-(phenylsulfonyl)cyclohexene (11i). The anion of **7** (1.00 g, 3.58 mmol) was prepared with 50% sodium hydride (274 mg, 5.71 mmol) in dimethylformamide (25 mL) and added to a solution of ethyl δ-iodovalerate (1.83 g) in 25 mL of the same solvent. Chromatography of the product on silica gel (elution with 20% ethyl acetate in hexane) afforded **11i** as a colorless, mobile oil: 1.34 g (92%); IR ($CHCl_3$) 3080–2875, 1735, 1450, 1305, 1240, 1145, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.3 (m, 5 H), 5.90 (d, J = 11 Hz, 1 H), 5.81 (d, J = 11 Hz, 1 H), 4.08 (q, J = 7 Hz, 2 H), 3.83 (s, 4 H), 2.4–1.2 (series of m, 12 H), 1.24 (t, J = 7 Hz, 3 H).

Hydrolysis of this product (1.27 g, 3.11 mmol) in wet acetone (25 mL) containing PPTS (300 mg) (reflux, 2 h), filtration through silica gel (20 g, elution with 20% ethyl acetate in hexane), and crystallization from ether gave 910 mg (80%) of enone **12i** as colorless needles: mp 56–59 °C; IR ($CHCl_3$) 3080–2860, 1735, 1695, 1450, 1380, 1310, 1190, 1145, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 6.60 (d, J = 11 Hz, 1 H), 6.15 (d, J = 11 Hz, 1 H), 4.07 (q, J = 7 Hz, 2 H), 2.61–1.2 (series of m, 12 H), 1.22 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{19}H_{24}O_5S$: C, 62.62; H, 6.64. Found: C, 62.78; H, 6.71.

4-(4-Carbethoxybutyl)-2-cyclohexenone (14i) and 4-(4-Carbethoxybutyl)-3-cyclohexenone (15i). Reductive desulfonylation of **11i** (342 mg, 0.84 mmol) with Na_2HPO_4 (550 mg) and 6% Na(Hg) (2.8 g) in the usual manner (20 mL of dry ethanol) for 1.5 h gave a mixture of ketals (159 mg, 71%) in a ratio of 56% β,γ and 44% α,β: IR (neat) 3000–2800, 1735, 1655, 1610, 1370, 1240, 1210, 1110, 1040, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.56 (br d, J = 5 Hz, 0.4 H), 5.30 (br s, 0.6 H), 4.89 (d, J = Hz, 0.4 H), 4.13 (q, J = 7 Hz, 2 H), 3.99 (s, 2.4 H), 3.84 (s, 1.6 H), 2.4–1.4 (series

of m, 13.6 H), 1.28 (t, J = 7 Hz, 3 H).

Deketalization was achieved without affecting the ester functionality by refluxing the above material (127 mg, 0.47 mmol) for 19 h in 95% ethanol (15 mL) containing *p*-toluenesulfonic acid (100 mg). The 69:31 mixture of **14i** and **15i** was separated into its components by preparative TLC on silica gel (elution with 40% ether in pentane). There was obtained 21 mg (20%) of **15i** and 59 mg (56%) of **14i**.

For **14i**: IR (neat) 3000–2800, 1735, 1680, 1450, 1410, 1370, 1240, 1180, 1090, 1025; ^{1}H NMR ($CDCl_3$) δ 6.85 (br d, J = 10 Hz, 1 H), 5.96 (dd, J = 10, 3 Hz, 1 H), 4.15 (q, J = 7 Hz, 2 H), 2.6–1.3 (series of m, 13 H), 1.29 (t, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 224.1412, obsd 224.1405.

For **15i**: IR (neat) 3000–2800, 1730, 1440, 1370, 1185, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.46 (br s, 1 H), 4.15 (q, J = 7 Hz, 2 H), 2.9–2.7 (br s, 2 H), 2.5–1.9 (series of m, 8 H), 1.8–1.3 (m, 4 H), 1.29 (t, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 224.1412, obsd 224.1405.

6,6-(Ethylenedioxy)-3-[3,3-(ethylenedioxy)butyl]-3-(phenylsulfonyl)cyclohexene (16). The anion of **7** (1.80 g, 6.42 mmol) was generated at 0 °C with 50% sodium hydride (503 mg, 10.48 mmol). 1-Bromo-3,3-(ethylenedioxy)butane (1.20 g, 6.15 mmol) was introduced, and the reaction mixture was stirred at room temperature for 1.5 h when an equivalent amount of electrophile was added. A third 1.20-g sample of bromide was added 18 h later. After a total reaction of 42 h, the slurry was poured into water (50 mL), and chloroform (100 mL) was added. The aqueous phase was extracted with chloroform (2 × 100 mL), and the combined organic layers were washed with water (6 × 50 mL) and brine (100 mL) before drying. Chloroform was removed on a rotary evaporator, and residual dimethylformamide was removed under high vacuum overnight. MPLC on silica gel (elution with 70% ethyl acetate in petroleum ether) afforded 990 mg of unreacted **7** and 946 mg (83%) of **16**: mp 114–116 °C (from ethyl acetate); IR ($CHCl_3$) 3040–2830, 1445, 1295, 1140 cm^{-1} ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.88 (d, J = 11 Hz, 1 H), 5.72 (d, J = 11 Hz, 1 H), 3.86 (s, 4 H), 3.82 (s, 4 H), 2.3–1.5 (series of m, 8 H), 1.28 (s, 3 H).

Hydrolysis of **16** (113 mg, 0.29 mmol) in wet acetone (15 mL) containing 100 mg of PPTS was complete after 23 h at the reflux temperature. The usual workup afforded 80 mg (90%) of **17** as a colorless oil which later crystallized: mp 110–112 °C (from dichloromethane–ether); IR ($CHCl_3$) 3100–2840, 1720, 1690, 1445, 1300, 1140, 1080; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 6.64 (d, J = 11 Hz, 1 H), 6.12 (d, J = 11 Hz, 1 H), 2.8–2.1 (series of m, 8 H), 2.17 (s, 3 H). This material was used without further purification.

Cyclization of 17. A solution of **17** (342 mg, 1.12 mmol) in 2% methanolic potassium hydroxide solution (20 mL) was stirred at room temperature for 4 h and poured into 50 mL of water previously saturated with ether. The product was extracted into ether (150 mL), and the resulting organic phase was washed with brine (50 mL) prior to drying and evaporation. MPLC on silica gel (elution with 70% ethyl acetate in petroleum ether) gave 246 mg (72%) of **19a** and 36 mg (11%) of **20a** as colorless crystalline solids.

For **19a**: mp 166–168 °C (from ether–pentane); IR ($CHCl_3$) 3600–3300, 3100–2840, 1680, 1445, 1375, 1305, 1145, 1080, 1010, 990, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.03 (dd, J = 11, 3 Hz, 1 H), 6.11 (d, J = 11 Hz, 1 H), 2.8–1.5 (series of m, 8 H), 1.20 (s, 3 H); ^{13}C NMR ($CDCl_3$) 198.32, 143.52, 134.84, 134.41, 132.59, 130.17, 129.26, 67.42, 64.50, 54.79, 32.83, 29.97, 28.52, 22.08 ppm, MS, m/e (M^+) calcd 306.0926, obsd 306.0933. Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92. Found: C, 62.69; H, 5.93.

For **20a**: mp 178–179 °C (from ether–pentane); IR ($CHCl_3$) 3600–3300, 3100–2840, 1675, 1445, 1375, 1305, 1145, 1080, 1000, 940, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.04 (dd, J = 10, 2 Hz, 1 H), 6.19 (d, J = 10 Hz, 1 H), 2.5–1.5 (series of m, 8 H), 1.40 (s, 3 H); ^{13}C NMR ($CDCl_3$) 198.58, 143.92, 134.93, 134.57, 133.60, 130.16, 129.33, 65.85, 64.15, 54.03, 33.15, 31.72, 26.31, 25.00 ppm.

4-(3-Oxobutyl)-3-cyclohexenone (18). Desulfonylation of **16** (596 mg, 1.51 mmol) was conducted during 1 h as before with 952 mg of Na_2HPO_4 and 4.84 g of 6% Na(Hg) in dry methanol (20 mL). The customary workup gave 368 mg (96%) of ketal isomers as a colorless liquid: IR ($CHCl_3$) 3000–2800, 1655, 1610, 1375, 1230, 1110, 1050, 940, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.56 (br d, J v 6 Hz, 0.4 H), 5.29 (br s, 0.6 H), 4.87 (d, J = 6 Hz, 0.4 H), 3.98 (s, 2.4 H), 3.94 (s, 4 H), 3.80 (s, 1.6 H), 2.3–1.6 (series of m, 9.6 H), 1.35 (s, 3 H).

Hydrolysis of this product (30 mg, 0.12 mmol) in the usual manner for 18 h furnished 16 mg (82%) of pure **18** as a colorless liquid; IR (neat) 3000–2800, 1720, 1420, 1360, 1190, 1160, 965, 785 cm^{-1} ^{1}H NMR ($CDCl_3$) δ 5.41 (br s, 1 H), 2.9–2.0 (series of m, 10 H), 2.17 (s, 3 H); MS, m/e (M^+) calcd 166.0994, obsd 166.0997.

Cyclization of 18. A solution of **18** (555 mg) in 2% methanolic potassium hydroxide (20 mL) was stirred at room temperature for 5 h, poured into water (50 mL), and extracted with chloroform (4 × 50 mL). The combined organic phases were washed with brine (50 mL), dried, and evaporated. Silica gel chromatography of the residue (elution with 40% ethyl acetate in petroleum ether) afforded 246 mg (51%) of **19b** and 68 mg of recovered **18**. Recrystallization of **19b** from ether–pentane yielded a fluffy white solid: mp 92–93.5 °C; IR ($CHCl_3$) 3600, 3560–3220, 3080–2820, 1670, 1440, 1380, 1300, 1260–1170, 1090, 970, 890, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.86 (m, 1 H), 6.01 (d, J = 9 Hz, 1 H), 2.7–1.3 (series of m, 9 H), 1.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) 201.42, 152.56, 130.41, 68.70, 55.47, 31.86, 30.40 (2C), 29.61, 22.09 ppm; MS, m/e (M^+) calcd 166.0994, obsd 166.0997. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.89; H, 8.48.

Hydrogenation **of 19b.** A solution of **19b** (164 mge in ethyl acette (9 mL) was hydrogenated in a Parr apparatus at 42 psi for 17 h over a 10% palladium on carbon catalyst. Filtration through Celite and evaporation of the filtrate gave 170 mg of dihydro derivative: mp 100–102 °C (from ether–pentane); IR ($CHCl_3$) 3600, 3560–3300, 3000–2820, 1695, 1450, 1380, 1295, 1225, 1100, 970, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.6–1.4 (series of m, 13 H), 1.18 (s, 3 H); MS, m/e (M^+) calcd 168.1150, obsd 168.1155.

***exo*-2,*endo*-8-Dimethylbicyclo[3.3.1]nonane-*endo*-2,*exo*-8-diol (21).** A cold (0 °C) solution of dihydro-**19b** (137 mg, 0.81 mmol) in dry ether (20 mL) and tetrahydrofuran (2 mL) was blanketed with nitrogen and treated with 1.90 mL of 1.3 M ethereal methyllithium (2.47 mmol). The reaction mixture was allowed to warm to room temperature where it was treated with additional methyllithium (0.70 mL) after 6 h. After a total reaction time of 11 h, saturated ammonium chloride solution (50 mL) was added, and the product was extracted into chloroform (2 × 75 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL), dried, and evaporated. MPLC of the residue on silica gel (elution with 45% ethyl acetate in petroleum ether) afforded 45 mg of unreacted **19b**, 19 mg of an unidentified substance, and 47 mg (46%) of **21**, a colorless solid: mp 148.5–149.5 °C (from dichloromethane–ether); IR (KBr) 3500–3200, 3000–2800, 1125, 1105, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.3–1.1 (series of m, 14 H), 1.47 (s, 3 H), 1.42 (s, 3 H); ^{13}C NMR (CD_3CN) 73.41 (2 C), 52.92, 36.85 (2 C), 33.11, 31.85, 30.78, 29.57, 29.37, 28.06 ppm; MS, m/e ($M^+ - H_2O$) calcd 166.1357, obsd 166.1361. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.45; H, 10.87.

6,6-(Ethylenedioxy)-3-(6-methyl-5-hepten-2-yl)-3-(phenylsulfonyl)cyclohexene (26). Inverse addition of the anion of **7** (6.00 g, 21.4 mmol), prepared as above, to 2-[(tolylsulfonyl)oxy]-6-methyl-5-heptene (10.29 g, 36.4 mmol) in a total volume of 100 mL of dimethylforamide, followed by preparative HPLC on a Waters Prep 500 instrument (silica gel, elution with 25% ethyl acetate in petroleum ether), afforded 857 mg (15%) of **27** and 2.75 g (47%) of **26** in addition to 1.87 g of unreacted **7**. The two diastereomers of **26** could be separated by careful MPLC purification (silica gel, elution with 30% ethyl acetate in petroleum ether).

For **27**: IR ($CHCl_3$) 3040–2820, 1595, 1445, 1310, 1260, 1150, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.85 (d, J = 9 Hz, 2 H), 7.6–7.4 (m, 3 H), 6.95 (d, J = 9 Hz, 2 H), 5.09 (br t, J = 6 Hz, 1 H), 4.2–3.3 (m, 5 H), 2.3–1.1 (series of m, 4 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.15 (d, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 388.1708, obsd 388.1716.

For **26a**: IR ($CHCl_3$) 3040–2800, 1400, 1385, 1290, 1215, 1135, 1115, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.80, 5.72 (AB q, J = 11 Hz, 2 H), 4.98 (br t, J = 6 Hz, 1 H), 3.80 (br s, 4 H), 2.4–1.0 (series of m, 9 H), 1.66 (s, 3 H), 1.59 (s, 3 H), 1.25 (d, J = 7 Hz, 3 H).

For **26b**: IR ($CHCl_3$) 3040–2800, 1445, 1385, 1290, 1135, 1115, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.82, 5.65 (AB q,

J = 11 Hz, 2 H), 5.10 (br m, 1 H), 3.81 (br s, 4 H), 2.3–1.0 (series of m, 9 H), 1.70 (s, 3 H), 1.63 (s, 3 H), 0.96 (d, J = 7 Hz, 3 H).

4-(6-Methyl-5-hepten-2-yl)-2-cyclohexenone. Desulfonylation of **26** (2.39 g, 6.13 mmol) was achieved in 1 h upon reaction with Na_2HPO_4 (3.0 g) and 6% Na(Hg) (12.5 g) in dry methanol (20 mL). The workup yielded 1.44 g (94%) of the isomeric ketals (54% β,γ; 46% α,β): IR (neat) 3000–2800, 1650, 1605, 1450, 1370, 1240, 1210, 1110, 1055, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.52 (d, J = 6 Hz, 0.5 H), 5.24 (br s, 0.5 H), 5.05 (br t, J = 7 Hz, 1 H), 4.86 (d, J = 6 Hz, 0.5 H), 3.95 (s, 2 H), 3.79 (s, 2 H), 2.3–1.0 (series of m, 10.5 H), 1.69 (s, 3 H), 1.60 (s, 3 H), 0.99 (d, J = 7 Hz, 3 H).

Exclusive formation of the β,γ-enone was realized upon refluxing this mixture (1.41 g, 5.63 mmol) in wet acetone (25 mL) containing 300 mg of PPTS for 5 h. Pure product was obtained following MPLC purification (silica gel, elution with 5% ethyl acetate in petroleum ether): 875 mg (75%); IR (neat) 3000–2820, 1725, 1450, 1370, 1185, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.42 (br s, 1 H), 5.05 (br t, J = 6 Hz, 1 H), 2.9–1.1 (series of m, 11 H), 1.69 (s, 3 H), 1.60 (s, 3 H), 1.02 (d, J = 6 Hz, 3 H); m/e (M^+) calcd 206.1670, obsd 206.1665.

The desired α,β-enone was obtained by treating the β,γ-unsaturated isomer (361 mg) with a methanolic sodium ethoxide solution (from 43 mg of sodium and 7 mL of dry methanol) at 60 °C for 5 min. The reaction mixture was poured onto ice (30 g) and acetic acid (1 mL). The product was extracted into ether (3 × 50 mL), and the combined organic layers were washed with 5% sodium bicarbonate solution (2 × 30 mL) and brine (50 mL) prior to drying and solvent evaporation. MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) led to the recovery of the β,γ isomer (105 mg) and the isolation of the conjugated enone: 148 mg (58%); IR (neat) 3000–2800, 1685, 1610, 1510, 1445, 1375, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.80 (br d, J = 10 Hz, 1 H), 5.96 (dd, J = 10 Hz, 1 H), 5.06 (br t, J = 6 Hz, 1 H), 2.6–1.0 (series of m, 10 H), 1.70 (s, 3 H), 1.62 (s, 3 H), 0.92 (d, J = 7 Hz, 1.5 H), 0.88 (d, J = 7 Hz, 1.5 H); MS, m/e (M^+) calcd 206.1670, obsd 206.1664.

Zingiberenol (24). A cold (0 °C) solution of the conjugated enone from above (75 mg, 0.36 mmol) in dry ether (7 mL) was blanketed with nitrogen and treated with ethereal methyllithium (0.35 mL of 1.3 M, 0.45 mmol). The reaction mixture was stirred at room temperature for 11 h prior to the addition of saturated ammonium chloride solution. Ether (150 mL) was introduced, and the organic layer was washed with water (50 mL) and brine (50 mL) before drying. Silica gel chromatography of the residue obtained upon solvent evaporation (elution with 10% ethyl acetate in petroleum ether) afforded 49 mg (61%) of zingiberenol (**24**) and 21 mg (26%) of its isomer **28**.

For **24**: IR (neat) 3350, 3000–2800, 1450, 1375, 1115, 1040, 970, 910, 735, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.6–5.3 (m, 2 H), 5.05 (br t, J = 6 Hz, 1 H), 2.2–1.0 (series of m, 11 H), 1.72 (s, 3 H), 1.64 (s, 3 H), 1.31 (s, 3 H), 0.84 (d, J = 6 Hz, 1.5 H), 0.80 (d, J = 6 Hz, 1.5 H); MS, m/e (M^+) calcd 222.1983, obsd 222.1990.

For **28**: IR (neat) 3350, 3000–2800, 1445, 1370, 1110, 900, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.7–5.4 (m, 2 H), 5.06 (br t, J = 6 Hz, 1 H), 2.2–1.0 (series of m, 11 H), 1.69 (s, 3 H), 1.62 (s, 3 H), 1.28 (s, 3 H), 0.86 (d, J = 6 Hz, 1.5 H), 0.82 (d, J = 6 Hz, 1.5 H); MS, m/e (M^+) calcd 222.1983, obsd 222.1990.

***trans*-3-Phenoxy-1-(phenylsulfonyl)propene (30b).** Allyl phenyl ether (0.60 g, 4.5 mmol) and *Se*-phenyl benzeneselenolsulfonate (1.1 g, 3.7 mmol) in carbon tetrachloride (15 mL) were irradiated at 2537 Å in a Rayonet reactor. After 1.5 h, the solvent was removed, and the residue was taken up in 20 mL of dichloromethane and treated at 0 °C with 4 mL of 15% hydrogen peroxide. Stirring was continued for 30 min at 0 °C and 30 min at room temperature, and then the product was worked up in the predescribed manner to afford 0.90 g (89%) of **30b**, mp 99–100 °C. Recrystallization from 25% ethyl acetate in petroleum ether gave analytically pure sulfone: IR (KBr) 3060, 3040, 1580, 1440, 1300, 1130, 950, 860, 800, 740, 705, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.7 (m, 2 H), 7.5–6.6 (m, 10 H), 4.6 (m, 2 H); MS, m/e (M^+) calcd 274.0663, obsd 274.0658. Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.54; H, 5.21.

(*E*)-(Trimethylsilyl)vinyl Phenyl Sulfone (30c). A solution of vinyltrimethylsilane (0.40 g, 4 mmol) and *Se*-phenyl benzeneselenolsulfonate (0.6 g, 2 mmol) in 8 mL of carbon tetrachloride was placed in a 10-mL Pyrex test tube and irradiated in a Rayonet chamber for 1.5 h, using a Rayonet 2537-Å photochemical reactor lamp. Removal of the solvent gave a yellow oil which was taken up in 20 mL of dichloromethane and treated at 0 °C with 4 mL of 15% hydrogen peroxide. After being stirred for 30 min at 0 °C and 30 min at room temperature, the solution was worked up in the usual manner to give a light yellow oil. Filtration through 30 g of silica gel removed traces of benzeneseleninic acid and afforded 0.41 g (84%) of pure **30c** identical in all respects with an authentic sample. ^1H NMR analysis of the crude product showed the E/Z ratio to be approximately 90:10.

3,3-Dimethoxy-1-(phenylsulfonyl)propene (30d). A solution of *Se*-phenyl benzeneselenolsulfonate (1.7 g, 5.7 mmol) and acrolein dimethyl acetal (1.2 g, 11 mmol) in carbon tetrachloride (15 mL) was irradiated through Pyrex in a Rayonet chamber by using 2537-Å lamps. After 1.5 h of irradiation, the solvent ws removed, and the residue was taken up in 40 mL of methylene chloride and stirred with ice cooling while 5 mL of 15% hydrogen peroxide was added via pipet. The solution was stirred for 30 min at 0 °C and for 30 min at room temperature, 30 mL of 10% aqueous sodium bicarbonate solution was added, and the layers were shaken and separated. The aqueous phase was reextracted with 20 mL of dichloromethane, and the combined organic phases were washed with saturated brine prior to drying and removal of solvent. Column chromatography (10% ethyl acetate in petroleum ether) furnished nearly pure **30d**: 101 g (73%); mp 55–57 °C. Final purification was achieved by recrystallization from 15% ethyl acetate in petroleum ether to deliver analytically pure **30d**: mp 57–59 °C; IR (KBr) 3060, 3040, 2940, 1640, 1580, 1470, 1440, 1300, 1230, 1140, 1060, 940, 860, 800, 740, 710, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.4 (m, 3 H), 6.7 (m, 2 H), 4.95 (d, J = 1 Hz, 1 H), 3.3 (s, 6 H); MS, (M^+ – 16) base peak at m/e 226. Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.46; H, 5.74.

5-*n*-Butyl-4-(phenylsulfonyl)-2-methylcyclohex-2-enone (32). A solution of **30a**[20,21] (0.74 g, 3.3 mmol) and diene **31** (0.74 g, 3.3 mmol) in 10 mL of xylene was heated at reflux for 28 h, cooled, and treated at room temperature with 5 mL of 1% hydrochloric acid and 5 mL of tetrahydrofuran. After 4 h, the product was extracted into 50 mL of ether, washed with brine, and dried. Removal of solvent gave an oil which was filtered through 30 g of silica gel. Elution with 10% ethyl acetate in petroleum ether furnished 0.68 g (68%) of **32a** as colorless crystals: mp 78–79 °C; IR (KBr) 3060, 2960, 2930, 2860, 1680, 1445, 1305, 1140, 1080, 900, 725, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.5 (m, 5 H), 6.45 (br d, J = 5 Hz, 1 H), 3.9 (br d, J = 5 Hz, 1 H), 3.0 (dd, J = 5, 16 Hz, 1 H), 2.9–2.6 (m, 1 H), 2.3 (dd, J = 16, 5 Hz, 1 H), 1.9 (br s, 3 H), 1.6–1.1 (m, 6 H), 0.9 (t, J = 4 Hz, 3 H); MS, m/e (M^+) calcd 306.1289, obsd 306.1297. Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24. Found: C, 66.65; H, 7.26.

5-(Phenoxymethyl)-4-(phenylsulfonyl)-2-methylcyclohex-2-(and 3-)enone (32b). A solution of **30b** (0.57 g, 2.1 mmol) and diene **31** (0.5 g, 2.2 mmol) in 10 mL of xylene was heated at reflux temperature for 20 h, cooled to room temperature, and stirred for 5 h with 5 mL of 1% hydrochloric acid and 5 mL of tetrahydrofuran. Extraction into ether and usual workup afforded a yellow oil consisting of α,β and β,γ double bond isomers of **32b**, in a ratio of ca. 2:1. Chromatography (MPLC, 15% ethyl acetate–petroleum ether) afforded pure α,β-unsaturated enone: mp 122 °C; IR (KBr) 3020, 2920, 1680, 1600, 1585, 1305, 1230, 1140, 1030, 900, 745, 715, 680, 590, 540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–7.6 (m, 2 H), 7.6–7.3 (m, 3 H), 7.2–6.9 (m, 2 H), 6.7 (m, 1 H), 6.7–6.45 (dd, J = 9, 1 Hz, 2 H), 6.35 (d, J = 5 Hz, 1 H), 4.1 (m, 1 H), 4.0–3.5 (m, 2 H), 3.1–2.6 (m, 2 H), 2.4–2.1 (m, 1 H), 1.7 (d, J = 1 Hz, 3 H); MS, m/e (M^+) calcd 356.1082, obsd 356.1075. Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.69. Found: C, 67.36; H, 5.65.

The remaining oily residue containing the β,γ-unsaturated isomer could be equilibrated to the α,β-unsaturated enone by stirring at room temperature in ethanol containing a catalytic amount of *p*-toluenesulfonic acid. The total combined yield was 0.59 g (79%).

5-(Dimethoxymethyl)-4-(phenylsulfonyl)-2-methylcyclohex-2-enone (32d). A solution of **30d** (0.30 g, 1.2 mmol) and diene

31 (0.40 g, 1.8 mmol) in 10 mL of xylene was stirred and heated at the reflux temperature for 30 h. Cooling followed by hydrolysis (5 mL of 1% hydrochloric acid and 5 mL of tetrahydrofuran, 5 h) and the usual workup afforded a light yellow oil. Filtration through silica gel (10% ethyl acetate–petroleum ether as the eluant) gave 0.30 g (77%) of **32d** as colorless crystals: mp 105–106 °C (from 20% ethyl acetate–petroleum ether); IR (KBr) 3060, 2960, 2930, 2830, 1675, 1180, 1145, 1120, 1100, 1060, 955, 920, 765, 735, 710, 685, 630, 565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.4 (br d, J = 5 Hz, 1 H), 4.3–4.05 (m, 2 H), 3.25 (s, 3 H), 3.18 (s, 3 H), 3.0–2.3 (series of m, 3 H), 1.85 (br s, 3 H); MS, no M^+, m/e 250, 218, 156, 136, 135 (base), 117, 108. Anal. Calcd for $C_{16}H_{20}O_5S$: C, 59.24; H, 6.21. Found: C, 59.11; H, 6.24.

5-*n*-Butyl-2-methylcyclohex-2-en-1-one (33a). To a solution of **32a** (0.21 g, 0.68 mmol) in 10 mL of glacial acetic acid was added activated zinc dust (0.45 g, 6.8 mmol) in one portion. The mixture was stirred magnetically at ambient temperature for 20 h, filtered, and concentrated in vacuo. The residue was taken up in ether and washed with 10% bicarbonate solution and brine prior to drying and removal of solvent. Purification by MPLC (5% ethyl acetate–petroleum ether) gave 89 mg (78%) of **33a** as a colorless oil: IR (neat) 3040, 2960, 2920, 2850, 1680, 1360, 895, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.6 (d, J = 5 Hz, 1 H), 2.6–1.8 (series of m, 5 H), 1.8 (br s, 3 H), 1.5–1.2 (m, 6 H), 0.8 (t, J = 5 Hz, 3 H); MS, m/e (M^+) calcd 166.1357, obsd 166.1360.

5-(Phenoxymethyl)-2-methylcyclohex-2-en-1-one (33b). To a solution of **32b** (0.23 g, 0.65 mmol) in 10 mL of glacial acetic acid was added activated zinc dust (0.4 g, 6.1 mmol) in one portion. The mixture was stirred for 20 h at ambient temperature, filtered, and concentrated in vacuo. The residue was taken up in ether and washed with sodium bicarbonate solution and brine prior to drying and removal of solvent. Purification by MPLC (10% ethyl acetate–petroleum ether) gave, in addition to several unidentified minor components, 0.088 g (63%) of **33b** as a colorless, crystalline solid: mp 65 °C; IR (KBr) 2940, 2910, 1655, 1235, 1040, 900, 810, 755, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.1 (m, 2 H), 7.0–6.6 (m, 4 H), 3.9 (d, J = 5 Hz, 2 H), 2.8–2.2 (m, 5 H), 1.75 (br s, 3 H); MS, m/e (M^+) calcd 216.1150, obs 216.1156. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.54; H, 7.52.

5-(Dimethoxymethyl)-2-methyl-2-cyclohexenone (33d) and 5-(Dimethoxymethyl)-2-methyl-3-cyclohexenone (34d). To a solution of **32d** (0.77 g, 2.4 mmol) in 10 mL of glacial acetic acid was added zinc dust (1.4 g, 21 mmol) in one portion. The solution was stirred for 3 h and filtered. The solid residue was washed with 50 mL of ether, and the combined organic filters were neutralized with saturated bicarbonate solution, washed with brine, dried, and concentrated. The resulting residue was partitioned into two oily fractions by medium-pressure chromatography (elution with 15% ethyl acetate in petroleum ether) which were identified as **33d** (0.19 g, 43%) and **34d** (0.15 g, 34%).

For **33d**: IR (neat) 2920, 2820, 1670, 1360, 1180, 1100, 1060, 960, 950, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.7 (m, 1 H), 4.2 (d, J = 3 Hz, 1 H), 3.38 (s, 6 H), 2.8–2.1 (series of m, 5 H), 1.8 (br s, 3 H); MS, m/e (M^+) calcd 184.1098, obsd 184.1104.

For **34d**: IR (neat) 2960, 2920, 2820, 1710, 1445, 1360, 1180, 1115, 1060, 965, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.7 (br s, 2 H), 4.2–4.0 (m, 1 H), 3.38 (s, 6 H), 3.0–2.75 (m, 2 H), 2.5–2.3 (m, 2 H), 1.2–1.0 (2 d, J = 7 Hz, 3 H); MS, m/e (M^+ – 31) 153 base peak.

***trans*-2-(3-Oxo-2-oxabicyclo[3.3.0]oct-6-yl)-1-(phenylsulfonyl)ethylene (36).** A solution of **35**[34] (0.32 g, 2.1 mmol) and *Se*-phenyl benzeneselenolsulfonate (0.63 g, 2.1 mmol) in 7 mL of carbon tetrachloride was irradiated at 2537 Å as described previously. After 3 h, the solvent was removed, and the residue was taken up in 10 mL of dichloromethane, cooled to 0 °C, and treated with 4 mL of 15% hydrogen peroxide. Stirring was continued for 0.5 h at 0 °C and 0.5 h at room temperature. The solution was shaken with 20 mL of 10% aqueous bicarbonate and worked up in the usual manner to give a light yellow oil which crystallized on standing. Recrystallization from 60% ethyl acetate in petroleum ether gave **36**: white needles; 0.44 g (72%); mp 133 °C; IR (KBr) 3040, 2970, 2830, 1765, 1620, 1445, 1310, 1180, 1140, 1080, 990, 820, 740, 710, 680, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.7 (m, 2 H), 7.7–7.3 (m, 3 H), 6.9 (dd, J = 6, 15 Hz, 1 H), 6.35 (d, J = 15 Hz, 1 H), 5.05 (t, J = 6 Hz, 1 H), 3.3–1.6 (series of m, 8 H); MS, m/e (M^+) calcd 292.0769, obsd 292.0777. Anal. Calcd for $C_{15}H_{16}O_4S$: C, 61.63; H, 5.52. Found: C, 61.51; H, 5.60.

***endo*-6-[5-Oxo-2-(phenylsulfonyl)cyclohex-3-enyl]-3-oxo-2-oxabicyclo[3.3.0]nonanes (37 and 38).** A solution of **36** (0.36 g, 1.2 mmol) and diene **10** (0.4 g, 2 mmol) in 10 mL of xylene was stirred at reflux in an inert atmosphere for 48 h, cooled to ambient temperature, and treated with 5 mL of 1% hydrochloric acid and 5 mL of tetrahydrofuran. After an additional 3 h at room temperature, the product was extracted into ethyl acetate (50 mL), washed with 20 mL of saturated bicarbonate solution and 20 mL of brine, dried, and concentrated. The resultant oil was chromatographed by MPLC with 35% petroleum ether in ethyl acetate to give 220 mg (50%) of **37** and 80 mg (18%) of **38**. Recrystallization from 50% ethyl acetate in petroleum ether gave the analytical samples.

For **37**: mp 165 °C; IR (KBr) 3050, 2930, 2860, 1780, 1680, 1450, 1310, 1180, 1145, 1080, 1000, 960, 900, 840, 790, 760, 725, 680, 620, 575, 545 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.6 (dd, J = 5, 11 Hz, 1 H), 6.2 (d, J = 11 Hz, 1 H), 4.9 (t, J = 7 Hz, 1 H), 3.85 (d, J = 5 Hz, 1 H), 3.2–2.9 (m, 2 H), 2.9–1.0 (series of m, 9 H); MS, m/e (M^+ – 125) 235 base peak. Anal. Calcd for $C_{19}H_{20}O_5S$: C, 63.32; H, 5.59. Found: C, 63.45; H, 5.78.

For **38**: mp 192 °C; IR (KBr) 3060, 2950, 1780, 1675, 1450, 1380, 1300, 1170, 1145, 1080, 1065, 1005, 895, 830, 750, 720, 700, 680, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.6 (dd, J = 5, 10 Hz, 1 H), 6.2 (d, J = 10 Hz, 1 H), 4.95 (t, J = 7 Hz, 1 H), 3.75 (d, J = 5 Hz, 1 H), 3.2–2.6 (m, 3 H), 2.6–1.2 (m, 8 H); MS, m/e (M^+ – 125) 235 base peak. Anal. Calcd for $C_{19}H_{20}O_5S$: C, 63.32; H, 5.59. Found: C, 63.26; H, 5.65.

***endo*-6-(5-Oxocyclohex-2-enyl)-3-oxo-2-oxabicyclo[3.3.0]-octane (39).** A solution of sulfones **37** and **38** (0.16 g, 0.44 mmol) in 5 mL of glacial acetic acid was stirred at ambient temperature while zinc dust (0.250 mg, 3.8 mmol) was added in one portion. Stirring was continued for an additional 24 h when the solution was filtered and concentrated. The residue was taken up in ethyl acetate and washed with saturated sodium bicarbonate solution and brine prior to drying and removal of the solvent. Medium-pressure chromatography (30% ethyl acetate–petroleum ether) furnished pure **39**: oil; 60 mg (60%); IR (neat) 3020, 2960, 2860, 1765, 1710, 1635, 1310, 1225, 1180, 1020, 995, 930, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (m, 2 H), 5.0 (t, J = 5 Hz, 1 H), 2.9 (br s, 2 H), 2.8–2.3 (m, 4 H), 2.3–1.2 (series of m, 7 H); MS, m/e (M^+) calcd 220.1099, obsd 220.1105.

***trans*-1-(Phenylsulfonyl)-4-(trimethylsilyl)-1-butene (41).** A solution of 4-(trimethylsilyl)-1-butene[35] (1.41 g, 11.0 mmol) and *Se*-phenyl benzeneselenolsulfonate (1.70 g, 5.7 mmol) in carbon tetrachloride (15 mL) was placed in two small Pyrex tubes and irradiated with a bank of 2537-Å lamps in a Rayonet reactor for 1.5 h. The solvent was evaporated, the residue was taken up in dichloromethane (50 mL), and 15% hydrogen peroxide (5 mL) was added with vigorous stirring at 0 °C. After 30 min, the reaction mixture was warmed to room temperature. Following an identical time interval, the solution was poured into 5% sodium bicarbonate solution (30 mL) and dichloromethane (20 mL). The organic phase was washed once more with the bicarbonate solution (30 mL) and brine (50 mL) before drying and evaporation. The resulting oil was chromatographed on silica gel (MPLC, elution with 10% ethyl acetate in petroleum ether) to give 1.43 g (93%) of **41** after removal of the solvent under high vacuum overnight: IR (neat) 2960–2860, 1625, 1445, 1320, 1250, 1145, 1080, 855, 830, 750, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.08 (dt, J = 15, 6 Hz, 1 H), 6.32 (d, J = 15 Hz, 1 H), 2.4–2.1 (m, 2 H), 0.8–0.6 (m, 2 H), 0.06 (s, 9 H); MS, m/e (M^+) calcd 268.0953, obsd 268.0971. Anal. Calcd for $C_{13}H_{20}O_2SSi$: C, 58.16; H, 7.51. Found: C, 57.76; H, 7.45.

***trans*-1-(Phenylsulfonyl)-6-[(*tert*-butyldimethylsilyl)-oxy]-1-hexene (44).** The silyl ether was prepared by reacting 5-hexen-1-ol (1.18 mL, 9.97 mmol) with imidazole (0.80 g) and *tert*-butyldimethylsilyl chloride (2.60 g) in dimethylformamide (50 mL) under nitrogen at room temperature for 20 h. The

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reaction mixture was poured into ether (200 mL) and extracted with water (100 mL, 2 × 50 mL) and brine (100 mL). After the mixture was dried and the solvent evaporated, distillation gave 1.39 g (65%) of product, bp 98 °C (20 torr).

Photolysis of this substance (1.34 g, 6.25 mmol) with *Se*-phenyl benzeneselenolsulfonate (1.20 g, 4.04 mmol) in carbon tetrachloride (15 mL) as before furnished 1.27 g (89%) of **44** after MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether): IR (neat) 2980–2810, 1620, 1440, 1320, 1245, 1140, 1080, 825, 770, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.5 (m, 5 H), 7.02 (dt, J = 15, 6 Hz, 1 H), 6.34 (d, J = 15 Hz, 1 H), 3.63 (m, 2 H), 2.5–2.2 (m, 2 H), 1.7–1.5 (m, 4 H), 0.93 (s, 9 H), 0.09 (s, 6 H); MS, m/e (M^+) calcd 339.1450, obsd 339.1458. Anal. Calcd for $C_{18}H_{30}O_3SSi$: C, 60.97; H, 8.53. Found: C, 60.94; H, 8.53.

***trans*-1-(Phenylsulfonyl)-3-[(*tert*-butyldimethylsilyl)oxy]-1-propene (47).** The *tert*-butyldimethylsilyl ether of allyl alcohol [bp 49–50 °C (20 torr); 1.14 g (6.61 mmol)] was similarly converted to **47** upon irradiation with the selenolsulfonate (1.02 g, 3.43 mmol) in carbon tetrachloride solution (15 mL). MPLC purification on silica gel (elution with 10% ethyl acetate in petroleum ether) gave 909 mg (85%) of **47** as a colorless solid which melted upon warming to room temperature: IR (neat) 2980–2820, 1630, 1440, 1310, 1250, 1140, 1080, 860, 830, 770, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.05 (dt, J = 14, 3 Hz, 1 H), 6.60 (dt, J = 14, 2 Hz, 1 H), 4.4–4.3 (m, 2 H), 0.92 (s, 9 H), 0.09 (s, 6 H); MS, m/e (M^+) calcd 297.0981, obsd 297.0987. Anal. Calcd for $C_{15}H_{24}O_3SSi$: C, 57.64; H, 7.74. Found: C, 57.57; H, 7.72.

Cycloaddition–Ketalization of 41. A solution containing **41** (3.98 g, 14.8 mmol) and Danishefsky's diene (3.30 g of 85% purity, 16.3 mmol) in xylene (16 mL) was refluxed under nitrogen for 55 h. The cooled reaction mixture was transferred to a larger round-bottomed flask, and benzene (20 mL), ethylene glycol (2 g), and a catalytic quantity of *p*-toluenesulfonic acid were added. Azeotropic removal of water was carried out over 24 h, followed by the customary workup. HPLC (silica gel, elution with 15% ethyl acetate in petroleum ether) afforded 1.07 g of unreacted **41** and 3.62 g (88%) of **42** as a mixture of the two isomers. Recrystallization of the mixture gave 1.92 g of Δ^3-**42**. The mother liquor was rechromatographed and recrystallized to provide an additional 0.50 g of Δ^3-**42** as a colorless crystalline solid, mp 76–78 °C (from ether–pentane). Careful MPLC of the residue (silica gel, elution with 16% ethyl acetate in petroleum ether) yielded pure Δ^2-**42** as a colorless oil.

For Δ^3-**42**: IR ($CHCl_3$) 3060–2820, 1630, 1440, 1300, 1140, 1080, 850, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 7.00 (t, J = 4 Hz, 1 H), 3.98 (s, 4 H), 2.8–2.5 (m, 2 H), 2.0–1.2 (series of m, 5 H), 0.6–0.2 (m, 2 H), −0.03 (s, 9 H).

For Δ^2-**42**: IR (neat) 3000–2800, 1440, 1300, 1240, 1150–1100, 1075, 1050, 1015, 940, 770, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.5 (m, 5 H), 5.89 (s, 2 H), 4.0–3.6 (m, 5 H), 2.4–1.5 (m, 5 H), 0.7–0.3 (m, 2 H), 0.01 (s, 9 H).

Cycloaddition–Ketalization of 44. A solution of **44** (1.21 g, 3.41 mmol) and Danishefsky's diene (760 mg of 85% purity, 3.75 mmol) in xylene (6 mL) was refluxed for 48 h under nitrogen. Ethylene glycol (650 mg), benzene (20 mL), and *p*-toluenesulfonic acid (25 mg) were added, and azeotropic removal of water was continued for 20 h. Workup as before but with ethyl acetate as the solvent gave **45** and some desilylated product. Reprotection of the hydroxyl group with imidazole (255 mg, 3.74 mmol) and *tert*-butyldimethylsilyl chloride (515 mg, 3.42 mmol) in dimethylformamide (18 mL) was therefore effected (22 h) prior to MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether). There was obtained 542 mg of unreacted **44** and 311 mg (35%) of Δ^3-**45**; IR (neat) 3000–2800, 1675, 1600, 1450, 1300, 1250, 1150–1000, 830, 770, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 7.0–6.8 (br t, 1 H), 4.0–3.8 (m, 4 H), 3.7–3.5 (m, 2 H), 2.7–2.5 (m, 2 H), 2.0–1.1 (series of m, 9 H), 0.95 (s, 9 H), 0.08 (s, 6 H).

Cycloaddition–Ketalization of 47. A solution of **47** (1.00 g, 3.2 mmol) and Danishefsky's diene (720 mg of 85% purity, 3.5 mmol) in xylene (5 mL) was refluxed until black (23 h) under nitrogen in base-washed glassware. The solution was transferred to a flask having twice the volume, and benzene (20 mL), ethylene glycol (600 mg), and *p*-toluenesulfonic acid (25 mg) were added. Removal of water azeotropically during 17 h followed by the predescribed workup but with ethyl acetate as the solvent afforded a ketal mixture. This oil was dissolved in dry dimethylformamide (18 mL) and resilylated with imidazole (240 mg, 3.5 mmol) and *tert*-butyldimethylsilyl chloride (480 mg, 3.2 mmol) at room temperature under nitrogen for 18 h. MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether) yielded 139 mg of unreacted **47** and 863 mg (74%) of **48** as a mixture of β,γ and α,β isomers (77:23): IR (neat) 3000–2800, 1465, 1440, 1390, 1355, 1300, 1250, 1150–1050, 1020, 940, 830, 770, 720, 680; ^1H NMR ($CDCl_3$) δ 8.0–7.5 (m, 5 H), 7.07 (t, J = 4 Hz, 0.8 H), 5.89 (s, 0.4 H), 4.0–3.6 (m, 6.2 H), 2.7–1.3 (series of m, 4.6 H), 0.90 (m, 9 H), 0.03 (m, 6 H).

Alkylation of 42. (A) 1-Bromo-4-*p*-tolylpentane. Alkylation of **42** (506 mg, 1.33 mmol) with sodium hydride (134 mg of 50% in oil, 2.79 mmol) and 1-bromo-4-*p*-tolylpentane (646 mg, 2.68 mmol) in dry dimethylformamide (25 mL) during 20 h, followed by the customary workup and MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether), gave 183 mg (20%) of dialkylated product and 444 mg (62%) of **49**: IR ($CHCl_3$) 3040–2800, 1510, 1440, 1290, 1240, 1220, 1130, 1075, 935, 850, 830, 680, 590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 7.06 (br s, 4 H), 6.0–5.1 (m, 2 H), 4.1–3.5 (m, 4 H), 2.31 (s, 3 H), 2.8–0.5 (series of m, 14 H), 1.22 (d, J = 8 Hz, 1.5 H), 1.20 (d, J = 8 Hz, 1.5 H), 0.02 (s, 9 H).

(B) Allyl Bromide. From 503 mg (1.32 mmol) of **42**, 144 mg (3.0 mmol) of 50% sodium hydride, and 0.23 mL (2.66 mmol) of allyl bromide (25 mL of dry DMF, room temperature, 22 h) there were isolated by MPLC on silica gel (elution with 17% ethyl acetate in petroleum ether) 65 mg (11%) of dialkylation products and 395 mg (71) of **53a**: IR (neat) 3100–2800, 1440, 1390, 1300, 1240, 1130, 1075, 1020, 925, 830, 765, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.2–5.1 (m, 3 H), 4.3–3.7 (m, 4 H), 3.2–1.2 (series of m, 7 H), 0.9–0.2 (m, 2 H), 0.13 (s, 9 H).

5-[2-(Trimethylsilyl)ethyl]-4-(4-*p*-tolylpentyl)-2-(and 3-)cyclohexenone (51/52). Deketalization was effected by refluxing a solution of **49** (385 mg, 0.71 mmol) and PPTS (90 mg) in wet acetone (12 mL) for 16 h. The usual workup and concentration under high vacuum afforded **50** (342 mg, 97%) as a colorless oil: IR (neat) 3100–2800, 1680, 1580, 1510, 1450, 1380, 1300, 1250, 1130, 1070, 880–800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.5 (m, 5 H), 7.3–7.0 (m, 5 H), 6.3–6.0 (m, 1 H), 2.30 (s, 3 H), 2.9–0.5 (series of m, 14 H), 1.23 (d, J = 7 Hz, 1.5 H), 1.19 (d, J = 7 Hz, 1.5 H), 0.04 (s, 9 H).

A solution of **50** (257 mg, 0.52 mmol) in glacial acetic acid (10 mL) was stirred with zinc dust (340 mg, 5.2 mmol) at room temperature under nitrogen for 24 h. The solution was filtered into 5% sodium bicarbonate solution (100 mL), and ether (150 mL) was added. Solid sodium bicarbonate was slowly added until neutralization was complete. The ethereal layer was washed again with the bicarbonate solution (50 mL) and brine (50 mL) prior to drying and solvent evaporation. MPLC of the residue on silica gel (elution with 5% ethyl acetate in petroleum ether) afforded 148 mg (80%) of **51** as a colorless liquid: IR (neat) 3000–2800, 1720, 1510, 1240, 1145, 870–800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.11 (s, 4 H), 5.37 (m, 1 H), 2.34 (s, 3 H), 2.9–1.1 (series of m, 14 H), 1.24 (d, J = 8 Hz, 3 H), 0.7–0.3 (m, 2 H), 0.00 (s, 9 H); MS, m/e (M^+) calcd 356.2535, obsd 356.2543.

Equilibration of the 2 isomer was cleanly achieved by refluxing a mixture of **51** (21 mg) and sodium carbonate (2 mg) in methanol (6 mL) for 9 h. The reaction mixture was cooled, poured into saturated brine, and extracted with ether. The combined organic layers were washed with water (25 mL) and brine (25 mL) before drying and solvent evaporation. MPLC on silica gel (elution as above) afforded recovered **51** (4 mg) and **52** (11 mg, 65%): IR (neat) 3040–2800, 1680, 1510, 1450, 1410, 1385, 1245, 870–800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (s, 4 H), 6.79 (dd, J = 10, 3 Hz, 1 H), 5.93 (br d, J = 10 Hz, 1 H), 2.36 (s, 3 H), 2.8–1.0 (series of m, 13 H), 1.24 (d, J = 7 Hz, 3 H), 0.7–0.3 (m, 2 H), 0.00 (s, 9 H); MS, m/e (M^+) calcd 356.2535, obsd 2545. Anal. Calcd for $C_{23}H_{36}OSi$: C, 77.46; H, 10.17. Found: C, 77.21; H, 10.14.

5-[2-(Trimethylsilyl)ethyl]-4-allyl-2-(and 3-)cyclohexenone (55a). The ketal sulfone **53a** (236 mg, 0.56 mmol) was reduced with 2.0 g of 6% Na(Hg) and 357 mg of Na_2HPO_4 in dry methanol (12 mL) during 3.5 h as before. The resulting double bond isomer mixture was directly taken up in wet acetone (12 mL) to which 40 mg of PPTS was added. This reaction mixture was heated at reflux for 17 h and worked up in the usual manner to furnish pure β,γ-unsaturated ketone (96 mg, 72%) after MPLC on silica

gel (elution with 5% ethyl acetate in petroleum ether): IR (neat) 3100–2800, 1720, 1630, 1410, 1240, 1160, 980, 900, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.0–5.6 (m, 1 H), 5.44 (br t, 1 H), 5.2–4.9 (m, 2 H), 2.9–2.7 (m, 4 H), 2.6–2.3 (m, 3 H), 1.7–1.2 (m, 2 H), 0.8–0.2 (m, 2 H), –0.03 (s, 9 H); MS, m/e (M^+) calcd 236.1596, obsd 236.1602.

Heating this substance (92 mg) with sodium carbonate (3 mg) in absolute methanol (20 mL) for 10 h, followed by the standard isolation procedure and MPLC (elution as before), furnished 12 mg of recovered Δ^3 isomer and 41 mg (51%) of **55a**: IR (neat) 3100–2800, 1680, 1390, 1245, 910, 855, 830, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.80 (dd, J = 10, 2 Hz, 1 H), 5.92 (br d, J = 10 Hz, 1 H), 6.0–5.5 (m, 1 H), 5.3–5.0 (m, 2 H), 2.7–1.7 (m, 5 H), 1.7–1.2 (m, 3 H), 0.7–0.3 (m, 2 H), –0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) 199.84, 153.37, 135.27, 129.04, 177.61, 41.40, 41.02, 40.03, 36.48, 26.97, 12.75, –1.84 ppm; MS, m/e (M^+) calcd 236.1596, obsd 236.1602. Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.12; H, 10.23. Found: C, 71.14; H, 10.14.

Alkylation of 45. (*E*)-2-(Trimethylsilyl)-4-iodo-2-butene. A 630-mg (1.35 mmol) sample of **45** was treated with 196 mg (4.08 mmol) of 50% sodium hydride and 1.03 g (4.05 mmol) of (*E*)-2-(trimethylsilyl)-4-iodo-2-butene in dimethylformamide (25 mL) for 17.5 h. Workup and solvent evaporation under high vacuum gave an oil which was chromatographed (MPLC) on silica gel (elution with 15% ethyl acetate in petroleum ether). There was obtained 171 mg (35%) of **53b** and 226 mg of unreacted **45**: IR (neat) 3000–2800, 1460, 1440, 1385, 1300, 1245, 1150–1050, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.1–5.8 (m, 2 H), 4.0–3.4 (m, 6 H), 1.73 (br s, 3 H), 2.4–1.1 (series of m, 11 H), 0.96 (s, 9 H), 0.10 (m, 15 H).

5-(4-Hydroxybutyl)-4-[3-(trimethylsilyl)-2-butenyl]-2-(and 3-)cyclohexenone (55b). Sulfone ketal **53b** (288 mg, 0.52 mmol) was reduced with 365 mg of Na_2HPO_4 and 3.2 g of 6% Na(Hg) in dry methanol (13 mL) for 1.5 h. The residue remaining after the workup was heated at reflux in a solution of PPTS (30 mg) in wet acetone (13 mL) for 22 h. MPLC on silica gel (elution with 44% ethyl acetate in petroleum ether) afforded 105 mg (69%) of isomerically pure β,γ-unsaturated enone: IR (neat) 3600–3200, 3000–2800, 1710, 1415, 1245, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.69 (m, 1 H), 5.36 (m, 1 H), 3.55 (t, J = 5 Hz, 2 H), 2.9–2.0 (series of m, 8 H), 1.66 (br s, 3 H), 1.6–1.1 (m, 6 H), 0.06 (s, 9 H); MS, m/e (M^+) calcd 294.2015, obsd 294.2023.

Equilibration of this substance (98 mg) was achieved by heating with sodium carbonate (2 mg) in absolute methanol under nitrogen for 6 h. MPLC on silica gel (elution with 44% ethyl acetate in petroleum ether) furnished 7 mg of recovered Δ^3 isomer and 61 mg (67%) of **55b**: IR (neat) 3600–3200, 3000–2800, 1680, 1245, 1055, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.76 (dd, J = 11, 2 Hz, 1 H), 5.93 (d, J = 11 Hz, 1 H), 5.7–5.5 (m, 1 H), 3.58 (t, J = 5 Hz, 2 H), 2.6–1.8 (m, 6 H), 1.67 (br s, 3 H), 1.6–1.1 (m, 9 H), 0.06 (s, 9 H); ^{13}C NMR ($CDCl_3$) 199.81, 153.75, 135.18, 129.05, 128.87, 62.78, 41.84, 41.24, 38.75, 33.11, 32.80, 30.92, 22.73, 14.72, –2.08 ppm; MS, m/e (M^+) calcd 294.2015, obsd 294.2023.

Alkylation of 48. (A) Geranyl Bromide. A 282-mg (0.66 mmol) sample of **48** was treated with 80 mg (1.67 mmol) of 50% NaH and 0.26 mL (1.31 mmol) of geranyl bromide in dry dimethylformamide (15 mL) for 19 h. A workup as before and MPLC on silica gel (elution with 17% ethyl acetate in petroleum ether) afforded 153 mg (41%) of **53c**: IR (neat) 3000–2800, 1450, 1390, 1300, 1250, 1135, 1080, 1030, 940, 830, 770, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5 H), 5.84 (s, 2 H), 5.3–4.9 (m, 2 H), 4.3–3.5 (m, 6 H), 2.2–1.8 (m, 6 H), 1.8–1.6 (m, 9 H), 1.6–1.1 (m, 3 H), 0.96 (s, 9 H), 0.13 (s, 6 H).

(B) 2-(Benzyloxy)ethyl Bromide. A 640-mg (1.51 mmol) sample of **48** was treated with 126 mg (2.62 mmol) of 50% NaH and 567 mg (2.63 mmol) of 2-(benzyloxy)ethyl bromide in dimethylformamide (25 mL) for 18.5 h. Workup and MPLC on silica gel (elution with 30% ethyl acetate in petroleum ether) led to the isolation of C-2-monoalkylated product (115 mg), dialkylation products (106 mg), and **53d**: 247 mg (29%); IR (neat) 3100–2800, 1450, 1385, 1360, 1290, 1250, 1200, 1150–1000, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 7.33 (s, 5 H), 6.1–5.8 (m, 2 H), 4.6–3.6 (series of m, 10 H), 2.6–1.5 (series of m, 5 H), 0.94 (2 s, 9 H), 0.09 (m, 6 H).

5-(Hydroxymethyl)-4-geranyl-3-cyclohexenone (56a). Reductive desulfonylation of **53c** (209 mg, 0.37 mmol) was accomplished with 260 mg of Na_2HPO_4 and 2.27 g of 6% Na(Hg) in dry methanol (12 mL) during 3.5 h. The residue after the workup was refluxed with 30 mg of PPTS in wet acetone (12 mL). MPLC on silica gel (elution with 44% ethyl acetate in petroleum ether) furnished 69 mg (71%) of **56a**: IR (neat) 3600–3100, 3000–2800, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.60 (m, 1 H), 5.3–5.0 (m, 2 H), 3.64 (AB, J = 4 Hz, 2 H), 3.0–2.8 (m, 4 H), 2.7–2.5 (m, 3 H), 2.2–2.0 (m, 4 H), 1.8–1.6 (m, 9 H); MS, m/e (M^+) calcd 262.1933, obsd 262.1939.

5-(Hydroxymethyl)-4-[2-(benzyloxy)ethyl]-3-cyclohexenone (56b). Reductive desulfonylation of **53d** (229 mg, 0.41 mmol) was accomplished with 260 mg of Na_2HPO_4 and 2.3 g of 6% Na(Hg) in dry methanol during 4 h. The resulting oil was hydrolyzed with 30 mg of PPTS in wet acetone (12 mL) at the reflux temperature (22 h). MPLC on silica gel (elution with 60% ethyl acetate in petroleum ether) afforded 80 mg (75% overall) of **56b** as the sole product: IR (neat) 3600–3200, 3100–2800, 1710, 1450, 1400, 1355, 1195, 1100–1000, 730, 690; ^1H NMR ($CDCl_3$) δ 7.36 (s, 5 H), 5.67 (br s, 1 H), 4.51 (br s, 2 H), 3.7–3.5 (m, 4 H), 2.9–2.3 (m, 8 H); MS, m/e (M^+) calcd 260.1412, obsd 260.1420.

Base-Promoted Equilibration of 56a. A solution of **56a** (60 mg) in absolute methanol (12 mL) containing sodium carbonate (1.5 mg) was heated at reflux for 6.5 h. A workup in the predescribed manner (dichloromethane extraction) and silica gel chromatography (MPLC, elution with 45% ethyl acetate in petroleum ether) gave unchanged **56a** (6 mg), the cyclized product **58a** (7 mg, 13%), and the conjugated enone **57a** (27 mg, 50%).

For **57a**: IR (neat) 3600–3100, 3100–2800, 1675, 1440, 1380, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86 (dd, J = 10, 3 Hz, 1 H), 5.98 (dd, J = 10, 2 Hz, 1 H), 5.3–4.9 (m, 2 H), 3.8–3.6 (m, 2 H), 2.6–1.8 (series of m, 10 H), 1.7–1.5 (m, 9 H), 1.5–1.2 (m, 1 H); ^{13}C NMR ($CDCl_3$) 199.39, 153.85, 138.16, 131.65, 128.81, 124.11, 120.82, 64.13, 41.22, 39.80, 29.42, 37.61, 30.67, 26.52, 25.70, 17.71, 16.29 ppm; MS, m/e (M^+) calcd 262.1933, obsd 262.1926.

For **58a**: IR (neat) 3000–2800, 1725, 1445, 1380, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.3–4.9 (m, 2 H), 4.3–3.7 (m, 3 H), 2.7–2.0 (m, 10 H), 1.8–1.6 (m, 9 H), 1.4–1.2 (m, 2 H); MS, m/e (M^+) calcd 262.1933, obsd 262.1941.

Base-Promoted Equilibration of 56b. Treatment of **56b** (75 mg) in a totally analogously manner afforded recovered starting material (6 mg), cyclized product **58b** (18 mg, 26%) and conjugated enone **57b** (26 mg, 38%).

For **57b**: IR (neat) 3600–3200, 3000–2800, 1675, 1450, 1120–1050, 740, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (s, 5 H), 6.85 (dd, J = 9, 3 Hz, 1 H), 5.98 (br d, J = 9 Hz, 1 H), 4.50 (s, 2 H), 3.7–3.4 (m, 4 H), 2.6–1.5 (series of m, 7 H); ^{13}C NMR ($CDCl_3$) 199.22, 153.57, 137.99, 128.64, 128.53, 127.87, 127.76, 73.31, 67.84, 64.23, 41.66, 39.47, 34.82, 32.42 ppm; MS, m/e (M^+) calcd 260.1412, obsd 260.1426.

For **58b**: IR (neat) 3000–2800, 1720, 1450, 1360, 1200, 1100, 735, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (s, 5 H), 4.51 (s, 2 H), 4.1–3.5 (m, 5 H), 2.6–1.5 (series of m, 8 H); MS, m/e (M^+) calcd 260.1412, obsd 260.1400.

1-(Phenylsulfonyl)cyclopentene (59a). A solution of cyclopentene (0.6 g, 8.8 mmol) and *Se*-phenyl benzeneselenolsulfonate (1.1 g, 3.7 mmol) in 12 mL of carbon tetrachloride was irradiated at 2537 Å for 1.5 h as described previously. Evaporation of the solvent gave a yellow oil which crystallized on standing (mp 64–65 °C). Treatment of dichloromethane solution (10 mL) of the crude selenolsulfone at 0 °C with 4 mL of 15% hydrogen peroxide for 1 h yielded, after the usual workup, 0.66 g (86%) of **59a**. Recrystallization from 25% ethyl acetate in petroleum ether gave an analytical sample: mp 65–66 °C; IR (KBr) 3060, 2960, 2920, 2840, 1610, 1580, 1440, 1300, 1150, 1085, 935, 825, 745, 710, 680, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.3 (m, 5 H), 6.6 (br s, 1 H), 2.6–2.2 (m, 4 H), 2.2–1.8 (m, 2 H); MS, m/e (M^+) calcd 208.0558, obsd 208.0553. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.49; H, 5.83.

3-(Phenylsulfonyl)-2,5-dihydrofuran (59b). A solution of 2,5-dihydrofuran (0.56 g, 8.1 mmol) and the selenolsulfonate (1.2 g, 4 mmol) in 12 mL of carbon tetrachloride was irradiated at 2537 Å for 1.5 h. Removal of solvent gave a yellow oil which was taken up in 20 mL of dichloromethane and treated at 0 °C with hydrogen peroxide (5 mL, 15%). Stirring was continued for 30 min at 0 °C and for 30 min at room temperature. The usual workup followed by filtration through 30 g of silica gel (elution with 10% ethyl acetate–petroleum ether) gave 0.63 g (75%) of **59b** (mp 62–63

°C) which was identical with the sulfone described by Böll.[33]

4-Oxo-3-methyl-1-(phenylsulfonyl)-*cis*-bicyclo[4.3.0]non-2-ene (60a). Vinyl sulfone **59a** (0.48 g, 2.3 mmol) was stirred with diene **31** (0.88 g, 2.3 mmol) in 10 mL of refluxing xylene for 65 h, cooled to 20 °C, and hydrolyzed by stirring for 5 h with 5 mL of 1% hydrochloric acid and 5 mL of tetrahydrofuran. Extraction into ether and a workup as described previously afforded a light yellow oil which was chromatographed by MPLC on silica gel (20% ethyl acetate–petroleum ether) to give unreacted starting material (0.12 g, 25%) and enone **60a**: 0.30 g (44%); mp 109–110 °C. Recrystallization of **60a** from 25% ethyl acetate in petroleum ether gave an analytical sample: IR (KBr) 3060, 2960, 2930, 2860, 1675, 1580, 1440, 1365, 1295, 1145, 1115, 1075, 955, 925, 900, 760, 720, 685, 595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95–7.3 (m, 5 H), 6.3 (br s, 1 H), 3.0 (m, 1 H), 2.7 (m, 1 H), 2.25 (d, J = 4 Hz, 2 H), 2.1–1.3 (multiplet including a methyl singlet at 1.85, total 8 H); MS, m/e (M^+) calcd 290.0976, obsd 290.0983. Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.24; H, 6.28.

1-(Phenylsulfonyl)-3-methyl-4-oxo-8-oxa-*cis*-bicyclo[4.3.0]non-2-ene (60b). A solution of **59b** (0.2 g, 0.95 mmol) and diene **31** (0.30 g, 1.6 mmol) in 10 mL of xylene was refluxed under nitrogen for 48 h. Hydrolysis with 5 mL of 1% hydrochloric acid and 5 mL of tetrahydrofuran at room temperature for 5 h followed by a standard workup gave the enone as a brown solid. Filtration through silica gel and recrystallization from 30% ethyl acetate in petroleum ether gave 0.19 g (69%) of **60b** as colorless needles: mp 164–165 °C; IR (KBr) 3060, 2920, 2870, 1675, 1640, 1580, 1475, 1370, 1300, 1150, 1140, 1060, 970, 915, 820, 750, 710, 680, 590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8 (dd, J = 7, 1 Hz, 2 H), 7.7–7.4 (m, 3 H), 6.4 (br s, 1 H), 4.65 (d, J = 9 Hz, 1 H), 4.2 (t, J = 3 Hz, 1 H), 3.85 (d, J = 9 Hz, 1 H), 3.6–3.3 (m, 2 H), 2.25 (m, 2 H), 1.90 (d, J = 1 Hz, 3 H); MS, small M^+ m/e 292, base peak 151 (M^+ – 141). Anal. Calcd for $C_{15}H_{16}O_4S$: C, 61.63; H, 5.52. Found: C, 61.58; H, 5.52.

3-Methylbicyclo[4.3.0]non-1-en-4-one (61a). A solution of **60a** (0.50 g, 1.7 mmol) in 10 mL of glacial acetic acid was stirred magnetically for 5 h with 1.0 g (15 mmol) of zinc dust. The solution was filtered and the solid washed with 50 mL of ether. The organic phase was neutralized with saturated sodium bicarbonate solution, washed with brine, dried, and concentrated to yield a yellow oil. Elution through silica gel (5% ethyl acetate–petroleum) gave pure **61a**: 0.21 g (80%); oil; IR (neat) 2920, 2860, 1710, 1440, 1295, 1145, 1070, 840, 750, 705, 680; ^1H NMR ($CDCl_3$) δ 5.5 (m, 1 H), 3.2–1.2 (series of m, 10 H), 1.2 (2 d, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 150.1044, obsd 150.1040.

3-Methyl-8-oxabicylo[4.3.0]non-1-en-4-one (61b). A solution of **60b** (0.58 g, 2.0 mmol) in 10 mL of glacial acetic acid was treated with 1.2 g (18 mmol) of zinc dust at ambient temperature. After 5 h, the solution was filtered and processed as described previously to deliver after MPLC chromatography on silica gel (15% ethyl acetate–petroleum) 0.25 g (83%) of enone **61b** as an oil: IR (neat) 2960, 2840, 1710, 1445, 1135, 1030, 905, 830, 790, 715, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.6–5.4 (m, 1 H), 4.4–4.0 (m, 3 H), 3.4–3.2 (m, 1 H), 3.2–1.8 (series of m, 4 H), 1.2–1.0 (2 d, J = 7 Hz, 3 H); MS, m/e (M^+) calcd 152.0836, obsd 152.0842.

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Registry No. **7**, 81841-89-6; **10**, 59414-23-2; **11a**, 81841-91-0; **11b**, 81841-92-1; **11c**, 81841-93-2; **11d**, 81841-94-3; **11e**, 81841-95-4; **11f**, 81841-96-5; **11g**, 81841-97-6; **11h**, 87640-73-1; **11i**, 81841-99-8; **12a**, 81842-30-0; **12b**, 81842-31-1; **12c**, 81842-32-2; **12d**, 81842-33-3; **12e**, 81842-34-4; **12f**, 81842-35-5; (*R**,*S**)-**12g**, 87640-74-2; (*R**,*R**)-**12g**, 87640-93-5; **12h**, 87640-75-3; **12i**, 81842-38-8; Δ^2-**13a**, 81842-08-2; Δ^3-**13a**, 33082-72-3; Δ^2-**13b**, 81842-09-3; Δ^3-**13b**, 81842-00-4; Δ^2-**13c**, 81842-10-6; Δ^3-**13c**, 81842-01-5; Δ^2-**13d**, 81842-11-7; Δ^3-**13d**, 81842-02-6; Δ^2-**13e**, 81851-45-8; Δ^3-**13e**, 81842-03-7; Δ^2-**13f**, 81842-12-8; Δ^3-**13f**, 81842-04-8; Δ^2-**13g**, 81842-13-9; Δ^3-**13g**, 81842-05-9; Δ^2-**13h**, 87640-26-4; Δ^3-**13h**, 87640-77-5; Δ^2-**13i**, 81842-15-1; Δ^3-**13i**, 81842-07-1; **14a**, 5515-76-4; **14b**, 4166-61-4; **14c**, 10071-61-1; **14d**, 81842-24-2; **14e**, 81842-25-3; **14f**, 81842-26-4; **14g**, 81842-27-5; **14h**, 87640-78-6; **14i**, 81842-29-7; **15a**, 5259-65-4; **15b**, 81842-16-2; **15c**, 81842-17-3; **15d**, 81842-18-4; **15e**, 81842-19-5; **15f**, 81842-20-8; **15g**, 81842-21-9; **15h**, 87640-79-7; **15i**, 81842-23-1; **16**, 81842-41-3; **17**, 81842-42-4; **18**, 81842-43-5; **19a**, 81842-44-6; **19b**, 81842-46-8; **19b** (dihydro), 81842-47-9; **20a**, 81842-45-7; **21**, 81873-86-1; **24** (isomer 1), 72346-46-4; **24** (isomer 2), 87680-38-4; **25**, 4582-61-0; (*R**,*R**)-**26**, 87640-80-0; (*R**,*S**)-**26**, 87640-81-1; Δ^2-**26** desulfonyl derivative, 87640-90-2; Δ^3-**26** desulfonyl derivative, 87640-91-3; Δ^2-**26** desulfonyl ketone, 1723-80-4; **27**, 87655-19-4; **28** (isomer 1), 72346-47-5; **28** (isomer 2), 87680-39-5; **29b**, 1746-13-0; **29c**, 754-05-2; **29d**, 6044-68-4; **30a**, 68969-25-5; **30b**, 77825-83-3; **30c**, 64489-06-1; **30d**, 84065-67-8; **31**, 72476-03-0; Δ^2-**32a**, 87640-82-2; Δ^2-**32b**, 84065-62-3; Δ^3-**32b**, 84065-63-4; Δ^2-**32d**, 87640-83-3; **33a**, 84065-66-7; **33b**, 84065-64-5; **33d**, 84065-70-3; **34d**, 84065-69-0; **35**, 84107-60-8; **36**, 84065-71-4; **37**, 84107-61-9; **38**, 84065-72-5; **39** (isomer 1), 87680-34-0; **39** (isomer 2), 87680-40-8; **40**, 763-13-3; **41**, 87640-84-4; Δ^2-**42**, 87640-85-5; Δ^3-**42**, 85807-89-2; **43**, 85807-84-7; **43**-01, 821-41-0; **44**, 87640-86-6; Δ^3-**45**, 85807-90-5; **46**, 74472-22-3; **47**, 87640-92-4; Δ^2-**48**, 87640-87-7; Δ^3-**48**, 85807-91-6; **49**, 85807-92-7; **50**, 85807-97-2; **51**, 85807-98-3; **52**, 85808-03-3; **53a**, 85807-93-8; **53b**, 87640-88-8; **53c**, 85807-95-0; **53d**, 85807-96-1; **55a**, 85808-04-4; **55b**, 87680-35-1; **56a**, 87640-89-9; **56b**, 85808-02-2; **57a**, 87680-36-2; **57b**, 85808-07-7; **58a**, 87680-37-3; **58b**, 85808-09-9; **59a**, 64740-90-5; **59b**, 41649-12-1; **60a**, 84065-59-8; **60b**, 84065-58-7; **61a**, 84065-61-2; **61b**, 84065-60-1; CH_2=$CHSO_2Ph$, 5535-48-8; CH_2=$CHCH_2Br$, 106-95-6; $(CH_3)_2C$=$CHCH_2Br$, 870-63-3; $PhCH_2Br$, 100-39-0; $Br(CH_2)_3CH(CH_3)C_6H_4$-*p*-CH_3, 19872-53-8; $Br(CH_2)_3SPh$, 3238-98-0; $I(CH_2)_4COOEt$, 41302-32-3; $PhSeSO_2Ph$, 60805-71-2; *t*-$BuMe_2SiCl$, 18162-48-6; (*E*)-ICH_2CH=$C(CH_3SiMe_3$, 52685-51-5; $Br(CH_2)_2OCH_2Ph$, 1462-37-9; 2-(iodomethyl)tetrahydrofuran, 5831-70-9; geranyl bromide, 6138-90-5; 1-bromo-3,3-(ethylenedioxy)butane, 37865-96-6; cyclopentene, 142-29-0; 2,5-dihydrofuran, 1708-29-8.