α-Haloalkanesulfonyl Bromides in Organic Synthesis. 5. Versatile Reagents for the Synthesis of Conjugated Polyenes, Enones, and 1,3-Oxathiole 1,1-Dioxides

Eric Block,*† Mohammad Aslam, Venkatachalam Eswarakrishnan, Kassu Gebreyes, John Hutchinson, Rajeshwari Iyer, Jean-Alex Laffitte, and Alan Wall

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222. *Received May 6, 1985. Revised Manuscript Received March 13, 1986*

Abstract: α-Haloalkanesulfonyl bromides including chloromethanesulfonyl bromide (**1**), bromomethanesulfonyl bromide (**2**), α-bromoethanesulfonyl bromide (**3**), and iodomethanesulfonyl bromide (**4**) undergo free radical addition to olefins giving adducts which upon treatment with base afford dienes by a process termed the vinylogous Ramberg–Bäcklund reaction. In appropriate cases regioselectivity and/or stereoselectivity is observed in both the first addition step and in subsequent base-promoted elimination steps. Using this two- or three-step procedure, 1-alkenes are converted into 1,3-alkadienes, 2-methyl-1-alkenes into 2-alkyl-1,3-butadienes, methylenecycloalkanes into 1-vinyl-1-cycloalkenes, cycloalkenes into 3-methylene-1-cycloalkenes, and 1-methylcycloalkenes into 1,2-dimethylenecycloalkanes among other examples. Reagents **1–4** can also be used to convert trimethylsilyl enol ethers into α-alkylidene ketones and 1,3-oxathiole 3,3-dioxides, 1,3-dienes into 1,3,5-trienes, and alkynes into enynes.

Base-induced conversion of α-haloalkyl sulfones into olefins (eq 1), known as the Ramberg–Bäcklund reaction, represents a synthetically useful method for introducing unsaturation into a variety of organic compounds.[1] Unfortunately, because the preparation of α-haloalkyl sulfones entails multistep procedures, e.g., preparation of sulfides followed by α-halogenation and oxidation or by oxidation and then α-halogenation, applications of the Ramberg–Bäcklund reaction have generally been limited. We have discovered a new series of readily prepared reagents, α-haloalkanesulfonyl bromides, $RCHXSO_2Br$, which package all the components required for the Ramberg–Bäcklund reaction into one reactive unit, requiring only an olefinic substrate and base and offering a convenient stereo- and regioselective approach to the synthesis of dienes and higher conjugated polyenes and enones, among other products. We describe below full details on the scope and mechanisms of our procedures.[2]

$$RCH_2SO_2CH_2X \xrightarrow{\text{base}} \underset{\underset{RCHSO_2CH_2}{\smile}}{RCHSO_2CH_2X} \xrightarrow{-X^-} RCH{=}CH_2 + SO_2 \quad (1)$$

Synthesis of α-Haloalkanesulfonyl Bromides

Our hope was to design α-haloalkanesulfonyl reagents which would readily afford adducts with unsaturated compounds which in turn could undergo Ramberg–Bäcklund-type reactions. Since it was known that chloromethanesulfonyl chloride, $ClCH_2SO_2Cl$, fails to add to unactivated olefins even in the presence of Cu(I)[3a] and bromomethanesulfonyl chloride, $BrCH_2SO_2Cl$, shows only 10% addition to 1-octene after irradiation for 1 h[3b] but that chloromethanesulfonyl bromide, $ClCH_2SO_2Br$ (**1**) with *tert*-butyl hydroperoxide–zinc dichloride catalysis, does add to olefins,[4] our attention was directed toward α-haloalkanesulfonyl bromides. An early report[5] describes the preparation of bromomethanesulfonyl bromide ($BrCH_2SO_2Br$, **2**) and α-bromoethanesulfonyl bromide (**3**) in low yields by bromination of 1,3,5-trithiane and 2,4,6-trimethyl-1,3,5-trithiane, respectively. We have found that **2** can be conveniently prepared in molar quantities in 42–48% yield by addition of 9.5 mol of bromine per mol of 1,3,5-trithiane to an aqueous suspension of the latter compound at 40 °C (eq 2). Compound **2** is a slightly yellow, distillable (bp 68 °C (0.01 mm)), stable oil. While compound **3** could be prepared in a manner similar to that used for **2**, but in lower yield, from 2,4,6-trimethyl-1,3,5-trithiane, a more efficient synthesis (66% overall yield) was developed involving treatment of α-bromoethanesulfonyl chloride[6] with aqueous sodium sulfite followed by bromine (eq 3). Two other reagents required in this study, chloro- and iodomethanesulfonyl bromides (**1**[4] and **4**, respectively), were synthesized as described in eq 4 and 5.

$$\underset{\underset{CH_2SCH_2SCH_2S}{\smile}}{CH_2SCH_2SCH_2S} \xrightarrow{9.5Br_2,\ H_2O} \underset{\mathbf{2}}{3\ BrCH_2SO_2Br} \quad (2)$$

$$CH_3CHBrSO_2Cl \xrightarrow{Na_2SO_3\text{–}H_2O,\ 0\ ^\circ C;\ Br_2} \underset{\mathbf{3}}{CH_3CHBrSO_2Br} \quad (3)$$

$$ClCH_2SO_2Cl \xrightarrow{Na_2SO_3\text{–}H_2O,\ 0\ ^\circ C;\ Br_2} \underset{\mathbf{1}}{ClCH_2SO_2Br} \quad (4)$$

$$CH_2I_2 \xrightarrow{Na_2SO_3\text{–}H_2O,\ \text{heat}} ICH_2SO_3Na \xrightarrow{PBr_5} \underset{\mathbf{4}}{ICH_2SO_2Br} + POBr_3 \quad (5)$$

Addition of α-Haloalkanesulfonyl Bromides to Olefins

Compound **2** was found to undergo a spontaneous, occasionally vigorously exothermic reaction upon mixing with olefins affording methylene dibromide and sulfur dioxide along with the olefin–**2** adducts. In those cases in which the thermally induced reaction was slow to start, a free-radical initiator proved useful. However in order to better control the addition and minimize the undesired side reaction producing methylene bromide and sulfur dioxide,

† Fellow of the John Simon Guggenheim Foundation, 1984–1985.

(1) Reviews: (a) Bordwell, F. G. In *Organosulfur Chemistry*; Janssen, M. J., Ed.; Interscience: New York, 1967; Chapter 16. (b) Paquette, L. A. *Org. React. (N. Y.)* **1977**, *25*, 1–71. (c) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; p 77.

(2) (a) The material covered in this paper is the subject of U.S. Patent Application No. 523276, filed by the Research Foundation of the State University of New York. (b) Preliminary communications. Part 1: Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1983**, *105*, 6164–6165. Part 2: Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *J. Am. Chem. Soc.* **1983**, *105*, 6165–6167. Part 3: Block, E.; Aslam, M.; Iyer, R.; Hutchinson, J. *J. Org. Chem.* **1984**, *49*, 3664–3666. Part 4: Block, E.; Eswarakrishnan, V.; Gebreyes, K. *Tetrahedron Lett.* **1984**, *25*, 5469–5472. Also see: Block, E.; Aslam, M. *Organic Syntheses*; Wiley: New York, in press.

(3) (a) Goldwhite, H.; Gibson, M. S.; Harris, C. *Tetrahedron* **1964**, *20*, 1613–1624. (b) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962–4971.

(4) Boll, W. *Liebigs Ann. Chem.* **1979**, 1665–1674.

(5) Kostova, A. G. *Tr. Voronezh. Gos. Univ.* **1935**, *88* 92–117; *Chem. Abstr.* **1938**, *32*, 6618.

(6) Carpino, L. A.; McAdams, L. V., III; Rynbrandt, R. H.; Spiewak, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 476–484.

0002-7863/86/1508-4568$01.50/0

it was preferable to dilute the olefin with an equal volume of methylene chloride, chill the solution to −20 °C, mix this with an equivalent amount of **2** in cold methylene chloride, and irradiate the mixture in a Pyrex tube at −20 °C for 30 min. In most cases this procedure gave olefin–**2** adducts in quantitative yields.

With mono-, 1,1-di-, and 1,1,2-trisubstituted olefins the addition is regiospecific, with attachment of bromine to the more substituted carbon, as illustrated by formation of products **5**, **6**, and **7**, from

$$C_6H_{13}CHBrCH_2SO_2CH_2Br$$
5

$$C_6H_{13}C(CH_3)BrCH_2SO_2CH_2Br$$
6

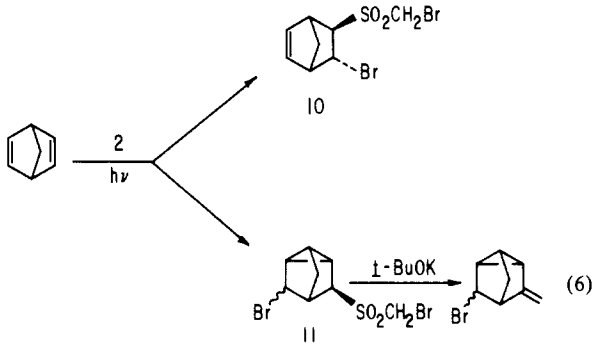
$$(CH_3)_2CBrCH(CH_3)SO_2CH_2Br$$
7

$$(CH_3)_2C{=}CHCH_2CH_2C(CH_3)BrCH_2SO_2CH_2Br$$
8

$$C_5H_{11}CH(Br)CH(CH_3)SO_2CH_2Br$$
9

1-octene, 2-methyl-1-octene, and 2-methyl-2-butene, respectively. In the case of molecules possessing both 1,1-di- and 1,1,2-trisubstituted double bonds, addition occurs exclusively to the less hindered 1,1-disubstituted double bond, as indicated by the formation of **8** from 2,6-dimethyl-1,5-heptadiene. Even unsymmetrical 1,2-disubstituted olefins show a high degree of regioselectivity in the addition, e.g., as seen by the formation of **9** as the major product (79%) from addition of **2** to 2-octene.

Single or double addition of **2** to *diolefins* can be achieved depending on the stoichiometry used. If 2 equiv of **2** are used per mol of diolefin, good yields of bis-adducts are obtained. If 1 equiv of **2** is used, or in some cases excess diolefin, addition of a single equivalent of **2** occurs. In the case of 1,5-cyclooctadiene, no products resulting from intramolecular rearrangement could be detected when **2** was added to an excess of the diene. On the other hand when **2** was reacted with excess nonbornadiene a 1:1 mixture of *endo*-6-bromo-*exo*-5-norbornen-2-yl bromomethyl sulfone (**10**) and 5-bromo-3-nortricyclyl bromomethyl sulfone (exo/endo mixture) (**11**) was isolated in 96% yield (eq 6).



(6)

The above data are consistent with the involvement of a free radical chain reaction detailed in Scheme I, analogous to free radical addition of other sulfonyl halides.[7] The superiority of sulfonyl bromide **2** compared to analogous sulfonyl chlorides is due to the weaker, more light-sensitive S–Br bond; it is also fortunate that the activation energy for the desulfonylation step (Scheme I, step d) is greater than that for the olefin-addition step (Scheme I, step b) so that desulfonylation is noncompetitive at −20 °C. The alkyl substituents in α-haloalkanesulfonyl bromides have little effect on the efficiency of olefin addition; chloro compound **1**, α-bromoethyl compound **3**, and iodo compound **4** all give excellent yields of olefin adducts. On the basis of previous studies of radical addition of benzenesulfonyl halides to norbornadiene,[7] the 1:1 ratio of **10**/**11** suggests that **2** is a more efficient radical chain transfer agent than benzenesulfonyl bromide.

Scheme I

$$BrCH_2SO_2Br \xrightarrow{h\nu} BrCH_2SO_2^{\bullet} + Br^{\bullet} \quad (a)$$

$$BrCH_2SO_2^{\bullet} + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2SO_2CH_2Br \quad (b)$$

$$R\dot{C}HCH_2SO_2CH_2Br + BrCH_2SO_2Br \rightarrow RCHBrCH_2SO_2CH_2Br + BrCH_2SO_2^{\bullet} \quad (c)$$

$$BrCH_2SO_2^{\bullet} \rightarrow BrCH_2^{\bullet} + SO_2 \quad (d)$$

$$BrCH_2^{\bullet} + BrCH_2SO_2Br \rightarrow CH_2Br_2 + BrCH_2SO_2^{\bullet} \quad (e)$$

We find that reagent **2** adds smoothly to the double bonds in unsaturated alcohols without prior protection of the OH group; an application of this reaction in a short synthesis of the sex pheromone of the red bollworm moth is given below. Reagent **2** also adds smoothly to allyltrimethylsilane and diallyldimethylsilane without complications due to elimination of the silyl group, as is observed with use of methanesulfonyl chloride/cuprous bromide (eq 7).[8] On the other hand, loss of the trimethylstannyl

$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{MeSO_2Cl_2,\ Cu_2Br_2} Me_3SiCl + CH_2{=}CHCH_2SO_2Me \quad (7)$$

group is observed on reaction of **2** with allyl trimethylstannane (eq 8).

$$Me_3SnCH_2CH{=}CH_2 \xrightarrow{2,\ h\nu} Me_3SnBr + CH_2{=}CHCH_2SO_2CH_2Br \quad (8)$$

Base Treatment of the α-Haloalkanesulfonyl Bromide–Olefin Adducts: The Vinylogous Ramberg–Bäcklund Reaction

Addition of **2** to olefins and subsequent reaction of the adducts with base is illustrated with 1-octene. Thus, 1-octene, diluted with an equal volume of methylene chloride and irradiated in a Pyrex tube for 30 min at −20 °C after addition of an equivalent amount of **2**, afforded a single 1:1 olefin–**2** adduct in 94% yield. Direct treatment of this crude adduct with triethylamine in methylene chloride at 0 °C for 15 min gave in 97% yield a 10:1 mixture of (*E*)- and (*Z*)-bromomethyl 1-octenyl sulfones (**12E** and **12Z**) (R = n-C_5H_{11}), respectively. The use of 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) at −23 °C in place of triethylamine gave a mixture containing >97% **12E**. Crystallization readily afforded a pure sample of **12E** while isomer **12Z** could be isolated from the mother liquor by preparative HPLC. Treatment of **12E** with 2.5 equiv of potassium *tert*-butoxide in 7:3 *t*-BuOH/THF at −20 °C for 1 h gave in 59% distilled yield a 83:17 mixture of (*Z*)- and (*E*)-1,3-nonadiene.[11a] In a similar manner **12Z** gave in 61% yield a 6:94 mixture of (*Z*)- and (*E*)-1,3-nonadiene. When lithium or cesium *tert*-butoxide was substituted for potassium *tert*-butoxide in the reaction with **12E**, the (*Z*)- to (*E*)-1,3-nonadiene ratio was 85:15 and 75:25, respectively, indicating only a minor change in stereoselectivity with metal ion.

The stereoselectivity of the reaction of **12E** with base, which may be termed a "vinylogous Ramberg–Bäcklund reaction", can be attributed to a stabilizing, attractive interaction between the developing negative charge at the α-position and the CH_2 group at the δ-position (a "syn effect"[9]) favoring transition state **12E′**

(7) Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727–1732. Cristol, S. J.; Davies, D. I. *J. Org. Chem.* **1963**, *28*, 372–379.

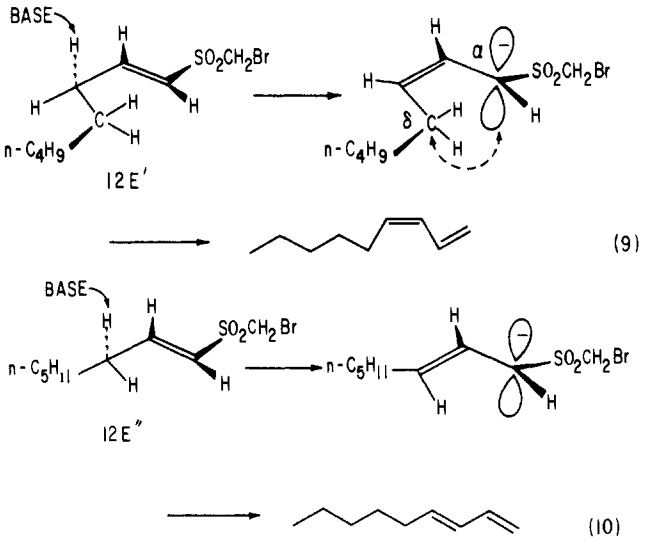
(8) Pillot, J. P.; Dunogues, J.; Calas, R. *Synthesis* **1977**, 469.

(9) (a) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199–7205. (b) Block, E.; Penn, R. E.; Bazzi, A. A.; Cremer, D. *Tetrahedron Lett.* **1981**, *22*, 29–32. (c) Houk, K. N.; Strozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chuaqui-Offermanns, N. *J. Am. Chem. Soc.* **1980**, *102*, 1426–1429 and references therein.

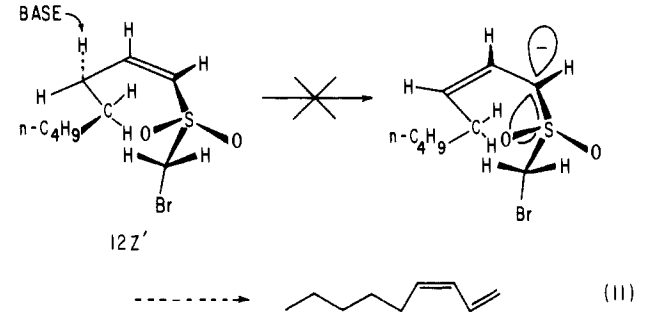
(10) Naf, F.; Decorzant, R.; Escher, S. D. *Tetrahedron Lett.* **1982**, *23*, 5043–5046.

(11) (a) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1982**, *23*, 3277–3280. (b) Babler, J. H.; Invergo, B. J. *J. Org. Chem.* **1979**, *44*, 3723–3724. (c) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 464–469. (d) Hayashi, T.; Yanagida, M.; Matsuda, Y.; Oishi, T. *Tetrahedron Lett.* **1983**, *24*, 2665–2668. (e) Yamamoto, Y.; Saito, Y.; Maruyama, K. *Tetrahedron Lett.* **1982**, *23*, 4597–4600 and refeences therein.

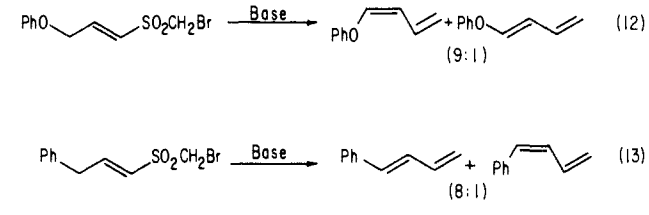
over **12E″** for deprotonation (eq 9 and 10). In a related example,



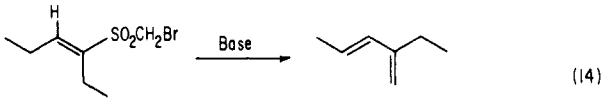
it has been reported that lithium dibutyl cuprate adds to (*E*)-1,3-butadienyl *p*-tolyl sulfone giving exclusively (*Z*)-2-octenyl *p*-tolyl sulfone.[10] In the case of **12Z** the possibility of a stabilizing syn interaction between the α- and δ-position is precluded for steric reasons (note the steric congestion in transition state **12Z′** leading to (*E*)-1,3-nonadiene (eq 11)). The syn effect is still seen with



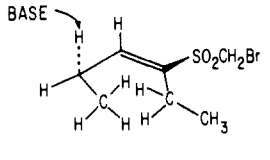
replacement of the δ-CH_2 in **12E** by oxygen but not by a phenyl group (eq 12 and 13). On the other hand, replacement of the



α-hydrogen in (*E*)-1-alkenyl bromomethyl sulfones by an alkyl group (see eq 14) results in *exclusive* formation of the *E* diene



upon treatment with base; syn interaction is sterically precluded in this case (see **13**). Table I illustrates the application of the



13

vinylogous Ramberg–Bäcklund reaction to the synthesis of terminal, branched internal, and heterosubstituted acyclic 1,3-dienes and bis 1,3-dienes, as well as 1-vinyl and 3-methylene 1-cycloalkenes and 1,2-dimethylenecycloalkanes. Among the examples is a simple synthesis from 10-undecenol of the acetate of (*E*,*Z*)-9,11-dodecadien-1-ol (entry 24), the sex pheromone of the red bollworm moth, *Diparopsis castanea*. While a number of other synthesis of this pheromone have been reported[11] our approach is particularly attractive because of its simplicity and high yield, the low cost of reagents, and its use of commerically available starting material. Also noteworthy is the conversion of allyltrimethylsilane and diallyldimethylsilane into 1-(trimethylsilyl)-1,3-butadiene[11f,g] and bis(1,3-butadienyl)dimethylsilane (entries 25 and 31), making these dienes readily available. Another application of our synthetic procedure is the attachment of methylene groups to interior carbon atoms in chains (e.g., entries 11, 12) or to ring carbon atoms (entries 17–19) providing access to compounds that would be otherwise difficult to prepare.

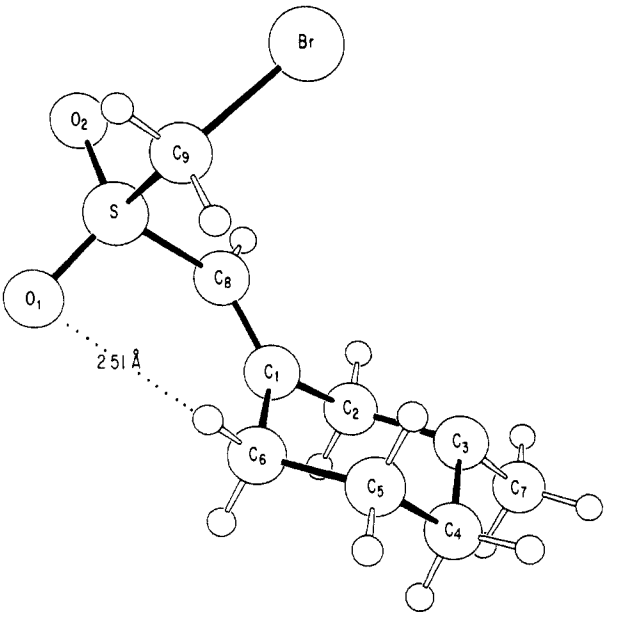
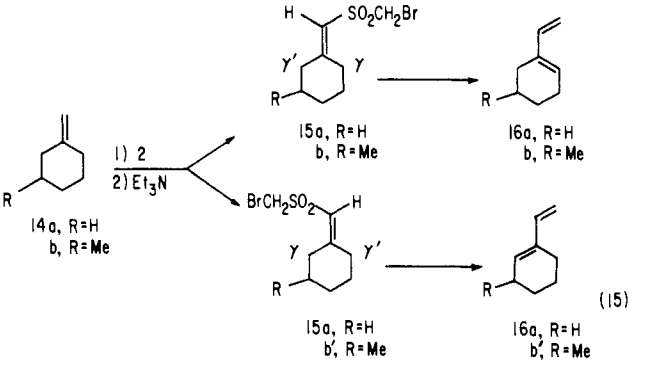


Figure 1. Perspective view of (*E*)-1-[[(bromomethyl)sulfonyl]-methylene]-3-methylcyclohexane showing the atom-labeling scheme. Relevant bond distances: C1–C8, 1.32 (1) Å; Br–C9, 1.891 (8) Å; S–C9, 1.784 (10) Å; O1···H2B, 2.51 Å (nonbonded closest O–H distance); for other data see supplementary material.

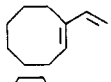
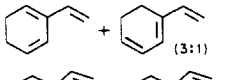
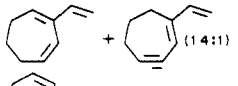
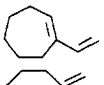
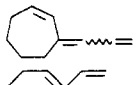
α,β-Unsaturated bromomethyl sulfones such as **15a** (eq 15)



could undergo vinylogous Ramberg–Bäcklund reaction by deprotonation syn (γ) and/or anti (γ′) to the sulfonyl group. In unsymmetrical systems this could give mixtures of products. Addition of **2** to 3-methyl-1-methylenecyclohexane (**14b**; prepared from the corresponding ketone with CH_2Br_2–$TiCl_4$–Zn[12] as described in the Experimental Section) followed by dehydrobromination with triethylamine gave a 1:1 mixture of **15b** and **15b′** in 94% overall yield. Fractional recrystallization of the mixture from CCl_4 afforded **15b**, mp 79–80 °C, homogeneous by capillary GC and HPLC. The structure of **15b** was established by X-ray crystallography, as shown in Figure 1 (see supplementary ma-

(12) Lombardo, L. *Tetrahedron Lett.* **1982**, *23*, 4293–4296.

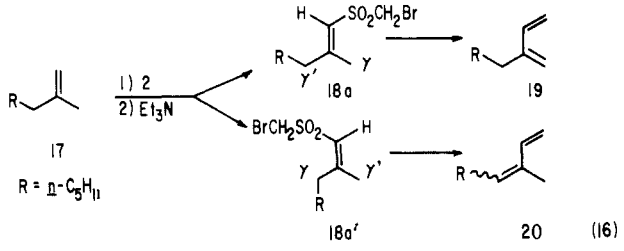
Table I. Diene, Polyene, and Enyne Synthesis with Bromomethanesulfonyl Bromide

entry	substrate	product (*Z*:*E* ratio)	yield, %[a,u]
1	*n*-$C_4H_9CH{=}CH_2$	*n*-$C_3H_7CH{=}CHCH{=}CH_2$ (2:1)	38 (52[43])
2	*n*-$C_6H_{13}CH{=}CH_2$	*n*-$C_5H_{11}CH{=}CHCH{=}CH_2$ (2:1)	61 (27[11a])
3	*n*-$C_7H_{15}CH{=}CH_2$	*n*-$C_6H_{13}CH{=}CHCH{=}CH_2$ (2:1)	52 (81[44])
4	*n*-$C_5H_{11}C(CH_3){=}CH_2$	$CH_2{=}CHC(=CH_2)C_5H_{11}$-*n*	79[b] (28[55])
5	*n*-$C_6H_{13}C(CH_3){=}CH_2$	$CH_2{=}CHC(=CH_2)C_6H_{13}$-*n*	73[c] (49[40])
6	$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CH_2$	$CH_2{=}CHC(=CH_2)CH_2CH_2CH{=}C(CH_3)_2$	65[d] (10[56])
7	$(CH_3)_2CHCH_2CH_2C(CH_3){=}CH_2$	$CH_2{=}CHC(=CH_2)CH_2CH_2CH(CH_3)_2$	63[e]
8	*n*-$C_9H_{19}C(CH_3){=}CH_2$	$CH_2{=}CHC(=CH_2)C_9H_{19}$-*n*	59[f] (48[45])
9	*c*-$C_6H_{11}C(CH_3){=}CH_2$	$CH_2{=}CHC(=CH_2)C_6H_{11}$-*c*	62 (5[46])
10	(*E*)-$C_2H_5CH{=}CHC_2H_5$	(*E*)-$CH_3CH{=}CHC(=CH_2)C_2H_5$	58[g] (30[47])
11	(*E*)-*n*-$C_4H_9CH{=}CH$-*n*-C_4H_9	(*E*)-*n*-$C_3H_7CH{=}CHC(=CH_2)C_4H_9$-*n*	68[g]
12	(*E*)-*n*-$C_6H_{13}CH{=}CH$-*n*-C_6H_{13}	(*E*)-*n*-$C_5H_{11}CH{=}CHC(=CH_2)C_6H_{13}$-*n*	71[g]
13	(*E*)-*n*-$C_5H_{11}CH{=}CHCH_3$	(*E*)-*n*-$C_4H_9CH{=}CHC(CH_3){=}CH_2$ + $CH_2{=}CHC(=CH_2)C_5H_{11}$-*n*	52 (16[48]) 15 (28[55])
14			53 (100[49])
15			74 (–[50])
16			75
17			41[h] (19[41])
18			31[h] (13[41])
19			49[h] (28[41])
20			51[h] (58[39])
21			43 (30[51])
22	$PhCH_2CH{=}CH_2$	$PhCH{=}CHCH{=}CH_2$ (1:8)	85 (51[52])
23	$PhOCH_2CH{=}CH_2$	$PhOCH{=}CHCH{=}CH_2$ (9:1)	54 (34[42])
24	$HO(CH_2)_9CH{=}CH_2$	$HO(CH_2)_8CH{=}CHCH{=}CH_2$ (5:1)	86 (54[11])
25	$(CH_3)_3SiCH_2CH{=}CH_2$	$(CH_3)_3SiCH{=}CHCH{=}CH_2$ (1:10)	41 (37[53])
26			35[h,j]
27	$CH_2{=}CH(CH_2)_6CH{=}CH_2$	$CH_2{=}CH(CH_2)_5CH{=}CHCH{=}CH_2$	49[i,j,k]
28	$CH_2{=}CH(CH_2)_4CH{=}CH_2$	$CH_2{=}CHCH{=}CH(CH_2)_2CH{=}CHCH{=}CH_2$	57[i,l] (50[54])
29	$CH_2{=}CH(CH_2)_6CH{=}CH_2$	$CH_2{=}CHCH{=}CH(CH_2)_4CH{=}CHCH{=}CH_2$	40[l,m] (14[54])
30	$CH_2{=}CH(CH_2)_{10}CH{=}CH_2$	$CH_2{=}CHCH{=}CH(CH_2)_8CH{=}CHCH{=}CH_2$	41[l]
31	$(CH_3)_2Si(CH_2CH{=}CH_2)_2$	$(CH_3)_2Si(CH{=}CHCH{=}CH_2)_2$	38[i,l]
32	$CH_3CH{=}CHCH{=}CH_2$	$CH_2{=}CHCH{=}CHCH{=}CH_2$	22[n] (28[23])
33	*n*-$C_3H_7CH{=}CHCH{=}CH_2$	$C_2H_5CH{=}CHCH{=}CHCH{=}CH_2$ (1.7:1 *EZ*/*EE*)	16[o] (22[25])
34	*n*-$C_6H_{13}CH{=}CHCH{=}CH_2$	$C_5H_{11}CH{=}CHCH{=}CHCH{=}CH_2$ (1.1:1 *EZ*/*EE*)	24[p] (47[24])
35	$CH_2{=}CHCH_2CH_2CH{=}CH_2$	$CH_3CH{=}CHCH{=}CHCH{=}CH_2$ (*E*,*E*)	21 (39[57])
36	(*E*)-$CH_3CH{=}CHC(C_2H_5){=}CH_2$	$CH_2{=}CHCH{=}C(C_2H_5)CH{=}CH_2$ + $CH_3CH{=}CHC(CH{=}CH_2){=}CHCH_3$	33[q] 17[q]
37		 (3:1)	47 (61[28])
38		 (14:1)	50
39			10[q]
40			53
41	$CH_2{=}CHCH_2CH_2CH{=}CH_2$[f]	$CH_2{=}CH(CH{=}CH)_2CH{=}CH_2$	8[s] (52[29b,c])
42	$CH_2{=}CHCH_2CH{=}CH_2$[r]	$CH_2{=}CH(CH{=}CH)_3CH_3$	8[t] (60[58])
43	$CH_2{=}CHCH_2CH_2CH_2CH{=}CH_2$[f]	$CH_2{=}CH(CH{=}CH)_3CH_3$	23 (60[58])
44	$CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CH_2$[f]	$CH_2{=}CH(CH{=}CH)_3CH{=}CH_2$	14[t] (9[29a])
45	$CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CHCH{=}CH_2$[f]	$CH_2{=}CH(CH{=}CH)_4CH{=}CH_2$	23[t] (1[29a])
46	$C_2H_5C{\equiv}CC_2H_5$	$C_2H_5C{\equiv}CC(C_2H_5){=}CH_2$	39
47	$C_5H_{11}C{\equiv}CH$	$C_4H_9C{\equiv}CCH{=}CH_2$	29 (63[59])

[a] Overall yield of distilled product. [b] 9% 3-methyl-1,3-octadiene. [c] 9% 3-methyl-1,3-nonadiene. [d] 11% 3,7-dimethyl-1,3,6-octatriene. [e] 8% 3,6-dimethyl-1,3-heptadiene. [f] 8% 3-methyl-1,3-dodecadiene. [g] GC analysis indicated <1% *Z* isomer. [h] Et_3N step omitted. [i] Isomers not resolved by GC. [j] Two equivalents of diene used. [k] Includes ca. 5% of 1,3,9,11-dodecatetraene. [l] Two equivalents of **2** used. [m] Ca. 80% *Z*,*Z*. [n] <2% *Z* isomer. [o] GC yield 24%. [p] At –26 °C ratio is 1.6:1. [q] Stereochemistry about trisubstituted double bond unknown. [r] $CH_3CHBrSO_2Br$. [s] Also contains ca. 3% yield of 1,3,5-cyclooctatriene. [t] Estimated by UV analysis. [u] For comparison purposes, when product is known overall yield for recent synthesis is given in parenthesis with literature reference as superscript. In many cases the starting materials for the published synthesis are not as readily available as the substrates indicated in the table.

terial). Preparative HPLC of the mother liquor from the above recrystallization afforded **15b'**, chromatographically and spectroscopically different from **15b**. Separate treatment of **15b** with KO-*t*-Bu and **15b'** with LiO-*t*-Bu in *t*-BuOH/THF gave, respectively, 5-methyl-1-vinylcyclohexene (**16b**) (GC retention time 8.02 min at 70 °C; ^{1}H NMR triplet at δ 5.66 due to ring CH_2CH=C) and 3-methyl-1-vinylcyclohexene (**16b'**) (GC retention time 7.90 min at 70 °C; ^{1}H NMR doublet at δ 5.59 due to ring $CH(CH_3)CH$=C), in each case regiospecifically in 77–78% yield. Reaction of **16b'** with LiO-*t*-Bu and excess 12-crown-4 gave a 4:1 mixture of **16b'**/**16b** while KO-*t*-Bu gave a 62:38 mixture of **16b'**/**16b**.

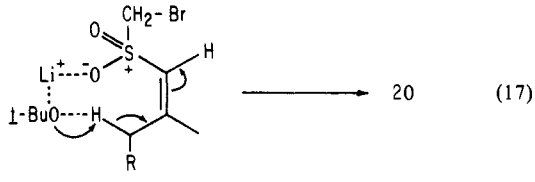
Treatment of 2-methyl-1-octene (**17**, eq 16) with **2** followed



(16)

by triethylamine gave in 87% yield a 2.8:1 mixture of **18a** and **18a'** which could be separated by HPLC. Compounds **18a** and **18a'**, showing ^{1}H NMR methyl resonances at 2.21 and 2.01 ppm, respectively, can be characterized as (*E*)- and (*Z*)-2-methyl-1-octenyl bromomethyl sulfone, respectively, based on the known deshielding of alkyl groups syn to the sulfonyl group in α,β-ethylenic sulfones.[13] Treatment of **18a** with KO-*t*-Bu or LiO-*t*-Bu led regiospecifically to 3-methylenenon-1-ene (**19**) while **18a'** gave mixtures of **19** and (*E*,*Z*)-3-methyl-1,3-nonadiene (**20**), in ratios varying from 7:93 (LiO-*t*-Bu) to 13:87 (LiO-*t*-Am-C_6H_6) to 29:71 (LiO-*t*-Bu, 12-crown-4) to 68:32 (KO-*t*-Bu).

The above observations on the regioselective deprotonation of bromomethyl sulfones **15b,b'** and **18a,a'** can be rationalized as follows: (1) Steric factors should favor deprotonation of compounds **15b,b'** and **18a,a'** with *tert*-alkoxides at the less hindered positions (remote from the R group) giving **16b** and **19**, in accord with earlier studies on enolate generation in analogous systems (treatment of 3-methylcyclohexanone with tritylithium is reported to give an 82:18 ratio of the 3-methyl to 5-methyl enolate[14]). (2) Coordination of the cations of alkali *tert*-butoxides by sulfonyl oxygen should favor deprotonation syn to the sulfonyl group. In particular we suggest that the lithium cation of LiO-*t*-Bu coordinates to the sulfonyl oxygen in **15b'** and **18a'** promoting removal of the γ-proton despite steric hindrance at that position. The X-ray structure of **15b** indicates that the sulfonyl oxygen is within 2.51 Å of the closest ring hydrogen, a value within the sum of the van der Waals radii of O and H, which should facilitate the type of coordination depicted in eq 17. When the extent of coordination



(17)

is diminished by substituting the "softer" (HSAB terminology) potassium for lithium or by complexing lithium with 12-crown-4, the relative proportion of α-deprotonation decreases. Our results are of interest because the sulfone group is not usually thought of as a group capable of metal coordination.[15] Eisch has previously noted without comment the greater kinetic activity of syn vs. anti methyl groups in α,β-ethylenic sulfones, presumably reflecting more favorable lithium coordination in the syn systems.[16] Similar kinetic acidity effects are also seen in α,β-unsaturated esters.[17]

For synthetic purposes, the crude mixture of isomers **18a,a'** may be used to prepare **19**. Thus when a solution of mixed isomers in *t*-BuOH/THF is added to 3 equiv of KO-*t*-Bu in *t*-BuOH/THF at −23 °C and the mixture is worked up, **19** is obtained in 84% yield and 91% purity. Additional examples of syntheses of 2-alkyl-1,3-butadienes by this route are given in Table I. Entry 6 is of interest because it demonstrates the preference of reagent **2** for addition to the terminal rather than internal double bond while entry 9 demonstrates that deprotonation can be regiospecific in particularly hindered cases.

While all of the above procedures employ sequential treatment of the olefin–**2** adducts with triethylamine followed by potassium *tert*-butoxide, it is possible to go directly from the adducts to dienes by using an excess of the latter base, as illustrated by the synthesis of 1,2-dimethylenecyclohexane from 1-methylcyclohexene (see Experimental Section). The advantages of the two-base procedure, when it can be employed, is that it conserves the more expensive *tert*-butoxide base and generally gives higher diene yields.

Reaction of α-Haloalkanesulfonyl Bromides with Trimethylsilyl Enol Ethers: Synthesis of α-Alkylidene Ketones and 1,3-Oxathiole 3,3-Dioxides

It was of interest to determine if reagents **1–4** could be added to olefins substituted with oxygen such as enol acetates, enol ethers, or enol silyl ethers since the initial adducts with these sulfonyl bromides might give α-haloalkylsulfonyl ketones or aldehydes upon hydrolysis (eq 18). While vinyl acetate and 1-cycloheptenyl

$$\mathrm{ROCR'{=}CH_2 + BrCH_2SO_2Br \rightarrow ROCR'BrCH_2SO_2CH_2Br \xrightarrow{H_2O} R'C(O)CH_2SO_2CH_2Br} \quad (18)$$

acetate proved unreactive toward **2**, 1-(trimethylsiloxy)-1-cycloheptene (**21**) reacted readily with **2** affording directly a mixture of 2-[(bromomethyl)sulfonyl]cycloheptanone (**22**) and cycloheptanone. Cycloheptanone presumably arises via hydrolysis of silyl ether **21**; its formation can be prevented by conducting the addition of **2** to **21** in ethylene oxide (an excellent acid scavenger which is unreactive toward free radicals) as solvent. Thus irradiation of a solution of **2** and **21** in ethylene oxide at −15 °C and concentration in vacuo gave directly **22** in 77% isolated yield. We suggest that a free radical chain reaction is involved in the formation of **22** as depicted in Scheme II. It should be noted that alkanesulfonyl chlorides undergo Cu(I)-catalyzed reaction with trimethylsilyl enol ethers giving β-keto sulfones and alkanesulfinyl chlorides undergo analogous reaction giving β-keto sulfoxides.[18] However, we were not able to get chloromethanesulfonyl chloride to add to silyl ether **21** under a variety of conditions.

Scheme II

$$\mathrm{XCH_2SO_2Br \xrightarrow{h\nu} XCH_2SO_2^{\bullet} + Br^{\bullet}} \quad (a)$$

$$\mathrm{XCH_2SO_2^{\bullet} + Me_3SiOCR{=}CHR' \rightarrow Me_3SiO\dot{C}RCHR'SO_2CH_2X} \quad (b)$$

$$\mathrm{Me_3SiO\dot{C}RCHR'SO_2CH_2X \rightarrow Me_3Si^{\bullet} + RC(O)CHR'SO_2CH_2X} \quad (c)$$

$$\mathrm{Me_3Si^{\bullet} + XCH_2SO_2Br \rightarrow Me_3SiBr + XCH_2SO_2^{\bullet}} \quad (d)$$

(13) Meyers, C. Y.; Sataty, I. *Tetrahedron Lett.* **1972**, 4323–4326. Sataty, I. Ph.D. Thesis, Southern Illinois University, Carbondale, IL, 1970. Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1978**, *43*, 2252–2258. Also note: Mikolajczyk, M.; Grzejzczak, S.; Zatorski, A. *J. Org. Chem.* **1975**, *40*, 1979–1984.

(14) Anthony, A.; Maloney, T. *J. Org. Chem.* **1972**, *37*, 1055–1056. Also see: Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495–498 for related work.

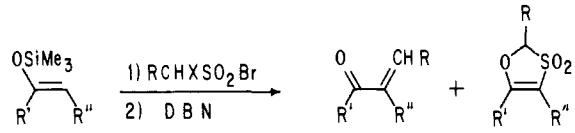
(15) Truce, W. E.; Amos, M. F. *J. Am. Chem. Soc.* **1951**, *73*, 3013–3017; Wolfe, S.; LaJohn, L. A.; Weaver, D. F. *Tetrahedron Lett.* **1984**, *25*, 2863–2866. Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396–405. Gais, H.-J.; Lindner, H. J.; Vollhardt, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 859–860.

(16) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279–3280.

(17) Harris, F. L.; Weiler, L. *Tetrahedron Lett.* **1984**, *25*, 1333–1336.

(18) Kuroki, Y.; Murai, S.; Sonoda, N.; Tsutsumi, S. *Organomet. Chem. Synth.* **1972**, *1*, 465–466. (b) Meanwell, N. A.; Johnson, C. R. *Synthesis* **1982**, 283–284.

Table II. Synthesis of α-Alkylidene Ketones and 1,3-Oxathiole 3,3-Dioxides from Trimethylsilyl Enol Ethers

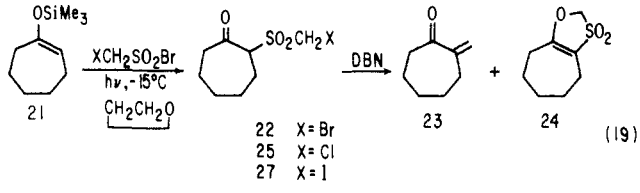


I II

entry	R'		R''	R	X	conditions[a,b]	products (overall isolated yield, %)
1		$(CH_2)_5$		H	Br	A	I (61), II (17)
2		$(CH_2)_5$		H	Br	B	I (45), II (16)
3		$(CH_2)_5$		H	Br	C	I (9), II (70)
4		$(CH_2)_5$		H	Cl	B	I (17), II (42)
5		$(CH_2)_5$		H	Cl	C	I (–), II (54)
6		$(CH_2)_5$		H	I	B	I (68), II (1)
7		$(CH_2)_5$		CH_3	Br	C	I (13),[c] II (2)
8		$(CH_2)_4$		H	Br	B	I (19), II (56)
9		$(CH_2)_4$		H	Br	C	I (–), II (46)
10		$(CH_2)_4$		H	I	B	I (32), II (32)
11		$(CH_2)_4$		CH_3	Br	C	I (12),[d] II (6)
12		$(CH_2)_3$		H	Br	B	I (30), II (–)
13	Ph		H	H	Br	B	I (–), II (43)
14	Ph		H	H	Cl	C	I (–), II (50)
15	*t*-Bu		H	H	Br	B	I (29), II (55)
16	*t*-Bu		H	H	Cl	C	I (–), II (57)
17	*t*-Bu		H	H	I	B	I (38), II (10)
18	C_2H_5		CH_3	H	Br	B	I (41), II (5)
19	C_2H_5		CH_3	H	Cl	C	I (–), II (54)

[a] Solvent is ethylene oxide (step 1); see Experimental Section for details. [b] DBN is base (step 2); A = CH_2Cl_2, −78 °C; B = CH_2Cl_2, −23 °C; C = EtOH, 23 °C. [c] 12:1 ratio of *E* to *Z* isomer. [d] 20:1 *E* to *Z* ratio.

Treatment of a methylene chloride solution of **22** with DBN at −78 °C followed by warming, washing with dilute acid, and distillation gave 2-methylenecycloheptanone[19] (**23**) in 77% yield (eq 19). A second compound, 8,10-oxathiabicyclo[5.3.0]dec-1-



(19)

(7)-ene 10,10-dioxide (**24**), a novel fused ring 1,3-oxathiole 3,3-dioxide, was isolated from the distillation residue in 21% yield as colorless needles. A higher yield of heterocycle **24** (88%) together with 12% of **23** was produced on reaction of an ethanol solution of **22** with DBN at room temperature. We have also utilized sulfonyl bromides **1**, **3**, and **4** in the preparation of α-alkylidene ketones and 1,3-oxathiole 3,3-dioxides. Thus reaction of **21** with **1**, **3**, and **4** gave 2-[(chloromethylsulfonyl]cycloheptanone (**25**) (67% yield), 2-[(1-bromoethyl)sulfonyl]cycloheptanone (**26**) (22% yield), and 2-[(iodomethyl)sulfonyl]cycloheptanone (**27**) (100% yield), respectively. Treatment of compound **25** with DBN in ethanol at room temperature gave **24** free from **23**, in 79% yield. On the other hand, treatment of **27** with 2.5 equiv of DBN in methylene chloride at −23 °C for 2 h gave **23** in 83% yield, with only trace amounts of **24**. Finally, treatment of 2-[(1-bromoethyl)sulfonyl]cycloheptanone with DBN in ethanol at room temperature led to a mixture of 39% (*E*)- and 3% (*Z*)-α-ethylidenecycloheptanone and 6% 9-methyl-8,10-oxathiabicyclo[5.3.0]dec-1(7)-ene 10,10-dioxide (**28**). This latter compound could also be obtained in 74% isolated yield by sequential treatment of **24** with *n*-butyllithium (THF, −78 °C) and methyl iodide. Other examples of the preparation of α-alkylidene ketones and 1,3-oxathiole 3,3-dioxides from trimethylsilyl enol ethers are given in Table II.

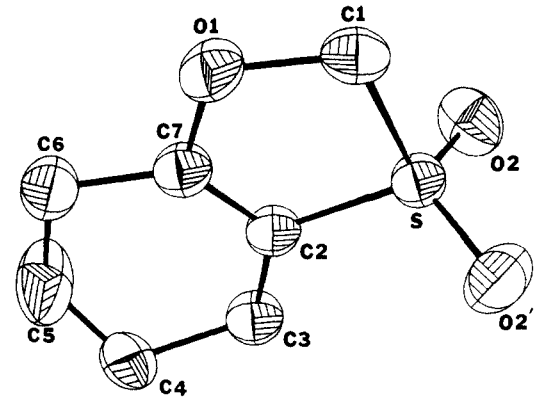
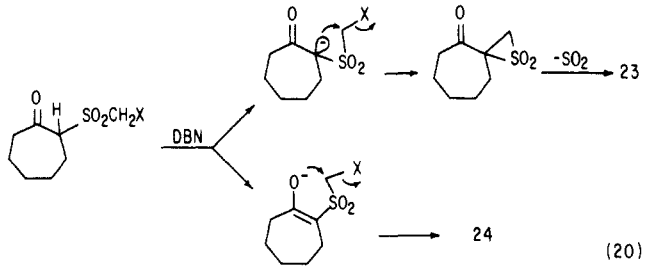


Figure 2. Perspective view of 7,9-oxathiabicyclo[4.3.0]non-1(6)-ene 9,9-dioxide showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Relevant bond distances and angles: S–C1, 1.809 (5) Å; S–C2, 1.727 (5) Å; S–O2, 1.430 (3) Å; C1–O1, 1.414 (6) Å; O1–C7, 1.373 (6) Å; C2–C7, 1.330 (6) Å; C1–S–C2, 92.1 (2)°; S–C1–O1, 107.4 (3)°; C1–O1–C7, 112.0 (3)°; O1–C7–2C2, 118.8 (4)°; C7–C2–S, 109.7 (3)°; for other data see supplementary material.

The 1,3-oxathiole 3,3-dioxide formed from 1-(trimethylsiloxy)-1-cyclohexene, 7,9-oxathiabicyclo[4.3.0]non-5-ene 9,9-dioxide, was further characterized by X-ray crystallography. The molecular geometry and the atom labeling are shown in Figure 2. The five-membered ring S–C1–O1–C7–C2 is rigorously planar, occupying the crystallographic mirror plane through $y = {}^1/_4$. The S–C2 distance is significantly shorter than S–C1, 1.727 (5) and 1.809 (5) Å, respectively, as a consequence of sp^2 hybridization at C2. The sulfone oxygen atoms O2 and O2′ are crystallographically equivalent, related through mirror symmetry. The six-membered ring C2–C3–C4–C5–C6–C7 is nonplanar, with C4 resting off the crystallographic mirror plane and disordered about the molecular plane. Other pertinent structural features are summarized in the figure caption.

As shown in eq 20, we suggest that reaction of **22**, **25**, and **27** with base generates an enolate ion which may undergo either intramolecular C-alkylation, giving an episulfone which loses sulfur dioxide affording enone **23** (Ramberg–Bäcklund reaction), or O-alkylation, giving heterocycle **24**. The preference for O-al-

(19) Kasandr, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180–1185; Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283–4286. Shono, T.; Nishiguchi, I.; Komamura, T.; Sasaki, M. *J. Am. Chem. Soc.* **1979**, *101*, 984–987. Danishefsky, S.; Prisbylla, M.; Lipisko, B. *Tetrahedron Lett.* **1980**, *21*, 805–808.



(20)

kylation in **25** (Cl leaving group) and C-alkylation in **27** (I leaving group) is in accord with the hard–soft acid–base principle.[20] The data in Table II suggest that O-alkylation is also favored by polar solvents, conjugation, and conformational factors but is disfavored when the Br is on a secondary carbon (steric effects[21]) and with smaller rings where the resultant heterocycle would be strained. While a few syntheses of 1,3-oxathiole 3,3-dioxides are known[22] our method should be useful because of its simplicity.

Reaction of α-Haloalkanesulfonyl Bromides and Conjugated Dienes: Synthesis of Conjugated Trienes and Polyenes

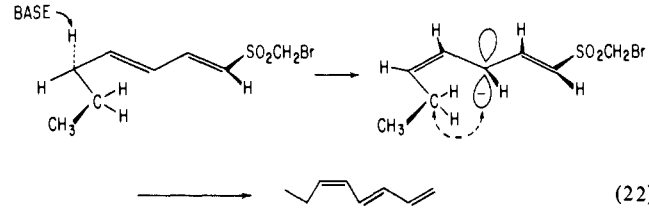
We have found that the two- or three-step olefin to conjugated diene transformation using **1**–**4**/base can be extended to the conversion of conjugated dienes to conjugated trienes (eq 21),

$$RCH_2CH{=}CHCH{=}CH_2 \xrightarrow{2;\ Et_3N} RCH_2CH{=}CHCH{=}CHSO_2CH_2Br \xrightarrow{t\text{-}BuOK} RCH{=}CHCH{=}CHCH{=}CH_2 \quad (21)$$

representing an extension of the "vinylogous Ramberg–Bäcklund reaction" to include the case with *two* intervening double bonds. Thus, light-initiated addition of **2** to (*E*)-1,3-pentadiene in methylene chloride followed by treatment of the adduct with triethylamine gave (*E*,*E*)-1,3-pentadienyl bromomethyl sulfone in 85% yield. Reaction of the latter dienyl sulfone with 2.25 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol gave (*E*)-1,3,5-hexatriene containing less than 1% of the *Z* isomer in 26% isolated yield. By comparison, the overall yield for the nonstereoselective and somewhat longer *Organic Syntheses* preparation of 1,3,5-hexatriene is 25%.[23]

A sequence similar to that described above gave, from 1,3-decadiene in 97% yield, (*E*,*E*)-1,3-decadienyl bromomethyl sulfone, which upon treatment with potassium *tert*-butoxide in *tert*-butyl alcohol/tetrahydrofuran under dilute conditions gave in 24% yield a 1.1:1 mixture of (*E*,*Z*)- and (*E*,*E*)-1,3,5-undecatriene, components of the essential oil from the Hawaiian seaweed *Dictyopteris*.[24] Under these same conditions 1,3-heptadiene was converted into a 1.7:1 mixture of (*E*,*Z*)- and (*E*,*E*)-1,3,5-octatriene in 16% overall yield. The former octatriene is known as fucoserratene, the female sex attractant from the ova of the seaweed *Fucus serratus* L.[25]

The stereoselectivity seen in the formation of linear trienes can be rationalized along lines similar to those used above to explain the stereoselectivity seen in diene synthesis. While the triene 3,4-double bond is derived with retention of stereochemistry from the *E*-1,2-double bond in the bromomethyl dienyl sulfones as indicated by the preferred formation of (*E*)-1,3,5-hexatriene, the modest preference of the triene 5,6-double bond for *Z* geometry can be rationalized in terms of an energetically favorable "syn effect" in the transition state leading to the anionic intermediate (see eq 22; it is assumed that some negative charge density develops



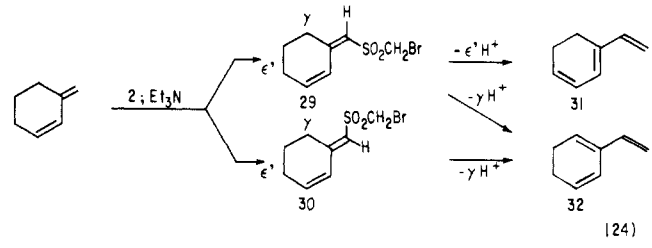
(22)

on carbon 3 in accord with the bonding in other pentadienyl anions[26]). Inasmuch as the dienes used in our methods may be prepared from olefins as already described, our triene synthesis involves a repetitive procedure in whch *both* the number of carbon atoms in the chain and the number of double bonds in conjugation increase by one in each cycle, e.g., eq 23. It is not possible to

$$RCH_2CH_2CH{=}CH_2 \xrightarrow{2;\ Et_3N;\ t\text{-}BuOK} RCH_2CH{=}CHCH{=}CH_2 \xrightarrow{\text{repeat}} RCH{=}CHCH{=}CHCH{=}CH_2 \quad (23)$$

convert conjugated trienes to conjugated tetraenes by using our procedure since trienes fail to give adducts with **2** either on direct irradiation or in the presence of zinc dichloride/*tert*-butyl hydroperoxide. We speculate that addition of the bromomethanesulfonyl radical to a conjugated triene gives a pentadienyl radical which is too stable[27] to abstract a bromine atom from **2**, thus effectively quenching the chain reaction. In fact we have observed that contamination of a sample of a conjugated diene with less than 1% of a conjugated triene is sufficient to prevent addition of **2** to the diene.

Addition of **2** to 3-methylene-1-cyclohexene followed by treatment of the adduct with triethylamine gives rise to a pair of doubly unsaturated bromomethyl sulfones **29** and **30** which can be separated by recrystallization and chromatography. The major, crystalline isomer, **29**, identified by NMR methods as (*Z*)-3-[[(bromomethyl)sulfonyl]methylene]-1-cyclohexene gives upon treatment with potassium *tert*-butoxide in *t*-BuOH/THF a 1:3 mixture of the known[28] trienes 1- and 2-vinyl-1,3-cyclohexadiene (**31** and **32**, respectively). The minor isomer **30** with the same base treatment gives only **32** (eq 24). These results can be



(24)

rationalized by invoking several different effects. The formation of **32** from **30** suggests that involvement of the sulfonyl group cation coordinating effect discussed above. In the absence of this effect (e.g., in **29**) deprotonation could occur either at the γ-position or the ε′-position. The somewhat stronger inductive or field effect of the sulfonyl group at the γ-position apparently favors deprotonation at that position.

We have used the diene to triene synthesis procedure to prepare polyenes with 3–6 conjugated double bonds (Table I, entries 41–45). The most direct approach involves base treatment of bis(bromomethyl sulfones) **33** to afford the polyenes (eq 25). An approach to methyl-substituted polyenes involves single or double

(20) Ho, T. L. *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic Press: New York, 1977.

(21) Since secondary carbons are considered *harder* than primary carbons, it is necessary to invoke steric effects to explain our results.

(22) (a) Dickore, K. *Liebigs Ann. Chem.* **1964**, *671*, 135–146. (b) Nozaki, H.; Takaku, M.; Hayashi, Y.; Kondo, K. *Tetrahedron* **1968**, *24*, 6563–6572. Elliott, A. J. In *Comprehensive Heterocyclic Chemistry*; Katrizky, A. R., Rees, C. W., Eds.; Pergamon Press: New York, 1984; Vol. 6, p 749.

(23) Hwa, J. C. H.; Sims, H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 608–612.

(24) Moore, R. E.; Pettus, J. A., Jr.; Mistysyn, J. *J. Org. Chem.* **1974**, *39*, 2201–2207. Näf, F.; Decorzant, R.; Thommen, W.; Willhalm, B.; Ohloff, G. *Helv. Chim. Acta* **1975**, *58*, 1016–1037. Giraudi, E.; Teisseire, P. *Tetrahedron Lett.* **1983**, *24*, 489–492. Hayashi, T.; Yanagida, M.; Matsuda, Y.; Oishi, T. *Tetrahedron Lett.* **1983**, *24*, 2665–2668.

(25) Jaenicke, L.; Seferiadis, K. *Chem. Ber.* **1975**, *108*, 225–232; Wiedenmann, B.; Hopf, H. *Z. Z. Naturforsch. B* **1977**, *32*, 119. Schneider, M. P.; Goldbach, M. *J. Am. Chem. Soc.* **1980**, *102*, 6114–6116.

(26) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, 199–204.

(27) Davies, A. W.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkins Trans. 2* **1981**, 633–641.

(28) Spangler, C. W. *Tetrahedron* **1976**, *32*, 2681–2684.

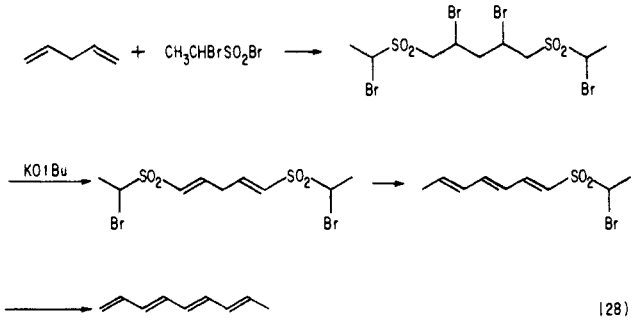
reaction according to eq 26 and 27 of mono- or bis(bromomethyl

$$\underset{\mathbf{33}}{BrCH_2SO_2(CH{=}CH)_mCH_2CH_2(CH{=}CH)_nSO_2CH_2Br} \xrightarrow{KO\text{-}t\text{-}Bu} H(CH{=}CH)_qH \quad (q = m{+}n{+}2) \quad (25)$$

$$H(CH{=}CH)_mCH_2CH_2(CH{=}CH)_nSO_2CH_2Br \xrightarrow{KO\text{-}t\text{-}Bu} \underset{\mathbf{34}}{H(CH{=}CH)_mCH_2(CH{=}CH)_{n+1}H} \xrightarrow{base} \underset{\mathbf{35}}{H(CH{=}CH)_pCH_3} \quad (p = m{+}n{+}1) \quad (26)$$

$$\underset{\mathbf{36}}{BrCH_2SO_2(CH{=}CH)_mCH_2CH_2CH_2(CH{=}CH)_nSO_2CH_2Br} \xrightarrow{KO\text{-}t\text{-}Bu} \underset{\mathbf{37}}{H(CH{=}CH)_{m+1}CH_2(CH{=}CH)_{n+1}H} \xrightarrow{base} H(CH{=}CH)_qCH_3 \quad (q = m{+}n{+}2) \quad (27)$$

sulfones) of type **34** or **36**, respectively, to generate *skipped* polyenes of type **35** or **37** which, under the basic reaction conditions, rearrange to the more stable fully conjugated terminal methyl-substituted polyenes. Another approach to the synthesis of methyl-substituted polyenes, illustrated in eq 28, involves ad-



(28)

dition of α-bromoethanesulfonyl bromide to 1,4-pentadiene followed by sequential Ramberg–Bäcklund reactions. This reaction apparently involves a vinylogous Ramberg–Bäcklund reaction through *three* intervening double bonds.

While these reactions involving several isolable intermediates all generated by base-induced elimination are cumbersome to represent, experimentally the procedure is simple. The initial single or double adducts of **1** or **2** with bis terminal olefins or dienes, e.g., **33**, can be treated with an excess of potassium *tert*-butoxide leading directly to formation of the polyenes in a two-step process or two repetitive two-step processes. The polyenes are easily isolated by extraction with pentane followed by washing and concentration. While the overall yields are only moderate and mixtures of geomeric isomers result, the synthesis have the advantage of simplicity and use of readily available starting materials for the preparation of polyenes that were either previously unknown or are quite difficult to prepare.[29,30]

Other Reactions of α-Haloalkanesulfonyl Bromides and Their Olefin Adducts: Reaction with Alkynes

Irradiation of **2** and excess 3-hexyne at −25 °C gives 1:1 adduct **38** in 90% yield.[31] This, upon treatment with potassium *tert*-butoxide–*t*-BuOH/THF gives 2-ethylpent-1-en-3-yne in 46% yield by a process presumably involving formation of 3-bromo-2-

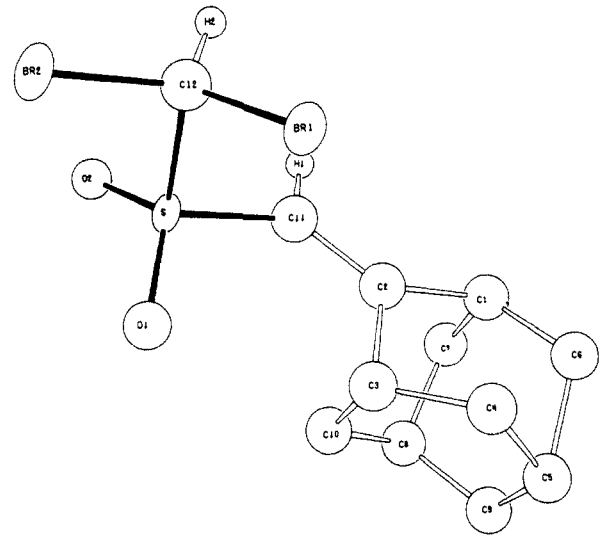
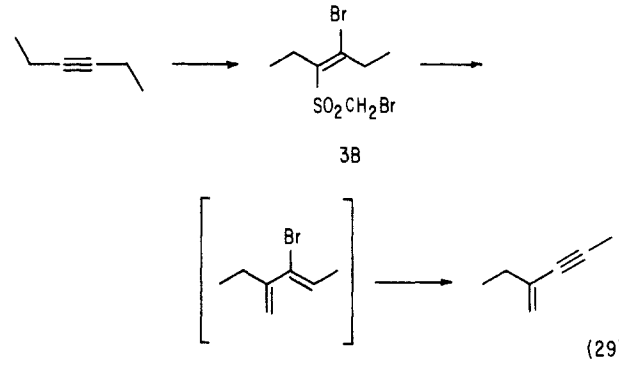


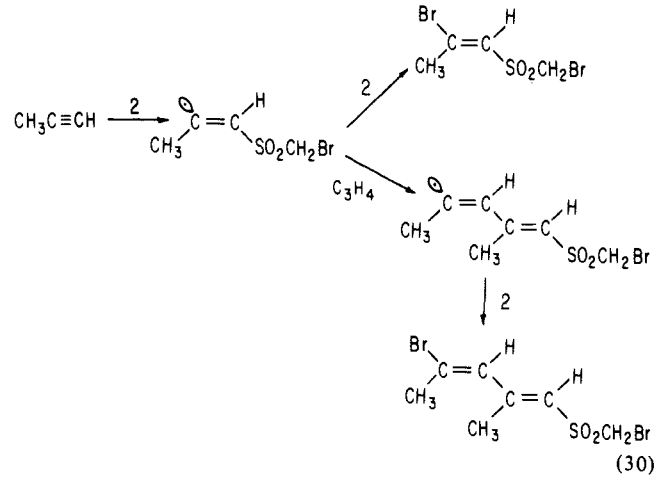
Figure 3. Perspective view of 2-[[(dibromomethyl)sulfonyl]methylene]-adamantane showing the atom-labeling scheme. Hydrogen atoms have been omitted from the adamantyl group for clarity. Relevant bond distances and angles: Br(2)–C(12), 1.912 (7) Å; Br(1)–C(12), 1.875 (7) Å; S–O(1), 1.442 (9) Å; S–O(2), 1.383 (10) Å; S–C(11), 2.213 (12) Å; Br–C12–Br, 130.9 (9)°; S–C11–C2, 149.6 (12)°; C3–C2–C11, 101.9 (16)°; O–S–O, 102.2 (13)°; C–S–C, 99.0 (14)°; for other data see supplementary material.

ethyl-1,3-pentadiene via vinylogous Ramberg–Bäcklund reaction followed by dehydrobromination (eq 29). In a similar manner



(29)

1-heptyne afforded oct-1-en-3-yne (29% overall isolated yield). Attempts to extend this procedure to propyne led to a surprising result, namely, formation of 4-bromo-2-methyl-1,3-pentadienyl bromomethyl sulfone in addition to the expected 2-bromo-1-propenyl bromomethyl sulfone. Apparently the intermediate propyne–sulfonyl radical adduct undergoes addition to a second molecule of propyne at a rate competitive with bromine atom extraction from **2** (eq 30), a process with some precedent.[32] We

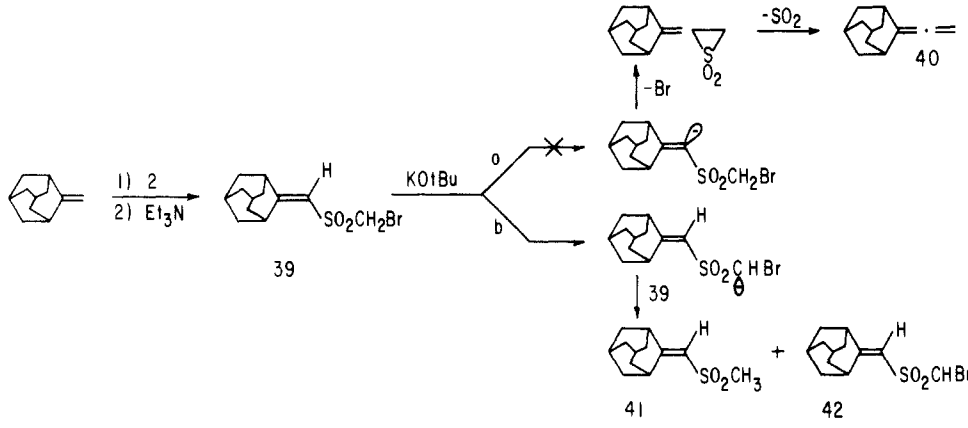


(30)

(29) (a) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675–1681. (b) D'Amico, K. L.; Manos, C.; Christensen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1777–1782. (c) Woods, G. F.; Schwartzman, L. H. *J. Am. Chem. Soc.* **1949**, *71*, 1396–1399. (d) Lippincott, E. R.; Feairheller, W. R., Jr.; White, C. E. *J. Am. Chem. Soc.* **1959**, *81*, 1316–1321. (e) Gavin, R. M., Jr.; Weisman, C.; McVey, J. K.; Rice, S. A. *J. Chem. Phys.* **1978**, *68*, 522–529. (f) Hayashi, T.; Hori, I.; Oishi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2909–2911.

(30) For other examples of syntheses of polyenes using the Ramberg–Bäcklund reaction, see: Buchi, G.; Freidinger, R. M. *J. Am. Chem Soc.* **1974**, *96*, 3332–3333. Näf, F.; Decorzant, R.; Escher, S. D. *Tetrahedron Lett.* **1982**, *23*, 5043–5046. Grieco, P. A.; Boxler, D. *Synth. Commun.* **1975**, *5*, 315–318.

(31) For other examples of addition of sulfonyl radicals to alkynes, see: Back, T. G.; Collins, S. *Tetrahedron Lett.* **1981**, 5111–5114. Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438–439 and ref 7.



(31)

were unable to prepare adducts of **2** with propargyl alcohol or chloride or with 3-phenoxy-1-propyne.

We have examined the reaction of **2** with 1,1-disubstituted alkenes that cannot undergo subsequent vinylogous Ramberg–Bäcklund rearrangement such as 1,1-diphenylethylene and 2-methyleneadamantane. While 1,1-diphenylethylene failed to react with **2** (paralleling the lack of reactivity of this olefin in other free radical additions[33]), addition of **2** to 2-methyleneadamantane followed by treatment with triethylamine gave unsaturated bromomethyl sulfone **39**. It was hoped that **39** would give allene **40** upon treatment with potassium *tert*-butoxide (see eq 31). Instead, base treatment of **39** lead to formation of an equimolar mixture of methyl sulfone **41** and dibromomethyl sulfone **42** (ca. 13% yield apiece) by a reaction presumably involving attack of an α-bromo α-sulfonyl carbanion on the bromine atom in **39**, a process seen in sulfonyl carbanion chemistry.[34] The olefinic and dibromomethyl protons in **42** are magnetically degenerate in deuteriochloroform which led to initial structural uncertainty. Thus the structural assignment was confirmed by X-ray crystallography, as summarized in Figure 3.

In systems capable of undergoing the Ramberg–Bäcklund reaction, reversible carbanion formation at the α-carbon bearing the halogen as well as at the non-halogenated position has been reported.[2] However, in contrast to these other systems, the Ramberg–Bäcklund reaction of **39** involving intramolecular SN_2 attack by an sp^2 carbanion (eq 31, path a) is apparently slow relative to the alternative process involving carbanion attack on halogen (eq 31, path b).

We have briefly examined the possibility of using **2** in diene synthesis via Michael-induced Ramberg–Bäcklund processes.[35] Thus 1,3-butadiene was converted into 1,3-butadienyl bromomethyl sulfone (**43**) via sequential treatment with **2** followed by triethylamine (eq 32). Treatment of **43** with sodium isopropoxide afforded a 3:1 mixture of (*E*)- and (*Z*)-1-isopropoxy-2,4-pentadiene.

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{2;\ Et_3N} CH_2{=}CHCH{=}CHSO_2CH_2Br \ (\mathbf{43}) \xrightarrow{i\text{-PrONa}} i\text{-}PrOCH_2CH{=}CHCH{=}CH_2 \quad (32)$$

Conclusion

We have demonstrated in this paper that reagents **1–4** may be easily prepared from readily available starting materials, that these reagents display high reactivity toward most olefins, dienes, silyl enol ethers, and alkynes, and that the adducts of **1–4** with these aforementioned substrates may be transformed rapidly, and in many cases stereo- and/or regioselectivity under mild conditions with common bases and in good yields, into products with additional unsaturation. In some of these cases we believe that use of reagents **1–4** will represent the method of choice for both small- and large-scale synthesis.

Experimental Section

General Procedures and Materials. General procedures and selected examples of synthetic applications of compounds **1–4** are given below. For many of the final products and intermediates obtained, whose identities are readily discerned by the usual analytical techniques, physical data are provided as supplementary material.

Chloromethanesulfonyl Bromide (1).[4] Chloromethanesulfonyl chloride[36] (31.0 g, 0.208 mol) was added to aqueous Na_2SO_3 (39.6 g, 0.31 mol, in 175 mL of water). The reaction mixture was stirred at room temperature until all of the chloromethanesulfonyl chloride had reacted (ca. 1 h). The aqueous layer was washed with CH_2Cl_2 (2 × 50 mL), cooled in ice, and treated dropwise with bromine (33.0 g, 0.206 mol). After consumption of the bromine, more bromine was added until the red color persisted. The product was extracted with CH_2Cl_2 (2 × 50 mL) and the organic layer washed with cold 2% $NaHSO_3$ (50 mL) and water, separated, dried ($MgSO_4$), and concentrated in vacuo to give an oil. Distillation gave **1** as a colorless liquid (22.5 g, 56%): bp 50–54 °C (0.6 mm); IR 1365 (vs), 1240 (s) 1160 (vs) 720 cm^{-1} (s); ^1H NMR δ 5.04 (s).

Bromomethanesulfonyl Bromide (2).[5] A 3-L three-necked round-bottomed flask equipped with a mechanical stirrer, a pressure-equalized dropping funnel, and a thermometer is charged with 100 g (0.73 mol) of *sym*-trithiane[37] suspended in 600 mL of water. Bromine (1136 g, 7.1 mol) is added with stirring while keeping the flask temperature around 40 °C (this is an exothermic reaction and no outside heating is required; if the temperature goes above 40 °C, the flask is cooled by ice). After the addition of half of the bromine, 600 mL of water is added and the bromine addition is continued. After all of the bromine has been added, the reaction mixture is stirred for 0.25 h. The mixture is transferred to a 4-L separatory funnel, the lower organic layer is separated, and the aqueous layer is extracted with two 200-mL portions of CH_2Cl_2. (In the first of these extractions, the upper phase is the organic one, while in the second extraction, the organic layer is at the bottom.) The organic extracts are combined, washed with one 100-mL portion of cold 5% $NaHSO_3$ and with 100 mL of water, dried ($MgSO_4$), and concentrated at 25 °C with a rotary evaporator to a light yellow oil. Distillation using a short column affords 218–249 g (42–48%) of bromomethanesulfonyl bromide as a light yellow oil: bp 60–68 °C, n^{20}_D 1.5706; IR (neat) 3040 (vs), 2960 (vs), 1362 (vs), 1205 (s), 1160 (vs), 1105 (ms), 830 (s), 680 cm^{-1} (s); ^1H NMR δ 5.05 (s).

α-Bromoethanesulfonyl Bromide (3).[5] A solution of Na_2SO_3 (26.7 g, 0.212 mol) in water (50 mL) is mixed with α-bromoethanesulfonyl chloride[6] (22 g, 0.106 mol) with stirring at 0 °C and allowed to warm to room temperature during the course of 1 h. The solution is again cooled in ice and treated dropwise with bromine (34 g, 0.213 mol) during 0.5 h. The product is extracted with CH_2Cl_2 (3 × 25 mL), washed with cold 5% $NaHSO_3$ (2 × 20 mL) and water (20 mL), dried ($MgSO_4$), and concentrated in vacuo. Distillation gave **3** (18 g, 66%) as a colorless oil:

(32) Leedham, K.; Haszeldine, R. N. *J. Chem. Soc.* **1954**, 1634–1638.
(33) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155–4158.
(34) Burger, J. J.; Chen, T. B. R. A.; de Waard, E. R.; Huisman, H. O. *Tetrahedron* **1980**, *36*, 1847–1850. Jonczyk, A.; Radwin-Pytlewski, T. *Chem. Lett.* **1983**, 1557–1560.
(35) Chen, T. B. R. A.; Burger, J. J.; de Waard, E. R.; Huisman, H. *Tetrahedron Lett.* **1977**, 4527–4530.
(36) Paquette, L.; Wittenbrook, L. S. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 231–234.
(37) Bost, R. W.; Constable, E. W. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, pp 610–611.

bp 50–58 °C (0.1 mm); IR (neat) 2950 (m), 1360 (s), 1250 (m), 1165 (s), 700 (s), 640 cm^{-1} (m); ^1H NMR δ 5.20 (q, 1 H, J = 6.5 Hz, CH), 2.10 (d, 3 H, J = 6.5 Hz, CH_3).

Iodomethanesulfonyl Bromide (4). Well-dried sodium iodomethanesulfonate[38] (24.4 g, 0.1 mol) was mixed with PBr_5 (43 g, 0.1 mol) and CH_2Cl_2 (150 mL). The reaction mixture was heated at 60 °C for 16 h, then cooled, and filtered through a small pad of silica gel which was rinsed with CH_2Cl_2 (50 mL). Evaporation of the solvent gave an orange-brown oil. Three recrystallizations of the oil with CS_2 at −72 °C in a low-temperature recrystallization apparatus to remove $POBr_3$ gave (11.4 g, 40% yield). Distillation gave a pale violet liquid: bp 78–80 °C (0.06 mm); ^1H NMR δ 5.25 (s); IR 1365 (s), 1165 (s), 1130 (s), 770 (m), 725 cm^{-1} (m).

Addition of Sulfonyl Bromides to Olefins: 1-Bromo-1-methyl-2-[(bromomethyl)sulfonyl]cyclohexane. General Procedure A. Four Pyrex test tubes (2.5 × 20 cm) are charged with 1-methylcyclohexene (5.0 g per test tube; total 20.0 g, 0.21 mol) and CH_2Cl_2 (12 mL per tube) and cooled in ice. An ice cold solution of **2** (13.6 g of **2** per test tube; total 54.4 g, 0.23 mol) in CH_2Cl_2 (12 mL) is added to each test tube with mixing at 0 °C. *On occasion **2** undergoes spontaneous, exothermic addition to olefins. Thus it is desirable to mix the reagents at low temperature to avoid a possible vigorous spontaneous reaction and to maximize the yield of adduct.* The test tubes are attached with the help of several rubber bands to a Pyrex immersion well equipped with a 450-W mercury lamp. The immersion well is cooled by circulation of ice water and immersed in a cooling bath kept at −15 °C. The reaction mixture is irradiated for 2 h. Solid K_2CO_3 (1.5 g) is added to each test tube and the contents of the test tube are filtered through a small column with a glass wool plug into a 250-mL round-bottomed flask. The solvent is removed, first on a rotary evaporator and then with a vacuum pump (1 mm), giving an oil which gradually solidifies (68.3 g, 98%). Recrystallization (100 mL of 95% EtOH) gives colorless crystals (54.3 g, 78%): mp 59–61 °C; IR 2960 (s), 1450 (m), 1380 (s), 1315 (vs), 1205 (s), 1140 (vs), 1090 (vs), 745 cm^{-1} (s); ^1H NMR δ 4.58 (AB q, J = 11 Hz, 2 H), 3.96 (dd, 1 H), 2.41–2.31 (m, 2 H), 2.16–2.08 (m, 2 H), 2.15 (s, 3 H), 1.82–1.56 (m, 4 H); ^{13}C NMR δ 67.2, 65.8, 44.4, 43.7, 29.7, 24.3, 23.3, 22.7.

Anal. Calcd for $C_8H_{14}Br_2O_2S$: C, 28.76; H, 4.22. Found: C, 28.82; H, 4.26.

Formation of 1,1-Disubstituted Olefins via Methylene–Titanium Reagent: 2-Methyloct-1-ene (17). General Procedure B. To a stirred suspension of zinc dust (28.8 g) in CH_2Br_2 (10.1 mL, 0.14 mol) and dry THF (200 mL) at −40 °C was added $TiCl_4$ (11.5 mL, 0.1 mol) during 40 min.[12] The mixture was brought to 5 °C and was stirred at 5 °C for 3 days to give a thick grey slurry. This slurry (150-mL portion) was added to 2-octanone (6.4 g, 0.05 mol) in CH_2Cl_2 (100 mL) at 25 °C, monitoring by GC for disappearance of the starting ketone (1 h). The product was then poured onto a mixture of $NaHCO_3$ (70 g) in water (150 mL) and CH_2Cl_2 (60 mL). The resultant mixture was filtered through a pad of Celite. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (75 mL), and the combined organic extracts were washed with water (4 × 25 mL), dried, filtered, and concentrated in vacuo, giving a colorless liquid. Flash distillation gave 2-methyloct-1-ene (3.5 g, 56%), ^1H NMR δ 4.77–4.49 (m, 2 H), 2.23–0.62 (m, 16 H).

Formation of 1-Alkenyl Bromomethyl Sulfones from Olefin–2 Adducts: (*E*,*Z*)-11-Hydroxy-1-undecenyl Bromomethyl Sulfone. General Procedure C. 2-Bromo-11-hydroxyundecyl bromomethyl sulfone (16.3 g, 0.04 mol) was dissolved in CH_2Cl_2 (150 mL), cooled in ice, and treated dropwise with stirring with a solution of Et_3N (4.85 g, 0.048 mol, 1.2 equiv) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 0.25 h and washed with dilute HCl (100 mL) and water (100 mL), and the organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo, giving a solid (12.9 g, 99%). Recrystallization (95:5 $CCl_4/CHCl_3$) gave colorless crystals of the *E* isomer: mp 60 °C; IR 3375 (OH, br), 1630 (m), 1325 (m), 1130 (vs), 1060 cm^{-1} (s); ^1H NMR δ 7.13 and 6.89 (1 H, td, J_d = 15, J_t = 6 Hz), 6.21 (1 H, J = 15 Hz), 4.32 (2 H, s), 3.57 (2 H, t), 2.30 (2 H, m), 1.96 (1 H, s), 1.35 (14 H, br s); ^{13}C NMR δ 153.9, 124.8, 62.8, 43.4, 32.7, 31.8, 29.3 (3 C), 29.1, 28.9, 25.7.

Anal. Calcd for $C_{12}H_{23}BrO_3S$: C, 44.04; H, 7.08. Found: C, 43.95; H, 7.09.

(*E*,*Z*)-1-Octenyl Bromomethyl Sulfone (12E,Z). As in procedure C, a 10:1 mixture of **12E**/**Z** was obtained in 97% yield. Recrystallization (pentane/CH_2Cl_2, 95:5) gave colorless crysals of **12E** (51%): mp 34–35 °C; IR 1625 (m), 1325 (vs), 1140 (vs), 855 cm^{-1} (s); ^1H NMR δ 7.10 and 6.86 (td, J_d = 15, 1 H), 6.24 (d, J = 15 Hz, 1 H), 4.34 (s, 2 H), 2.33 (m, 2 H), 1.34 (br s, 8 H), 0.89 (t, 3 H); ^{13}C NMR δ 153.8, 125.0, 43.5, 31.9, 31.5, 28.7, 27.5, 22.5, 14.0.

Anal. Calcd for $C_9H_{17}BrO_2S$: C, 40.15; H, 6.37. Found: C, 40.32; H, 6.36.

Preparatory HPLC (hexane/THF 92:3) of the mother liquor gave **12Z** as an oil (5%): IR 1620 (m), 1320 (vs), 1140 (vs), 880 cm^{-1} (m); ^1H NMR δ 6.65 and 6.53 (td, J_d = 11 Hz, 1 H), 6.25 (d, J = 11 Hz, 1 H), 4.36 (s, 2 H), 2.69 (m, 2 H), 1.33 (br s, 8 H), 0.89 (t, 2 H); ^{13}C NMR δ 152.9, 124.7, 44.0, 31.5, 28.8 (2 C), 28.3, 22.5, 14.0.

(*E*,*Z*)-2-Methyl-1-octenyl Bromomethyl Sulfone (18a,a'). As in procedure A addition of **2** to 2-methyloct-1-ene gave 2-bromo-2-methyloctyl bromomethyl sulfone in 95% yield as an oil: ^1H NMR δ 4.42 (s, 2 H), 3.88 (s, 2 H), 2.09 (s, 3 H), 1.96–1.10 (m, 10 H), 1.03–0.65 (m, 3 H). Following procedure C, a 2.7:1 mixture of the title compounds was obtained as an oil (92%). HPLC separation of a 0.18-g sample of the mixture of isomers (99.5% hexane, 0.5% isopropyl alcohol) gave 0.10 of **18a** (*E*), >98% pure by GC analysis, and 0.03 g of **18a'** (*Z*) as colorless oils (GC t_R 9.62 and 8.69 min, respectively, at 195 °C). The *E* isomer had ^1H NMR δ 6.05 (q, 1 H), 4.36 (s, 2 H), 2.21 (d, 3 H, J = 2 Hz, CH_3 syn to SO_2), 2.40–1.92 (2.16 av, m, 2 H, CH_2 anti to SO_2), 1.68–1.03 (m, 8 H), 1.03–0.69 (t, 3 H); ^{13}C NMR δ 163.9, 120.0, 44.3, 40.9, 31.5, 28.7, 27.1, 22.5, 18.3, 14.0. The *Z* isomer had ^1H NMR δ 6.05 (q, 1 H), 4.30 (s, 2 H), 2.81–2.44 (2.63 average, m, 2 H, CH_2 syn to SO_2), 2.01 (d, 3 H, J = 2 Hz, CH_3 anti to SO_2), 1.58–1.06 (m, 8 H), 1.06–0.69 (t, 3 H); ^{13}C NMR δ 164.1, 120.2, 44.3, 33.0, 31.6, 29.3, 28.4, 25.0, 22.5, 14.0.

(*E*,*Z*)-1-[[(Bromomethyl)sulfonyl]methylene]-3-methylcyclohexane (15). As in procedure A, addition of **2** to 3-methyl-1-methylenecyclohexane gave 1-bromo-1-[[(bromomethyl)sulfonyl]methyl]-3-methylcyclohexane (95%) as an oil: ^1H NMR δ 4.56 (s, 2 H), 3.98 (s, 2 H), 2.54–1.37 (m, 9 H), 0.96 (d, 3 H). Procedure C gave a mixture of the title compounds (93%) as an oil. Fractional crystallization (CCl_4) gave the *E* isomer as colorless needles: mp 79–80 °C; ^1H NMR δ 6.04 (br s, 1 H), 4.36 (s, 2 H), 3.64–3.19 (m, 1 H), 2.44–1.27 (m, 8 H), 0.98 (d, 3 H); ^{13}C NMR δ 166.7, 117.9, 45.9, 44.5, 35.0, 33.9, 29.3, 26.6, 21.9.

Anal. Calcd for $C_9H_{15}BrSO_2$: C, 40.46; H, 5.66. Found: C, 40.59; H, 5.50.

Preparatory HPLC of the mixture (99% hexane, 1% *i*-PrOH) gave the *Z* isomer as an oil: ^1H NMR δ 6.05 (br s, 1 H), 4.36 (s, 2 H), 3.58–3.21 (m, 1 H), 2.52–1.32 (m, 8 H), 1.01 (d, 3 H); ^{13}C NMR δ 166.7, 117.9, 44.6, 37.5, 34.5, 34.0, 27.2, 22.1.

Formation of Dienes Directly from Olefin-2 Adducts: 1,2-Dimethylenecyclohexane. General Procedure D. An oven-dried 1-L three-necked round-bottomed flask equipped with a mechanical stirrer and a pressure-equalized dropping funnel is charged with KO-*t*-Bu (59.5 g, 0.53 mol) in *t*-BuOH–THF (9:1; 400 mL total) and cooled in ice in an argon atmosphere. A solution of 1-bromo-1-methyl-2-[(bromomethyl)sulfonyl]cyclohexane (54.0 g, 0.16 mol) in *t*-BuOH–THF (9:1; 100 mL) is added dropwise during 1 h. The reaction mixture is stirred at 25 °C for 0.5 h and then is poured into a 2-L separatory funnel containing water (500 mL). This solution is extracted with pentane (2 × 150 mL); the combined pentane extracts are washed with water (8 × 500 mL; the first four washings are done with gentle agitation to avoid emulsion formation), dried ($MgSO_4$), and filtered. The pentane is removed by distillation at atmospheric pressure using an efficient Vigreux column, and the residue is distilled under reduced pressure to give 11.4 g (65%) of the title compound as a colorless liquid: bp 69–70 °C [90 mm; lit.[39] 60–61 °C, (90 mm)] shown by GC analysis to be 93% pure; n^{20}_D 1.4722; IR 3090 (s), 2940 (s), 2870 (s), 1635 (s), 1440 (s), 895 cm^{-1} (vs); ^1H NMR δ 4.93–4.92 (m, 2 H), 4.65–4.64 (m, 2 H), 2.27–2.24 (m, 4 H), 1.66–1.62 (m, 4 H); ^{13}C NMR δ 149.7, 107.8, 35.4, 36.9.

5-Methyl-1-vinyl-1-cyclohexene (16b). Reaction of pure (*E*)-1-[[(bromomethyl)sulfonyl]methylene]-3-methylcyclohexane with KO-*t*-Bu as in procedure D gave, after distillation, **16b** (78%): IR 1650, 1620, 1460, 1000, 900 cm^{-1}; ^1H NMR δ 6.62–6.04 (m, 1 H), 5.66 (t, 1 H), 5.25–4.70 (m, 2 H), 2.47–1.13 (m, 7 H), 1.01 (d, 3 H); ^{13}C NMR δ 140.1, 135.8, 129.3, 109.6, 32.4, 30.8, 28.4, 25.8, 22.0.

3-Methyl-1-vinyl-1-cyclohexene (16b'). A solution of LiO-*t*-Bu (0.0023 mol) in *t*-BuOH was prepared by adding *n*-butyllithium (1.5 mL, 1.55 M) in THF to *t*-BuOH (3 mL). This solution was added dropwise to a refluxing solution of (*Z*)-1-[[(bromomethyl)sulfonyl]methylene]-3-methylcyclohexane (0.17 g, 0.64 mmol) in 4:1 THF–*t*-BuOH (2.5 mL). The mixture was maintained at reflux for 1 h. and then diluted with water (10 mL) and extracted with pentane (2 × 10 mL). The combined pentane extracts were washed with water (6 × 10 mL), dried ($MgSO_4$), and concentrated in vacuo to give **16b'** (0.06 g, 77%): ^1H NMR δ 6.59–5.97 (m, 1 H), 5.59 (d, 1 H), 5.18–4.63 (m, 2 H), 2.40–1.03 (m, 7 H), 0.93 (d, 3 H); ^{13}C NMR δ 140.3, 136.0, 135.3, 110.1, 31.3, 30.9, 23.8, 21.5, 21.4.

(38) Lauer, W. M.; Langkammerer, C. M. *J. Am. Chem. Soc.* **1935**, *57*, 2361–2362.

(39) Bailey, W. J.; Golden, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 4780–4782. Blomquist, A. T.; Longone, D. T. *J. Am. Chem. Soc.* **1957**, *79*, 3916–3919.

5-Methyl-1-vinyl-1-cyclohexene (16b) and 3-Methyl-1-vinyl-1-cyclohexene (16b'). Treatment of a 1:1 mixture of (*E*,*Z*)-1-[[(bromomethyl)sulfonyl]methylene]-3-methylcyclohexane with KO-*t*-Bu as in procedure D gave after flash distillation a mixture of **16b** and **16b'** (1.9:1; 69%) as determined by capillary GC (t_R at 70 °C 8.03 and 7.90 min, respectively) as well as NMR methods.

Formation of Dienes from 1-Alkenyl Bromomethyl Sulfones: (*E*,*Z*)-1,3-Nonadiene.[11a] General Procedure E. (*E*,*Z*)-1-Octenyl bromomethyl sulfone (**12E,Z**; 5.4 g, 0.02 mol) was dissolved in THF–*t*-BuOH (1:9, 20 mL) and added dropwise to an ice-cold solution of KO-*t*-Bu (6.75 g, 0.0l mol) in THF–*t*-BuOH (1:9, 100 mL). The reaction mixture was stirred in ice for 1 h and at 25 °C for 0.5 h, then diluted with water (200 mL), and extracted with pentane (2 × 75 mL). The combined organic layer was washed with water (4 × 150 mL), separated, dried ($MgSO_4$), filtered, and concentrated to give an oil. Distillation gave the title compound[11a] (1.79 g, 72%; 2:1 *Z*/*E*): IR 1642 (m), 1602 (m), 1465 (s), 1002 (vs), 902 cm^{-1} (vs); ^1H NMR δ 6.94–4.62 (m, 5 H), 2.10 (m, 2 H), 1.30 (br m, 6 H), 0.84 (t, 3 H); ^{13}C NMR δ (*E*) 137.5, 135.5, 131.1, 114.5, 32.6, 31.6, 29.0, 22.7, 14.0, (*Z*) 133.0, 132.5, 129.3, 116.6, 31.6, 29.4, 27.8, 22.7, 14.0; MS, *m*/*e* 124 (M^+, 65), 95 (20), 81 (34), 67 (66), 54 (100).

3-Methylenenon-1-ene (19).[40] As in procedure E (except treated with base at −23 °C; THF:*t*-BuOH ratio was 1:5), (*E*,*Z*)-2-methyl-1-octenyl bromomethyl sulfone was converted into the title compound (82%; 9% of 3-methyl-1,3-nonadiene).

6-Methylene-4-decene. As in procedure A addition of **2** (50% excess) to 5-decene gave 5-bromo-6-[(bromomethyl)sulfonyl]decane as a thick oil (95%), ^1H NMR δ 4.85–4.3 (m, 1 H), 4.52 (s, 2 H), 3.9 (m, 1 H), 2.41–0.69 (br m, 18 H). Procedure C gave a 6:1 mixture of (*E*)- and (*Z*)-5-[(bromomethyl)sulfonyl]-5-decene (100%): ^1H NMR δ 6.79 (t, *Z* isomer) and 6.25 (t, *E* isomer, total area for both 1 H), 4.45 and 4.3 (2 s, 2 H total), 2.9–1.87 (m, 4 H), 1.46 (br s, 8 H), 0.95 (t, 6 H). Application of procedure *E* gave the title compound as a colorless liquid (75%).

1-Vinylcycloheptene. Methylenecycloheptane was treated with 1 equiv of **2** by procedure A. Application of procedure C to the resulting thick oil gave [[(bromomethyl)sulfonyl]methylene]cycloheptane (96%). Procedure E gave after distillation the title compound (85%) as a colorless liquid.

3-Methylenecyclooctene.[41] Cyclooctene was treated with an equiv of **2** by procedure A. Application of procedure D to the product (80%) gave after distillation the title compound as a colorless oil (57%).

(*E*,*Z*)-1,3-Butadienyl Phenyl Ether.[42] Application of procedure C to 2-bromo-3-phenoxypropyl bromomethyl sulfone gave (*E*,*Z*)-3-phenoxy-1-propenyl bromomethyl sulfone (97%); recrystallization (CCl_4) gave colorless crystals of the *E* isomer, mp 76–77 °C. Application of procedure E to the above sulfone gave the title compound[42] (58%; 1:9 *E*/*Z*).

Preparation of Conjugated Trienes: (*E*)-1,3,5-Hexatriene.[23] As in procedure A **2** (14.3 g, 0.06 mol) was added to 1,3-pentadiene (4.08 g, 0.06 mol) to afford 4-bromo-2-pentenyl bromomethyl sulfone (17.9 g, 98%). Procedure C gave (*E*,*E*)-1,3-pentadienyl bromomethyl sulfone (11.5 g, 88%) as a colorless solid: mp 65–67 °C (from CCl_4); IR 1640 (s), 1585 (m), 1315 (vs), 1135 (vs), 820 cm^{-1} (m); ^1H NMR δ 7.44–6.89 (m, 1 H), 6.5–5.94 (m, 3 H), 4.37 (s, 3 H), 1.89 (d, 3 H); ^{13}C NMR δ 148.3, 144.7, 127.3, 121.3, 43.8, 18.9. The latter compound (4.5 g, 0.02 mol) in *t*-BuOH (25 mL) was added tp KO-*t*-Bu (5.0 g, 0.045 mmol) in *t*-BuOH (100 mL) and the mixture was stirred for 0.5 h. Water (100 mL) was added and the reaction mixture was extracted with dodecane (2 × 50 mL). The combined dodecane layer was washed (4 × 200 mL of water) and dried ($MgSO_4$). Flash distillation [50 °C (1 mm)] gave (*E*)-1,3,5-hexatriene (0.40 g, 25%; <2% of *Z* isomer): IR 1430 (m), 1010 (s), 900 cm^{-1} (s); ^1H NMR δ 6.77–5.89 (m, 4 H), 5.48–4.81 (m, 4 H); ^{13}C NMR δ 136.9, 133.7, 117.8.[23]

(*E*,*Z*)- and (*E*,*E*)-1,3,5-Undecatriene.[24] 1,3-decadiene was treated with 1 equiv of **2** as in procedure A to give a 1:1 adduct (100%) as an oil: ^1H NMR δ 6.52–5.45 (m, 2 H), 4.87–4.22 (m, 3 H), 4.00 (d, 2 H), 2.33–1.68 (m, 2 H), 1.68–1.06 (m, 8 H), 1.06–0.58 (m, 3 H). Procedure C (50% excess of Et_3N) gave 1,3-decadienyl bromomethyl sulfone (97%). Recrystallization (pentane–CH_2Cl_2) gave (*E*,*E*)-1,3-decadienyl bromomethyl sulfone, mp 54–55 °C.

This latter compound (4.43 g, 15 mmol) in THF (143 mL)–*t*-BuOH (286 mL) and a solution of KO-*t*-Bu (4.2 g, 37 mmol) in THF (143 mL) and *t*-BuOH (286 mL) were separately added simultaneously via syringe drive during 24 h to *t*-BuOH (715 mL) in a three-necked flask in an argon atmosphere and in the dark. The resulting solution was diluted with water (1200 mL) and extracted with pentane (2 × 150 mL), and the pentane extract was washed with water (12 × 100 mL), dried ($MgSO_4$), and concentrated to give a red liquid which upon flash distillation gave a 1.1:1 mixture of (*E*,*Z*)- and (*E*,*E*)-1,3,5-undecatriene[24] (0.55 g, 24%) as a pale yellow liquid: GC t_R 10.65 and 11.16* min (oven 100 °C), respectively; IR (thin film) 2950 (s), 1480 (m), 1010 (s), 900 cm^{-1} (m); UV (hexane) λ_{max} 253, 268, 273 nm; ^1H NMR δ 6.96–4.77 (m, 7 H), 2.50–1.82 (q, 2 H), 1.58–1.10 (m, 6 H), 1.06–0.69 (t, 3 H); ^{13}C δ NMR 137.3*, 136.1*, 133.6*, 132.9, 131.0*, 130.2*, 128.7, 128.3, 116.7, 116.1*, 32.8*, 31.5*, 29.4, 29.0*, 27.9, 22.6*, 14.0*. An authentic sample of (*E*,*E*)-1,3,5-undecatriene was prepared to confirm some of the above data (indicated by asterisk). The stereoselectivity could be increased to 1.6:1 *E*,*Z*/*E*,*E* (at the expense of the yield) by running the reaction at −24 °C. Neither the yield nor stereoselectivity of the undecatrienes was changed by using 1,3-decadientyl iodomethyl sulfone, prepared as above by using iodomethanesulfonyl bromide.

1,3,5-Heptatriene. Three equivalents of 1,5-hexadiene was treated with 1 equiv of **2** as in procedure A to give 2-bromo-5-hexenyl bromomethyl sulfone (86%) as an oil: ^1H NMR δ 6.21–5.49 (m, 1 H), 5.39–4.87 (m, 2 H), 4.73–4.18 (m, 3 H), 4.08–3.53 (dd, 2 H), 2.64–1.82 (m, 4 H). Procedure C (50% excess of Et_3N) gave 1,5-hexadienyl bromomethyl sulfone (97%), bp 110–111 °C (0.02 mm). Treatment of the latter compound with KO-*t*-Bu as above gave after flash distillation a mixture of isomeric 1,3,5-heptatrienes (24%) as a colorless liquid: UV (hexane) λ_{max} 248, 258, 269; ^1H NMR δ 7.24–5.3 (m, 5 H), 5.30–4.80 (m, 2 H), 1.72 (d, 3 H); ^{13}C NMR δ 137.2, 133.5, 132.3, 131.0, 130.8, 130.2, 129.2, 128.3, 127.6, 127.0, 124.4, 117.1, 116.8, 116.1, 18.7, 18.3. If the reaction with KO-*t*-Bu was done at −23 °C, a 3:1 mixture of 1,3,5-heptatrienes and 1,3,6-heptatrienes was found; at 25 °C KO-*t*-Bu converted the 1,3,6-heptatrienes into 1,3,5-heptatrienes.

1-Vinyl-1,3-cyclohexadiene and 2-Vinyl-1,3-cyclohexadiene.[28] 3-Methylenecyclohexene was treated with 1 equiv of **2** as in procedure A to give a 1:1 adduct (96%) as an oil: ^1H NMR δ 6.23 (d, 1 H), 5.08–4.75 (m, 1 H), 4.46 (br s, 2 H), 3.91 (d, 2 H), 2.62–1.59 (m, 6 H). Procedure C (25% excess of Et_3N) gave a 5:1 mixture of (*Z*)- and (*E*)-3-[[(bromomethyl)sulfonyl]methylene]cyclohexene (92%) as an oil: GC t_R 9.18 and 8.67, respectively (225 °C). Crystallization (CCl_4) gave the *Z* isomer as colorless crystals: mp 47–47.5 °C; IR (KBr) 2950 (m), 1620 (s), 1580 (s), 1310 (s), 1210 (m), 1140 (s), 1100 (s), 890 (m), 850 cm^{-1} (m); ^1H NMR δ 7.24 (d, J = 10 Hz, 1 H), 6.62–6.21 (m, 1 H), 5.90 (br s, 1 H), 4.46 (s, 2 H), 2.74–2.09 (m, 4 H), 2.09–1.58 (m, 2 H); ^{13}C NMR δ 155.2, 142.2, 122.3, 116.2, 44.8, 32.4, 25.9, 22.0.

Anal. Calcd for $C_8H_{11}SO_2Br$: C, 38.26; H, 4.42. Found: C, 37.63; H, 4.35.

Preparatory HPLC (85% hexane, 15% THF) of the crude mixture gave the *E* isomer. Procedure E on the *E*,*Z* mixture gave after flash distillation a 3:1 mixture of 2-vinyl-1,3-cyclohexadiene and 1-vinyl-1,3-cyclohexadiene (53%), GC t_R 9.87 and 10.06 (50 °C), respectively, identified by comparison with a known mixture[28] of the two isomers. GC experiments established that (*E*)-3-[[(bromomethyl)sulfonyl]-methylene]cyclohexene gave *only* 2-vinyl-1,3-cyclohexatriene upon treatment with KO-*t*-Bu while the *Z* isomer gave a mixture of the title trienes.

1,3,5,7,9,11-Dodecahexaene.[29a] The adduct of 1,3,7,9-decatetraene (0.62 g, 4.6 mmol) and 2 equiv of **2** (2.22 g, 9.3 mmol) was prepared in nearly quantitative yield by procedure A as an oil: ^1H NMR δ 6.40–5.49 (m, 4 H), 4.78–4.24 (m, 6 H), 4.01 (d, 4 H), 2.38–1.80 (m, 4 H). Treatment of this adduct (1,10-bis[(bromomethyl)sulfonyl]-4,7-dibromo-2,8-decadiene; 2.8 g, 4.6 mmol) with Et_3N (16 mmol, 1.64 g) as in procedure C gave 1,10-bis[(bromomethyl)sulfonyl]-1,3,7,9-decatetraene (1.83 g, 92%; mixture of isomers): ^1H NMR δ 7.72–6.93 (m, 2 H), 6.86–6.11 (m, 6 H), 4.39 (s, 4 H), 2.74–2.13 (m, 4 H). This latter product (3.2 g, 7.1 mmol) in THF (143 mL)–*t*-BuOH (50 mL) and a solution of KO-*t*-Bu (6.4 g, 57 mmol) in THF (143 mL) and *t*-BuOH (50 mL) were separately added simultaneously via syringe drive during 7 h to *t*-BuOH (1100 mL) in a three-necked flask in an argon atmosphere and in the dark. The resulting dark red solution was diluted with water (1200 mL) and extracted with pentane (4 × 100 mL), and the pentane extract was washed with water (15 × 100 mL), dried ($MgSO_4$), and filtered to give a solution of a mixture of isomers of 1,3,5,7,9,11-dodecahexaene with a UV spectrum identical with that reported[29a] (λ_{max} 308, 324, 341, 362 nm) in 25% yield (calculated on the basis of the reported[29a] extinction coefficient (138 000) for the 362-nm maximum): IR (in $CDCl_3$) 3050 (m), 1610 (m), 1270 (m), 1090 (m), 1010 (s), 860 cm^{-1} (m); ^1H NMR δ 7.00–5.69 (m, 10 H), 5.45–4.80 (m, 4 H); ^{13}C NMR δ 137.1, 135.1, 134.5, 134.2, 133.8, 133.4, 130.2, 130.1, 129.6, 128.8, 128.5, 128.2, 124.8, 118.2, 118.0, 117.7, 117.5; MS, *m*/*e* 158 (M^+, 17%), 130, 129, 117, 115, 91, 86, 84, 80, 79, 78 (100%), 77.

(40) Ueno, Y.; Sano, H.; Aoki, S.; Okawara, M. *Tetrahedron Lett.* **1981**, *22*, 2675–2678.

(41) Dauben, W. G.; Poulter, C. D.; Suter, C. *J. Am. Chem. Soc.* **1970**, *92*, 7408–7412. Short, M. R.; *J. Org. Chem.* **1972**, *37*, 2201–2202.

(42) Everlardus, R. H.; Peterse, A.; Vermeer, P.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 90–91.

1,3,5,7-Octatetraene.[29c] A mixture of 1,5-hexadiene (1.64 g, 20 mmol) and **2** (14.28 g, 60 mmol) in acetone (6 mL) was irradiated at −20 °C for 1 h. Acetone was then evaporated and the resulting semisolid was washed with CH_2Cl_2. Removal of traces of solvent gave a colorless solid insoluble in most solvents (7.2 g, 65%), ^{1}H NMR (acetone-d_6) δ 4.87 (s, 4 H), 4.77–4.39 (m, 2 H), 4.01 (dd, 4 H), 2.54–2.16 (m, 4 H). With a solid addition funnel, this latter compound (1,6-bis[(bromomethyl)-sulfonyl]-2,5-dibromohexane; 4.3 g, 7.7 mmol) was added slowly under argon to a solution of KO-*t*-Bu (9.1 g, 80 mmol) in *t*-BuOH (170 mL) and THF (50 mL). The mixture was then stirred at 45 °C for 2 h, diluted with water, and extracted with pentane (3 × 50 mL) and the pentane extract washed with water (7 × 25 mL), dried, filtered, and concentrated in vacuo to give a semisolid. Flash distillation gave a 4:1 mixture (by GC; >90% pure) of 1,3,5,7-octatetraene and 1,3,5-cyclo-octatriene as a colorless solid (0.15 g, 18%): UV λ_{max} 302, 287, 276, 265 nm; IR 2975 (s), 1830 (m), 1630 (m), 1430 (m), 1410 (m), 1250 (m), 1020 (s), 860 cm^{-1} (s); ^{1}H NMR δ 7.13–5.56 (m, 6 H), 5.45–4.80 (m, 4 H); ^{13}C NMR δ 137.0, 133.9, 133.0, 117.5 (major peaks). A catalytic amount of iodine was added to a sample of the mixture of 1,3,5,7-octatetraene and 1,3,5-cyclooctatriene in $CDCl_3$, and the solution was exposed to a sunlamp for 1 h. The product was then washed with sodium thiosulfate solution and water, dried, and filtered to give a solution of 1,3,5-cyclooctatriene in deuteriochloroform (>90% pure by GC): ^{1}H NMR δ 6.09–5.57 (m, 6 H), 2.54–2.23 (br s, 4 H); ^{13}C NMR δ 135.5, 126.7, 126.0, 28.0; UV λ_{max} 263 nm.

1,3,5,7-Nonatetraene. Method 1. Following procedure A, reaction of **2** (2.1 equiv) with 1,6-heptadiene gave a bis-adduct, 1,7-bis[(bromomethyl)sulfonyl]-2,6-dibromoheptane (96%) as an oil: ^{1}H NMR δ 4.53 (dd, 4 H), 4.42–4.12 (m, 2 H), 3.81 (dd, 4 H), 2.30–1.65 (m, 6 H). The latter compound was treated with KO-*t*-Bu (10 equiv) in *t*-BuOH–THF as above (15 h addition) to give after flash distillation 1,3,5,7-nonatetraene as a mixture of isomers (24%): IR 3040 (m), 1620 (m), 1440 (m), 1010 (m), 990 (s), 910 (s), 810 (w), 660 cm^{-1} (m); UV λ_{max} 306, 292, 280, 270 nm; ^{1}H NMR δ 7.01–5.57 (m, 7 H), 5.40–4.89 (m, 2 H), 1.77 (d, 3 H); ^{13}C NMR δ 141.2, 137.2, 134.4, 133.8, 133.6, 133.1, 132.3, 131.9, 130.9., 130.3, 129.6, 129.2, 127.8, 127.4, 125.5, 118.0, 117.7, 116.6, 18.7, 18.4.

1,3,5,7-Nonatetraene. Method 2. Addition of 2.2 equiv of α-bromoethanesulfonyl bromide (**3**) to 1,4-pentadiene as in procedure A gave 1,5-bis[(α-bromoethyl)sulfonyl]-2,4-dibromopentane as a viscous oil, (91%): ^{1}H NMR 5.6 (q, 2 H), 4.8 (m, 2 H), 3.7 (m, 2 H), 2.7 (t, 2 H), 2.3 (d, 4 H), 2.0 (d, 6 H). Procedure C on the latter product with 3.5 equiv of Et_3N gave 1,5-bis[(α-bromoethyl)sulfonyl]-1,4-pentadiene (66%) as a mixture of isomers. Reaction of the latter compound with 5 equiv of KO-*t*-Bu as above gave a pentane solution with a UV spectrum identical with that described in method 1 above. The yield estimated by UV analysis was 14%.

1,3,5,7,9-Decapentaene.[29a] 1,3,7-Octatriene was prepared in 81% distilled yield via addition of a 3-fold excess of allylmagnesium bromide to 2,4-pentadienyl bromide[27] in ether in the presence of 3 mol % cuprous bromide. The 1:2 adduct of 1,3,7-octatriene (1.08 g, 10 mmol) and **2** (4.76 g, 20 mmol) was prepared in nearly quantitative yield by procedure A; ^{1}H NMR δ 6.27–5.65 (m, 2 H), 4.43 (d, 2 H), 4.35 (s, 4 H), 4.01 (d, 2 H), 2.72 (m, 2 H), 1.87–2.54 (m, 4 H). Procedure A on the latter product (1.1 g; 2.6 equiv of Et_3N) gave 1,10-bis[(bromomethyl)-sulfonyl]-1,3,7-octatriene (0.66 g, 83%) as a brown solid (mixture of isomers), ^{1}H NMR δ 6.69–7.56 (m, 2 H), 5.86–6.69 (m, 4 H), 4.42 (s, 4 H), 2.16–2.78 (m, 4 H). To a solution of the latter compound (0.01 g) in THF (10 mL) was added dropwise a solution of KO-*t*-Bu (6 equiv) in *t*-BuOK (32 mL) and THF (4 mL). The solution was stirred at 0 °C for 1 h and at 25 °C for 1 h, diluted with water (20 mL), and extracted with hexane; the hexane layer was washed with water (6 times), dried ($MgSO_4$), and diluted with hexane to 100 mL. The solution showed a UV spectrum identical with that reported for 1,3,5,7,9-decapentaene (λ_{max} 333, 317, 302, 289 nm); the yield calculated on the basis of the reported[29a] extinction coefficient of 121 000 at 333 nm was 18%.

Addition of 2 to Alkynes and Reaction of the Adducts with Base: 2-Ethylhex-1-en-3-yne. General Procedure F. A mixture of 3-hexyne (1.6 g, 0.02 mol) and **2** (2.38 g, 0.01 mol) in CH_2Cl_2 (3 mL) was irradiated at −20 °C as above for 2 h. A small amount of solid K_2CO_3 was added and then removed by filtration. The solution was concentrated in vacuo to give 3-bromo-4-[(bromomethyl)sulfonyl]-hex-3-ene (2.73 g, 85% yield) as a solid (from EtOH): mp 96–97 °C; IR 2970 (m), 1610 (s), 1320 (s), 1160 (s), 1130 (s), 750 cm^{-1} (m); ^{1}H NMR δ 4.42 (s, 2 H), 3.12 (q, 2 H), 2.69 (q, 2 H), 1.51–0.93 (m, 6 H); ^{13}C NMR δ 151.1, 137.2, 43.6, 33.8, 29.2, 14.2, 12.5.

Anal. Calcd for $C_7H_{12}Br_2O_2S$: C, 26.27; H, 3.78. Found: C, 26.45; H, 3.88.

The latter compound (3.2 g, 0.01 mol) was dissolved in 15 mL of 1:2 THF/*t*-BuOH and added dropwise to an ice cold solution of KO-*t*-Bu (4.5 g, 0.04 mol) in 66 mL of 1:10 THF/*t*-BuOH. The reaction mixture was diluted with water and extracted with pentane. The combined organic layer was washed with water, dried ($MgSO_4$), and filtered and the solvent removed by distillation to give an oil. Flash distillation gave 0.43 g (46% yield) of 2-ethylhex-1-en-3-yne: IR 2250, 1620, 1470, 900 cm^{-1}; ^{1}H NMR δ 5.25–4.94 (m, 2 H), 2.37–1.75 (m, 5 H), 1.37–0.72 (m, 3 H); ^{13}C NMR δ 133.9, 118.5, 85.4, 30.7, 12.9, 4.1.

Reaction of 2 with Propyne. A mixture of propyne (3.2 g, 0.08 mol) and **2** (4.76, 0.02 mol) in CH_2Cl_2 was irradiated at −23 °C for 1 h. The solution then was concentrated in vacuo to give an oil which was dissolved in CH_2Cl_2, washed with $NaHSO_3$ solution (2×), water, and brine, and dried ($MgSO_4$). Concentration and flash chromatography (silica gel, CH_2Cl_2) gave 2-bromopropenyl bromomethyl sulfone (1.39 g, 25%) and 4-bromo-2-methyl-1,3-pentadienyl bromomethyl sulfone (0.53 g, 8%). The former compound was a colorless solid: mp 60–61 °C; IR 3030 (m), 2945 (m), 1618 (s), 1369 (vs), 1328 (vs), 1140 (vs), 1160 cm^{-1} (vs); ^{1}H NMR δ 6.76 (q, 2 H), 4.41 (s, 2 H), 2.85 (d J = 2 Hz, 3 H); ^{13}C NMR δ 146.3, 126.4, 44.1, 26.0.

Anal. Calcd for $C_4H_6Br_2O_2S$: C, 17.28; H, 2.18. Found: 17.45; H, 2.21.

The second compound was a colorless glass-wool-like solid: mp 103–106 °C; ^{1}H NMR δ 7.36 (q, 1 H), 6.67 (q, 1 H), 4.45 (s, 2 H), 2.81 (d, 3 H, J = 2 Hz), 2.54 (d, 3 H, J = 2 Hz); ^{13}C NMR δ 155.6, 146.8, 130.8, 127.1, 43.4, 25.8, 12.8.

Addition of 2 to Silyl Enol Ethers and Conversion of Adducts to α-Alkylidene Ketones: 2-Methylenecycloheptanone (23).[19] **General Procedure G.** A solution of 1-(trimethylsiloxy)cycloheptene[43a] (**21**) (1.84 g) and **2** (3.33 g) in 4 mL of ethylene oxide was irradiated at −15 °C for 1.5 h. The reaction mixture was diluted with 10 mL of CH_2Cl_2, a small quantity of K_2CO_3 was added, and the solution was filtered, concentrated in vacuo, and subjected to high vacuum for 1 h giving 2.1 g (69% yield) of 2-[(bromomethyl)sulfonyl]cycloheptanone (**22**) which was distilled giving a thick pale yellow oil: bp 152–154 °C (0.035 mm); IR 1700 (vs), 1460 (s), 1320 (vs), 1145 (vs), 840 cm^{-1}; ^{1}H NMR δ 4.63 (AB q, J = 10.5, 2 Hz, 2 H), 4.32 (dd, 1 H), 2.88–1.03 (br m, 10 H). The latter compound (0.54 g) was dissolved in 10 mL of CH_2Cl_2 and cooled to −78 °C at which temperature it was treated dropwise with stirring with a solution of DBN (0.62 g) in 10 mL of CH_2Cl_2. The reaction mixture was allowed to warm slowly to room temperature and then was stirred for 0.5 h. The reaction mixture was washed with dilute HCl (2 × 25 mL) and water (25 mL). The organic layer was separated and dried and the solvent removed in vacuo giving an oil. Distillation gave 0.19 g of 2-methylenecycloheptanone (**23**; 77% yield) as a colorless oil: IR 1690 (vs), 1610 (s), 1005 (m), 940 cm^{-1} (s); ^{1}H NMR δ 5.91 (d, 1 H), 5.22 (m, 1 H), 2.54 (br s, 4 H), 1.75 (br s, 6 H); ^{13}C NMR δ 203.6, 148.4, 122.5, 43.5, 33.9, 31.3, 30.6, 25.4.

2-[(Bromomethyl)sulfonyl]-3-pentanone. Following procedure G, **2** was added to 3-(trimethylsiloxy)-2-pentene giving 2-bromomethanesulfonyl-3-pentanone, an oil (81%) which solidified. Recrystallization (CCl_4) gave colorless crystals, mp 57–58 °C.

[(Iodomethyl)sulfonyl]acetophenone. As in procedure G, **4** was added to 1-(trimethylsiloxy)-1-phenylethylene giving the title compound as a solid (100%). Recrystallization (CH_2Cl_2–hexane) gave light yellow crystals, mp 99–100 °C.

(43) (a) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336. (b) Hauser, C. F.; Brooks, T. W.; Miles, M. L.; Raymond, M. A.; Butler, G. B. *J. Org. Chem.* **1963**, *28*, 372–379.
(44) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, 191–194.
(45) Halazy, S.; Krief, A. *Tetrahedron Lett.* **1980**, *21*, 1997–2000.
(46) Nunomoto, S.; Kawakami, Y.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2831–2832.
(47) Frey, H. M.; Solly, R. R. *J. Chem. Soc. A* **1969**, 733–735.
(48) Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898–3903.
(49) Markgraf, J. H.; Greeno, E. W.; Miller, M. D.; Zaks, W. J. *Tetrahedron Lett.* **1983**, *24*, 241–244.
(50) Salomon, R. G.; Sinha, A.; Salomon, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 520–526.
(51) Van Straten, J. W.; Van Norden, J. J.; Van Schauk, T. A. M.; Franke, G. T.; De Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 105–106.
(52) Corey, E. J.; Cane, D. E. *J. Org. Chem.* **1969**, *34*, 3053–3057.
(53) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1983**, *24*, 1247–1250.
(54) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036–2045.
(55) Dare, D. L.; Entwistle, I. D.; Johnstone, R. A. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1130–1134.
(56) Vig, O. P.; Vig, A. K.; Kumar, S. D. *Indian J. Chem.* **1975**, *13*, 1244–1246.
(57) Alder, K.; Brachel, H. V. *Justus Liebigs Ann. Chem.* **1957**, *608*, 195–215.
(58) Hubert, A. J. *Chem. Ind. (London)* **1968**, 975–976.
(59) Anzilotti, W. F.; Vogt, R. R. *J. Am. Chem. Soc.* **1939**, *61*, 572–573.

Preparation of 1,3-Oxathiole 3,3-Dioxides: 4-Methyl-5-ethyl-1,3-oxathiole 3,3-Dioxide. General Procedure H. 2-[(Chloromethyl)sulfonyl]-3-pentanone (0.99 g, 5 mmol) was dissolved in EtOH (25 mL), and a solution of DBN (1.55 g, 13 mmol) in EtOH (10 mL) was added dropwise. The reaction mixture was stirred at 25 °C for 1 h and concentrated and the residue taken up in CH_2Cl_2 and washed with dilute HCl (50 mL) and water (50 mL), and the organic layer was separated, dried ($MgSO_4$), and concentrated to give an oil. Kugelrohr distillation (100 °C, 0.1 mm) gave a colorless liquid (0.44 g, 54%): IR 1670 (s), 1440 (m), 1300 (vs), 1155 (vs), 1070 cm^{-1}; ^1H NMR δ 4.83 (s, 2 H), 2.37 (q, 2 H), 1.93 (s, 3 H), 1.15 (t, 3 H); ^{13}C NMR δ 163.2, 106.8, 80.1, 21.9, 10.2, 4.2.

8,10-Oxathiabicyclo[5.3.0]dec-1(7)-ene 10,10-Dioxide (24). As in procedure H, 2-[(chloromethyl)sulfonyl]cycloheptanone gave **24** as a solid (81%) which gave colorless crystals, mp 55–56 °C, from petroleum ether: IR 1660 (s), 1440 (m), 1290 (vs), 1130 (vs), 810 (m), 790 cm^{-1} (m); ^1H NMR δ 4.85 (s, 2 H), 2.44 (br s, 4 H), 1.77 (br s, 6 H); ^{13}C NMR δ 165.58 112.7, 80.7, 31.5, 29.9, 27.4, 24.4, 18.8.

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.04; H, 6.43; S, 17.03. Found: C, 51.11; H, 6.36; S, 17.31.

9-Methyl-8,10-oxathiabicyclo[5.3.0]dec-1(7)-ene 10,10-Dioxide (28). A solution of 8,10-oxathiabicyclo[5.3.0]dec-1(7)-ene 10,10-dioxide (0.75 g, 4 mmol) in dry THF (20 mL) was placed in a dry three-necked flask under argon and then treated at −78 °C with *n*-butyllithium (4 mmol). After 15 min a solution of methyl iodide (0.57 g, 4 mmol) in dry THF (5 mL) was added. The reaction mixture was warmed to 25 °C, water (50 mL) was added, the product was extracted with CH_2Cl_2 (50 mL), and the organic layer was separated, dried ($MgSO_4$), and concentrated to give an oil. Kugelrohr distillation (0.025 mm) gave a colorless liquid (0.6 g, 74%).

(E,Z)-2-Ethylidenecycloheptanone and 28. As in procedure G, **3** was added to 1-(trimethylsiloxy)cycloheptene giving 2-[(1-bromoethyl)sulfonyl]cycloheptanone as a solid (28%), mp 98 °C (CH_2Cl_2–pentane). Treatment of this product with DBN in CH_2Cl_2 at −78 °C according to procedure G gave an oil (54% yield) which by GC and NMR analysis was found to consist of 48% (*E*)- and 4% (*Z*)-2-ethylidenecycloheptanone (GC t_R 7.35 and 5.78 min at 120 °C) and 3% of **28** (identical with authentic material as prepared above); IR 2950 (s), 1700 (s), 1680 cm^{-1} (s); ^1H NMR δ 6.40 (q, J = 2.5 Hz, *E* isomer), 5.63 (q, J = 2.5 Hz, *Z* isomer), 2.50 (t, 2 H), 1.70 (m, 13 H).

Preparation of 1-Isopropoxy-2,4-pentadiene from 1,3-Butadiene. A solution of 1,3-butadiene (6.4 g, 0.12 mol) in CH_2Cl_2 (6 mL) at −20 °C was mixed with a solution of **2** (23.8 g, 0.1 mol) in CH_2Cl_2 (8 mL). The reaction mixture was irradiated for 1 h and worked up as in procedure A to give 4-bromo-2-butenyl bromomethyl sulfone (27.0 g, 93%), ^1H NMR δ 5.96 (2 H, m), 4.40 (2 H, s), 3.94 (4 H, d). Application of procedure C to the latter sulfone (27.0 g, 0.092 mol) using 1.2 equiv of Et_3N gave 1,3-butadienyl bromomethyl sulfone (13 g, 95%), ^1H NMR δ 7.53–5.43 (5 H, m), 4.50 (2 H, s). A solution of this latter compound (4.22 g, 0.02 mol) in dry *i*-PrOH (25 mL) was added dropwise to a solution prepared by dissolving sodium (1.38 g, 0.06 mol) in dry *i*-PrOH (50 mL). The mixture was stirred for 1 h, diluted with water (100 mL), and extracted with pentane (2 × 30 mL). The combined pentane extracts were washed with water (3 × 100 mL), dried ($MgSO_4$), and concentrated, and the residue was purified by trap-to-trap distillation giving (*E*) and (*Z*)-1-isopropoxy-2,4-pentadiene (1.4 g, 56%; 49% overall yield from 1,3-butadiene) in a 3:1 ratio (by GC) as a colorless oil: ^1H NMR δ 6.68–4.78 (m, 5 H), 3.99 (d, 2 H), 3.6 (m, 1 H), 1.16 (d, 6 H); ^{13}C NMR δ 138.6, 136.5, 132.5, 131.0, 117.0, 115.7, 79.0, 71.0, 68.6, 68.2, 22.4, 22.2.

Preparation of 2-[[(Bromomethyl)sulfonyl]methylene]adamantane (39) and Reaction with KO-*t*-Bu. 2-Methyleneadamantane was prepared in 66% yield from 2-adamantanone by procedure B. Addition of **2** to 2-methyleneadamantane via procedure A gave 2-bromo-2-[[(bromomethyl)sulfonyl]methyl]adamantane in nearly quantitative yield. Procedure C gave with this latter compound (3.85 g, 0.01 mol; refluxing $CHCl_3$) **39** as a colorless solid (2.66 g, 88%): ^1H NMR δ 5.96 (s, 1 H), 4.31 (s, 2 H), 3.72 (br s, 1 H), 2.47 (br s, 1 H), 1.95 (br s, 12 H); ^{13}C NMR δ 175.7, 113.6, 44.6, 41.5, 40.0, 39.6, 39.2, 36.3, 33.0, 27.4.

Sulfone **39** (1.21 g, 4 mmol) was dissolved in *t*-BuOH–THF (40 mL/8 mL), cooled in ice, and treated with KO-*t*-Bu (1.4 g, 12 mmol). The reaction mixture was stirred for 3 h at 25 °C, diluted with water (50 mL), and extracted with pentane (2 × 25 mL). The pentane layer was washed with water (2 × 25 mL), dried, and concentrated giving a solid (0.62 g). Preparatory TLC (CH_2Cl_2) gave equal amounts of three components, namely, unreacted **39**, and compounds identified as 2-[[(dibromomethyl)sulfonyl]methylene]adamantane (**42**), and 2-[(methylsulfonyl)methylene]adamantane (**41**). Compound **42** (0.2 g, 13%), after recrystallization from hexane, gave colorless crystals: mp 137–138 °C; IR 1615 (s), 1315 (s), 1140 (vs), 815 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.07 (s, 2 H), 3.8 (br s, 1 H), 2.55 (br s, 1 H), 1.95 (br s, 12 H); ^1H NMR (C_6D_6) δ 5.87 (s, 1 H), 5.64 (s, 1 H), 3.91 (br s, 1 H), 1.96 (br s, 1 H), 1.58 (br s, 12 H); ^{13}C NMR δ 179.2, 109.6, 51.2, 42.1, 40.1 (2 C), 39.4 (2 C), 36.4, 33.3, 27.5 (2 C).

Anal. Calcd for $C_{12}H_{16}Br_2O_2S$: C, 37.52; H, 4.20. Found: C, 37.60; H, 4.23. MW calcd 384, found (cryoscopically) 367.

Compound **41**: IR 1620 (m), 1290 (vs), 1130 cm^{-1} (vs); ^1H NMR δ 6.00 (1 H, s), 3.69 (br s, 1 H), 2.90 (s, 3 H), 2.41 (br s, 1 H), 1.93 (br s, 12 H); ^{13}C NMR δ 170.5, 118.7, 44.5, 40.8, 39.8 (2 C), 36.4, 32.8, 27.4 (2 C).

Acknowledgment. We thank Professor Jon Zubieta for assistance in the determination of the X-ray structures and gratefully acknowledge support from the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Societe Nationale Elf Aquitaine (EB), and the National Institutes of Health (K.G., J. H.). The SUNY-Albany 300-MHz NMR facility is funded in part by a grant from the National Science Foundation.

Supplementary Material Available: Analytical techniques and physical data for identifying products and intermediates and tables of X-ray crystal structure data for (*E*)-1-[[(bromomethyl)sulfonyl]methylene]-3-methylcyclohexane, 7,9-oxathiabicyclo[4.3.0]non-1(6)-ene 9,9-dioxide, and 2-[[(dibromomethyl)sulfonyl]methylene]adamantane (25 pages). Ordering information is given on any current masthead page.