Acknowledgment is made to the Indiana University Office of Research and Graduate Development, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Stauffer Chemical Co. for support of this research. NATO Grant 070-82 and the consultation of David Hoffman, Jan Teuben, and Reinder Bouma were of crucial importance to this work. We thank Scott Horn for skilled technical assistance. The high-field NMR spectrometer employed was purchased under NSF Grant CHE-81-05004.

Registry No. $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$, 86690-01-9; $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$, 86690-03-1; $VCl_2(THF)_2$, 21729-44-2.

Supplementary Material Available: Table of fractional atomic coordinates, thermal parameters, and structure factors for $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$ (18 pages). Ordering information is given on any current masthead page.

α-Haloalkanesulfonyl Bromides in Organic Synthesis. 1. Formation and Base-Induced Reactions of α,β-Unsaturated Halomethyl Sulfones[1a,b]

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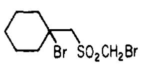
The Ramberg–Bäcklund reaction is a synthetically useful process in which α-haloalkyl sulfones afford olefins upon treatment with base (eq 1).[2] We report a novel variant of the Ramberg–Bäcklund reaction in which α,β-unsaturated α′-bromoalkyl sulfones **1** afford 1,3-dienes on base treatment (eq 2). This communication describes a general synthesis of previously unknown compounds of type **1**, using the useful reagent $BrCH_2SO_2Br$ (**2**, bromomethanesulfonyl bromide), as well as unusual stereochemical features of the reaction of **1** with base. The accompanying communication[1c] illustrates the broad utility of this reaction.

$$\mathrm{RCH_2SO_2CH_2X \xrightarrow{base} R\overset{-}{C}HSO_2CH_2X \xrightarrow{-X^-} R\overline{CHSO_2C}H_2 \rightarrow RCH{=}CH_2 + SO_2} \quad (1)$$

$$\underset{\mathbf{1}}{\mathrm{RCH_2CH{=}CHSO_2CH_2Br}} \xrightarrow{\text{base}} \mathrm{R\overline{C}H\overset{-}{\overline{C}}H\overline{C}HSO_2CH_2Br \xrightarrow{-Br^-} RCH{=}CH\overline{CHSO_2C}H_2 \rightarrow RCH{=}CHCH{=}CH_2 + SO_2} \quad (2)$$

Compounds **1** are formed in excellent yield in a two-step process involving light-catalyzed addition of **2** to olefins at −20 °C followed by treatment of the adduct with triethylamine (eq 3). Reagent **2** may be conveniently prepared in 46% yield by bromination of an aqueous slurry of 1,3,5-trithiane.[3,4] Olefin–**2** adducts are formed in nearly quantitative yields by a process that most likely involves a free radical chain reaction analogous to free radical additions of other sulfonyl halides.[2,6,7] We find the light-catalyzed process to be cleaner and more easily controlled than thermal addition of **2**. A wide range of olefins react with **2**. With mono-, 1,1-di-, and 1,1,2-trisubstituted olefins the addition is regiospecific, consistent with formation of the more stabilized radical intermediate (see products **3**, R = n-C_5H_{11}, **4**, and **5**, from 1-octene, methylenecyclohexane, and 2-methyl-2-butene, respectively[8]). Even unsymmetrical 1,2-disubstituted olefins show a high degree of regioselectivity in the addition, e.g., as demonstrated by the formation of **6** as the major (79%) adduct from addition of **2** to 2-octene. The facile S–Br bond homolysis of **2** makes it superior to sulfonyl chlorides such as $BrCH_2SO_2Cl$, which showed only 10% addition to 1-octene after irradiation for 1 h.[7,10]

$$\mathrm{RCH_2CH{=}CH_2 + \underset{\mathbf{2}}{BrCH_2SO_2Br} \xrightarrow[30\ min,\ -20\ ^\circ C]{h\nu,\ CH_2Cl_2} \underset{\mathbf{3}}{RCH_2CHBrCH_2SO_2CH_2Br} \xrightarrow{Et_3N} \underset{\mathbf{1}}{RCH_2CH{=}CHSO_2CH_2Br}} \quad (3)$$



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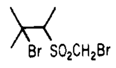

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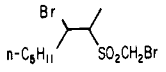

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Addition of **2** to olefins and subsequent reaction of the adducts with base is nicely illustrated with 1-octene. Thus, 1-octene, diluted with an equal volume of CH_2Cl_2 and irradiated in a Pyrex tube for 30 min at −20 °C after addition of an equivalent amount of **2**, afforded a single 1:1 olefin–**2** adduct in 94% yield. Direct treatment of this crude adduct with Et_3N in CH_2Cl_2 at 0 °C for 15 min gave in 97% yield a 10:1 mixture of (E)- and (Z)-bromomethyl 1-octenyl sulfones, **1E** and **1Z** (R = n-C_5H_{11}), respectively.[8,9] Crystallization readily afforded a pure sample of **1E** while isomer **1Z** could be isolated from the mother liquor by preparative HPLC. Treatment of **1E** with 2.5 equiv of t-BuOK in 7:3 *tert*-butyl alcohol/THF at −20 °C for 1 h gave in 59% distilled yield a 83:17 mixture of (Z)- and (E)-1,3-nonadiene. In a similar manner **1Z** gave in 61% distilled yield a 6:94 mixture of (Z)- and (E)-1,3-nonadiene.

The remarkable stereoselectivity of the reaction of **1E** with base, which may be termed a "*vinylogous Ramberg–Bäcklund reaction*", is attributed to a "syn effect"[11] involving interaction between the developing negative charge at the α-position and the CH_2 group at the δ-position favoring transition state **1E′** over **1E″** for deprotonation (eq 4 and 5). Our observation that (E)-1-octenyl phenyl sulfone undergoes base-catalyzed isomerization to (Z)-2-octenyl phenyl sulfone[8,12] provides support for this model, if it

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[1] (a) The material covered in this communication is the subject of a U.S. Patent Application filed by the Research Foundation of the State University of New York. (b) Presented in part at the International Symposium on Heteroatoms for Organic Synthesis, Montreal, August 16, 1983 and at the 186th ACS National Meeting, Washington, D.C., September 1, 1983. (c) Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *J. Am. Chem. Soc.*, following communication in this issue.

[2] 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.

[3] Kostsova, A. G. *Tr. Voronezh. Gos. Univ.* **1935**, *8*, 92–117; *Chem. Abstr.* **1938**, *32*, 6618; a 15% yield of **2** is claimed.

[4] Bromine (9.5 equiv) is added dropwise to a vigorously stirred aqueous slurry of 1,3,5-trithiane at or below 35 °C. The product is extracted into CH_2Cl_2, and the organic phase is washed with ice-cold 5% $NaHSO_3$ and water, dried, concentrated, and distilled giving **2** as a pale yellow liquid: $bp_{0.025mm}$ 62 °C, NMR δ 4.92 (s); IR 1362 (vs), 1205 (s), 1160 (vs), 1105 (m), 830 (s), 680 (s) cm^{-1}. Compound **2** is stable at 25 °C for at least 2 weeks. An alternative synthesis of **2** is given in ref 5.

[5] Block, E.; Aslam, M. *Tetrahedron Lett.* **1982**, *23*, 4203–4206.

[6] Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727–1732. Also cf.: Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155–4158.

[7] Goldwhite, H.; Gibson, M. S.; Harris, C. *Tetrahedron* **1964**, *20*, 1613–1624.

[8] All new compounds have been fully characterized by spectral means.

[9] 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% **1E**.

[10] (a) 1-Octene fails to add $ClCH_2SO_2Cl$ on heating in the presence of Cu^I: Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962–4971. (b) t-BuOOH/$ZnCl_2$-catalyzed addition of $ClCH_2SO_2Br$ to 2,5-dihydrofuran and Et_3N treatment gives 3-(chloromethylsulfonyl)-2,5-dihydrofuran in 26% yield: Böll, W. *Liebigs Ann. Chem.* **1979**, 1665–1674.

[11] (a) Block, E.; Penn, R. E.; Bazzi, A. A.; Cremer, D. *Tetrahedron Lett.* **1981**, *22*, 29–32. (b) 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.

[12] Product stereochemistry in the base-induced isomerization of α,β-unsaturated sulfones to β,γ-unsaturated sulfones[13] has not been previously reported. Exclusive formation of (Z)-2-octenyl tosyl sulfone when Bu_2CuLi adds to (E)-1,3-butadienyl tosyl sulfone[14] is consistent with a syn effect in the anionic intermediate.

[13] O'Connor, D. E.; Lyness, W. I. *J. Am. Chem. Soc.* **1964**, *86*, 3840–3846. Broaddus, C. D. *Ibid.* **1968**, *90*, 5504–5511.

[14] Näf, F.; Decorzant, R.; Escher, S. D. *Tetrahedron Lett.* **1982**, *23*, 5043–5046.

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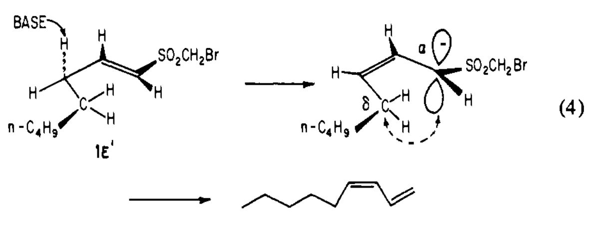

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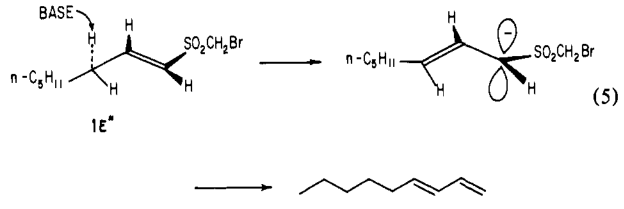
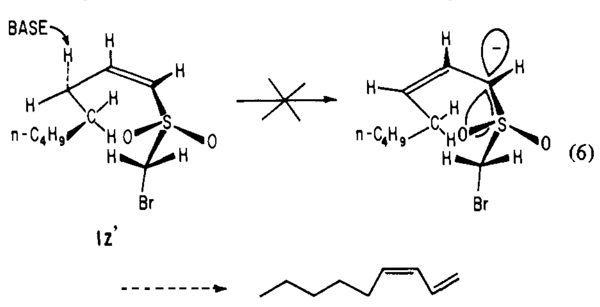


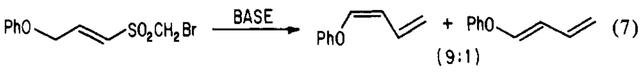
(5)

is assumed that the isomerization is kinetically controlled. In **1Z** the possibility of a stabilizing syn interaction between the α- and δ-position is precluded for steric reasons if **1Z'**, eq 6, is assumed



(6)

to be the transition state required for formation of *Z* diene. The syn effect is still seen with the replacement of the δ-CH_2 group in **1E** by oxygen[15] but not by a phenyl group (eq 7 and 8). On



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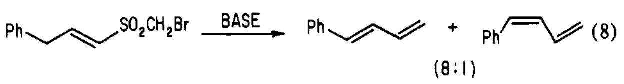
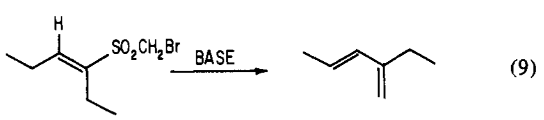


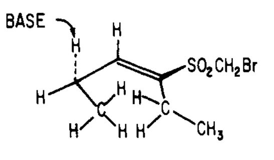
(8)

the other hand, replacement of the α-hydrogen in (*E*)-1-alkenyl bromomethyl sulfones by an alkyl group (see eq 9) results in



(9)

exclusive formation of the *E* diene upon treatment with base; syn interaction is sterically precluded here (see **7**).



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Acknowledgment. We gratefully acknowledge support for this work by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Prof. Shelton Bank and Henry Kuivila for helpful discussions and the Callery Chemical Co. for chemical samples.

Registry No. **1E** (R = n-C_5H_{11}), 86823-63-4; **1E** (R = C_6H_5O), 86823-64-5; **1E** (R = C_6H_5), 86823-65-6; **1Z** (R = n-C_5H_{11}), 86823-66-7; **2**, 54730-18-6; **3** (R = n-C_5H_{11}), 86823-67-8; **4**, 86823-68-9; **5**, 86823-69-0; **6**, 86823-70-3; (*Z*)-1,3-nonadiene, 77192-27-9; (*E*)-1,3-nonadiene, 56700-77-7; (*E*)-1-octenyl phenyl sulfone, 77144-81-1; (*Z*)-2-octenyl phenyl sulfone, 86823-71-4; (*E*)-3-((bromomethyl)sulfonyl)-3-hexene, 86823-72-5; (*Z*)-1-phenoxy-1,3-butadiene, 25752-60-0; (*E*)-1-phenoxy-1,3-butadiene, 52752-61-1; (*E*)-1-phenyl-1,3-butadiene, 16939-57-4; (*Z*)-1-phenyl-1,3-butadiene, 31915-94-3; (*E*)-2-ethyl-1,3-pentadiene, 69530-49-0; 1,3,5-trithiane, 291-21-4; 1-octene, 111-66-0; methylenecylohexane, 1192-37-6; 2-methyl-2-butene, 513-35-9; 2-octene, 111-67-1.

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[15] Compare halogen syn effects: Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1963**, *10*, 622.

α-Haloalkanesulfonyl Bromides in Organic Synthesis. 2. A Useful New 1,3-Diene Synthesis[1]

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The preceding communication[1c] describes a new reaction whereby α,β-unsaturated bromomethyl sulfones are converted into 1,3-dienes with base. Since these sulfones can be made from olefins by addition of readily accessible[1c] bromomethanesulfonyl bromide ($BrCH_2SO_2Br$, **1**) followed by dehydrobromination, the overall process is a three-step transformation of olefins into 1,3-dienes bearing one more carbon atom. The same process can be achieved in two steps if the olefin–**1** adducts are treated with an excess of base (eq 1). We wish to report that these sequential

$$RCH_2CH{=}CH_2 \xrightarrow{1} RCH_2CHBrCH_2SO_2CH_2Br \xrightarrow{\text{base}} RCH_2CH{=}CHSO_2CH_2Br \xrightarrow{\text{base}} RCH{=}CHCH{=}CH_2 \quad (1)$$

reactions work admirably with a wide range of acyclic and cyclic olefins and diolefins, constituting an easy and economical synthesis of dienes, and that this procedure represents a fundamentally new synthetic method for attachment of methylene groups to interior carbon atoms in chains (eq 2) or to ring carbon atoms, providing access to compounds that would be otherwise difficult to prepare.[2]

$$RCH_2CH{=}CHCH_2R \xrightarrow[2.\ \text{base}]{1.\ 1} (E)\text{-}RCH_2C({=}CH_2)CH{=}CHR \ (60\text{–}70\%) \quad (2)$$

Table I illustrates the application of our procedure 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-bismethylenecycloalkanes. In a representative case, (*E*)-7-tetradecene (0.02 mol; Table I, entry 2) in CH_2Cl_2 (1:1 v/v) in a Pyrex tube is chilled to −15 °C[3] and treated with **1** (0.03 mol) in CH_2Cl_2 (1:1 v/v). After 2-h irradiation at −15 °C,[4] Et_3N (0.03 mol) in 90 mL of CH_2Cl_2 was

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[1] (a) The material covered in this communication is the subject of a U.S. Patent Application filed by the Research Foundation of the State University of New York. (b) Presented in part at the International Symposium on Heteroatoms for Organic Synthesis, Montreal, August 16, 1983 and at the 186th ACS National Meeting, Washington, D.C., September 1, 1983. (c) Part 1: Block, E.; Aslam, M. *J. Am. Chem. Soc.*, preceding communication in this issue.

[2] Lengthy syntheses are required for 3-methylenecycloalkenes: 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.

[3] Components should be chilled to −15 °C before mixing since **1** undergoes vigorous, spontaneous, exothermic reactions with particularly reactive olefins. Due caution should be exercised in scaling up reactions of **1**.

[4] A 450-W Hanovia lamp was used. With more reactive olefins irradiation times can be reduced to as short as 15 min and 1 equiv of **1** can be used.