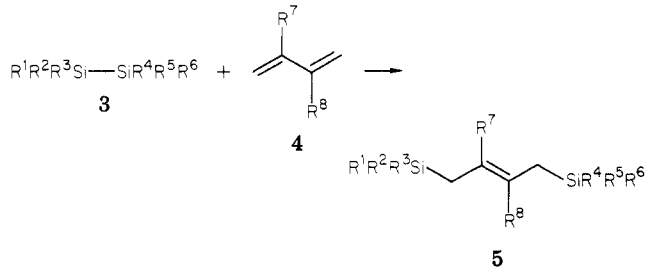
product was established.[17] Formation of dimeric product (i.e., 1,3-butadiene/disilane, 2:1) was less than 3% as revealed by GLC assay of the crude products.

The reaction was applied to various disilanes (**3**) and 1,3-butadienes (**4**) to produce 1,4-disilyl-2-butenes (**5**) (Table I). Salient features of the reaction are summarized as follows.



3 **4** **5**

(1) Reaction conditions are extremely mild (neutral reagent, room temperature, atmospheric pressure) compared with the reductive disilylation[15] or the transition-metal-catalyzed disilylation[16] of 1,3-dienes.

(2) Oligomerization of 1,3-dienes is suppressed compared with the reductive disilylation.[15] These oligomers are easily separated by simple distillation or chromatography.

(3) *E* Isomers of **5** are produced with high selectivity. 1,2-Disilylation products were not produced to any measurable extent.

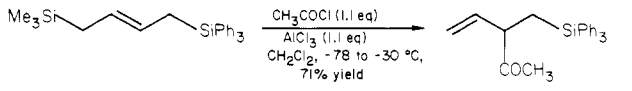
(4) Scrambling of silyl group does not take place. For example, unsymmetric disilanes such as 1,1,1-trimethyl-2,2,2-triphenyldisilane (entries 3 and 8 of Table I) give **5** having a silyl group at each end. In view of the selective attack of fluoride ion to the less hindered silicon atom, the reaction seems to be initiated here by triphenylsilyl anion.

(5) Use of equimolar amounts of 1,3-dienes and disilanes is essential for effective *E* olefin formation. When a 7:1 mole ratio of isoprene and disilane with 7 mol % of TBAF in HMPA was employed for the reaction of run 4 in Table I, the yield of 2:1 product increased only 30% at the slight expense of *E* selectivity. Reaction in concentrated solutions decreased the total yield of products with somewhat increased formation of the 2:1 product.

(6) Aprotic polar solvent such as HMPA or 1,3-dimethyl-2-imidazolidinone (DMI) is particularly essential for the reaction (cf. run 4, Table I; in DMI 47% yield with 89% *E*). Dimethylformamide or THF turned out to be ineffective.

(7) The disilylation is sensitive to the substitution pattern, as 1,3-dienes having substituents on the 1 and/or 4 carbon(s) were recovered unchanged. The olefinic bond remains intact as shown by the reaction of myrcene (entry 9).

The products obtained herein should have wide applicability in view of synthetic reactions exploited by Calas and others.[18] Particular attention should be paid to unsymmetrically substituted 1,4-disilyl-2-butenes. For example, 1-(trimethylsilyl)-4-(triphenylsilyl)-2-butene was selectively transformed into 3-((triphenylsilyl)methyl)-4-penten-2-one (selectivity more than 95%). Further synthetic applications are in progress in our laboratories.[19]



(17) For the assignment of the configuration, see ref 15c.

(18) (a) Calas, R.; Dunogues, J.; Pillot, J.-P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149. (b) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 97-124. (c) Kumada, M. et al. *J. Synth. Org. Chem., Jpn.* **1982**, *40*, 462-590.

(19) We are indebted to Dr. Kohei Tamao, Department of Synthetic Chemistry, Kyoto University, for helpful discussions and to Shin-etsu Chemical Co., Ltd., for the generous gift of disilanes.

Registry No. **1**, 84824-61-3; **2**, 84812-32-8; **3** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et), 1633-09-6; **3** ($R^1 = R^2 = R^4 = R^5$ = Me; $R^3 = R^6$ = Ph), 1145-98-8; **3** ($R^1 = R^2 = R^4 = R^5$ = Me; $R^3 = R^6$ = CH=CH_2), 1450-29-9; **4** (R^7 = H; R^8 = Me), 78-79-5; **4** ($R^7 = R^8$ = Me), 513-81-5; **4** (R^7 = H; R^8 = Me_2C=$CHCH_2CH_2$), 123-35-3; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Me; $R^7 = R^8$ = H), 16054-35-6; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et; $R^7 = R_8$ = H), 84812-44-2; (*E*)-**5** ($R^1 = R^2 = R^3$ = Me; $R^4 = R^5 = R^6$ = Ph; $R^7 = R^8$ = H), 84812-45-3; (*Z*)-**5** ($R^1 = R^2 = R^3$ = Me; $R^4 = R^5 = R^6$ = Ph; $R^7 = R^8$ = H), 84812-46-4; (*E*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^8$ = Me; R^7 = H), 16109-36-7; (*Z*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5$ = R6 = R^8 = Me; R^7 = H), 16054-36-7; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et; R^7 = H; R^8 = Me), 84812-47-5; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8$ = Me), 16054-38-9; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et; $R^7 = R^8$ = Me), 84812-48-6; (*E*)-**5** ($R^1 = R^2 = R^3 = R^7 = R^8$ = Me; $R^4 = R^5 = R^6$ = Ph), 84812-49-7; (*Z*)-**5** ($R^1 = R^2 = R^3 = R^7 = R^8$ = Me; $R^4 = R^5 = R^6$ = Ph), 84812-50-0; (*E*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Me; R^7 = H; R^8 = Me_2C=$CHCH_2CH_2$), 84812-51-1; (*Z*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Me; R^7 = H; R^8 = Me_2C=$CHCH_2CH_2$), 84812-52-2; **5** ($R^1 = R^2 = R^4 = R^5$ = Me; $R^3 = R^6$ = Ph; $R^7 = R^8$ = H), 84812-53-3; (*E*)-**5** ($R^1 = R^2 = R^4 = R^5 = R^8$ = Me; $R^3 = R^6$ = Ph; R^7 = H), 84812-54-4; (*Z*)-**5** ($R^1 = R^2 = R^4 = R^5 = R^8$ = Me; $R^3 = R^6$ = Ph; R^7 = H), 84812-55-5; **5** ($R^1 = R^2 = R^4 = R^5 = R^7 = R^8$ = Me; $R^3 = R^6$ = Ph), 84812-56-6; **5** ($R^1 = R^2 = R^4 = R^5 = R^7 = R^8$ = Me; $R^3 = R^6$ = CH=CH_2), 84812-57-7; TBAF, 429-41-4; $Me_3SiSiMe_3$, 1450-14-2; $Me_3SiSiPh_3$, 1450-18-6; $Me_2(EtO)SiSi(OEt)Me_2$, 18419-84-6; *n*-C_3H_7CHO, 123-72-8; *i*-C_3H_7CHO, 78-84-2; *t*-C_4H_9CHO, 630-19-3; CH_2=O, 50-00-0; C_6H_5CHO, 100-52-7; *p*-$BuOC_6H_4CHO$, 5736-88-9; *p*-$MeOC_6H_4CHO$, 123-11-5; *p*-$Me_2NC_6H_4CHO$, 100-10-7; *p*-ClC_6H_4CHO, 104-88-1; 1-naphthyl-CHO, 66-77-3; *n*-$C_{10}H_{21}CH(OH)SiPh_3$, 84812-35-1; *n*-$C_3H_7CH(OH)SiPh_3$, 84812-36-2; *i*-$C_3H_7CH(OH)SiPh_3$, 84812-37-3; *t*-$C_4H_9CH(OH)SiMe_3$, 84812-38-4; *t*-$C_4H_9CH(OH)SiPh_3$, 20083-30-1; $HOCH_2SiPh_3$, 18670-80-9; $C_6H_5CH(OH)CH(OH)C_6H_5$, 492-70-6; *p*-$MeOC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-OMe, 4464-76-0; *p*-$BuOC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-OBu, 84812-39-5; *p*-$Me_2NC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-$NMe_2$, 54322-62-2; *p*-$ClC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-Cl, 38152-44-2; 1-naphthyl-CH(OH)CH(OH)-1-naphthyl, 84812-40-8; undecanal, 112-44-7; 1,3-butadiene, 106-99-0; trimethylsilyl fluoride, 420-56-4; 1-(trimethylsilyl)-1-((trimethylsilyl)oxy)undecane, 84812-33-9; undecyl trimethylsilyl ether, 17957-64-1; 1-(trimethylsilyl)-1-undecanol, 84812-34-0; 3-((triphenylsilyl)methyl)-4-penten-2-one, 84812-41-9; *p*-(dimethylamino)-α-(trimethylsilyl)benzyl alcohol, 84812-42-0; 1-naphthylmethanol, 4780-79-4; 2,2′-bis(3-(trimethylsilyl)cyclohexanone), 84812-43-1.

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Conjugate Addition of Moderately Soft Anions to a Vinyl Sulfone[1]

Summary: The potassium and, in part, lithium anions of ethyl acetate, dimethyl acetamide, acetonitrile, acetophenone, pinacalone, and (trimethylsilyl)acetylene undergo conjugate addition to 3-(*tert*-butyldimethylsiloxy)-1-cyclohexenyl *tert*-butyl sulfone. The resultant α-sulfonyl anions may be protonated or trapped with an electrophile (MeI) stereospecifically. The usefulness of these reactions

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(1) Syntheses via Vinyl Sulfones **10**. For paper 9, see: S. G. Pyne, D. C. Spellmeyer, S. Chen, and P. L. Fuchs, *J. Am. Chem. Soc.*, **104**, 5728 (1982).

0022-3263/83/1948-0914$01.50/0

is illustrated by further transformations of the methylated (trimethylsilyl)acetylene adduct.

Sir: During the course of our synthetic studies, we have come to appreciate the value of a triply convergent strategy involving the conjugate addition of "hard" anions to vinyl sulfones (**1** to **2**, Scheme I) followed by subsequent functionalization of the resulting α-sulfonyl anion by a variety of electrophiles (**2** to **3**/**4**).[2]

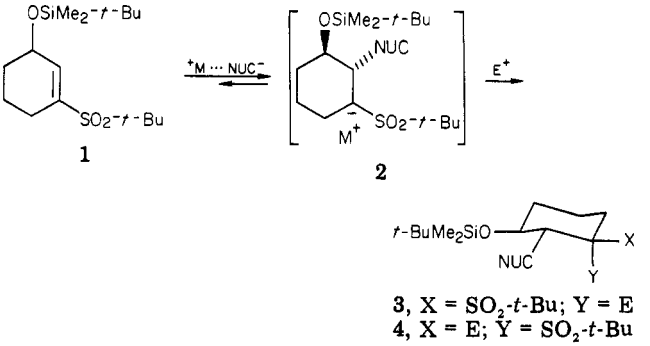
In applying this strategem we have been guided by the dictum that only anions having pK_a values greater than 25 (the approximate value of **2**) would be expected to undergo facile addition to the starting vinyl sulfone **1**.[3] Unfortunately this would apparently exclude a vast array of highly synthetically useful fragments such as enolates, acetylide anions, and nitrile anions. Consequently, we have examined several of these species and find that they do, in fact, undergo excellent conjugate additions to vinyl sulfone **1** under appropriately defined conditions.

Our initial investigation involved the conjugate addition of a series of monoactivated primary anions MCH_2W (**5**)[4] to vinyl sulfone **1** followed by simple protonolysis of the resulting α-sulfonyl anion **2** ((NUC≡CH_2W). Protonation of intermediate **2** occurred with good axial selectivity to produce mainly the all-equatorial sulfones **3a–d** (Y = H) in high isolated yield (Table I).[5] Several additional features about these reactions are worthy of mention. The potassium anions **5** (M = K^+) were substantially more reactive and in several instances yielded products where the lithium counterion had failed completely. This effect was particularly dramatic in the case of the less basic (pK_a = 18–20) ketone enolates **5d** and **5e** where the lithium enolates fail to yield any product. Ketone enolates **5d** and **5e** also reveal what appears to be the first incidence of reversability in the conjugate-addition reaction, since increasing the concentration of ketone enolate from 1.5 to 3.0 or 5.0 equiv results in a more complete conversion of vinyl sulfone **1** to adduct **2**.[6]

We next turned our attention to the reaction of vinyl sulfone **1** with (trimethylsilyl)acetylide anion **6a**. Treatment of (trimethylsilyl)acetylene with 1.1 equiv of a 1:1 mixture of *n*-butyllithium/KO-*t*-Bu[7] in THF at −78 °C followed by addition of vinyl sulfone **1** and allowing the solution to warm to 0 °C for 0.5 h generates α-sulfonyl anion intermediate **7**. (Reaction of **1** with *lithium* acetylide **6b** is far more sluggish under comparable conditions.)

Quenching of the intermediate **7** at −78 °C with aqueous NH_4Cl or methyl iodide affords a 95:5 mixture of α-functionalized sulfones **8a**/**9a** and **8b**/**9b**, respectively (Scheme II).

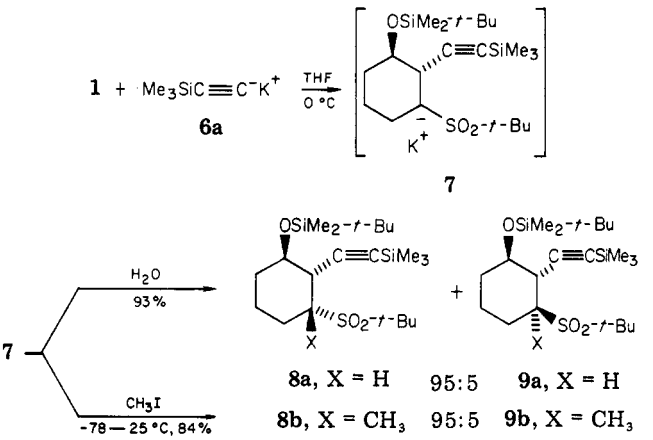
Scheme I



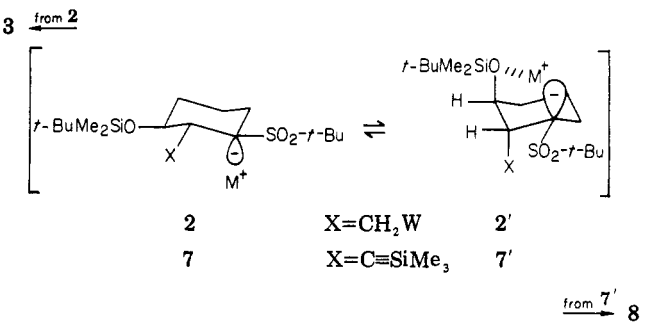
1 2

3, X = SO_2-*t*-Bu; Y = E
4, X = E; Y = SO_2-*t*-Bu

Scheme II



Scheme III



As can be seen in Schemes II and III, functionalization of acetylenic α-sulfonyl anion **7** has occurred with almost total stereochemical control, *but in the opposite sense* than that observed with the sp^3-functionalized sulfone anion **2**.[8] These two series provide a particularly nice example of stereocontrol via the synergistic combination of steric and electronic effects. In the case of intermediate **2**, it is clear that the sp^3-hybridized CH_2W group will prefer to occupy the less encumbered equatorial position. The example of intermediate **7** shows, in addition to the substantially diminished steric requirements for an axial acetylene (**7'**), that there may be a significant *associative 1,3-diaxial interaction* between the (potassium) ion pair and the α-silyloxy moiety.[9]

Acid-catalyzed deprotection[10] of the silyl ether moiety of **8b** (the use fluoride also cleaves the acetylenic silane)

(2) For application of this strategy to the total synthesis of chiral prostaglandin E_2, see: R. E. Donaldson and P. L. Fuchs, *J. Am. Chem. Soc.*, **103**, 2108 (1981).

(3) By contrast, it is well-known that "soft" nucleophiles such as amines, mercaptides, and cyanide add to vinyl sulfones *under protic conditions* where the insipient α-sulfonyl anion intermediate **2** is rapidly quenched. Clearly this is not acceptable if further *in situ* functionalization of [2] is desired. See: (a) J. J. Eisch and J. E. Galle, *J. Org. Chem.*, **45**, 4534 (1980); (b) A. H. Ford-More, R. A. Peters, and R. W. Wakelin, *J. Chem. Soc.*, 1754 (1949); (c) D. F. Taber and S. A. Saleh, *J. Org. Chem.*, **46**, 4817, (1981).

(4) Prepared by addition of CH_3W to a slight excess of LDA (KDA) in THF at −78 °C. The KDA was prepared by the method of Raucher and Koolpe (*J. Org. Chem.*, **43**, 3794 (1978)).

(5) Experimental details, including fully decoupled 470-MHz ^1H NMR and ^{13}C NMR spectral evidence for compounds **3a–e**, **4a**, **4d**, **8a**, **8b**, **10**, **11**, **12**, **13**, and **14** will appear in the supplementary material.

(6) A more detailed examination of this "equilibrium reaction" was not undertaken since under the reaction conditions containing excess enolate (and lithium *tert*-butoxide from the preparation of KDA[4]), several additional secondary processes take place. The most serious of these involves allylic isomerization of the starting vinyl sulfone **1** to a β-sulfonyl silyl enol ether.

(7) M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 508 (1973).

(8) Addition of dry diisopropyl amine to the solution of **7** prior to the ammonium chloride quench has no effect on the **8a**/**9a** ratio. This control eliminates the possibility of an amine hydrogen-bonded species as being responsible for the change in stereochemistry from intermediate **2** to intermediate **7**.

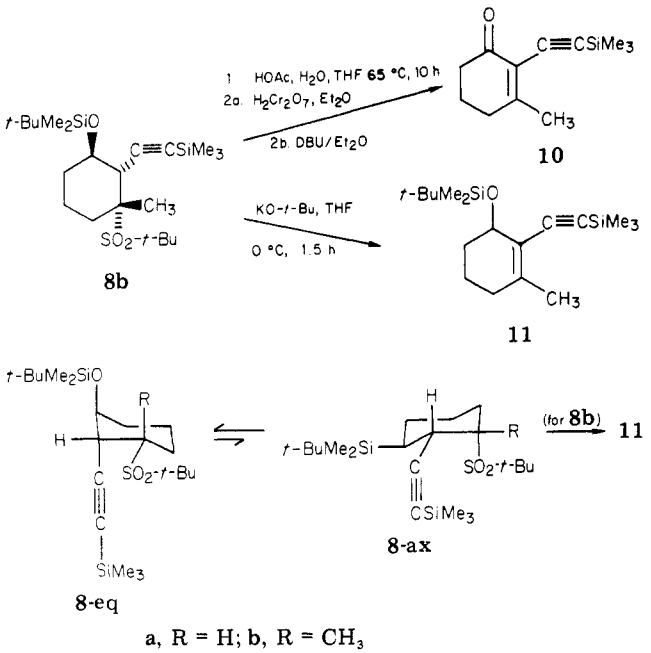
(9) For simplicity, α-sulfone carbanions **2** and **7** are represented as being pyramidal although a sp^2-hybridized anion would not substantially alter the stereochemical interpretation. For a discussion of α-sulfone carbanion geometry, see: P. D. Magnus, *Tetrahedron*, **33**, 2019 (1977), and references contained therein.

Table I

entry	NUC (equiv)	conditions,[a] °C, h	products, % yield[b] (3/4 ratio)[c]	comments
A-1	$LiCH_2CN$ (1.1)	−50, 0.25	**3a**, 98 (>99:1)	3/4 = 70:30, 0 °C quench
A-2	KCH_2CN (1.1)	−50, 0.25	**3a**, 95 (>99:1)	3/4 = 70:30, 0 °C quench
B-1	$LiCH_2CON(CH_3)_2$ (1.1)	−78-0	**3b** + **4b**, 70 (84:16)	10% **1** recovered[c]
B-2	$KCH_2CON(CH_3)_2$ (1.1)	−78-0	**3b** + **4b**, 95 (96:4)	
C-1	$LiCH_2CO_2C_2H_5$ (1.2)	0, 0.75	**3c**, 0	35% **1** recovered,[c] 15% β keto ester[d]
C-2	$KCH_2CO_2C_2H_5$ (1.1)	0, 0.5	**3c**, 88 (>99:1)	
D-1	$LiCH_2COC_6H_5$ (1.1)	0, 1.0	**3d**, 0	
D-2	$KCH_2COC_6H_5$ (1.5)	0, 1.0	**3d** + **4d**, 78 (75:25)	trace **1** recovered,[c] trace isomerized **1**[c,e]
D-3	$KCH_2COC_6H_5$ (1.5)	25, 1.0	**3d** + **4d**, 54 (75:25)	isomerized **1** present[e]
D-4	$KCH_2COC_6H_5$ (5.0)	25, 1.0	**3d** + **4d**, 77 (75:25)	trace isomerized **1**[e]
E-1	$LiCH_2CO$-*t*-Bu (1.5)	0, 1.0	**3e**, 0	
E-2	KCH_2CO-*t*-Bu (1.5)	0, 1.0	**3e** + **4e**, 51 (88:12)	31% **1** recovered, trace isomerized **1**[c,e]
E-3	KCH_2CO-*t*-Bu (3.0)	0, 1.0	**3e** + **4e**, 69 (88:12)	9% **1** recovered, trace isomerized **1**,[c,e] 3% cyclopropyl ketone[f]

[a] All reactions conducted in dry THF and quenched at the temperature indicated by a saturated aqueous solution of NH_4Cl. [b] Isolated yield of pure products (**3** + **4**). [c] Ratio prior to purification on the basis of NMR integration. [d] β-Keto ester **12**[g] resulting from the Claisen condensation of **3c** with lithioethyl acetate. [e] Via allylic isomerization of **1** to produce a β-sulfonyl silyl enol ether. This silyl enol ether **13**[g] can be prepared by KO-*t*-Bu catalyzed deconjugation of **1**. [f] Formally resulting from enolization and intramolecular displacement of *tert*-butyl sulfinate. The cyclopropyl ketone **14**[g] is the major product at higher temperature. [g] Structures of **12-14** are drawn in the supplementary material.

Scheme IV



followed by oxidation to the ketone and β-elimination of sulfinate anion via our previously described methodology[11] affords enone **10** (67% overall yield from **8b**).

We have also developed a procedure for the *direct* 1,2-elimination of sulfinic acid from homopropargylic sulfone **8b**, *which avoids the need for prior modification of the silyl ether moiety*. This is effected by further treatment of the methyl iodide quenched reaction mixture of **8b** with anhydrous potassium *tert*-butoxide (5 equiv added portionwise) to afford vinyl acetylene **11** in 71% yield. The base-catalyzed 1,2-elimination of phenylsulfinic acid from homoallylic sulfones has been previously observed,[12,13] but in those instances the deprotonation occurred at an exocyclic methylene group to generate an acyclic[12a] or exocyclic[12b] 1,3-diene. The case at hand provides more insight with regard to the conformational and stereoelectronic demands of this reaction.

As can be seen in Scheme IV, acetylenic sulfones **8a** and **8b** can exist in a conformational equilibrium between the (nonreactive) form where the sulfone moiety is in an equatorial position (8-eq) and the (reactive) form where the sulfone group and propargylic proton exist in a trans diaxial relationship (8-ax). Substitution at the sulfone-bearing carbon (b series) provides two beneficial effects: (1) changing the sulfonyl center from secondary to tertiary presumably facilitates bond breaking in the E_2 transition state and simultaneously (2) shifts the equilibrium more toward the reactive 8-ax form by the introduction of a new 1,3-diaxial interaction with the silyloxy moiety which results in destabilization of the nonreactive 8-eq conformer.[14] Application of this elimination strategy to more highly functionalized examples where the virtue of preserving the silyl ether stereochemistry becomes more apparent will be published in due course.

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Supplementary Material Available: Preparation of and experimental data for addition compounds (7 pages). Ordering information is given on any current masthead page.

(10) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

(11) (a) P. C. Conrad and P. L. Fuchs, *J. Am. Chem. Soc.*, **100**, 346, (1978); (b) D. L. Barton, P. C. Conrad, and P. L. Fuchs, *Tetrahedron Lett.*, 1811 (1980).

(12) (a) K. C. Nicolaou, D. A. Claremon, D. P. Paphatjis, and R. L. Magolda, *J. Am. Chem. Soc.*, **103**, 6969 (1981); (b) S. G. Pyne and P. L. Fuchs, unpublished results.

(13) For 1,2-eliminations of sulfinic acid, see: A. K. Colter and R. E. Miller, Jr., *J. Org. Chem.*, **36**, 1898 (1971).

(14) Similar base-catalyzed treatment of secondary sulfone **8a** is far less efficacious.

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