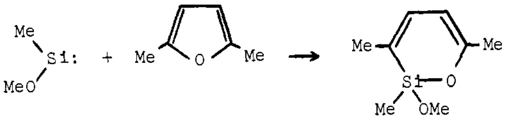
d of t, J_{AB} = 14, $J_{AD} \sim J_{AC}$), 6.54 (H_D, overlapped with H_B), 6.71 (H_B, d of d of d, $J_{BD} \sim$ 1 Hz); mass spectrum *m/e* (rel intensity) 126 (19.5), 111 (M − CH_3, 100), 85 (M − CH_3 + C_2H_2, 14), calcd for $C_6H_{10}OSi$ 126.0501, obsd 126.0498.

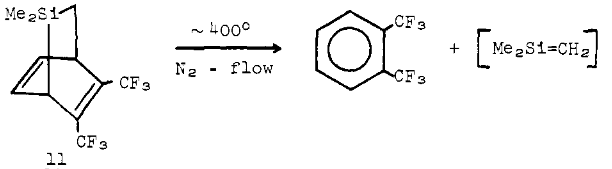
The formation of **9** is easily rationalized when it is recognized that the methoxyl oxygen of **6** is in close proximity to an undoubtedly polar silicon-carbon double bond. Silicon-oxygen bond formation to produce zwitterion **8** would render the methoxyl methyl labile with regard to involvement in the elimination of tetramethylsilane.[6]

Oxasilin **9** is the second example of this ring system to be reported. Weber obtained 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5-diene (**10**) in yields of "... never better than a few percent ..." from the reaction of methoxymethylsilylene and 2,5-dimethylfuran.[7] Unfortunately, an insufficient amount of **10** was accumulated to attempt any chemical investigations.

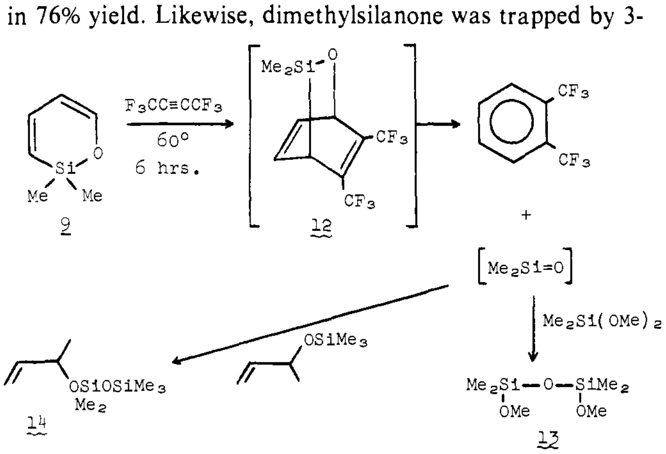


10

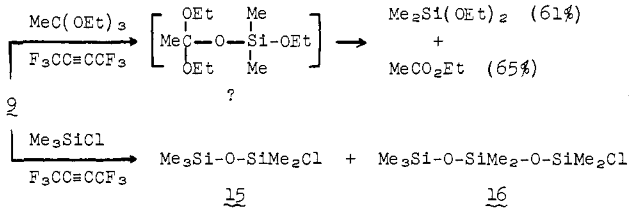
The 1,2-oxasilin ring system is one which we have long coveted, as we viewed it as a potential penultimate precursor to silanones—compounds containing a silicon-oxygen (p-p)π double bond. It has been established that 7-silabicyclo[2.2.2]-octadiene ring system **11** extrudes the silene bridge at high temperatures (~400 °C) in the gas phase.[8] Thus, we thought to react **9** with an acetylene in a Diels-Alder fashion to produce the corresponding bicyclic silanone precursor. To our surprise, while perfluoro-2-butyne reacts completely with **9** in ~1 day at room temperature (6 h at 60 °C), *o*-bis(trifluoromethyl)-benzene is formed at the same rate (as observed by NMR). We have never observed the intermediate adduct **12**.[9] Thus, it appears that the initial adduct **12** quickly decomposes even at room temperature through extrusion of the silanone bridge. This assumption was dramatically verified by conducting the cycloaddition in the presence of excess dimethoxydimethylsilane and obtaining the dimethylsilanone insertion product **13**[10] in 76% yield. Likewise, dimethylsilanone was trapped by 3-trimethylsiloxy-1-butene to afford disiloxane **14** in 67% yield.[11]



11



With this mild, convenient route to dimethylsilanone we are, for the first time, in a position to systematically investigate the chemistry of this intriguing system. Indeed, at this time we can report the first example of silanone insertion into a silicon-chlorine bond. When **9** is reacted with perfluoro-2-butyne and excess trimethylchlorosilane (65 °C, 8 h), siloxanes **15** (37%) and **16** (17%) are obtained.[12] This represents the first report of silanone trapping by the Si-Cl bond. When **9** is reacted with perfluoro-2-butyne in the presence of excess triethyl orthoacetate, a 61% yield of dimethyldiethoxysilane[10] is obtained.



Presumable this arises from silanone insertion into a C-O bond, followed by disproportionation of the resulting ortho ester.

Acknowledgment. We thank the Dow Corning Corporation for partial support of this work.

References and Notes

(1) Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. C. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) NMR (CCl_4) δ 0.13 (9 H, s), 0.21 (6 H, s), 3.85 (3 H, s), 4.50 (1 H, d, J = 7 Hz), 5.62 (1 H, d, J = 7 Hz); mass spectrum *m/e* (rel intensity) 2.2 (0.9), 211 (0.3), 197 (74), 171 (70), 73 (100), calcd for $C_{10}H_{19}OSi_2$ 211.0975, obsd 211.0977.

(3) The procedure followed was from Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068.

(4) NMR (CCl_4) δ 0.03 (9 H, s), 0.15 (6 H, s), 3.63 (3 H, s), 5.05 (H_C, d of d of d, J_{BC} = 12, J_{CD} = 6.5, J_{AC} = 1.0 Hz), 5.32 (H_A, d of t, J_{AB} = 14, J_{AD} = 1.0 Hz), 5.84 (H_D, d of t, J_{BD} = 0.5 Hz), 7.01 (H_B, d of d of d); mass spectrum *m/e* (rel intensity) 199 (M − CH_3, 10.5), 111 (54), 89 (21), 73 (100), calcd for $C_9H_{19}OSi_2$ 199.0975, obsd 199.0971.

(5) Tetramethylsilane was identified as a product of this pyrolysis by gas chromatographic-mass spectral comparison with an authentic sample.

(6) We cannot exclude the possibility of a mechanistic route to **9** involving homolytic cleavage of the Si-Si bond followed by S_H2 displacement on oxygen by silyl radical. However, the 1,5-silyl migration is precedented while S_H2 displacement from ether oxygen is very rare.

(7) Childs, M. E.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 1799.

(8) Barton, T. J.; Kline, E. *J. Organomet. Chem.* **1972**, *42*, C21.

(9) Reaction of **9** with maleic anhydride does produce the expected, stable Diels-Alder adduct. Other dienophiles are currently being investigated.

(10) Identified by NMR and mass spectral comparison with an authentic sample.

(11) NMR (CCl_4) δ 0.04 (6 H, s), 0.10 (9 H, s), 1.26 (3 H, d, J = 3 Hz), 4.46 (1 H, m), 5.19 (2 H, m), 5.98 (1 H, m); *m/e* (rel intensity) 218 (10), 203 (24), 149 (100), 147 (41), 73 (10), 55 (44), calcd for $C_9H_{22}O_2Si_2$ 218.1158, obsd 218.1158.

(12) **15:** NMR (CCl_4) δ 0.15 (9 H, s), 0.42 (6 H, s); *m/e* (rel intensity) 169 (43), 167 (100, M − CH_3), 147 (10, M − Cl), 76 (13), 73 (14). **16:** δ 0.10 (15 H, s), 0.42 (6 H, s); *m/e* (rel intensity) 243 (29), 241 (68, M − CH_3), 221 (4), 133 (11), 113 (11), 73 (100). Yields are based on *o*-bis(trifluoromethyl)-benzene.

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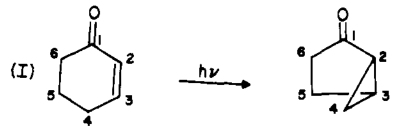
Spin-Inversion and Orbital Symmetry Conspiracy in Type A Lumiketone Rearrangements

Sir:

Type A lumiketone rearrangement is known to originate from a triplet state[1,2] with evidence suggesting a ${}^3\pi\pi^*$ reactive state.[2b-d] The reaction (I) can be viewed as a formal $[2_\pi + 2_\sigma]$



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cycloaddition, in which $\sigma_{4,5}$ adds in a cross-bonding fashion to $\pi_{2,3}$.

Recently, Schuster et al.[3] have demonstrated that the reaction of optically active 4-substituted cyclohexenones is stereospecific. The authors have concluded that the photorearrangement is apparently concerted and consistent with the symmetry-allowed[4] $[_{\pi}2_a + {}_{\sigma}2_a]$ cycloaddition. They also concluded that spin inversion may have occurred directly from the triplet surface to the ground-state surface without prior formation of a singlet diradical.

Since the type A rearrangement is stereospecific, its analysis may be pivotal to the understanding of triplet reaction mechanisms. We now provide a rationale for the postulate that in certain classes of triplet reactions product formation can be attended by concomitant spin inversion.

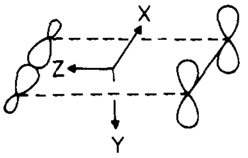
Orbital-symmetry allowedness is not a sufficient condition for stereospecificity in triplet reactions. Even if the triplet complex of a symmetry-allowed reaction is formed,[5] the combination of its *stereochemically different spin-inversion mechanisms, caused by the different symmetries of the triplet sublevels* (T_x, T_y, T_z), *could result in a nonstereospecific appearance.*[6,7]

The symmetry properties of the triplet sublevels, T_x, T_y, and T_z are given by the direct products of the representation (Γ) of the orbital (ν) part of the triplet state (T^{ν}) and the three representations of the spin parts which transform as the rotation vectors, $\mathbf{R}_x$, $\mathbf{R}_y$, and $\mathbf{R}_z$.[8,9] Since the ground state is always totally symmetric (unless degeneracies are involved), the representations of the motions (Q_k) which couple the sublevels of the triplet state with the ground state and promote spin inversion are simply[6b,7,10]

$$\Gamma(Q_k) = \Gamma(T^{\nu}) \times \Gamma(\mathbf{R}_k) \quad (k = x, y, z) \tag{1}$$

Let us now apply this principle and discover the motions which induce spin inversion in the $^3\pi\pi^*$ state of cyclohexenone. A system (II) consisting only of the reacting π and σ bonds will serve as a model for describing stereochemical features of spin-inversion mechanisms. Symmetries will be designated with respect to the mirror plane (yz) which bisects both π and σ bonds. The orbital (spatial) part of the $^3\pi\pi^*$ state is antisymmetric (A) with respect to this plane. Similarly, $\mathbf{R}_z$ and $\mathbf{R}_y$ which are perpendicular to the plane (yz) have an A symmetry, whereas $\mathbf{R}_x$ which is in the plane is symmetric (S). The symmetries of the corresponding spin-inversion motions, Q_k, are then

(II)

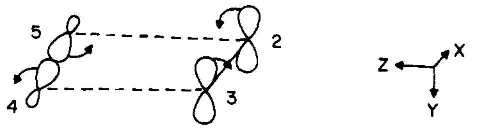


$$\Gamma(Q_x) = \mathrm{A} \times \mathrm{S} = \mathrm{A} \tag{2}$$

$$\Gamma(Q_y) = \Gamma(Q_z) = \mathrm{A} \times \mathrm{A} = \mathrm{S} \tag{3}$$

In addition to the symmetry specifications, in order to be efficient these *motions should generate perpendicular atomic orbital (AO) pairs along neighboring centers.*[6,7,11] Hence, the induction of spin inversion in the x sublevel of $^3\pi\pi^*$ can be achieved by an antisymmetric motion (eq 2) which generates perpendicular p_z–p_y AO pairs. A motion which meets these requirements is (III) which consists of a disrotation of the π bond and a conrotatory cleavage of the σ bond; both motions are antisymmetric with respect to the mirror plane (yz).

(III)



The spin-inversion efficiency associated with this motion can be estimated by evaluating the spin orbit (SO) coupling matrix element, $\langle \mathrm{T}|\hat{H}_{\mathrm{SO}}|\mathrm{S}_0\rangle$, between the triplet state and the ground state. This matrix element can be reduced to the angular momentum ($\hat{l}_k$) matrix element of the HOMO and the LUMO of the reaction complex. The expression is given by

$$\langle \hat{H}_{\mathrm{SO}}\rangle_k = \frac{A}{\sqrt{2}\hbar}\left\langle \mathrm{HOMO}\left|\frac{\hat{l}_k}{r^3}\right|\mathrm{LUMO}\right\rangle \quad (k = x, y, z) \tag{4}$$

where A is a constant.[9] The HOMO and the LUMO can be expressed as a function of the rotation angle, θ (around $\pi_{2,3}$) and the cleavage angle, ϕ (of $\sigma_{4,5}$).[7,12] This leads to the following expression for the x component of the SO coupling (N and N' are normalization factors):

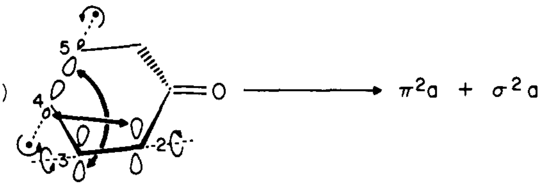
$$\langle \hat{H}_{\mathrm{SO}}\rangle_x = \sqrt{2}\, iANN'\{2V^{\pi}_{32}\sin\theta\cos\theta - (V^{\sigma}_{34} + V^{\pi}_{34})\sin\phi\cos\theta\} \tag{5}$$

V^{σ} and V^{π} describe σ- and π-type interactions, respectively.[7,11b] For example

$$V^{\sigma}_{34} = \left\langle p_{3z}\left|\frac{1}{r_3^3} + \frac{1}{r_4^3}\right|p_{4z}\right\rangle \text{ and } V^{\pi}_{32} = \left\langle p_{3y}\left|\frac{1}{r_3^3} + \frac{1}{r_2^3}\right|p_{2y}\right\rangle$$

These terms behave similarly to the corresponding overlap integrals. This similarity refers to their signs and relative magnitudes, namely, $V^{\sigma}_{34} < 0$, whereas $V^{\pi} > 0$ and $|V^{\sigma}_{34}| > V^{\pi}_{34}$. Consequently, the second term in eq 5 is additive. At $\phi = 0°$, the expression reaches maximum at $\theta = 45°$ where the olefinic portion has a perpendicular conformation. In this geometry the system inverts a spin and relaxes to a ground-state reactant.[13] Alternatively, a higher maximum of $\langle H_{\mathrm{SO}}\rangle_x$ is reached at $\theta = 45°$ and $\phi = 90°$. In this geometry all the orbitals are aligned to form the new bonds; the inversion at carbon 4 is taking place and leads to a formal $[_{\pi}2_a + {}_{\sigma}2_a]$ allowed cycloaddition as illustrated for cyclohexenone in (IV). Thick double headed arrows indicate the newly forming bonds.[14] Repeating the procedure for $\langle H_{\mathrm{SO}}\rangle_y$ and $\langle H_{\mathrm{SO}}\rangle_z$ leads to much smaller SO coupling expressions. Therefore, spin inversion will occur faster in the x sublevel.

(IV)



In conclusion, an efficient[7,11] spin-inversion mechanism (III) was found to be identical with the orbital-symmetry-allowed pathway $[_{\pi}2_a + {}_{\sigma}2_a]$.[14] Thus, the type A rearrangement is a case where orbital-symmetry and spin-inversion requirements conspire to yield the same product. Whenever both spin-inversion and orbital-symmetry requirements are met along *the same reaction coordinate*, the reaction can be stereospecific.[5] This can be typically realized in $[2_{\pi} + 2_{\sigma}]$ and/or in $[2_{\pi} + 2_{\pi}]$ intramolecular cycloadditions.[7]

Further insight into the role of spin inversion in these reactions can be gained by selective excitation of the x, y, and z sublevels of the triplet state which could react with differing efficiencies. Recent developments in this area[15,16] can hopefully be extended to stereochemical studies.

Acknowledgment. The author thanks Professor R. Hoffmann for his support and E. D. Jemmis, R. Goddard, and A. Pinhas for enlightening discussions.

References and Notes

(1) For a recent review, see O. L. Chapman and D. S. Weiss in "Organic Photochemistry", Vol. 3, O. L. Chapman, Ed., Marcel Dekker, New York, 1973, and references therein.

(2) (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159, 1965 (1966); (b) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969); (c) G. Marsh, D. R. Kearns, and K. Schaffner, *J. Am. Chem. Soc.*, **93**, 3129 (1971); (d) W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *ibid.*, **93**, 3674 (1971).

(3) D. I. Schuster, R. H. Brown, and B. M. Resnick, *J. Am. Chem. Soc.*, **100**, 4504 (1978).

(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1971.

(5) Commonly, formation of loose triplet diradicals competes with the formation of symmetry-allowed triplet complexes. The reason is that the stabilization gained in the symmetry-allowed geometry may not always be sufficient to override the overlap repulsion (exchange repulsion of the identical-spin electrons) which can be relieved at loose geometries. The competition between diradical and symmetry-allowed pathways is discussed in detail in ref 7. The role of diradicals in triplet cycloadditions has been theoretically considered by (a) S. Kita and K. Fukui, *Bull. Chem. Soc., Jpn.*, **42**, 66 (1969); (b) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **92**, 1411 (1970), **94**, 8749 (1972); (c) J. Michl, *Top. Curr. Chem.*, **46**, 1 (1974).

(6) (a) S. Shaik and N. D. Epiotis, *J. Am. Chem. Soc.*, **100**, 18 (1978); (b) S. Shaik, Ph.D. Dissertation, University of Washington, Seattle, Wash., 1978.

(7) S. S. Shaik, *J. Am. Chem. Soc.*, in press.

(8) For example, $\mathbf{R}_x$ is a rotation about the x axis and is described as a rotation vector in the yz plane. See E. P. Wigner, "Group Theory and Its Applications to the Quantum Mechanics of Atomic Spectra", Academic Press, New York, 1959 (translated from German by J. J. Griffin).

(9) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969.

(10) See also the analyses of (a) T. Lee, *J. Am. Chem. Soc.*, **99**, 3909 (1977); (b) E. A. Halevi and C. Trindle, *Isr. J. Chem.*, **16**, 283 (1977).

(11) The significance of perpendicular AO pairs for creating strong SO coupling interactions has been discussed in (a) M. Kasha, H. R. Rawls, and M. A. El-Bayoumi, *8th European Congress on Molecular Spectroscopy, Copenhagen, 1965*; (b) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(12) A similar approach was used by C. Trindle and H. Ö. Pamuk, *Tetrahedron*, **34**, 747 (1978).

(13) Either cis or trans (noncis) cyclohexenone may result. A noncis cyclohexenone was observed spectroscopically by T. D. Goldfarb, cited in R. Bonneau, J. Joussot-Doubien, L. Salem, and A. J. Yarwood, *J. Am. Chem. Soc.*, **98**, 4329 (1976).

(14) If the rearrangement is viewed as a 1,2-sigmatropic shift of carbon 5 to carbon 3, it can be seen that the reaction complex is topologically equivalent to trimethylenemethane which has a triplet ground state: W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977). Thus, a T-S surface crossing is expected during the rearrangement in a geometry close to the one discussed in the text. This facilitates spin inversion (see also ref 12).

(15) Selective population of the triplet sublevels is reviewed in M. A. El-Sayed, *Annu. Rev. Phys. Chem.*, **26**, 235 (1975).

(16) Different rates of decomposition were observed for the sublevels of the first triplet state of dimethyl-*s*-tetrazine. See B. Dillinger, R. M. Hochstrasser, and A. B. Smith III, *J. Am. Chem. Soc.*, **99**, 5834 (1977).

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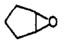
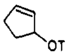
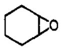
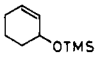
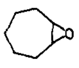
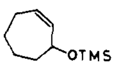
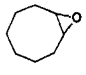
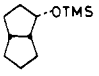
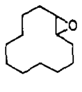
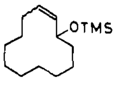
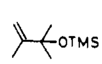
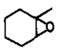
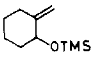
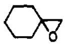
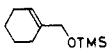
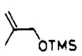
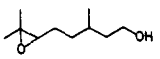
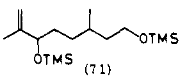
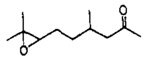
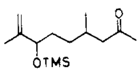
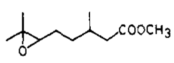
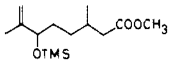
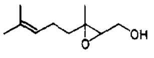
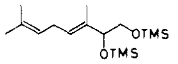
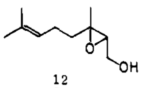
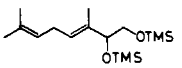
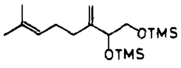
A New Method for Converting Oxiranes to Allylic Alcohols by an Organosilicon Reagent

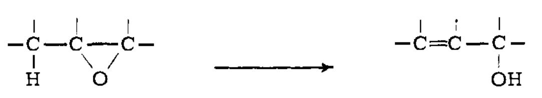
Sir:

The oxirane to allylic alcohol isomerization (eq 1) is an essential operation in organic synthesis and a variety of reagents have been elaborated for this purpose. The recently discovered dialkylaluminum amides[1] and a dialkylboron trifluoromethanesulfonate[2] are applicable to the reaction of *trans*-2,3-dialkylated oxiranes (but not cis or common cyclic derivatives) or further alkylated substrates. The conversion of oxiranes derived from five- to seven-membered cyclic olefins may be effected by strongly basic lithium amide reagents in refluxing solvents.[3] A mild, two-step procedure via an organoselenium reagent was also developed; nucleophilic displacement of oxiranes with sodium phenylselenide followed by hydrogen peroxide oxidation of the resulting hydroxy selenides, causing elimination of phenylselenic acid, affords the desired allylic alcohols.[4] We here disclose a new procedure based on the use of an organosilicon compound. This method requires only very mild reaction conditions and is employable satisfactorily to the reaction of cyclic substrates as well as 2,2-di-, tri-, and tetrasubstituted oxiranes.

Table I. Reaction of Oxiranes and Trimethylsilyl Trifluoromethanesulfonate (**1**)[a]

Entry	Oxirane	Conditions	Products (% yield[b])
1		1, DBU, 29 °C, 5 h	 (59[c])
2		1, DBU, 22 °C, 20 h	 (87)
3		1, DBU, 22 °C, 14 h	 (40, 100[d])
4	 2	1. 1, Lu, -50 °C, 3h 2. 26 °C, 40 h	 3 (100)
5		1, DBU, 27 °C, 40 h	 (38)
6		1. 1, Lu, -78 °C, 4 h 2. DBU, 15 °C, 5 h	 (87[c])
7	 4	1. 1, Lu, -78 °C, 3 h 2. DBU, 24 °C, 3 h	 5 (80)
8		1. 1, Lu, -78 °C, 3 h 2. DBU, 30 °C, 14 h	 (72)
9		1. 1, Lu, -78 °C, 10 h 2. DBU, 13 °C, 0.5 h	 (62[c])
10		1. 1,[e] Lu,[e] -78 °C, 5 h 2. DBU, 28 °C, 4 h	 (71)
11	 6	1. 1, Lu, -78 °C, 4 h 2. DBU, 20 °C, 0.5 h	 7 (69)
12	 8	1. 1, Lu, -78 °C, 4 h 2. DBU, 15 °C, 2 h	 9 (79)
13	 10	1. 1,[e] Lu,[e] -78 °C, 5 h 2. DBU, 30 °C, 54 h	 11 (66)
14	 12	1. 1,[e] Lu,[e] -78 °C, 3 h 2. DBU, 32 °C, 14 h	 11 (65)  13 (16)

[a] TMS = trimethylsilyl. Lu = 2,6-lutidine. Unless otherwise stated, the reaction was carried out in benzene (room temperature) or toluene (low temperature) using 1 equiv of **1**, Lu, and DBU. [b] Isolated yield. [c] Determined by GLC analysis. [d] Conversion was 40%. The value was based on the consumed starting material. [e] Two equivalents.



$$\underset{\text{H}}{\overset{|}{\text{—C}}}\text{—}\overset{|}{\text{C}}\text{—}\overset{|}{\text{C}}\text{—}\ (\text{C—C bridged by O}) \longrightarrow \text{—}\overset{|}{\text{C}}\text{=}\overset{|}{\text{C}}\text{—}\underset{\text{OH}}{\overset{|}{\text{C}}}\text{—} \qquad (1)$$

When an oxirane dissolved in aromatic hydrocarbon was treated with equimolar amounts of trimethylsilyl trifluoromethanesulfonate (**1**)[5] and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (or an equimolar mixture of **1** and 2,6-lutidine and then DBU), the corresponding allylic alcohol protected as a tri-

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