(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).

Sason S. Shaik
Department of Chemistry, Cornell University
Ithaca, New York 14853

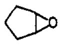
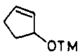
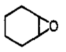
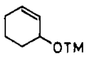
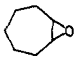
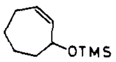
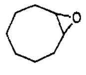
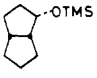
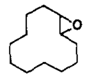
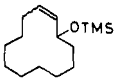
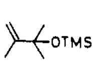
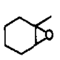
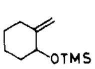
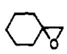
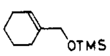
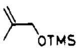
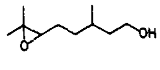
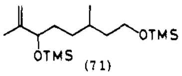
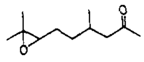
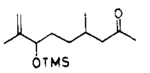
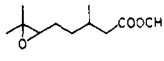
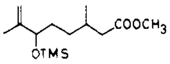
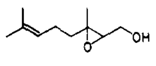
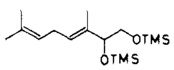
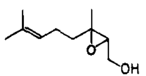
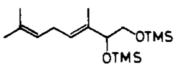
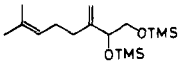
Received November 21, 1978

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)

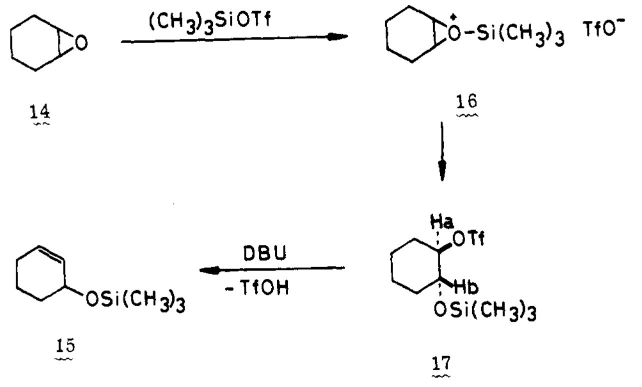
[a] TMS = trimethylsilyl. Lu = 2,6-lutidine. Unless otherwise stated, the reaction was carried out in benzene (room temperature) or toluene (low temperature) using 1 equiv of **1**, Lu, and DBU. [b] Isolated yield. [c] Determined by GLC analysis. [d] Conversion was 40%. The value was based on the consumed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

$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underbrace{\overset{|}{C}-\overset{|}{C}}_{O}- \longrightarrow -\overset{|}{C}=\overset{|}{C}-\underset{OH}{\overset{|}{\underset{|}{C}}}- \qquad (1)$$

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-

0002-7863/79/1501-2738$01.00/0

Scheme I



methylsilyl ether was obtained in a reasonable yield. The trimethylsilyl group was readily removed by treating with dilute hydrochloric acid or KF in methanol. Several examples of this transformation are given in Table I. The reaction of cyclic substrates possessing ordinary ring size (entries 1–3) proceeded at room temperature to give the desired allyl trimethylsilyl ethers. The reaction of epoxycyclooctane (**2**), however, led to the transannular cyclization product **3** (entry 4). Tetra-, tri-, and 2,2-disubstituted oxiranes reacted with **1** at dry ice temperature (entries 6–14).[6] Notably the reaction of 1,2-epoxy-1-methylcyclohexane (**4**) afforded specifically product **5** possessing an exocyclic methylene group (entry 7). Since hydroxy group reacts with **1** spontaneously, giving a trimethylsilyl ether, alcoholic oxiranes could be subjected to the reaction with 2 equiv of **1** directly without any protection (entries 10, 13, and 14). Reaction of the bifunctional compounds **6** and **8** with 1 equiv of **1** led chemoselectively to the corresponding allyl trimethylsilyl ethers **7** and **9**, respectively, leaving the keto or ester group intact.[7] *trans*-2,3-Epoxycitronellol (**10**) was converted stereoselectively to the olefin **11** having *E* configuration (entry 13). The cis analogue **12** led to a mixture of the isomeric olefins **11** and **13** with the former predominating (4:1 ratio) (entry 14). Thus this simple isomerization method, complementary to the existing techniques, would provide a useful tool in the synthesis of complex organic molecules.

Unlike epoxycycloalkanes, ordinary 2,3-dialkylated oxiranes were inert to the standard reaction conditions. Monoalkylated substrates did not react either. Under forcing conditions, these oxiranes underwent ring opening to produce alkenyl silyl ethers as the major or exclusive product.[8]

A representative procedure for the oxirane to allyl silyl ether conversion follows. A solution of **1** (2.26 g, 10.2 mmol) in benzene (20 mL) was placed under argon atmosphere and to this was added a mixture of 1,2-epoxycyclohexane (**14**, 1.06 g, 10.7 mmol) and DBU (2 mL) in benzene (5 mL) at 22 °C. The mixture was stirred at this temperature for 20 h and poured onto a column of silica gel (15 g) which had been treated with ammonia. The column was eluted with hexane-ether mixture (2:1, 300 mL). The elute was concentrated in vacuo (200 mmHg) at room temperature and distilled. Redistillation of the fraction boiling at 50-60 °C (50 mmHg) gave pure 3-trimethylsiloxycyclohexene (**15**, 1.51 g, 87% yield).

Apparently the efficiency of this isomerization reaction is ascribed to the eminent affinity of silicon for oxygen and high electronegativity of trifluoromethanesulfonyl group.[9] Convincing evidence was obtained for operation of the addition-elimination mechanism as outlined in Scheme I. When a mixture of **1**, **14**, and triethylamine (1:1:1 ratio) in hexane was allowed to stand at 19 °C, a single, labile adduct **17** was obtained. The trans stereochemistry was substantiated by the ^{1}H NMR spectrum (CCl_4 solution) exhibiting characteristic H_a and H_b signals at δ 4.47 (ddd) and 3.57 (ddd), respectively, with vicinal coupling constant of 10 Hz.[10] This product upon treatment with DBU in benzene afforded the allyl silyl ether **15**. As would be expected, the electrophilically induced nucleophilic ring opening is made more rapid by increased alkyl substitution. When an unsymmetrically trisubstituted oxirane is used, the ring opening occurs preferentially at the more substituted carbon.[11] Thus the sense of the regioselectivity of this process is opposite that observed in the cleavage of oxiranes with sodium phenylselenide[4] in which the displacement takes place at the less substituted carbon. In the second olefin-forming step (**17** → **15**), proton abstraction occurs away from the trimethylsiloxy group. The observed selectivity, particularly with the stereoisomeric oxiranes, **10** and **12**, suggests the operation of an E2 mechanism with anti stereochemistry rather than intramolecular syn elimination.

Acknowledgment. This work was supported financially by the Ministry of Education, Japanese Government (Grant-in-aid, No. 303023).

References and Notes

(1) Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6513. Yamamoto, H.; Nozaki, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 169.

(2) Inoue, T.; Uchimaru, T.; Mukaiyama, T. *Chem. Lett.* **1977**, 1215.

(3) Cope, A. C.; Lee, H. H.; Petree, H. E. *J. Am. Chem. Soc.* **1958**, *80*, 2849. Cope, A. C.; Brown, M.; Lee, H. H. *ibid.* **1958**, *80*, 2855. Cope, A. C.; Berchtold, G. A.; Peterson, P. E.; Sharman, S. H. *ibid.* **1960**, *82*, 6370. Rickborn, B.; Thummel, R. P. *J. Org. Chem.* **1969**, *34*, 3583. Thummel, R. P.; Rickborn, B. *J. Am. Chem. Soc.* **1970**, *92*, 2064. Kissel, C. L.; Rickborn, B. *J. Org. Chem.* **1972**, *37*, 2060. Sheng, M. N. *Synthesis* **1972**, 194. Crandall, J. K.; Crawley, L. C. *Org. Synth.* **1974**, *53*, 17. Whitesell, J. K.; White, P. D. *Synthesis* **1975**, 602.

(4) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.

(5) Schmeisser, M.; Sartori, P.; Lappsmeier, B. *Chem. Ber.* **1970**, *103*, 868. Roesky, H. W.; Giere, H. H. *Z. Naturforsch. B* **1970**, *25*, 773. Marsmann, H. C.; Horn, H. G. *ibid.* **1972**, *27*, 1448.

(6) Starting oxiranes disappeared at this temperature (operation 1 in Table I).

(7) Reaction of ketones and esters with **1** in the presence of triethylamine forms alkenyl silyl ethers: Simchen, G.; Kober, W. *Synthesis* **1976**, 259; Emde, H.; Simchen, G. *ibid.* **1977**, 867.

(8) Reaction of *trans*-2,3-dihexyloxirane, **1**, and pyridine in benzene at 70 °C for 10 h produced trimethylsilyl ethers of 8-tetradecen-7-ol (17%) and 6- and 7-tetradecen-7-ols (65%). 2-Octyloxirane upon treatment with **1** and 2,6-lutidine (benzene, 80 °C, 14 h) and then DBU (25 °C, 8 h) gave (*Z*)-1-decen-1-ol trimethylsilyl ether in 80% yield.

(9) The actual active species under these conditions may be trimethylsilylammonium trifluoromethanesulfonates: Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649.

(10) Gaudemer, A. "Stereochemistry, Fundamentals and Methods", Kagan, H. B. Ed.; Georg Thieme: Stuttgart, 1977; Vol. 1, p 95.

(11) Theoretical account: Pocker, Y.; Ronald, B. P. *J. Am. Chem. Soc.* **1978**, *100*, 3122.

S. Murata, M. Suzuki, R. Noyori*
Department of Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

Received December 28, 1978

2,2′-Bisallylmethane: Thermal Degenerate Rearrangement of 1,3-Dimethylenecyclopentane. Partly Stereospecific Generation of a Biradical

Sir:

Upon thermolysis 1,5-diene systems undergo a [3,3]-sigmatropic shift (Cope rearrangement)[1] unless steric constraints prevent the termini of the diene from strongly interacting. Under these circumstances [1,3] shifts intervene,[2] the stereochemistry of which has been interpreted as resulting from the operation of both Woodward–Hoffmann orbital symmetry conservation and Berson–Salem subjacent orbital control.[3] In an effort to delineate the crossover point between concerted [3,3] shifts and other processes, the pyrolyses of 1,4-dimethylenecycloalkanes have been investigated. 1,4-Dimethylenecyclohexane (DMCH) undergoes a [3,3] shift via a

0002-7863/79/1501-2739$01.00/0