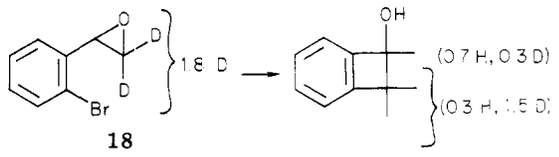


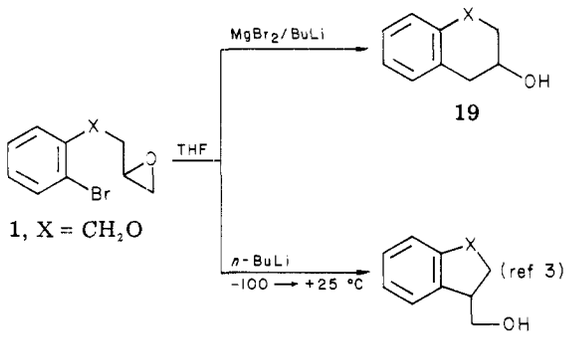
18

nistic proposals and to delineate more clearly the effect of substituents, both on the aromatic ring and on the epoxide ring, on the course of the reaction are in progress.

In agreement with the above two-path process is the observation that β,β-dideuterio-*o*-styrene oxide **18**, prepared from *o*-bromobenzaldehyde and trimethylsulfonium chloride in $D_2O/NaOD/PhCH_2{}^+N(Et)_3Cl^-$, gave benzocyclobutenol in which the deuterium labels were found to the extent of 0.3 atoms of D on the carbon bearing the hydroxyl group and 1.5 atoms of D at the methylene carbon. The results suggest that **3b** is converted to **4** by a combination of path a (70%) and path b (30%).

A typical procedure follows: 492 mg (2.0 mmol) of *o*-iodosytrene oxide was dissolved in 30 mL of dry THF at −78 °C under N_2. To this was added 1.6 mL of $MgBr_2$ (2.5 M in ether) which caused a white precipitate, followed by 1.4 mL of *n*-BuLi (1.6 M in hexane). The reaction mixture was stirred for 15–20 min at −78 °C, allowed to warm to room temperature, and quenched with saturated NH_4Cl solution. Typical workup followed by chromatography of the crude product on silica gel (1:2 ethyl acetate–hexane eluent) gave 200 mg (83%) of benzocyclobutenol, mp 56–58 °C.

Finally, as expected from our previous results, the epoxides 1[3] can be converted in good yield into the six-membered-ring derivatives **19** if the metalation is carried out with *n*-BuLi in THF at −78 °C in the presence of $MgBr_2$ or at −100 °C with *n*-BuLi[3] followed by addition of $MgBr_2$ at −78 °C and subsequent warming to room temperature. These results again point out the value of the $RLi/MgBr_2$ combination in the various intramolecular epoxide ring-opening reactions.



Acknowledgment. The financial support of NSERC (Canada) and Hoffmann-LaRoche (Nutley, N.J.) is gratefully acknowledged.

Registry No. 1 (X = CH_2), 71813-52-0; 1 (X = O), 22421-56-3; **3a**, 62717-50-4; **3b**, 71636-51-6; **3c**, 72525-47-4; **4**, 35447-99-5; **5** (*E* isomer), 72525-48-5; **5** (*Z* isomer), 72525-49-6; **7**, 72525-50-9; **8**, 72525-51-0; **9**, 72525-52-1; **10**, 72525-53-2; **11**, 72525-54-3; **12**, 19164-60-4; **18**, 72525-55-4; **19** (X = CH_2), 530-91-6; **19** (X = O), 21834-60-6; 2-methyl-4-methoxybenzaldehyde, 52289-54-0; 2-methyl-4-methoxybenzoic acid, 6245-57-4.

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Electrophilic Conversion of Oxiranes to Allylic Alcohols with *tert*-Butyldimethylsilyl Iodide

Summary: *tert*-Butyldimethylsilyl iodide (**1**) is prepared from the reaction of iodine with (phenylseleno)-*tert*-butyldimethylsilane in acetonitrile. The reaction of oxiranes with **1** followed by treatment with 1,5-diazabicyclo[4.3.0]non-5-ene gives acceptable yields of allylic alcohols isolated as their *tert*-butyldimethylsilyl ethers. Ring opening involves cleavage of the bond to the more highly substituted carbon.

Sir: Oxiranes have been isomerized to allylic alcohols by a variety of reagents including organoselenium compounds,[1] dialkylaluminum amides,[2] dialkylboron trifluoromethanesulfonates,[3] and various lithium dialkylamides.[4] Recently, a method was reported for rearranging oxiranes to allylic alcohols with trimethylsilyl trifluoromethanesulfonate.[5] This method is satisfactory for cyclic 2,2-di-, tri-, and tetrasubstituted oxiranes but fails with acyclic 2,3-dialkyl- and monoalkyloxiranes. In this communication, we report a more general procedure using *tert*-butyldimethylsilyl iodide (**1**, TBDSI) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). The reaction conditions are mild, and the method is satisfactory for cyclic di-, tri-, and tetrasubstituted oxiranes. The allylic alcohols are obtained as the hydrolytically stable *tert*-butyldimethylsilyl ethers.[6] Regiochemical results parallel those reported for trimethylsilyl trifluoromethanesulfonate, but some significant differences are noted.

$$\underset{\mathbf{2}}{PhSeSi(CH_3)_2\text{-}t\text{-}Bu} + {}^1/_2I_2 \rightarrow \underset{\mathbf{1}}{ISi(CH_3)_2\text{-}t\text{-}Bu} + {}^1/_2PhSeSePh \quad (1)$$

Treatment of (phenylseleno)-*tert*-butyldimethylsilane (**2**)[7] with 0.5 equiv of iodine in acetonitrile gave **1** and diphenyl diselenide as the only products (eq 1). Attempted isolation of TBDSI by vacuum sublimation gave a white solid that rapidly turned to a red oil containing iodine and bis(*tert*-butyldimethyl)disilane. Therefore, the reagent was generated and used in situ.

Reactions with oxiranes were run by generating **1** in an addition funnel under argon and adding this solution dropwise to a cooled (0 °C) solution of substrate in acetonitrile. Immediately after the addition, the reaction mixture was diluted with saturated sodium bicarbonate solution. The products were extracted with methylene chloride, and the extract was dried and concentrated. The residue was taken up in tetrahydrofuran (THF) and 1.5

(1) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.
(2) 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.
(3) Inoue, T.; Uchimara, T.; Mukaiyama, T. *Chem. Lett.* **1977**, 1214.
(4) For example and references cited therein: Whitesell, J. K.; White, P. D. *Synthesis* **1975**, 602. Sheng, M. N. *Ibid.* **1972**, 194. Kissel, C. L.; Rickborn, B. *J. Org. Chem.* **1972**, *37*, 2060. Rickborn, B.; Thummel, R. P. *Ibid.* **1969**, *34*, 3583. Cope, A. C.; Berchtold, G. A.; Peterson, P. E.; Sharman, S. H. *J. Am. Chem. Soc.* **1960**, *82*, 6370.
(5) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 2739.
(6) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(7) Selenosilane **2** [bp 60–52 °C (0.2 torr)] was prepared from diphenyl diselenide, sodium, and *tert*-butyldimethylsilyl chloride in THF in a manner analogous to the procedure described in: Detty, M. R. *Tetrahedron Lett.* **1978**, 5087.
(8) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247. Jung, M. E.; Blumenkopf, T. A. *Tetrahedron Lett.* **1978**, 3657. Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 417.

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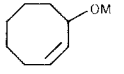
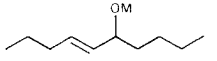
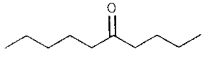
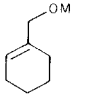
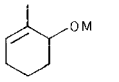
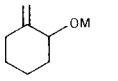
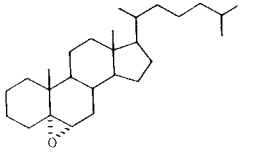
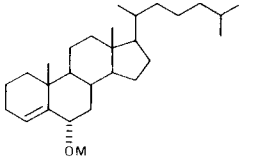
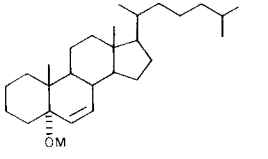
Table I. Reaction of Oxiranes and *tert*-Butyldimethylsilyl Iodide (1)[a]

entry	oxirane	conditions	products	% yld[b]
1		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 48 h		81
2		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 48 h		90
3		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 14 h		78
4		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 12 h		68
5		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 15 h		80
				2
6		**1**, CH_3CN, 0 °C		78
7	 **4**	1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C		58
				38

entry	oxirane	conditions	products	% yld[b]
8		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 1 h		52
				6
			 **5**	23
9		**1**, DBN, CH_3CN, 25 °C, 2 h		85
10		1. **1**, CH_3CN, 0 °C 2. DBN, THF, 65 °C, 16 h		35[c]
				35[c]

[a] M = *tert*-butyldimethylsilyl. 1 equiv of **1** and 1.5 equiv of DBN (where noted) were used. [b] Isolated yield. [c] Relative yield determined by ^1H NMR examination of product mixture.

equiv of DBN was added.[9] After refluxing for the appropriate time, the reaction mixture was diluted with ether and washed first with 10% HCl and then with saturated $NaHCO_3$. Chromatography on silica gel gave allylic alcohol as the *tert*-butyldimethylsilyl ether in good yield as well as diphenyl diselenide in more than 95% yield. Several representative examples of this transformation are given in Table I.[10] The protecting group is removed by treatment with tetraalkylammonium fluoride in moist dimethyl sulfoxide or THF or with KF in the presence of a catalytic amount of 18-crown-6.

The reaction of trimethylsilyl iodide[8] with oxiranes is not clean. Mixtures of deoxygenated and ring-opened products, silylated and unsilylated, were obtained. The use of TBDSI eliminates the problem of deoxygenation with alkyl-substituted oxiranes as well as the problem of facile hydrolysis of the silyl ether.

The following features of the method are worthy of note. The reaction of cyclic five-, six-, seven-, and eight-membered oxiranes (entries 1–4) gave the protected allylic alcohols in good yield. The smooth conversion of cyclooctene oxide (3) to the cyclooct-2-enol derivative is in marked contrast to the reaction of 3 with trimethylsilyl trifluoromethanesulfonate, in which only transannular cyclization is observed.[5] 2,3-Dialkyloxiranes gave good yields of the corresponding trans allylic alcohols. Thus, *trans*-2,3-dibutyloxirane gave the *tert*-butyldimethylsilyl ether of *trans*-4-decen-5-ol in 80% yield (entry 5). None of the cis isomer was detected by ^1H NMR spectroscopy or gas chromatography with a lower limit of detectability of less than 1%. A small amount of 5-decanone (2%) was also isolated. 2,2-Dimethyl-3-ethyloxirane reacted with 1 to give the allylic alcohol derivative without added base (entry 6). Spirocyclic oxirane 4 gave, in addition to the expected 1-(hydroxymethyl)cyclohexane derivative, substantial amounts of 1-(iodomethyl)cyclohexanol *tert*-butyldimethylsilyl ether (entry 7). Similarly, 1-methylcyclohexene oxide gave 23% of the trans silylated iodohydrin 5 in addition to the 2-methylcyclohex-2-enol and methylenecyclohexane derivatives (entry 8).[11] The endocyclic/exocyclic olefin ratio observed in this system was 9:1, which complements the strictly exocyclic stereochemistry observed when trimethylsilyl trifluoromethanesulfonate was used.[5,12] 5α,6α-Cholestene oxide gave an inseparable mixture of both possible allylic alcohol silyl ethers (entry 10).[13]

Monoalkylated oxiranes reacted with TBDSI to give primary iodides predominantly, which reacted slowly with DBN in refluxing THF to give 1-alken-2-ol silyl ethers. Secondary iodides were isolated as minor products from these oxiranes.

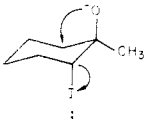
The isomerization of the oxiranes is presumably initiated by electrophilic attack of silicon on oxygen to give an onium species. This species then undergoes ring-opening displacement by iodide to give a trans iodohydrin derivative or cleaves to a tertiary carbenium ion. This ion, in turn, may lose a proton to form the allylic alcohol directly or may trap iodide. Trisubstituted and 2,2-disubstituted oxiranes preferentially give ring opening at the more highly substituted carbon. Significant amounts of ring opening at the less substituted carbon occur in cyclic six-membered oxiranes in which a trans diaxial ring opening is possible (entries 7, 8, and 10).

Registry No. 1, 72726-45-5; 2, 72726-46-6; 3, 286-62-4; 4, 185-70-6; 5, 72726-47-7; ii, 72726-48-8; 6-oxabicyclo[3.1.0]hexane, 285-67-6; 7-oxabicyclo[4.1.0]heptane, 286-20-4; 8-oxabicyclo[5.1.0]octane, 286-45-3; *trans*-2,3-dibutyloxirane, 2165-61-9; 2-ethyl-3,3-dimethyloxirane, 1192-22-9; 1-methyl-7-oxabicyclo[4.1.0]heptane, 1713-33-3; tetramethyloxirane, 5076-20-0; 5α,6α-5,6-epoxycholestane, 20230-22-2; 3-(*tert*-butyldimethylsiloxy)cyclopentene, 68845-73-8; 3-(*tert*-butyldimethylsiloxy)cyclohexane, 72726-49-9; 3-(*tert*-butyldimethylsiloxy)cycloheptane, 72726-50-2; 3-(*tert*-butyldimethylsiloxy)cyclooctane, 72726-51-3; (*E*)-6-(*tert*-butyldimethylsiloxy)dec-4-ene, 72726-52-4; 5-decanone, 820-29-1; 2-methyl-3-(*tert*-butyldimethylsiloxy)pent-1-ene, 72726-53-5; 1-(*tert*-butyldimethylsiloxy)-cyclohexene, 62791-22-4; 1-(iodomethyl)-1-(*tert*-butyldimethylsiloxy)cyclohexane, 72726-54-6; 1-methyl-6-(*tert*-butyldimethylsiloxy)cyclohexene, 72726-55-7; 2-methylene-1-(*tert*-butyldimethylsiloxy)cyclohexane, 72726-56-8; 2,3-dimethyl-3-(*tert*-butyldimethylsiloxy)but-2-ene, 72726-57-9; 6α-6-(*tert*-butyldimethylsiloxy)cholestane, 72749-02-1; 5α-5-(*tert*-butyldimethylsiloxy)cholestane, 72726-58-0.

(9) Adding DBN directly to the acetonitrile solution gave poorer yields of allylic alcohol silyl ethers.

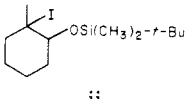
(10) All compounds gave satisfactory ^1H NMR, IR, and mass spectral data.

(11) The trans stereochemistry was assigned after treatment of 5 with tetra-*n*-butylammonium fluoride in THF gave complete conversion to 1-methylcyclohexene oxide, presumably via i.



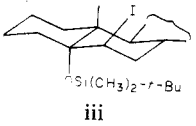
i

(12) The initial reaction of 1-methylcyclohexene oxide with 1 gave endocyclic olefin in 9% yield, exocyclic olefin in 4% yield, and a 65:35 mixture of tertiary iodide ii and secondary iodide 5 in 70% yield. Treatment of the iodide mixture with DBN gave endocyclic olefin in >95% regiochemical purity and unreacted secondary iodide.



ii

(13) The initial reaction of 5α,6α-cholestene oxide with 1 gave a mixture of both olefinic products and a labile secondary iodide assigned structure iii. Treatment of iii with fluoride gave elimination, not oxirane formation.



iii

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