mild conditions for silylations with in situ formed trimethylsilyl triflate reagent.

Experimental Section

Typical Procedure for the Preparation of Trimethylsilyl Benzoate. To a mixture of benzoic acid (1.22 g, 10 mmol) and allyltrimethylsilane (1.4 g, 12 mmol) in carbon tetrachloride (20 mL) solution was added with good stirring 2–3 drops of triflic acid under nitrogen atmosphere. Immediate reaction took place, resulting in the dissolution of benzoic acid and the copious liberation of propene. the ^{1}H NMR of this clear solution revealed that the reaction was complete. To this solution 2–3 drops of pyridine was added to neutralize triflic acid and the evaporation of solvent afforded crude trimethylsilyl benzoate, which was distilled under reduced pressure to obtain pure product, bp 43–45 °C (0.75 mm) (lit. bp 97–99 °C (100 mm)), 1.4 g, 71% yield.

General Procedure for the Preparation of Trimethylsilyl Enol Ethers. To an ice-cold solution of allyltrimethylsilane (1.5 mol equiv per mole of carbonyl group) in dry methylene chloride contained in a three-neck round-bottom flask was carfully added trifluoromethanesulfonic acid (1.5 mol equiv per mole of carbonyl group) under a nitrogen atmosphere. An exothermic reaction took place, generating trimethylsilyl triflate. The solution was stirred for 15–20 min during which time it was allowed to warm up to room temperature. From a dropping funnel, a solution of triethylamine (2 mol equiv per mole of carbonyl group) and the carbonyl compound in methylene chloride was slowly added to the above solution. After the addition was complete, the reeaction mixture was stirred for the required time. After the completion of the reaction, solvent was removed in vacuo. This resulted in two layers. The lighter product layer was separated and the denser layer was extracted with carbon tetrachloride. the extract was combined with product layer. Carbon tetrachloride was removed in vacuo and the resulting crude product was purified by fractional distillation under reduced pressure.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. Cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; acetophenone, 98-86-2; 2,3-butanedione, 431-03-8; 1-phenyl-2-propanone, 103-79-7; 2-methylcyclohexanone, 583-60-8; (1-cyclohexen-1-yloxy)trimethylsilane, 6651-36-1; (1-cyclopenten-1-yloxy)-trimethylsilane, 19980-43-9; trimethyl[(1-phenylethenyl)oxy]silane, 13735-81-4; 1,1'-[[1,2-bis(methylene)-1,2-ethanediyl]bis(oxy)bis(trimethyl)silane, 31411-71-9; trimethyl[[(1-phenylmethyl)ethenyl]-oxy]silane, 59021-31-7; trimethyl[(1-methyl-2-phenylethenyl)oxy]silane, 43108-63-0; trimethyl[(6-methyl-1-cyclohexen-1-yl)oxy]silane, 19980-33-7; trimethyl[(2-methyl-1-cyclohexen-1-yl)oxy]silane, 19980-35-9; cyclohexanol, 108-93-0; benzyl alcohol, 100-51-6; phenol, 108-95-2; α-*oluenethiol, 100-53-8; benzenethiol, 108-98-5; *m*-toluenethiol, 108-40-7; benzoic acid, 65-85-0; acetic acid, 64-19-7; indole-2-carboxylic acid, 1477-50-5; cyclohexyl trimethylsilyl ether, 13871-89-1; benzyl trimethylsilyl ether, 14642-79-6; phenyl trimethylsilyl ether, 1529-17-5; trimethylsilyl thiobenzoxide, 14629-67-5; trimethylsilyl thiophenoxide, 4551-15-9; trimethylsilyl thio-*m*-tolyl ether, 79255-62-2; trimethylsilyl benzoate, 2078-12-8; trimethylsilyl acetate, 2754-27-0; trimethylsilyl indole-2-carboxylate, 79255-63-3; allyltrimethylsilane, 762-72-1; triflic acid, 1493-13-6.

Regio- and Stereoselective Cleavage of Epoxides with Cyanoborohydride and Boron Trifluoride Etherate[1]

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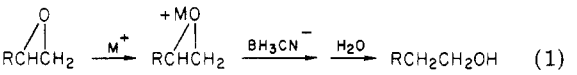
As expected for SN_2 processes, nucleophilic hydride transferring reagents attack epoxides at the less substituted position to afford the more highly substituted alcohol.[2] With electrophilic hydride reagents (i.e., BH_3, AlH_3, etc.), reverse opening is often observed to produce the less substituted alcohol, but mixtures usually result.[2,3]

We envisioned that the unique acid stability of cyanoborohydride[4] might be advantageous for regioselective opening of epoxides in which the less substituted alcohol would be preferentially produced by trapping of hydride at the site best able to accomodate a carbonium ion[5] (eq 1). Activation of epoxides toward nucleophilic attack by



(1)

complexation with a Lewis acid is required since this moiety is essentially inert toward cyanoborohydride in neutral or basic media.[6] After considerable exploration the combination of boron trifluoride etherate in dry THF was demonstrated to offer the most reliable and convenient reductive system. Other acidic reagents including protonic examples (H_2SO_4, CF_3COOH resulted in considerable polymerization of the epoxides while others (i.e., $SbCl_3$) were reduced by the reagent. Results using the BH_3CN^-/BF_3 system for a variety of epoxides are presented in Table I and illustrate important features of the conversions. First, the ring severing is highly regioselective and afford predominately the less substituted alcohols (entries 5–9) in good to excellent yields. Reactive epoxides (i.e., styrene oxide, cyclohexane oxide) are effectively reduced at 5 °C (ice bath), while aliphatic examples require ambient or refluxing (66 °C) temperatures for adequate conversions. In addition, the stereoselectivity greatly favors anti cleavage since 1-methylcyclohexane oxide (entry 5) produced almost exclusively *cis*-2-methylcyclohexanol resulting from backside diaxial opening of the intermediate complexed ring.

Limitations of the reductions were uncovered in that certain aryl and other epoxides prone to rearrangement gave products steming from migration. Thus, *trans*-stilbene oxide (entry 10) afforded predominately 2,2-diphenylethanol resulting from initial BF_3 induced rear-

(1) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, CA, Sept 1976; ORG 173.

(2) Discussions of reductive opening of epoxides with hydride reagents are contained in the following: (a) Hajos, A. "Complex Hydrides"; Elsevier: New York, 1979. (b) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry, Part B"; Plenum Press: New York, 1977. (c) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 103–104.

(3) Electrophilic reagents which have been utilized with varying degrees of success include the following: (a) AlH_3; Yoon, N. M.; Brown, H. C.; Lamke, W. E. *J. Org. Chem.* **1967**, *32*, 537. Lansbury, P. T.; Sharf, D. J.; Pattison, V. A. *ibid.* **1968**, *32*, 1748. Ashby, E. C.; Cooke, B. J. *J. Am. Chem. Soc.* **1968**, *90*, 1625. (b) Diisobutylaluminum hydride; Zakharkin, L. I.; Khorlina, I. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, 862. Lenox, R. S.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 957. (c) BH_3 + BF_3; Brown, H. C.; Yoon, N. M. *Chem. Commun.* **1968**, 1549. Lyle, R. E.; Krueger, W. E. *J. Org. Chem.* **1967**, *32*, 2873. (d) BH_3 + BH_4^-; Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1968**, *90*, 2686. Bessiere-Chretien, Y.; Meklati, B. *Tetrahedron Lett.* **1971**, 621. Fu, Y. L.; Bobek, M. *J. Org. Chem.* **1980**, *45*, 3836.

(4) For reviews of cyanoborohydride chemistry, see (a) Hutchins, R. O.; Natale, N. R. *Org. Prep. Proced. Int.* **1979**, *11*, 201. (b) Lane, C. F. *Synthesis* **1975**, 131.

(5) The use of acid in combination with cyanoborohydride to generate ions which are trapped by hydride has been successful for conversions of triphenylmethanol to triphenylmethane [Kreevoy, M. M.; Johnston, D. C. *Croat. Chem. Acta* **1973**, *45*, 511], acetals to ethers [Horne, D. A.; Jordan, A. *Tetrahedron Lett.* **1978**, 1357], and the conversion of certain reactive allylic alcohols to alkenes [Hutchins, R. O.; Kandasamy, D. *J. Org. Chem.* **1975**, *40*, 2530].

(6) Hutchins, R. O.; Kandasamy, D.; Maryanoff, C. A.; Masilamani, D.; Maryanoff, B. E. *J. Org. Chem.* **1977**, *42*, 82.

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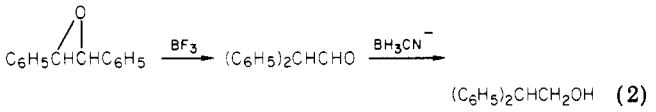
Table I. Reductions of Epoxides with Cyanoborohydride–Boron Trifluoride Etherate

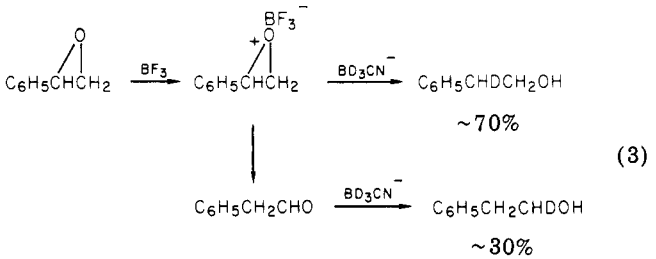
entry	epoxide	T, °C (time, h)	product(s) (rel ratio)[a]		% yield[b]
1	cyclohexene	5 (0.75)	cyclohexanol		63, 96[c]
2	cyclooctene	5 (4)	cyclooctanol		60
3	cyclododecene	66 (22)	cyclododecanol		94
4	cyclooctadiene (monoepoxide)	25 (20)	cyclooctan-2-en-1-ol (89)	cyclooctan-3-en-1-ol (11)	79
5	1-methylcyclohexene	25 (6)	2-methylcyclohexanol, cis (97),[d] trans (trace)	1-methylcyclohexanol (3)	87
6	styrene	5 (4)	2-phenylethanol (97)	1-phenylethanol (3)	79
7	β-methylstyrene	25 (4)	2-phenyl-1-propanol (99)	2-phenyl-2-propanol (1)	94
8	1-dodecene	66 (4)	1-dodecanol (89)	2-dodecanol (11)	83
9	2-methylundecene	66 (2)	2-methyl-1-undecanol (95)	2-methyl-2-undecanol (5)	73
10	*trans*-stilbene	66 (4)	1,2-diphenylethanol (12)	2,2-diphenylethanol (88)	80

[a] Ratios of products determined by GC. [b] Yields represent isolated, distilled products unless otherwise indicated. [c] GC yield, corrected for detector response. [d] Analyzed as the acetates.

rangement to diphenylacetaldehyde prior to reduction[7] (eq 2). In addition, the reduction of styrene oxide with



(2)



(3)

$NaBD_3CN$ afforded 2-phenylethanol-*d* with approximately 30% of the deuterium located at the 1-carbon, indicating partial rearrangement prior to reduction (eq 3). Note that such rearrangement and subsequent reduction results in production of the same product (2-phenylethanol) in the absence of the deuterium tag. Norbornene epoxide gave a complex mixture of products, some of which contained fluorine. In no other cases was evidence of rearrangement observed.

In conclusion, BH_3CN^-–BF_3OEt_2 provides an effective combination for the regio- and stereoselective cleavage of most epoxides to the less substituted alcohols resulting from anti ring opening. Further, the inertness of BH_3CN^- toward several other functional groups in acidic media (ester, acid, amide, cyano, nitro)[4,8] recommends the reagent system when chemoselectivity is important.

Experimental Section

General Methods. The epoxides used were either commercially available or prepared from the corresponding alkene and *m*-chloroperbenzoic acid in $CHCl_3$.[9] GC analyses were performed on either a Hewlett-Packard Model 5750 or a Varian Model 3700 equipped with a Columbia Scientific Industries Model CSI 38 digital integrator, and product identification was accomplished by comparison with authentic samples.

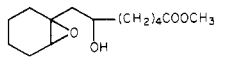
Reduction of Epoxides. General Procedure. The general reaction procedure was straightforward. A solution of the epoxide (10 mmol), $NaBH_3CN$ (14–30 mmol), and a small quantity of bromocresol green indicator in 40 mL of dry THF was stirred, while BF_3OEt_2 in a few milliliters of THF was added dropwise until a color change to yellow was noted and stirring was continued at the temperatures in Table I for the durations listed. For some examples, additional BF_3OEt_2 was required periodically to maintain the acidity. Upon completion the reactions were diluted with brine and exhaustedly extracted with ether. After the solution was dried (Na_2SO_4), solvent was removed on a rotary evaporator and the residue distilled on a Kugelrohr apparatus and analyzed by GC.

Acknowledgment. We thank the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for support of this work.

Registry No. Cyclohexene epoxide, 286-20-4; cyclooctene epoxide, 286-62-4; cyclododecene epoxide, 286-99-7; cyclooctadiene epoxide, 637-90-1; 1-methylcyclohexene epoxide, 1713-33-3; styrene epoxide, 96-09-3; 3-methylstyrene epoxide, 4436-22-0; 1-dodecene epoxide, 2855-19-8; 2-methylundecene epoxide, 54125-40-5; *trans*-stilbene epoxide, 1439-07-2; sodium cyanoborohydride, 25895-60-7; boron trifluoride etherate, 109-63-7.

(7) (a) House, H. O.; Reif, D. J. "Organic Syntheses", Collect. Vol. 4; Wiley: New York, 1963; p 375. Collins, D. J. *J. Chem. Soc.* **1959**, 3919. (b) Reduction of *trans*-stilbene oxide with R_3SiH/BF_3 also proceeds via initial rearrangement to 1,1-diphenylethanal; Fry, J. F.; Marz, T. J. *Tetrahedron Lett.* **1979**, 849.

(8) The method has been successfully utilized to convert epoxide i to ii (70% + 30% of the tertiary alcohol; 80% yield); G. C. de Magalhaes (University of Brasilia), personal communication. In this case the amount of attack at the less substituted site is perhaps augmented by hydride deliverance at this position by cyanoborohydride complexed to the secondary alcohol.



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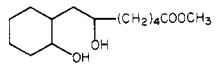

ii

(9) Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 135.

Organic *N*-Halogeno Compounds. 14.[1] Preparation of *N*-(*N*-Halomethoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimines

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Received July 22, 1981

Sulfilimines are unique in reactivity, and many intensive studies on them have been performed.[2] Sulfilimines of

(1) Part 13: T. Fuchigami and T. Nonaka, *Chem. Lett.*, 829 (1979).

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