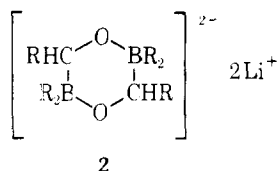


is consumed. Thus the triethylborane serves as a catalyst in this reaction.

The product of this reaction must be an intermediate corresponding to 1 ($R = \text{ethyl}$), or an association product. Simple evaporation of the THF permits isolation of this intermediate. The ^{11}B NMR spectrum exhibits a broad singlet at $\delta -2.74$ in the lithium case, suggesting its possible existence as an "ate" complex in the form of the dimer 2. However, instead of ex-



ploring the structure of these intermediates at this time, we preferred to establish that hydrolysis with base provided the homologated alcohols (RCH_2OH), and oxidation with hydrogen peroxide provided the corresponding aldehydes (RCHO), both in excellent yields. The procedure also provides a valuable new route to the intermediate, free of the aluminum alkoxides which accompanied earlier carbonylation procedures.

The reaction appears to be quite general. It was applied to representative trialkylboranes without difficulty. It also works quite satisfactorily with *B*-alkyl-9-BBN derivatives. The results are summarized in Table II.

The reaction was also successfully applied to lithium triphenylborohydride. Addition of a small amount of excess triphenylborane resulted in rapid carbonylation. (However, subsequent hydrolysis gave diphenylmethane, indicating a second migration.)

The reaction of alkali metal hydrides with trialkylboranes provides a convenient route, with only a few exceptions, to the alkali metal trialkylborohydrides.^{8,9} This circumvents the need in most cases for utilizing either lithium trimethoxyaluminumhydride^{4,5} or lithium tri-*tert*-butoxyaluminumhydride,¹⁰ thereby avoiding the presence of the corresponding aluminum alkoxide in the reaction mixture.

The following procedure for the carbonylation of lithium tri-*sec*-butylborohydride is representative. A dry 200-mL flask fitted with magnetic stirring bar and septum inlet was attached to the automatic gasimeter,^{11,12} adapted for carbonylation as previously described.¹³ The system was flushed with nitrogen while the flask cooled. It was then immersed in a dry ice/*o*-xylene bath at -25°C . Lithium tri-*sec*-butylborohydride (9.6 mL, 1.04 M) in THF (10 mmol) was introduced. The system was flushed with carbon monoxide and vigorous stirring was begun. Carbon monoxide (10 mmol) was absorbed in approximately 18 min. The system was flushed with nitrogen and the reaction flask was transferred to a reflux condenser. Aqueous sodium hydroxide (10 mL, 3 N) was added and the mixture was heated to reflux for 2 h. After cooling, the flask was immersed in an ice bath and 4 mL of 30% hydrogen peroxide was added. The ice bath was removed and stirring was continued for 1 h at room temperature. *n*-Hexadecane (5 mmol; 1.46 mL) was added as an internal standard. Anhydrous potassium carbonate (14 g) was added and dissolved. The THF layer was separated and dried over anhydrous magnesium sulfate, and then powdered 3 Å molecular sieves. GLC analysis revealed 9.4 mmol of 2-methyl-1-butanol.

The present development emphasizes the value of ^{11}B NMR in understanding the unusual phenomena often encountered in borane chemistry. We are continuing to explore the synthetic potential of this novel reaction.

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References and Notes

- (1) C. A. Brown, *J. Am. Chem. Soc.*, **95**, 4100 (1973); C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).
- (2) C. A. Brown, 172nd National Meeting of the American Chemical Society, San Francisco, California, Aug. 29–Sept 3, 1976, Abstract ORGN-153; C. A. Brown, *J. Organomet. Chem.*, **156**, C17 (1978).
- (3) For example, oxidation yields the aldehyde (RCHO), alkaline hydrolysis yields the methylol (RCH_2OH), and mild protonolysis yields the borinic acid (RB(OH)CHR_2) (ref 4 and research in progress).
- (4) H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Am. Chem. Soc.*, **90**, 499 (1968).
- (5) H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Am. Chem. Soc.*, **91**, 2144 (1969).
- (6) J. L. Hubbard, Ph.D. Thesis, Purdue University, 1976.
- (7) The proposed reduction of the carbonyl adduct is similar to the reduction of transition metal carbonyls by lithium triethylborohydride as recently described: J. A. Gladysz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, C1 (1977).
- (8) H. C. Brown, S. Krishnamurthy, and J. L. Hubbard, *J. Am. Chem. Soc.*, **100**, 3343 (1978).
- (9) C. A. Brown and S. Krishnamurthy, *J. Organomet. Chem.*, **156**, 111 (1978).
- (10) H. C. Brown and R. A. Coleman, *J. Am. Chem. Soc.*, **91**, 4606 (1969).
- (11) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1976, pp 218–221.
- (12) The gasimeter used was a commercial model available from Delmar Scientific Laboratories, Inc., Maywood, Ill. An improved model is now available from Ace Glass, Inc., Vineland, N.J.
- (13) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 2606 (1966).

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1-(Trimethylsilyl)benzene Oxides: Synthesis, Aromatization, and Reactions of Carbanions from Desilylation

Summary: The synthesis, acid-catalyzed aromatization, and reaction of carbanions from desilylation of 1-(trimethylsilyl)benzene oxides are described.

Sir: Cleavage of the Si–O or, in certain cases, the Si–C bond by F^- has become a useful transformation for organic synthesis.¹ Application of the reaction to simple α -(trimethylsilyl)oxiranes affords the corresponding oxiranyl anion that abstracts H^+ (or D^+) from the reaction medium to afford the desilylated epoxide.²

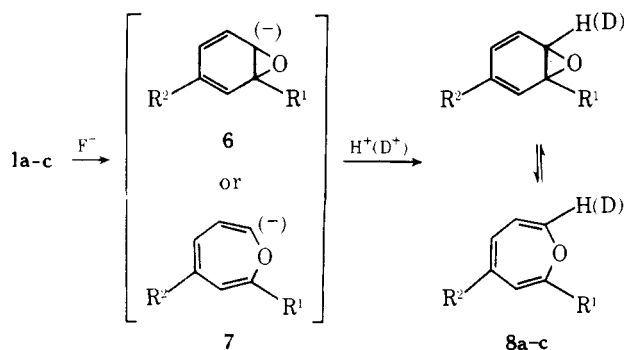
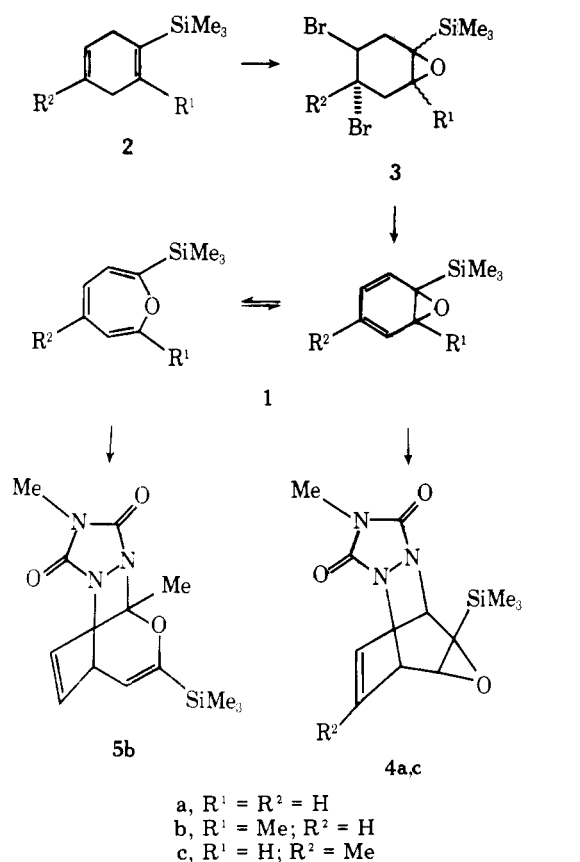
We wish to report the preparation and quantitative desilylation of 1-(trimethylsilyl)benzene oxide–oxepins **1a–c** with F^- under various conditions. Synthesis of **1a–c** was effected by conversion of the known dienes **2a–c**³ to **3a–c**⁴ and subsequent elimination of HBr with DBN in THF to afford the arene oxides.^{5,6} Whereas **1a** and **1c** reacted with 4-methyl-1,2,4-triazoline-3,5-dione to afford the expected Diels–Alder adducts **4a** and **4c**^{7,8} from the benzene oxide valence isomer, **1b** afforded adduct **5b**^{5,8} (100%) from reaction of the oxepin valence isomer. It is interesting to note that 2,7-dimethyloxepin reacts with azodicarboxylate esters to afford similar adducts from the oxepin valence isomer that are not stable but undergo Claisen rearrangement to a cyclopropyl ketone.⁹ Adduct **5b** is stable at room temperature.

Reaction of **1a–c** with F^- affords an anionic intermediate (**6** or **7**) that quantitatively abstracts H^+ (or D^+) from the reaction medium to afford exclusively **8a–c**, i.e., no tautomerism of the anionic intermediate to phenoxide anion occurs under the reaction conditions (Table I). In acetonitrile the rate of desilylation of **1a** with the different F^- sources follows the order $(n\text{-Bu})_4\text{NF} \gg \text{Et}_4\text{NF} > \text{KF/crown ether}$. The reaction in acetonitrile is immeasurably slow if an excess (20 equiv) of H_2O is added, but the reaction in both acetonitrile and dimethyl sulfoxide occurs with 1 equiv of H_2O (D_2O) present.

Table I. Desilylation of 1a-c by F⁻ ^a

	F ⁻ source	solvent	product (% D incorp.) ^b
1a	Et ₄ N ⁺ F ⁻	CH ₃ CN	8a
1a	Et ₄ N ⁺ F ⁻	CD ₃ CN	8a (85)
1a	Et ₄ N ⁺ F ⁻	CD ₃ SOCD ₃	8a (<15)
1a	Et ₄ N ⁺ F ⁻	CD ₃ SOCD ₃ + 1 equiv D ₂ O	8a (69)
1a	(<i>n</i> -Bu) ₄ N ⁺ F ⁻	CH ₃ CN	8a
1a	KF/18-crown-6	CD ₃ CN	8a (79)
1b	Et ₄ N ⁺ F ⁻	CD ₃ CN	8b (88)
1c	Et ₄ N ⁺ F ⁻	CD ₃ CN	8c (81)

^a Reagents and solvent were predried over Linde 4A molecular sieves and, except for the reaction where D₂O was added, the reaction mixture was kept at room temperature over sieves. ^b Analysis by ¹H NMR and mass spectrometry of the product and of the Diels-Alder adduct with 4-methyl-1,2,4-triazoline-3,5-dione.

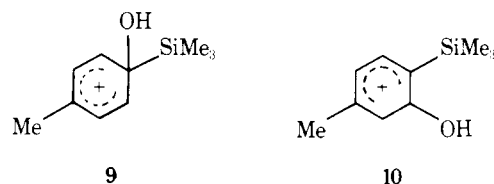


Since the H⁺ (or D⁺) source follows the acidity order H₂O > CH₃CN > R₄N⁺ > CH₃SOCH₃, proper choice of the reaction medium (CD₃CN or CD₃SOCD₃ + 1 equiv of D₂O) provides a high degree of deuterium incorporation with R₄N⁺F⁻

and only a small proportion of neutralization of the intermediate anion by H⁺ transfer from the α position of R₄N⁺.¹⁰ The reaction thus provides a convenient single-step route to selective deuterium labeling at one of the epoxy carbon atoms of arene oxides for investigations of their mechanism of aromatization. The method should be equally applicable to the synthesis of the analogous deuterium-labeled arene oxides of polycyclic aromatic hydrocarbons.

Whether the nucleophilic displacement at silicon by F⁻ occurs on the benzene oxide or oxepin valence isomer of 1a-c is open to question. Argument in favor of anion 6 is supported by the formation of oxiranyl anions from reaction of α-(trimethylsilyl)oxiranes with F⁻ and reports that cleavage of the silicon-vinyl carbon bond is difficult.¹¹ On the other hand desilylation of the oxepin valence isomer is not unreasonable since 1-chloro-1-(trimethylsilyl)-2-methylpropene undergoes dehalosilylation with Me₄N⁺F⁻ to generate a carbene species that is trapped by olefins.¹² 1-Chloro-2-methylpropene is observed as a minor product in this latter reaction, and it becomes the major product if 1 equiv of H₂O is added to the reaction mixture to trap the intermediate vinyl anion.

Acid-catalyzed aromatization of 1a and 1b (CF₃CO₂H in CDCl₃) affords phenol and *o*-cresol, respectively, in quantitative yield. Aromatization of 1c under the same conditions gives a 1:1 mixture of *m*- and *p*-cresol. The latter reaction must occur through acid-catalyzed ring opening of 1c to afford 9 and 10 in equivalent amounts. Since the 4-methyl group of



1c would favor acid-catalyzed oxirane ring opening in the direction to afford 9,¹³ the aromatization of 1a must occur predominantly or entirely by acid-catalyzed cleavage of the C₁-O bond to afford a cationic intermediate analogous to 10 (i.e., 4-H instead of 4-Me). Although localization of positive charge at the α position to silicon is reported to be disfavored,¹ nucleophilic addition to the α position of α-silyloxiranes occurs readily under acid catalysis;¹⁴ and evidence has been presented for incipient carbonium ion formation α to silicon.¹⁵ Ring silylated phenols from aromatization of 1a-c would be desilylated under the acidic conditions of the reaction.¹⁶

Additional studies of the reaction of anions derived from 1a-c with electrophiles, including T⁺, and of the mechanism of aromatization of 1a-c are in progress.

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References and Notes

- P. F. Hudrlik, in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, 1976, p 127; E. W. Colvin, *Chem. Soc. Rev.*, **7**, 15 (1978); I. Fleming, *Chem. Ind. (London)*, 449 (1975).
- T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 2667 (1976); T. H. Chan and B. S. Ong, *J. Org. Chem.*, **43**, 2994 (1978). Oxiranyl anions have also been generated by proton abstraction with an alkyl lithium, and their reaction with electrophiles has been investigated: J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, **98**, 4646 (1976).
- C. Eaborn, R. A. Jackson, and R. Pearce, *J. Chem. Soc., Perkin Trans. 1*, 470 (1975); H. Hopff, J. M. Deuber, P. Gallegra, and A. Said, *Helv. Chim. Acta*, **54**, 117 (1971).
- Dienes 2a-b were epoxidized (*m*-CPBA/CH₂Cl₂, 60-67%), and the epoxides were brominated (Br₂/CH₂Cl₂, 84-100%) to afford 3a-b. Diene 2c was brominated (Br₂/CH₂Cl₂, -78 °C), and the dibromide was oxidized (CF₃CO₂H/CH₂Cl₂) to afford 3c. All materials were characterized by elemental analysis (except 3c) and spectral data.

- (5) Satisfactory high-resolution mass spectral analysis. The high-resolution mass spectra were provided by the facility sponsored by National Institutes of Health Grant RR00317 (Principal Investigator Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.
- (6) Spectral data for **1a-c**. **1a**: $^1\text{H NMR}$ (CDCl_3) δ 0.16 (s, 9 H), 5.5–5.8 (m, 1 H), 5.8–6.1 (m, 2 H), 6.1–6.5 (m, 2 H); UV max (isooctane) 297 nm (ϵ 1457). **1b**: $^1\text{H NMR}$ (CDCl_3) δ 0.17 (s, 9 H), 1.87 (s, 3 H), 5.31 (m, 1 H), 5.73 (m, 1 H), 5.95 (m, 2 H); UV max (isooctane) 317 nm (ϵ 1217). **1c**: $^1\text{H NMR}$ (CDCl_3) δ 0.13 (s, 9 H), 1.82 (s, 3 H), 5.30 (d, 1 H), 5.55–6.05 (m, 3 H); UV max (MeOH) 287 nm (ϵ 1050).
- (7) Satisfactory combustion analysis (C, H, N).
- (8) **4a**: mp 140–141 °C; $^1\text{H NMR}$ (CDCl_3) δ 0.20 (s, 9 H), 2.95 (s, 3 H), 3.45 (d, 1 H, $J = 4$ Hz), 5.12 (m, 2 H), 6.01 (m, 2 H). **4c**: mp 155–156 °C; $^1\text{H NMR}$ (CDCl_3) δ 0.10 (s, 9 H), 1.76 (d, 3 H, $J = 1$ Hz), 2.85 (s, 3 H), 3.34 (d, 1 H, $J = 4.5$ Hz), 4.85 (m, 2 H), 5.34–5.62 (m, 1 H). **5b**: mp 98–100 °C; $^1\text{H NMR}$ (CDCl_3) δ 0.07 (s, 9 H), 2.13 (s, 3 H), 3.04 (s, 3 H), 4.54 (dt, 1 H, $J = 7, 1.5$ Hz), 5.18 (d, 1 H, $J = 7$ Hz), 5.60 (dd, 1 H, $J = 8, 1.5$ Hz), 6.50 (dd, 1 H, $J = 8, 7.5$ Hz); mass spectrum m/e 293 (34%) $[\text{M}]^+$, 179 (47%) $[\text{M} - \text{C}_5\text{H}_9\text{OSi}]^+$. There is no peak in the mass spectrum of **5b** at m/e 237 $[\text{M} - \text{C}_3\text{H}_4\text{O}]^+$.
- (9) W. H. Rastetter and T. J. Richard, *Tetrahedron Lett.*, 2999 (1978).
- (10) The extent to which proton transfer occurs from trace quantities of water vs. R_4N^+ have not been determined.
- (11) See ref 1 and 2 and references cited therein.
- (12) R. F. Cunico and Y-K Han, *J. Organomet. Chem.*, **105**, C29 (1976).
- (13) Acid-catalyzed aromatization of 4-methylbenzene oxide gives only *p*-cresol: D. M. Jerina, J. W. Daly, and B. Witkop, *J. Am. Chem. Soc.*, **90**, 6523 (1968).
- (14) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, *J. Am. Chem. Soc.*, **99**, 1993 (1977); P. F. Hudrlik, J. P. Arcoleo, R. H. Schwartz, R. N. Misra and R. J. Rona, *Tetrahedron Lett.*, 591 (1977); C. M. Robbins and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 697 (1976); M. Obayashi, K. Ultimoto, and H. Nozaki, *Tetrahedron Lett.*, 1383 (1978).
- (15) J. J. Eisch and J. E. Galle, *J. Org. Chem.*, **41**, 2615 (1976).
- (16) Desilylation of trimethylsilyl-substituted benzene derivatives occurs readily with strong acid (see ref 1). 2,6-Bis(trimethylsilyl)toluene is converted rapidly to toluene and 4-(trimethylsilyl)-2-methylbenzene oxide aromatizes with desilylation to afford *o*-cresol under our reaction conditions ($\text{CF}_3\text{CO}_2\text{H}$ in CDCl_3).
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