Experimental Section

Materials. The majority of reagents and solvents used in this investigation were obtained from commercial sources. Compounds synthesized in our laboratory were ethyl 2-bromo-3-methylbutanoate, ethyl 2-bromo-3,3-dimethylbutanoate, and ethyl 2-bromo-2-ethylbutanoate prepared from the corresponding nonbrominated acids,[20] bromotricarbethoxymethane prepared from the corresponding nonbrominated triester,[21] and 3-propoxypropene prepared by a standard Williamson synthesis.[22] All materials were purified before use. Properties agreed with the literature values.

Determination of Selectivities. A standard competitive kinetic approach was used.[23] Stock solutions of either 3-propoxypropene or 1-methylcyclohexene, 1-octene, ethyl 2-bromo carboxylate, chlorobenzene (internal GLC standard), benzoyl peroxide (radical chain initiator), and benzene (solvent) were prepared in approximate relative molar ratios of 1:1:4:1:0.1:13. The solution was divided among several reaction tubes. Air was removed from the samples by repeated freeze–thaw cycles. Tubes were sealed while samples were under a nitrogen atmosphere at reduced pressure. One tube was reserved as a starting mixture sample, and the remainder were put in a 70.0 ± 0.1 °C constant-temperature bath for 24 h. Relative rates of disappearance of the two competing alkenes were determined by GLC evaluation of relative concentrations. All GLC analyses were carried out on a Varian 200 chromatograph. A 15 ft × $^1/_4$ in. packed column of 5% SE-30 on Chromasorb-W was used throughout this study. The 24-h reaction time employed corresponded to 15-35% disappearance of each alkene in any given run.

Acknowledgment. M.K. expresses his graditude to the Orgeon State University Undergraduate Honors Program for providing financial support.

Registry No. $BrCH_2CO_2Et$, 105-36-2; $BrCH(Me)CO_2Et$, 535-11-5; $BrCN(Et)CO_2Et$, 533-68-6; $BrCN(i\text{-}Pr)CO_2Et$, 609-12-1; $BrCH(t\text{-}Bu)CO_2Et$, 20201-39-2; $BrC(Me)_2CO_2Et$, 600-00-0; $BrC(Et)_2CO_2Et$, 6937-28-6; $\cdot CH_2CO_2Et$, 21946-41-8; $\cdot CH(Me)CO_2Et$, 37999-08-9; $\cdot CH(Et)CO_2Et$, 105019-17-8; $\cdot CH(i\text{-}Pr)CO_2Et$, 105019-18-9; $\cdot CH(t\text{-}Bu)CO_2Et$, 105019-19-0; $\cdot C(Me)_2CO_2Et$, 37999-09-0; $\cdot C(Et)_2CO_2Et$, 105019-20-3; 3-propoxypropene, 1471-03-0; 1-octene, 111-66-0; 1-methylcyclohexene, 591-49-1.

(20) Allen, C. F.; Kalm, M. J. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 616.
(21) Carothers, W. H. *J. Am. Chem. Soc.* **1926**, *48*, 3197.
(22) Williamson, A. W. *J. Chem. Soc.* **1852**, *4*, 229.
(23) Gleicher, G. J. *J. Org. Chem.* **1968**, *33*, 332.

Epoxide Opening with *tert*-Butyldimethylsilyl Cyanide–Zinc Iodide. Evidence for a Stepwise Process in the Opening of a Sterically Hindered Epoxide

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Recently, we have described the opening of oxiranes (epoxides)[2] and oxetanes[3] with trimethylsilyl cyanide–zinc iodide to produce high yields of **1** and **2**, respectively. Because of the ease with which **1** could be converted into β-amino alcohols **3**, and **2** could serve as a source of γ-amino alcohols **4**, these reactions appeared to have considerable potential as a new synthetic route to these bifunctional molecules. In order to establish whether we could introduce the more stable *tert*-butyldimethylsilyl protecting group via this method, we investigated the opening of epoxides with *tert*-butyldimethylsilyl cyanide[4]–zinc iodide. This paper presents the details of this investigation.

Scheme I

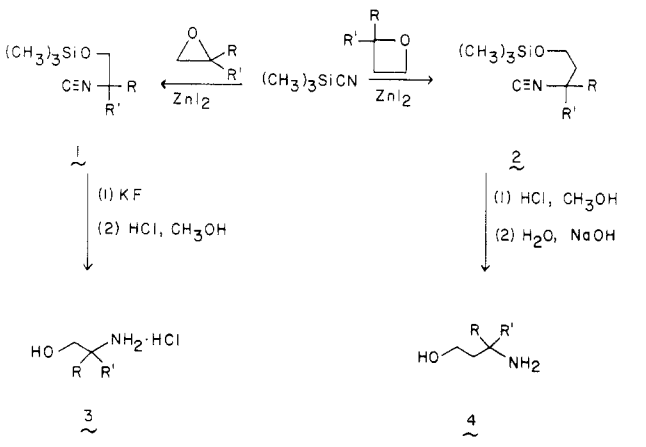
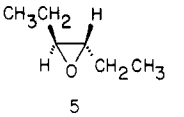
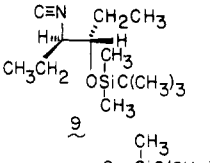
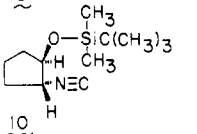
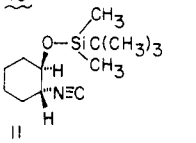
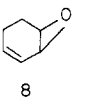
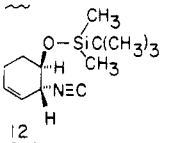


Table I. Opening of Epoxides with *tert*-Butyldimethylsilyl Cyanide–Zinc Iodide in Refluxing Methylene Chloride

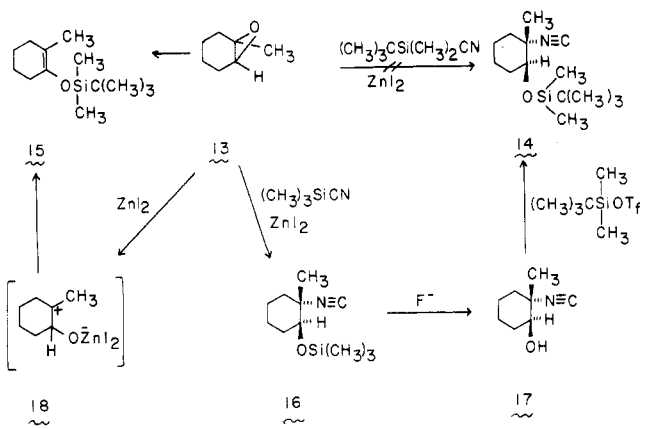
epoxide	product	reactn time, h	% yield
 5	 9	48	74
 6	 10	48	81
 7	 11	48	87
 8	 12	48	87

As shown in Table I, when a series of epoxides **5–8** was allowed to react with *tert*-butyldimethylsilyl cyanide and zinc iodide in methylene chloride, the corresponding *tert*-butyldimethylsilyl ether of the β-hydroxy isonitriles **9–12**, respectively, were obtained in 74–87% yield. In most respects these reactions paralleled the related opening of these same epoxides with trimethylsilyl cyanide–zinc iodide.[2] However, certain differences did exist. The first major difference involved the rate of the epoxide ring opening. In general, those reactions involving *tert*-bu-

(1) 3M Fellow, 1984–1985.
(2) Gassman, P. G.; Guggenheim, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 5849. Gassman, P. G.; Gremban, R. S. *Tetrahedron Lett.* **1984**, *25*, 3259. See also: Spessard, G. O.; Ritter, A. R.; Johnson, D. M.; Montgomery, A. M. *Ibid.* **1983**, *24*, 655.
(3) Gassman, P. G.; Haberman, L. M. *Tetrahedron Lett.* **1985**, *26*, 4971. See also: Carr, S. A.; Weber, W. P. *Synth. Commun.* **1985**, *15*, 775.
(4) *tert*-Butyldimethylsilyl cyanide could be prepared either by the method of Treichel and Shaw[5] or through an adaptation of the procedure of Zubrick, Dunbar, and Durst.[6]
(5) Treichel, P. M.; Shaw, D. B. *J. Organomet. Chem.* **1977**, *139*, 21. Although our melting point approached that of these authors, NMR analysis indicated the presence of 35–40% contamination of the *tert*-butyldimethylsilyl cyanide by *tert*-butyldimethylsilyl chloride.
(6) Zubrick, J. W.; Dunbar, B. I.; Durst, H. D. *Tetrahedron Lett.* **1975**, 71.

0022-3263/86/1951-5010$01.50/0

Scheme II

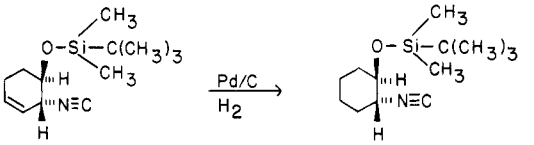


tyldimethylsilyl cyanide occurred 10–20 times slower than those involving trimethylsilyl cyanide.[2] This implies that the *tert*-butyldimethylsilyl cyanide was involved in the rate-determining step. The rate retardation could be attributed to the added steric effect resulting from the replacement of a methyl by a *tert*-butyl group. While this rate retardation and the rigorous trans stereochemistry of the products suggested an S_N2-type attack on a Lewis acid complexed epoxide, other evidence pointed to the intermediacy of a discrete carbocation in at least one example.

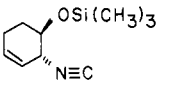
In contrast to the very acceptable yields of ring-opened products obtained from the epoxides **5**–**8**, the epoxide **13** gave neither an isonitrile nor a nitrile on treatment with *tert*-butyldimethylsilyl cyanide–zinc iodide. No trace of the expected product **14** could be detected. Instead, a 63% yield of the silyl enol ether **15**[7] was obtained. In order to determine whether **14** might have been formed in the usual manner only to suffer loss of hydrogen cyanide to produce **15** under the reaction conditions, **14** was prepared by an alternate synthetic route. Utilizing the literature procedure,[2] **13** was converted into **16**, and **16** was desilylated with fluoride ion to produce **17**. Treatment of **17** with *tert*-butyldimethylsilyl triflate gave an authentic sample of **14**. When **14** was subjected to the reaction conditions, it was found to be stable. It was not converted to **15**. Thus, **15** appeared to a primary product.

Mechanistically, it seems probable that **13** was converted to **18** in the presence of zinc iodide. Silylation and proton loss would then have given **15**. This should not be misconstrued to mean that carbocations are involved in all of the epoxide-opening reactions discussed above. If discrete carbocations were formed, it would be extremely difficult to rationalize the very well-defined stereochemical relationships of the observed products. The formation of **15** would be consistent with the slow conversion of **13** into **15** in the presence of the slowly reacting, sterically encumbered *tert*-butyldimethylsilyl cyanide. When trimethylsilyl cyanide was present, **13** converted into **16** more rapidly than it was converted into **15**. Thus, it would appear that a competition does exist in this epoxide-opening reaction between E1 and S_N2 mechanisms.[8]

Special attention was merited by the very clean conversion of **8** into **12**. The opening of 1,3-cyclohexadiene monoepoxide has been studied under a wide variety of ring-opening conditions.[9-11] In general, those reactions that involved nucleophilic opening of the epoxide moiety occurred via an S_N2 mechanism rather than through a formal S_N2' process. Thus, alkoxides, amines, and mercaptides reacted with 1,3-cyclohexadiene monoepoxide to give either exclusively[9] or predominately[10] 3,4-disubstituted cyclohexenes. In contrast, the opening of 1,3-cyclohexadiene monoepoxide with organocopper reagents generally yields the 3,6-disubstituted cyclohexene.[11] In view of these literature precedents, it is interesting to note that **8** gave only the 3,4-disubstituted cyclohexene **12**. This would be most consistent with an S_N2-type attack of the nitrogen, which eventually becomes the bonding atom of the isonitrile moiety. The opening of **8** with *tert*-butyldimethylsilyl cyanide–zinc iodide was paralleled by the reaction of **8** with trimethylsilyl cyanide–zinc iodide, which gave **19** in 78% yield.



Structural evidence for **12**, and by analogy and spectral comparison with **19**, was obtained through the conversion of **12** into **11** by catalytic hydrogenation over 5% palladium on carbon. This reduction, which occurred in 83% yield, gave material that was identical with that obtained from **7** by direct reaction with *tert*-butyldimethylsilyl cyanide–zinc iodide.



As indicated in the Experimental Section, all of the ring-opened products were definitively identified through extensive spectroscopic studies. Of particular significance was the coupling of the isonitrile nitrogen to the isonitrile carbon and to the substrate carbon to which the isonitrile group was attached.[2,3,12]

In summary, we have expanded our understanding of the opening of epoxides with trialkylsilyl cyanide–zinc iodide.

Experimental Section[13]

***tert*-Butyldimethylsilyl Cyanide.** The procedure of Durst and co-workers[6] for preparation of trimethylsilyl cyanide was

(7) For an alternate synthesis of **15**, see: Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4462.

(8) It should be reiterated that the observed stereochemistry of the difunctional products precludes the intermediacy of a free (uncomplexed) carbocation and, as a result, of an S_N1 process without neighboring group participation.

(9) For a leading reference, see: Knapp, S.; Sebastian, M. J.; Ramanathan, H. *J. Org. Chem.* **1983**, *48*, 4786. See also: Kozlov, N. S.; Zhavnerko, K. A.; Yakubovich, L. S.; Perishchepenko, V. M. *Dokl. Akad. Nauk SSSR* **1975**, *19*, 812.

(10) For leading references, see: Posner, G. H.; Rogers, D. Z. *J. Am. Chem. Soc.* **1977**, *99*, 8214. See also: Berti, G.; Mastrorilli, E.; Bronzetti, G. *Gazz. Chim. Ital.* **1983**, *113*, 449.

(11) Staroscik, J.; Rickborn, B. *J. Am. Chem. Soc.* **1971**, *93*, 3046. Johnson, C. R.; Herr, R. W.; Wieland, D. M. *J. Org. Chem.* **1973**, *38*, 4263. Marino, J. P.; Farina, J. S. *Ibid.* **1976**, *41*, 3213. Marino, J. P.; Hatanaka, N. *Ibid.* **1979**, *44*, 4467. Marino, J. P.; Jaën, J. C. *Tetrahedron Lett.* **1983**, *24*, 441.

(12) The nitrogen of the isonitrile group couples with the attached carbons to provide a triplet resonance for these carbons in the proton-decoupled ^{13}C NMR: Stephany, R. W.; de Bie, M. J. A.; Drenth, W. *Org. Magn. Reson.* **1974**, *6*, 45. Koole, N. J.; Knol, D.; de Bie, M. J. A. *J. Magn. Reson.* **1976**, *21*, 499. Kuntz, I. D., Jr.; Schleyer, P. v. R.; Allerhand, A. *J. Chem. Phys.* **1961**, *35*, 1533. Spiesecke, J. *Z. Naturforsh., A* **1968**, *23A*, 467.

(13) Boiling points and melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian CFT-20/HFT-80 nuclear magnetic resonance spectrometer or on a Nicolet NT-300 wide-bore NMR spectrometer. Elemental analyses were performed by the Scandinavian Microanalytical Laboratories, Herlev, Denmark.

modified for the preparation of *tert*-butyldimethylsilyl cyanide. A 1-L, three-necked Morton flask, equipped with a nitrogen inlet, reflux condenser, and a motor-driven stirrer, was charged with 200 mL of dry methylene chloride, 65.1 g (1.0 mol) of potassium cyanide, 45.0 g (0.3 mol) of *tert*-butyldimethylsilyl chloride, and 2.0 g of 18-crown-6. The reaction mixture was refluxed with vigorous stirring for 48 h. The reaction mixture was cooled to room temperature and filtered, and the solvent was removed by distillation in a nitrogen atmosphere. After the solvent was completely removed, the residue was sublimed to give 37.6 g (89%) of *tert*-butyldimethylsilyl cyanide, mp 72–77 °C (lit.[5] mp 76–78 °C). This crude product was used without further purification.

Starting Epoxides. All of the epoxides used in this study were either commercially available or previously reported in the literature. Cyclohexene epoxide was purchased from Aldrich Chemical Co. and used without further purification.

trans-3-Hexene epoxide (**5**) was prepared in 68% yield from the reaction of *trans*-3-hexene with *m*-chloroperbenzoic acid at 0 °C; bp 103–106 °C (lit.[14] bp 104–106 °C).

Cyclopentene epoxide (**6**) was prepared in 57% yield from the reaction of cyclopentene with *m*-chloroperbenzoic acid at 0 °C; bp 98–100 °C (lit.[15] bp 99–100 °C).

1,3-Cyclohexadiene monoepoxide (**8**) was prepared according to the procedure of Crandall and co-workers;[16] bp 60–63 °C (47 mm) [lit.[16] bp 62–64 °C (65 mm)].

1-Methylcyclohexene epoxide (**13**) was prepared in 78% yield through the reaction of 1-methylcyclohexene with *m*-chloroperbenzoic acid in methylene chloride at 0 °C: bp 76–79 °C (91 mm) (lit.[17] bp 137–138 °C).

[*erythro*-1-Ethyl-2-isocyanobutoxy]-*tert*-butyldimethylsilane (9). To a refluxing solution of 7.90 g (56 mmol) of *tert*-butyldimethylsilyl cyanide and 1.28 g of zinc iodide in 67 mL of methylene chloride was added 4.00 g (39 mmol) of **5** dissolved in 67 mL of methylene chloride. The reaction mixture was refluxed for 48 h,[18] cooled, and filtered through a silica gel plug. The solvent was removed under reduced pressure, and the residue was distilled to give 7.14 g (74% yield) of **9**: bp 58–63 °C (8.0×10^{-5} mm); IR (neat) 2130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95–3.20 (2 H, br m), 2.27–0.95 (10 H, br m), 0.90 (9 H, s), 0.08 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 156.21 (t, J_{CN} = 5.5 Hz), 73.75 (d), 60.64 (dt, J_{CN} = 5.6 Hz), 25.80 (t), 25.80 (q), 23.65 (t), 18.07 (s), 10.61 (q), 8.64 (q), -4.33 (q), -4.56 (q). Anal. Calcd for $C_{13}H_{27}NOSi$: C, 64.67; H, 11.27; N, 5.80. Found: C, 64.68; H, 11.20; N, 5.93.

[*trans*-(2-Isocyanocyclopentyl)oxy]-*tert*-butyldimethylsilane (10). To a refluxing solution of 10.08 g (71 mmol) of *tert*-butyldimethylsilyl cyanide and 1.52 g of zinc iodide in methylene chloride (79 mL) was added 4.00 g (48 mmol) of **6** in 79 mL of methylene chloride. The reaction mixture was refluxed for 48 h, cooled, and filtered through a silica gel plug. The solvent was removed under reduced pressure, and the residue was distilled to give 8.73 g (81% yield) of **10**: bp 55–59 °C (2.2×10^{-4} mm); IR (neat) 2140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30–4.05 (1 H, br m), 3.70–3.55 (1 H, br m), 2.40–1.00 (6 H, br m), 0.88 (9 H, s), 0.10 (3 H, s), 0.08 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 156.20 (t, J_{CN} = 5.5 Hz), 78.94 (d), 60.50 (dt, J_{CN} = 6.1 Hz), 32.78 (t), 30.86 (t), 25.66 (q), 20.53 (t), 17.92 (s), -4.79 (q), -4.85 (q). Anal. Calcd for $C_{12}H_{23}NOSi$: C, 63.94; H, 10.29; N, 6.21. Found: C, 64.03; H, 10.29; N, 6.26.

[*trans*-(2-Isocyanocyclohexyl)oxy]-*tert*-butyldimethylsilane (11). To a refluxing solution of 2.16 g (15.3 mmol) of *tert*-butyldimethylsilyl cyanide and 326 mg of zinc iodide in 17 mL of methylene chloride was added 1.00 g (10.2 mmol) of **7** in 17 mL of methylene chloride. The reaction mixture was refluxed for 48 h, cooled, and filtered through a silica gel plug. After removal of the solvent under reduced pressure, the residue was distilled to give 2.13 g (87% yield) of **11**: bp 50–55 °C (1×10^{-4} mm); mp 36–37 °C; IR (neat) 2140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.75–3.10 (2 H, br m), 2.40–1.00 (8 H, br m), 0.91 (9 H, s), 0.14 (3 H, s), 0.10 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 155.42 (t, J_{CN} = 5.4 Hz), 76.91 (d), 59.83 (dt, J_{CN} = 6.4 Hz), 32.75 (t), 30.61 (t), 25.63 (q), 22.68 (t), 22.50 (t), 17.87 (s), -4.64 (q), -4.71 (q). Anal. Calcd for $C_{13}H_{25}NOSi$: C, 65.21; H, 10.52; N, 5.85. Found: C, 65.25; H, 10.50; N, 5.88.

[*trans*-(2-Isocyanocyclohex-3-enyl)oxy]-*tert*-butyldimethylsilane (12). To a refluxing solution of 11.76 g (83 mmol) of *tert*-butyldimethylsilyl cyanide and 1.33 g of zinc iodide in methylene chloride (70 mL) was added 4.00 g (42 mmol) of **8** in methylene chloride (70 mL). The reaction mixture was refluxed for 48 h, cooled, and filtered through a silica gel plug. The solvent was removed under reduced pressure, and the residue was distilled to afford 8.58 g (87% yield) of **12**: bp 76–82 °C (1×10^{-4} mm); IR (neat) 2135 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95–5.40 (2 H, br m), 4.10–3.55 (2 H, br m), 2.55–1.05 (4 H, br m), 0.91 (9 H, s), 0.17 (3 H, s), 0.12 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 155.35 (t, J_{CN} = 5.0 Hz), 130.28 (d), 122.66 (d), 71.45 (d), 57.63 (dt, J_{CN} = 6.6 Hz), 29.32 (t), 25.64 (q), 23.76 (t), 17.89 (s), -4.63 (q), -4.69 (q). Anal. Calcd for $C_{13}H_{23}NOSi$: C, 65.77; H, 9.76; N, 5.90. Found: C, 65.87; H, 9.77; N, 6.02.

[(2-Methylcyclohexenyl)oxy]-*tert*-butyldimethylsilane (15).[7] To a refluxing solution of 8.5 g of *tert*-butyldimethylsilyl cyanide (60.0 mmol, 1.5 equiv) and 1.28 g of zinc iodide (10 mol %) in 67 mL of methylene chloride was added 4.5 g of 1-methylcyclohexene epoxide (40.0 mmol) in 67 mL of methylene chloride. The reaction mixture was refluxed for 48 h, cooled, and filtered through a silica gel plug. The solvent was removed under reduced pressure, and the residue was distilled to afford 5.67 g (63% yield) of **15**: bp 81–87 °C (0.1 mm). Preparative HPLC gave a sample having the following spectral properties: IR (neat) 1690 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.20–1.20 (9 H, br m), 1.13 (2 H, t, J = 5.5 Hz), 0.89 (9 H, s), 0.25 (3 H, s), 0.19 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 141.35 (s), 111.49 (s), 32.04 (t), 29.73 (t), 25.66 (q), 25.16 (q), 23.86 (t), 23.31 (t), 16.20 (s), -3.80 (q), -4.19 (q).

***trans*-2-Isocyano-2-methylcyclohexanol (17).** This compound was prepared according to the literature procedure of Gassman and Guggenheim.[2]

[*trans*-(2-Isocyano-2-methylcyclohexyl)oxy]-*tert*-butyldimethylsilane (14). To an ice-cold solution of 4.8 g of pyridine (2.0 equiv) and 4.20 g of **17** in 30 mL of dry acetonitrile was added slowly 9.6 g of *tert*-butyldimethylsilyl triflate (36.2 mmol, 1.2 equiv). The reaction mixture was stirred for 5 h at room temperature and then poured into 200 mL of saturated sodium bicarbonate solution at 0 °C. The solution was extracted thoroughly with hexane, and the organic extracts were dried over anhydrous potassium carbonate and filtered. Removal of the solvent under reduced pressure followed by distillation of the residue gave 6.29 g (82% yield: bp 50–54 °C (2×10^{-4} mm). An analytical sample was prepared by preparative HPLC: IR (neat) 2120 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.70–3.40 (1 H, br m), 2.60–0.95 (11 H, br m), 0.82 (9 H, s), 0.06 (3 H, s), 0.05 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 154.75 (t, J_{CN} = 4.6 Hz), 73.17 (d), 61.14 (t, J_{CN} = 4.9 Hz), 34.24 (t), 29.58 (t), 25.72 (q), 25.50 (q), 21.24 (t), 19.89 (t), 17.94 (s), -4.43 (q), -4.97 (q). Anal. Calcd for $C_{14}H_{27}NOSi$: C, 66.34; H, 10.74; N, 5.53. Found: C, 66.26; H, 10.70; N, 5.63.

[*trans*-(2-Isocyanocyclohex-3-enyl)oxy]trimethylsilane (19). To a refluxing solution of 10.3 g of trimethylsilyl cyanide (104 mmol, 2.0 equiv) and 0.83 g of zinc iodide (5 mol %) in 87 mL of methylene chloride was added 5.0 g (52 mmol) of 1,3-cyclohexadiene monoepoxide in 87 mL of methylene chloride. The reaction mixture was refluxed for 30 min, cooled, and filtered through a silica gel plug. The solvent was removed under reduced pressure, and the residue was distilled to give 7.95 g (78% yield) of **19**: bp 56–61 °C (0.1 mm). An analytical sample was prepared by HPLC: mp 29–30 °C; IR (neat) 2140, 1655 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 5.85–5.51 (2 H, br m), 4.04–3.80 (2 H, br m), 2.19–1.48 (4 H, br m), 0.19 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 155.37 (t, J_{CN} = 4.4 Hz), 130.17 (d), 122.71 (d), 71.34 (d), 57.57 (dt, J_{CN} = 4.4), 29.35 (t), 23.73 (t), 0.00 (q). Anal. Calcd for $C_{10}H_{17}NOSi$: C, 61.49; H, 8.77; N, 7.17. Found: C, 61.58; H, 8.99; N, 7.18.

Catalytic Hydrogenation of [*trans*-(2-Isocyanocyclohex-3-enyl)oxy]-*tert*-butyldimethylsilane (12) to [*trans*-(2-Isocyanocyclohexyl)oxy]-*tert*-butyldimethylsilane (11). A 250-mL, three-necked, round-bottomed flask equipped with a gas

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inlet tube, reflux condenser, and magnetic stir bar was charged with 100 mL of dry methylene chloride, 2.0 g (8.42 mmol) of **12**, and 200 mg of 5% palladium on carbon. The system was purged with hydrogen and stirred at room temperature until 189 mL (8.42 mmol, 1 equiv) of hydrogen was used (4.5 h). Filtration through silica gel followed by removal of the solvent afforded 1.68 g (83% yield) of **11**, which had spectral properties identical with those of the sample of **11** obtained from **7**. Additional purification by HPLC on silica gel using 1% ethyl acetate–99% hexane gave a sample; mp 36–37 °C.

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Registry No. **5**, 36611-93-5; **6**, 285-67-6; **7**, 286-20-4; **8**, 6705-51-7; **9**, 105162-55-8; **10**, 105162-56-9; **11**, 105162-57-0; **12**, 105162-58-1; **13**, 1713-33-3; **14**, 105162-59-2; **15**, 20152-33-4; **17**, 83152-89-0; **19**, 105162-60-5; $(CH_3)_3CSi(CH_3)_2CN$, 56522-24-8; ZnI_2, 10139-47-6; $(CH_3)_3CSi(CH_3)_2Cl$, 18162-48-6; $(CH_3)_3CSi(CH_2)_2OTf$, 69739-34-0; $(CH_3)_3SiCN$, 7677-24-9.

Use of ^{33}S Chemical Shifts To Determine pK_a's of Arenesulfonic Acids

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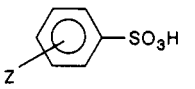
The ^{33}S chemical shifts of several arenesulfonic acids were recently determined in 1–3 M aqueous solution where they are completely ionized.[2] It was observed that substitution on the aromatic ring led to a change in the ^{33}S chemical shift of the sulfonate sulfur. In a general sense the chemical shift is related to the electron density on the probe nucleus, other things being equal. If the ^{33}S chemical shift is related to the electron density on sulfur, then it is also related to the electron distribution in the sulfonate ion. The pK_a of an arenesulfonic acid should also be directly influenced by the electron distribution in the sulfonate ion conjugate base, and therefore we investigated whether ^{33}S chemical shifts could be utilized in some manner for the determination of the pK_a's of arenesulfonic acids.

Currently it is necessary to carry out pK_a determinations of sulfonic acids in concentrated sulfuric acid solution where appreciable amounts of both the free sulfonic acid and its conjugate base are present. The concentrations are determined by either UV or ^1H NMR methods in solutions of varying Hammett acidity (H_0). The pK_a is obtained by extrapolation of these plots to dilute solution.[3] As a consequence of these experimental difficulties, not a large number of these values have been reported. Measurement of ^{33}S chemical shifts would be a vast improvement over current methods if pK_a values could be derived from them.

We report that substituent effects on the ^{33}S chemical shifts of arenesulfonates are accurately described by a dual-substituent parameter (DSP) treatment and that ^{33}S chemical shifts of arenesulfonates are linearly related to pK_a's of the sulfonic acids. In addition we report a simple method for the preparation of pure samples of arenesulfonic acids.

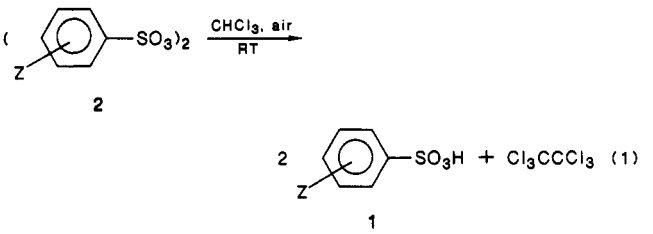
Results and Discussion

The series of arenesulfonic acids **1a–g** was utilized in this study as the free acid dissolved in water. Concentrations



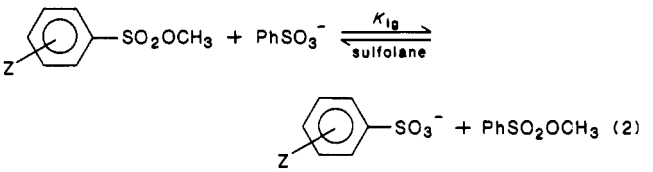
1a, Z = H
b, Z = *m*-CH_3
c, Z = *p*-CH_3
d, Z = *p*-Br
e, Z = *m*-CF_3
f, Z = *m*-NO_2
g, Z = *p*-NO_2

were normally about 2.4 M. Experiments with both methanesulfonic acid and benzenesulfonic acid showed that over the concentration ranges used in this study (2.0–2.7 M) changes in ^{33}S chemical shifts were within the experimental error. Acids **1a–c** were available commercially. Acids **1d–g** were prepared in generally high yields by decomposition of the corresponding bis(arenesulfonyl peroxide) (**2**) in chloroform (eq 1).



2 **1**

Table I contains the chemical shift data, measured relative to an external 4.0 M ammonium sulfate reference, for this series of acids as well as pK_a values, which were measured by Cerfontain[3] or extrapolated by us.[4] Included in Table I are pK_{lg} values, which are derived from the equilibrium constants for methyl transfer between a substituted methyl arenesulfonate and benzenesulfonate in sulfolane solution[5,6] (eq 2).



A Hammett plot of δ (^{33}S) vs. σ followed the relationship of eq 3. A linear relationship of $\delta(^{33}S)$ and σ was reported earlier for a limited set of arenesulfonic acids.[7] The fit was greatly improved by using a dual-substituent parameter fit to σ_I and σ_R (eq 4 and 5).[8] A plot of the chemical shifts calculated from eq 4 and 5 vs. the observed values gives excellent agreement (r = 0.997), and the slope of this

$$\delta(^{33}S) = -8.75\sigma - 11.89 \quad (r = 0.986) \qquad (3)$$

$$\delta(^{33}S_m) = -6.39\sigma_I - 10.08\sigma_R - 11.98 \quad (r = 0.997) \qquad (4)$$

$$\delta(^{33}S_p) = -7.37\sigma_I - 11.6\sigma_R - 12.43 \quad (r = 0.994) \qquad (5)$$

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