radical cyclizations.[12] At least, this result serves as a cautionary note to those intending to incorporate such cyano radical cyclizations in projected syntheses.

Experimental Section

All melting points are uncorrected. ^{1}H nuclear magnetic resonance spectra were recorded on Varian EM-390 or Bruker AM-500 instruments and are reported in parts per million from internal tetramethylsilane on the δ scale. Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, integration, interpretation]. ^{13}C magnetic resonance spectra were recorded on a Bruker WP-80 instrument and are recorded in parts per million from internal tetramethylsilane: chemical shift (multiplicity). Infrared spectra were recorded using a Perkin-Elmer 457 spectrometer. Mass spectra were recorded using a Kratos MS-30. The parent ions of some compounds were not observed. In these cases, fragmentation patterns were in accord with the assigned structures. Combustion analyses were performed by Micro-Analysis, Inc., Wilmington, DE.

Solvents and reagents were purified prior to use. All reactions were carried out under a blanket of nitrogen or argon in flame-dried flasks unless stated otherwise. Column chromatography was peformed over EM Laboratories silica gel (70–230 mesh) or LoBar columns (medium pressure).

***rel*-(1*S*,5*S*)-1-(2-Cyanoethyl)-5-methyl-6-oxabicyclo-[3.2.1]oct-2-en-7-one (2).** To a solution of 1.08 g (3.39 mmol) of iodo nitrile 1[5] in 50 mL of dry benzene under reflux was added a solution of 1.83 g (6.3 mmol) of tri-*n*-butyltin hydride[6] and 20 mg of azo(bisisobutyronitrile) (AIBN) in 15 mL of dry benzene via syringe pump at a rate of 1.7 mL h^{-1}. The mixture was warmed under reflux for an additional 10 h, cooled to room temperature, and concentrated in vacuo. The residue was partitioned between 20 mL of acetonitrile and 20 mL of hexane. The acetonitrile layer was concentrated in vacuo to yield a brown oil which was chromatographed over 15 g of silica gel (ethyl acetate–hexane, 1:4) to afford 616 mg (95%) of cyano lactone 2: mp 76–77 °C; IR (CH_2Cl_2) 2250, 1765 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.5 (s, 3 H, CH_3), 2.1 (m, 4 H, CH_2), 2.45 (m, 4 H, =CCH_2 and CH_2CN), 5.6–6.0 (m, 2 H, =CH).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81. Found: C, 68.70; H, 6.98.

***meso*- and *dl*-*rel*-(1*R*,5*S*,6*S*)-6-Methyl-10-oxo-11-oxatricyclo[4.3.2.0^{1,5}]undec-8-en-4-ylidenehydrazine [6 (*meso*) and 7 (*dl*)].** A solution of 1.0 g (3.15 mmol) of iodo nitrile 1 and 2.17 g (6.63 mmol) of hexamethyldistannane[9] in 60 mL of dry benzene was irradiated for 52 h under argon using a 450-W medium-pressure Hanovia lamp and Pyrex filter. The solution was concentrated and most of the tin residues were removed in vacuo (0.7 mm, room temperature for 30 min). The residual oil was subjected to MPLC (Lobar size B column; ethyl acetate–hexane, 1:4) to give 418 mg (42%) of starting iodo lactone 1, 94 mg (16%) of *meso*-azine 6, and 61 mg (10%) of *dl*-azine 7. Azine 6: mp 160–220 °C dec; IR (CH_2Cl_2) 1775, 1395, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.72 (s, 6 H, CH_3), 1.80 (ddd, J = 13, 10.5, 8.5 Hz, 2 H), 2.30 (dddd, J = 19.3, 10.9, 8.7, 2.2 Hz, 2 H), 2.48–2.56 (m, 6 H), 2.62 (ddd, J = 19.3, 9.1, 1.0 Hz, 2 H), 2.70 (d, J = 2.2 Hz, 2 H), 5.8 (dt, J = 9.3, 2.1 Hz, 2 H, =CH), 6.06 (dt, J = 9.3, 2.1 Hz, 2 H, =CH); ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 25.8 (t), 29.9 (t), 41.1 (t), 55.6 (s), 56.2 (d), 84.3 (s), 128.6 (d, two =CH), 166.6 (s), 177.1 (s); exact mass calcd for $C_{22}H_{24}N_2O_4$ m/e 380.1737, found m/e 380.1734.

Anal. Calcd for $C_{22}H_{24}N_2O_4$: C, 69.47; H, 6.32. Found: C, 68.92; H, 6.40.

Azine 7: mp 270–272 °C; IR (CH_2Cl_2) 1775, 1395, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.70 (s, 6 H, CH_3), 1.82 (ddd, J = 13.0, 10.5, 8.5 Hz, 2 H), 2.18 (dddd, J = 19.3, 10.7, 8.5, 2.3 Hz, 2 H), 2.48–2.56 (m, 6 H), 2.74 (d, J = 2.3 Hz, 2 H), 2.82 (dd, J = 19.3, 8.2 Hz, 2 H), 5.8 (dt, J = 9.3, 3.2 Hz, 2 H, =CH), 6.06 (dt, J = 9.3, 2.1 Hz, 2 H, =CH); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 25.9 (t), 30.3 (t), 41.1 (t), 55.6 (s), 56.6 (d), 84.1 (s), 128.6 (d, two =CH), 166.9 (s), 176.8 (s); exact mass calcd for $C_{22}H_{24}N_2O_4$ m/e 380.1737, found m/e 380.1765.

***rel*-(1*S*,5*S*)-1-(3-Cyanopropyl)-5-methyl-6-oxabicyclo-[3.2.1]oct-2-en-7-one (10) and *rel*-(1*S*,4*R*,5*R*,8*S*)-4-Cyano-8-methyl-9-oxatricyclo[6.2.1.0^{1,5}]undecan-10-one (12).** To a solution of 1.05 g (3.18 mmol) of iodo nitrile 8 in 50 mL of dry benzene under reflux was added a solution of 1.8 g (6.19 mmol) of tri-*n*-butyltin hydride and 20 mg of AIBN in 15 mL of dry benzene via syringe pump at a rate of 1.7 mL h^{-1}. The mixture was warmed under reflux for an additional 8 h, cooled to room temperature, and concentrated in vacuo. The residue was chromatographed over 40 g of silica gel (ethyl acetate–hexane, 1:4) to give 86 mg (13%) of tricyclic nitrile 12 and 463 mg (71%) of cyanolactone 10. Lactone 12: mp 78–80 °C; IR (CH_2Cl_2) 2240, 1775 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.5 (s, 3 H, CH_3), 1.8–2.2 (m, 8 H), 2.26 (dt, J = 9, 9 Hz, 1 H, C*H*CHCN), 2.36 (m, 2 H), 3.13 (dt, J = 9, 3.5 Hz, 1 H, CHCN); ^{13}C NMR ($CDCl_3$) δ 20.99 (t), 25.7 (q), 29.69 (t), 30.52 (t), 32.04 (t), 35.43 (d), 40.24 (t), 42.98 (d), 51.06 (s), 83.92 (s), 120.22 (s), 179.87 (s); mass spectrum, m/e (relative intensity) 205 (27), 161 (100), 146 (92), 133 (51), 119 (47), 111 (57), 106 (75); exact mass calcd for $C_{12}H_{15}NO_2$ m/e 205.1103, found m/e 205.1136.

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.24; H, 7.32. Found: C, 70.52; H, 7.63.

Lactone 10: IR (CH_2Cl_2) 2250, 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.52 (s, 3 H, CH_3), 1.8 (m, 6 H, CH_2), 2.4 (m, 4 H, =CCH_2 and CH_2CN), 5.6–5.9 (m, 2 H, =CH); ^{13}C NMR ($CDCl_3$) δ 17.55 (t), 20.94 (t), 25.20 (q), 31.33 (t), 37.61 (t), 43.14 (t), 47.78 (s), 81.52 (s), 119.24 (s), 128.53 (d), 130.98 (d), 177.08 (s).

Acknowledgment. We thank the National Science Foundation for financial support. We thank Richard Weisenberger for recording mass spectra at the Ohio State University Campus Chemical Instrument Center.

Registry No. 1, 99310-22-2; 2, 99310-23-3; 6, 99310-24-4; 7, 99310-25-5; 8, 99310-26-6; 10, 99310-27-7; 12, 99310-28-8.

Supplementary Material Available: Crystallographic details and ORTEP drawings are available for compounds 7 and 12 (32 pages). Ordering information is given on any current masthead page.

(12) Ogibin has reported the cyclization of several ϵ-cyano radicals having α-hydrogens to give cyclohexanones in low yield.[3] On the other hand, Johns has provided an example of an ϵ-cyano radical cyclization which gives cyclohexanones in good yield.[4] In this case, the nitrile had no α-hydrogens.

Preparation and Some Reactions of 1-(Trimethylsilyl)cyclopropanol and Its Trimethylsilyl Ether

Robert F. Cunico* and Chia-Piao Kuan

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

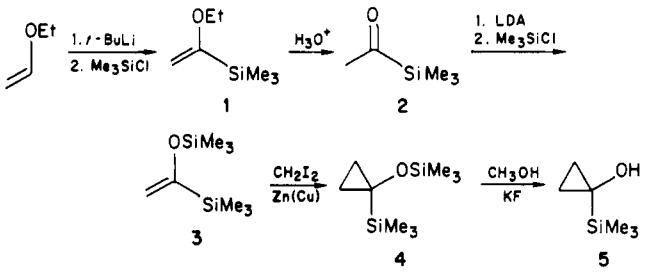
Received April 16, 1985

The chemistry of cyclopropylsilanes[1] has recently found synthetic applications in the area of cyclopentannulation through the thermal rearrangement of 1-(1-silylcyclopropyl)alkenes.[2] However, studies directed toward utilizing cyclopropylsilanes with electrophiles to afford ring-opened products are as of yet less promising, as the systems thus far explored at times exhibit carbocation rearrangements and variations in bond selectivity which limit generality.[3] In contrast, the facile ring-opening of

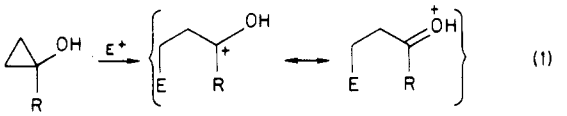
(1) Review: Paquette, L. A. *Isr. J. Chem.* **1981**, *21*, 128.
(2) (a) Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron Lett.* **1982**, *23*, 263. (b) Yan, T.-H.; Paquette, L. A. *Tetrahedron Lett.* **1982**, *23*, 3227. (c) Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron* **1983**, *39*, 913. (d) Paquette, L. A.; Yan, T.-H.; Wells, G. J. *J. Org. Chem.* **1984**, *49*, 3610.
(3) Daniels, R. G.; Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 2901.

0022-3263/85/1950-5410$01.50/0

Scheme I



cyclopropanols with electrophiles is a well-established process which leads exclusively to C(1)–C(2) fission with formation of a stable α-oxo cation (eq 1).[4] Reactions of



(1)

1-silylcyclopropanols, of which **5** is the parent species, with electrophiles might thus serve as entry routes to functionalized acylsilanes, compounds of some current synthetic interest.[5]

Previous chemistry initiated in our laboratories had provided a convenient source of acetyltrimethylsilane (**2**),[6] leading us to envision the sequence of Scheme I for access to the prototype silylcyclopropanol **5**. Adaptation of the method of Baldwin to the metalation of ethyl vinyl ether[7] afforded (1-ethoxyethenyl)trimethylsilane (**1**) which was readily hydrolyzed to **2**. Metalation of this ketone with lithium diisopropylamide gave an enolate which was trapped by silylation to produce **3**. This enol ether was resistant to cyclopropanation under standard conditions,[8] and modification with a zinc–silver couple[9] proved ineffective. Satisfactory results were finally obtained in hot dioxane as solvent, although still necessitating a large excess (three- to fourfold) of cyclopropanating reagents. The apparent lower reactivity of **3** relative to other silyl enol ethers may find its origin in reduced π-bond nucleophilicity accompanying the placement of a silyl group on the double bond system.[10] The transetherification of **4** to afford alcohol **5** was effected only slowly in neat methanol but was rapid in the presence of catalytic amounts of potassium fluoride.

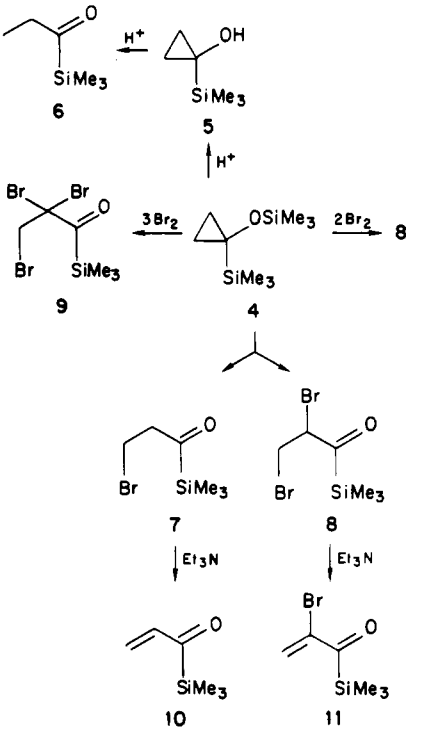
Both silyl ether **4** and the alcohol **5** were examined in order to determine their behavior toward various electrophilic agents. When **4** was mixed with an equivalent amount of trifluoroacetic acid at 0 °C, complete conversion to **5** occurred within 15 min. Subsequent protonolysis to ketone **6** proceeded much more slowly. More extensive data on this latter transformation were obtained by utilizing **5** directly with a series of acids of varying proton-donating abilities (Table I). These results indicate that a range of kinetic compatibility exists for **5** under acid conditions. If quantitative protonolysis is a desired end, 24-h contact with trifluoroacetic acid affords the acylsilane **6** in synthetically useful yields (Scheme II).

Table I. Half-Lives of 5 with Acids[a]

acid	pK_a[b]	$t_{1/2}$ (h)
CF_3SO_3H		0.25
$BF_3{\cdot}Et_2O$		23
CF_3CO_2H	0.23	1.5
$CHCl_2CO_2H$	1.29	7
CH_2ClCO_2H	2.86	120
HCO_2H[c]	3.77	530
CH_3CO_2H	4.76	199

[a] At 25 °C. Mixtures comprised of 0.28 mmol of **5** and 0.28 mmol of acid in 350 μL of $CDCl_3$; for CF_3SO_3H and $BF_3{\cdot}Et_2O$, 0.28 mmol of **5** and 0.032 mmol of acid. [b] Brown, H. C.; McDaniel, D. H.; Haflinger, O. In "Determination of Organic Structures by Physical Methods"; Brande, E. A., Nachod, F. C., Eds.; Academic Press; New York, 1955; Vol. 1, p 567. [c] 90% HCOOH.

Scheme II



Brominolysis of cyclopropanols is known to be complicated by simultaneous protonolysis of the starting alcohols by HBr liberated in situ. Murai and co-workers have reported that this problem can be circumvented by employing the trimethylsilyl ethers of the alcohols as surrogate substrates.[11] These species liberate the unreactive bromotrimethylsilane in lieu of HBr and thus afford excellent yields of monobrominated ketones. When equimolar amounts of bromine were added to **4** at −78 °C, protonolysis was indeed suppressed (albeit not eliminated), but the product consisted of a 4:1 mixture of monobrominated **7** and dibrominated **8** acylsilane (Scheme II). Although an 11:1 ratio of these products could be generated by reducing the Br_2:**3** ratio to 0.55, a survey of other conditions and brominating agents failed to disclose experimental parameters under which **7** could be made the sole product. This situation was complicated further by our

(4) (a) DePuy, C. H.; Breitbeil, F. W.; DeBruin, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 3347. (b) DePuy, C. H. *Acc. Chem. Res.* **1968**, *1*, 33. (c) DePuy, C. H. *Fortschr. Chem. Forsch.* **1973**, *40*, 73. (d) Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605.

(5) (a) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119. (b) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949. (c) Cunico, R. F. "Synthetic Aspects of Acylsilane Chemistry", in "Silicon Compounds, Register and Review", Petrarch Systems Inc.: Bristol, PA, 1984.

(6) (a) Cunico, R. F.; Han, Y. K., unpublished results. See: Dexheimer, E. M.; Spialter, L. *J. Organomet. Chem.* **1976**, *107*, 229. (b) The preparation of **2** from methyl vinyl ether has also been reported: Soderquist, J. A.; Grace, J. H. *Organometallics* **1982**, *1*, 830.

(7) Baldwin, J. E.; Holfe, G. A.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125. Convenience dictated the use of ethyl vinyl ether.

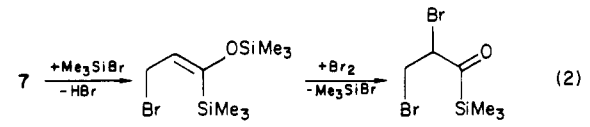
(8) Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973**, *38*, 4354.

(9) Denis, J. M.; Girard, C.; Conia, J. M. *Synthesis* **1972**, 549.

(10) Seyferth, D.; Dertouzos, H. *J. Organomet. Chem.* **1968**, *11*, 263.

(11) Murai, S.; Seki, Y.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1974**, 1032.

inability to separate **7** from **8** in large part due to the thermal instability of **7**, which slowly decomposed even on storage at −25 °C. An explanation for the disparity of these results vs. those of Murai et al. may rest on a more facile enolization of **7** relative to its asilyl counterparts; the HBr liberated in this way would also account for the small amounts of protonolysis product (ketone **6**) accompanying these runs (eq 2). As forsaged by these results, poly-



(2)

brominated products arose readily from **4**, and both dibromo ketone **8** and tribromo ketone **9** could be obtained in high yields by employing, respectively, 2 and 3 equiv of bromine in the reaction with **4**.

α,β-Unsaturated acylsilanes, and in particular, those bearing halogen substitution, are still relatively novel species.[5] Ketones **7** and **8** were recognized as possible precursors to inital members within these classes, and their dehydrobromination was investigated. Treatment of the 4:1 mixture of **7** and **8** obtained above with triethylamine easily led to the expected mixture of **10** and **11**, isolable by distillation in 60% and 10% overall yields from **5**. The method of choice for obtaining the previously unknown **11**, of course, employed pure **8**, resulting in an 84% yield of the bromovinyl ketone. Unfortunately, we were unable to establish conditions under which the readily available **8** could be debrominated to afford **10**.

Various attempts to induce the reaction of **4** with carbon electrophiles [t-BuCl/$TiCl_4$, t-BuCHO/$TiCl_4$, and $CH_2(OMe)_2$/Me_3SiOTf] were unproductive.[12] The use of acetyl triflate did not result in ring-opening but instead afforded (1-acetoxycyclopropyl)trimethylsilane (**12**).

Experimental Section

Infrared spectra were determined from neat films by using a Sargent-Welch Model 3-200 spectrophotometer. NMR spectra were determined on $CDCl_3$ solutions ($CHCl_3$ taken as δ 7.27 as reference) with a Varian Model A60A spectrometer. VPC analyses employed a Varian Associates Model 1720 chromatograph and 20% SE-30 columns of various lengths. Elemental analyses were performed by P. Rider of these laboratories or by Spang Microanalytical Laboratory, Eagle Harbor, MI. Unless stated otherwise, all reactions were carried out under a nitrogen atmosphere, and anhydrous magnesium sulfate was used to dry organic phases after workup. Diethyl ether and THF were distilled from sodium benzophenone ketyl immediately prior to use. Distillations were carried out on short-path apparatus unless otherwise stipulated. VPC quantitations are based on uncorrected peak integrals.

(1-Ethoxyethenyl)trimethylsilane (1). A cooled (−78 °C) mixture of 21.7 g (0.30 mol) of ethyl vinyl ether in 80 mL of THF was treated dropwise with 203 mL of a 1.48 M (0.30 mol) *tert*-butyllithium in pentane solution. Dry ice was removed from the cold bath, and its temperature was allowed to slowly rise to −25 °C. After 15 min at −25 °C, the mixture was recooled to −78 °C, and 32.6 g (0.30 mol) of chlorotrimethylsilane was added dropwise. After having been stirred overnight, the mixture was poured into dilute $KHCO_3$, and the organic layer was washed with water, dried, and concentrated to 50 mL. The residual solution was distilled through a 6-in. vacuum-jacketed Vigreux column to give 32.4 g of material, bp 50–63 °C (100 mmHg). VPC showed this to be 90% pure, indicating a yield of 29.2 g (67%) of **1**. The major impurity was identified as bis(trimethylsilyl)acetylene. ^1H NMR of **1**: δ 0.06 (s, 9 H), 1.24 (t, 3 H), 3.68 (q, 2 H), 4.25 (d, 1 H); IR 3045, 1585, 1250, 1220, 1055, 970, 865, 755 cm^{-1}.

Anal. Calcd for $C_7H_{16}OSi$: C, 58.28; H, 11.18. Found: C, 58.41; H, 11.24.

Acetyltrimethylsilane (2).[13] Hydrochloric acid (50 mL, 3 N) was added to a solution of 27.9 g (0.19 mol) of **1** in 50 mL ether. After 1.5 h of vigorous stirring, workup gave 20.2 g of **2**, bp 108–110 °C (6-in. Vigreux), which VPC indicated was 95% pure. This represents a 95% yield based on the 90% purity of **1**.

[1-[(Trimethylsilyl)oxy]ethenyl]trimethylsilane (3).[14] A mixture of 18.8 g (0.186 mol) of diisopropylamine and 150 mL of THF was cooled in ice and treated dropwise with 93 mL of 2.0 N (0.186 mol) methyllithium in ether. After 1 h at 25 °C, the solution was cooled to −78 °C, and 21.6 g (0.186 mol) of **2** was added dropwise over 1 h. Ten minutes later, 20.2 g (0.186 mol) of chlorotrimethylsilane was added rapidly by syringe. The dry ice bath was removed. When the reaction mixture reached 25 °C, it was poured into aqueous $NaHCO_3$–pentane, and the organic layer was washed with $NaHCO_3$ solution and saturated with NaCl (2×). After drying and concentration, distillation yielded 26.6 g of material with bp 50–70 °C (50 mmHg) [most at 66–69 °C], which VPC showed to be 90% pure; the calculated yield is 23.7 g (68%).

[1-[(Trimethylsilyl)oxy]cyclopropyl]trimethylsilane (4). Conditions reported for the cyclopropanation of alkyl-substituted silyl enol ethers[8,9] gave unsatisfactory results in the case of **3**, and the following procedure was followed instead. A mixture of Zn dust (5.7 g, 0.088 mol, Fisher Scientific No. Z-5), CuCl[15] (5.6 g, 0.088 mol), and 100 mL of p-dioxane (distilled from sodium benzophenone ketyl) was held at reflux 45 min. The enol ether **3** (8.25 g, 0.044 mol) was added at once, followed by dropwise addition of 17.7 g (0.066 mol) of CH_2I_2 over 40 min. VPC monitoring showed that 30 min later, the CH_2I_2 had been consumed and **3** and **4** were present in a 2:3 ratio. A repeat addition of all reagents was then carried out, and after an additional reflux time of 1 h 40 min, only **4** was present. Any excess CH_2I_2 is not easily separable from **4**, and the reaction mixture should be checked for its absence by VPC. Remaining diiodide may be removed by additional contact time with extra Zn dust.

Pentane was added to the mixture, and solids were removed by filtration through Celite. After a pentane trituration of the solids and a second filtration, the organic phases were washed with NH_4Cl solution and aqueous NaCl, dried, and concentrated. Distillation gave 5.84 g (66%) of **4**, bp 42–46 °C (8 mmHg): ^1H NMR δ 0.02 (s, 9 H), 0.11 (s, 9 H), 0.52 (m, 2 H), 0.75 (m, 2 H); IR 3085, 3005, 2965, 2905, 1255, 1205, 1045, 1005, 905, 840, 755 cm^{-1}.

Anal. Calcd for $C_9H_{22}OSi_2$: C, 53.41; H, 10.96. Found: C, 53.54; H, 10.93.

1-(Trimethylsilyl)cyclopropanol (5). A sample of **4** (2.17 g, 0.011 mol) was added to a solution of 0.3 g (0.005 mol) of KF in 6 mL of CH_3OH. After 2 h 45 min at 25 °C, the mixture was diluted with water, extracted with pentane (3×), dried, and distilled. There was obtained 1.14 g (81%) of distillate, bp 56–62 °C, which partially solidified upon standing: ^1H NMR δ 0.00 (s, 9 H), 0.43 (m, 2 H), 0.61 (m, 2 H), 1.42 (s, 1 H); IR 3270, 3085, 3005, 2960, 2920, 1420, 1370, 1250, 1180, 1020, 965, 935, 865, 840, 770, 750, 695, 640 cm^{-1}. Dissolution of **4** in methanol alone led to very slow transetherification, with significant amounts of **4** remaining after 6 days at 25 °C.

Anal. Calcd for $C_6H_{14}OSi$: C, 55.38; H, 10.76. Found: C, 55.45; H, 10.71.

The p-toluenesulfonate of **5** was prepared by treating the alcohol in THF with an equivalent amount of methyllithium in ether followed by overnight stirring with an equivalent amount of p-toluenesulfonyl chloride. Workup and recrystallization from cold (−25 °C) pentane afforded a semisolid: ^1H NMR δ 0.10 (s, 9 H), 0.60 (m, 2 H), 1.07 (m, 2 H), 2.42 (s, 3 H), 7.53 (m, 4 H).

Anal. Calcd for $C_{13}H_{20}O_3SSi$: C, 54.89; H, 7.09. Found: C, 54.48; H, 7.23.

(12) A statement as to a similar lack of reactivity for alkyl-substituted cyclopropyl silyl ethers appeared during our investigations: Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121. This is a useful review of (silyloxy)cyclopropane chemistry.

(13) (a) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95. (b) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431.

(14) Murai, S.; Ryu, I.; Iriguchi, J.; Sonada, N. *J. Am. Chem. Soc.* **1984**, *106*, 2440 and references cited therein.

(15) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

Protonolysis of 4 and 5. A mixture of 4 (2.0 g, 0.010 mol), 1.1 g (0.010 mol) of trifluoroacetic acid, and 25 mL of dry CH_2Cl_2 was prepared at 0 °C. After 15 min, all of 4 had been converted to 5. After an additional 24 h at 25 °C, only 2,2-dimethyl-2-sila-3-pentanone (6) was present. Workup with aqueous $NaHCO_3$ followed by drying and distillation gave 1.0 g (78%) of 6,[16] bp 50–58 °C (100 mmHg), containing some minor impurities. Data for half-life determinations of the reaction of 5 with various acids were obtained in $DCCl_3$ by ^1H NMR as indicated in Table I.

Brominolysis of 4. (A) One Equivalent of Bromine. A solution of 1.89 g (0.0118 mol) of Br_2 in 50 mL of dry CH_2Cl_2 was added dropwise to a solution of 2.38 g (0.0118 mol) of 4 in 50 mL of CH_2Cl_2 at −78 °C. The flask was wrapped with aluminum foil. After addition, volatiles (which VPC indicated contained small amounts of 6) were removed by evacuation at 5 mmHg to give 2.26 g of crude product. ^1H NMR analysis showed this to consist of 78% 2,2-dimethyl-5-bromo-2-silapentan-3-one (7) and 22% 2,2-dimethyl-4,5-dibromo-2-silapentan-3-one (8). The monobromo product is quite unstable; storage of this mixture at −25 °C for 7 days resulted in the total decomposition of 7. Efforts to separate 7 from 8 by rapid chromatography, VPC, or distillation were unsuccessful. ^1H NMR of 7: δ 0.19 (s, 9 H), 3.36 (m, 4 H).

(B) Two Equivalents of Bromine. The procedure of A was followed with 2.0 g (0.010 mol) of 4 and 3.2 g (0.020 mol) of Br_2. The mixture was allowed to warm to 25 °C and stirred 30 min, whereupon the initial red color had turned to yellow. A water wash was followed by drying and distillation to give 2.5 g (87%) of 7, bp 44–50 °C (0.4 mmHg) which VPC indicated was 98% pure: ^1H NMR δ 0.31 (s, 9 H), 3.57 (dd, 1 H), 3.98 (t, 1 H), 4.82 (dd, 1 H); IR 1645, 1250, 850 cm^{-1}.

Anal. Calcd for $C_6H_{12}Br_2OSi$: C, 25.02; H, 4.20. Found: C, 25.09; H, 4.13.

(C) Three Equivalents of Bromine. The procedure of A was followed with 1.0 g (0.0050 mol) of 4 and 2.4 g (0.015 mol) of Br_2. After addition, the reaction mixture was stirred at 25 °C for 20 h. The color of the solution remained red, but titration of an aliquot with standard $Na_2S_2O_3$ solution indicated only 1.4% unreacted Br_2. The reaction mixture was washed with 0.1 N $Na_2S_2O_3$ and water, dried, and concentrated. Distillation gave 1.67 g (91%) of 4,4,5-tribromo-2,2-dimethyl-2-silapentan-3-one (9), bp 62–70 °C (0.2 mmHg), which VPC showed to be 99% pure: ^1H NMR δ 0.42 (s, 9 H), 4.23 (s, 2 H); IR 1650, 850 cm^{-1}.

Anal. Calcd for $C_6H_{11}Br_3OSi$: C, 19.64; H, 3.02. Found: C, 19.81; H, 3.13.

(D) Under Other Brominating Conditions. The use of Br_2 and pyridine, Br_2 and polyvinylpyridine, *N*-bromosuccinimide, cupric bromide, or *tert*-butyl hypobromite with 4 all afforded mixtures of 6, 7, and 8.

Preparation of Enones 10 and 11. The crude reaction mixture obtained from 2.38 g of 4 and 1.89 g of Br_2 as described above was evacuated at 5 mmHg and added to a mixture of 1.19 g (0.0118 mol) of triethylamine in 50 mL of CH_2Cl_2. After 2 h at 25 °C, the clear solution was diluted with 100 mL of pentane to form a precipitate which was removed by sintered frit filtration. Kugelrohr distillation of the concentrated filtrate gave 0.92 g (61%) of 4,4-dimethyl-4-sila-1-penten-3-one (10),[5a] bp 25 °C (5 mmHg), and 0.24 g (10%) of 2-bromo-4,4-dimethyl-4-sila-1-penten-3-one (11), bp 50 °C (0.5 mmHg): ^1H NMR (11) δ 0.30 (s, 9 H), 6.78 (s, 2 H); IR 1625, 1595, 1250, 850 cm^{-1}.

Anal. Calcd for $C_6H_{11}BrOSi$: C, 34.79; H, 5.35. Found: C, 35.03; H, 5.40.

In a completely parallel experiment, but employing 2.52 g of pure 8, short-path distillation gave 1.36 g (84%) of 11, bp 64–70 °C (8 mmHg).

Attempts at the debromination of 8 with Zn/Et_2O, $Zn/ZnBr_2/Et_2O$, $Zn/ZnBr_2/p$-dioxane (80 °C), or Ph_3P did not afford 10.

Attempted Reaction of 4 with Carbon Electrophiles. Attempted reaction of 4 with *t*-BuCl/$TiCl_4$, *t*-BuCl/Me_3SiOTf, $CH_2(OCH_3)_2/Me_3SiOTf$, or $Me_3CCHO/TiCl_4$, first at −78 °C and then at 25 °C, gave only varying amounts of protonolysis product 6. The reaction of 4 with acetyl triflate (from acetyl chloride and silver triflate in chloroform) gave only (1-acetoxycyclopropyl)-trimethylsilane: ^1H NMR δ 0.10 (s, 9 H), 0.72 (m, 4 H), 1.94 (s, 3 H); IR 3085, 1735, 1250, 1170 cm^{-1}.

Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.81; H, 9.30. Found: C, 55.74; H, 9.51.

(16) Brook, A. G.; Dillon, D. J.; Pearce, P. *Can. J. Chem.* **1971**, *49*, 133.

$Mo(CO)_6$-Promoted Reductive Cleavage of the Carbon–Sulfur Bond[1]

Tien-Yau Luh* and Chi Sang Wong

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Received May 21, 1985

The hydrodesulfurization process is important in the purification of fossil fuels.[2] The commonly used catalyst for this transformation consists of molybdenum sulfide with cobalt or nickel compounds as a promoter.[3] However, the actual mode of this process is not well understood. The reaction is essentially the reductive cleavage of a carbon–sulfur bond. There are scattered examples of the use of homogeneous organometallic reagents to promote reductive cleavage of carbon–sulfur bonds. To illustrate this, metal carbonyls such as $Fe(CO)_5$,[4] $Fe_3(CO)_{12}$,[5] $Os_3(CO)_{12}$,[6] $Mn_2(CO)_{10}$,[7] and $Co_2(CO)_8$[4a,8] are effective desulfurization reagents. Recently, Alper and Blais reported that molybdenum species generated by the adsorption of $Mo(CO)_6$ on silica was an active reagent which would react with dibenzothiophene to give biphenyl.[9] No desulfurization occured when dibenzothiophene was exposed to $Mo(CO)_6$ in THF.[9] Similar reaction was observed when various thiols were treated with a preheated acetic acid solution of $Mo(CO)_6$.[10] In continuing our long time interest in the reductive cleavage of C–X bonds promoted by metal carbonyl,[11] including group VI (6)[17] metal carbonyls,[11c] we felt that $Mo(CO)_6$ itself may be able to selectively reduce other kinds of more reactive carbon sulfur bonds. We have tested this viewpoint by reacting various organosulfur compounds with $Mo(CO)_6$ and now wish to describe our results.

Results and Discussion

A THF solution of organosulfur compounds and $Mo(CO)_6$ was refluxed for 12–16 h, and after workup, the cor-

(1) Part 12 of the series "Transition-Metal Promoted Reactions". Part 11: Luh, T.-Y.; Wong, C. S. *J. Organomet. Chem.* **1985**, *287*, 231.
(2) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245.
(3) For review, see: Mitchell, P. C. H. *Catalysis* **1981**, 175.
(4) (a) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694. (b) Alper, H.; Paik, H.-N. *J. Org. Chem.* **1977**, *42*, 3522. (c) Ayral-Kalonstaan, S.; Agosta, W. C. *Synth. Commun.* **1981**, *11*, 1011. (d) Daub, J.; Erhardt, G.; Jogun, K. H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowske, J. J. *Chem. Ber.* **1982**, *115*, 1787.
(5) (a) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 3198. (b) Alper, H.; Sibtain, F.; Heveling, J. *Tetrahedron Lett.* **1983**, *24*, 5329.
(6) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235.
(7) Alper, H. *J. Organomet. Chem.* **1974**, *73*, 359.
(8) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147.
(9) Alper, H.; Blais, C. *Fuel* **1980**, *59*, 670.
(10) Alper, H.; Blais, C. *J. Chem. Soc., Chem. Commun.* **1980**, 169.
(11) (a) Luh, T.-Y.; Lai, C. H.; Tam, S. W. *Tetrahedron Lett.* **1978**, 5011. (b) Luh, T.-Y.; Lai, C. H.; Lei, K. L.; Tam, S. W. *J. Org. Chem.* **1979**, *44*, 641. (c) Luh, T.-Y. *J. Organomet. Chem.* **1979**, *174*, 169. (d) Luh, T.-Y.; Lai, C. H.; Tam, S. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 444. (e) Luh, T.-Y. *Synth. Commun.* **1981**, *11*, 829. (f) Luh, T.-Y.; Lee, K. S.; Tam, S. W. *J. Organomet. Chem.* **1981**, *219*, 345. (g) Luh, T.-Y.; Lee, K. S.; Tam, S. W. *J. Organomet. Chem.* **1983**, *248*, 221.

0022-3263/85/1950-5413$01.50/0