Anal. Calcd for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97. Found: C, 70.11; H, 5.04.

1-Hydroxy-4,5,8-trimethoxynaphthalene (6). Compound 10 (200 mg, 0.59 mmol) and Dowex 2X-8 resin (200 mg, OH^- form) were placed in degassed absolute ethanol (20 mL) under N_2 and refluxed for 3 h. The reaction mixture was filtered to remove the resin and the filtrate cooled in an ice bath. The product crystallized from the filtrate and was collected to afford 88.0 mg of **6**. The mother liquor was evaporated and the residue crystallized from $CHCl_3$/hexane to afford an additional 12.5 mg of **6**: total yield 100.5 mg (73%); mp 148–149 °C; IR 2.95 (OH), 6.27, 6.60, 6.85, 6.95, 7.10, 7.28, 7.81, 8.00, 8.35, 8.78, 8.90, 9.38, 9.72, 9.98, 11.00, 12.15, 12.45, 13.40, 13.75, 14.70 μm; NMR δ 3.90, 3.92 (2 s, 6, 4- and 5-OMe's), 4.03 (s, 3, 8-OMe), 6.76 (s, 2, 6- and 7-H's), 6.85 (m, 2, 2- and 3-H's), 9.43 (s, 1, OH); UV (MeOH) λ_{max} 223 nm (ϵ 50400), 310–134 (8400), 334 (7800), 353 (8600); TLC ($CHCl_3$) R_f 0.6.

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.62; H, 6.01.

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Registry No. 1, 475-38-7; **2**, 15013-16-8; **3**, 4923-61-9; **4**, 81194-55-0; **6**, 81194-56-1; **7**, 81194-57-2; **8**, 81194-58-3; **9**, 81194-59-4; **10**, 81194-60-7.

Mechanism of Reaction of Oxetanes, Sodium, and Dimethyldichlorosilane. Synthesis of 1-Oxa-2-silacyclopentanes

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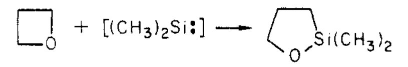
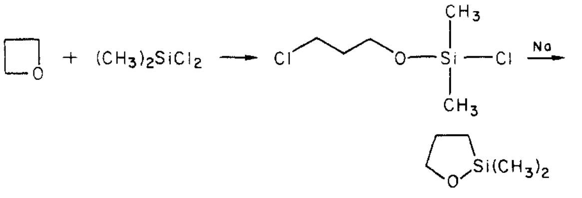
Reaction of dimethyldichlorosilane, sodium metal, and oxetane in refluxing toluene yields 2,2-dimethyl-1-oxa-2-silacyclopentane (42%, eq 1), while a similar reaction with 3,3-dimethyloxetane gives 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane (47%).



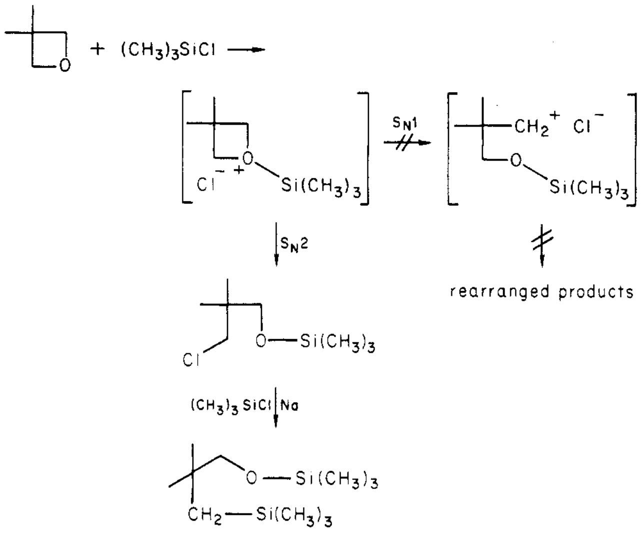
(1)

Since photochemically generated dimethylsilylene is known to react with oxetanes to yield similar products,[1] one might be led to propose that dimethyldichlorosilane undergoes reduction by sodium metal under these reaction conditions to form dimethylsilylene. While this explanation is economical, we are reasonably certain that it is not correct. Rather we have evidence that the reaction probably occurs by the following sequence of events. Initial reaction of dimethyldichlorosilane with oxetane (eq 2) yields (3-chloropropoxy)dimethylchlorosilane[2] which then undergoes reductive cyclization with sodium to form 2,2-dimethyl-1-oxa-2-silacyclopentane. Independent experiments are consistent with this interpretation. Oxetane does react with dimethyldichlorosilane to give (3-chloropropoxy)dimethylchlorosilane in virtually quantitative yield. In addition, 2,2-dimethyl-1-oxa-2-silacyclopentane has been prepared by treatment of (3-chloropropoxy)dimethylchlorosilane with sodium metal.[3] The ethyl iodide catalyzed reaction of tetrahydrofuran with dimethyldichlorosilane and magnesium metal to yield 2,2-dimethyl-1-oxa-2-silacyclohexane is probably closely related.[4-6] In addition, we have found that oxetane reacts with trimethylchlorosilane and sodium metal in refluxing toluene to yield [3-(trimethylsiloxy)propyl]trimethylsilane (55%) and (3-chloropropoxy)trimethylsilane (8%). Similar reactions of 2-methyloxetane and 3,3-dimethyloxetane yield, respectively, [3-methyl-3-(trimethylsiloxy)propyl]trimethylsilane (52%) and [2,2-dimethyl-3-(trimethylsiloxy)propyl]trimethylsilane (48%).

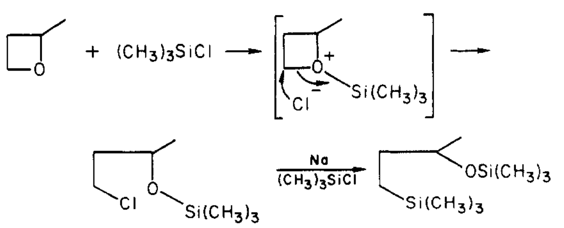


(2)

Scheme I



These observations, we believe, provide insight into the mechanism of carbon–oxygen bond cleavage of oxetanes by chlorosilanes. The cleavage of epoxides by chlorosilanes has been thoroughly studied.[7-9] The following sequence of events is consistent with our data. Nucleophilic attack by oxygen lone pairs of electrons of the oxetane on the silyl center of the halosilane leads to a silyl-substituted oxonium ion/chloride ion pair (eq 3). Nucleophilic attack by chloride on the least substituted alpha carbon of the silyl substituted oxonium ion results in carbon-oxygen bond



(3)

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scission and formation of (3-chloropropoxy)trimethylsilanes. In the presence of sodium metal these undergo further reaction.

An alternative possibility, $\mathrm{S_N}1$ cleavage (Scheme I) of the silyl-substituted oxonium ion/chloride ion pair to a carbocation/chloride ion pair, can be eliminated since no products resulting from a neopentyl rearrangement are observed with 3,3-dimethyloxetane.[10] Neopentyl rearrangement would rapidly convert a primary carbocation to a more stable tertiary carbocation via a 1,2 Wagner–Meerwein rearrangement. In addition, 2-methyloxetane would be expected to open to a more stable secondary carbocation rather than a primary one if the silyl-substituted oxonium ion underwent $\mathrm{S_N}1$-type cleavage. No products predicted from such an $\mathrm{S_N}1$ cleavage are observed.

We believe these results provide additional evidence that great caution should be used in proposing the existence of dimethylsilylene in the solution-phase reaction of dimethyldichlorosilane and sodium metal.[11] In addition, our results provide evidence for the mechanism of C–O cleavage of oxetanes by chlorosilanes.

Experimental Section

IR spectra were recorded as 2% CCl_4 solutions on a Perkin-Elmer 281 spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode by using 1% solutions in $CDCl_3$ with an internal standard of chloroform. Elemental analysis were performed by Galbraith Laboratories, Inc. Samples of all compounds for spectra and elemental analyses were purified by preparative vapor-phase chromatography on a Hewlett-Packard F&M 700 using a 26 ft × 0.25 in. 20% SE-30 on Chromosorb W (60–80 mesh) column.

Oxetane, 3,3-dimethyloxetane, and 2-methyloxetane were purchased from Aldrich Chemical Co. Trimethylchlorosilane and dimethyldichlorosilane were purchased from Silar Chemical Co.

Reaction of Oxetanes with Dimethyldichlorosilane and Sodium. A typical run of dimethyldichlorosilane, oxetane, and sodium is described below. Oxetane (0.05 mol), sodium (2.3 g, 0.1 mol), and 20 mL of toluene were placed in a 100-mL, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a Teflon-covered magnetic stirring bar. Freshly distilled dimethyldichlorosilane (0.055 mol) in 20 mL of toluene was added dropwise to the refluxing, stirred solution. After the addition was complete, the solution was refluxed for 8 h. The reaction mixture was cooled to room temperature. Ethanol was added to the solution to destroy residual sodium. The reaction mixture was washed with water, dried over Na_2SO_4, and filtered. The filtrate was subjected to GLPC analysis.

2,2-Dimethyl-1-oxa-2-silacyclopentane[3] was obtained from the reaction of dimethyldichlorosilane, oxetane, and sodium in toluene as above: 42% yield; NMR δ 3.85 (t, 2 H, J = 6 Hz), 2.02–1.70 (m, 2 H), 0.70 (t, 2 H, J = 8 Hz), 0.18 (s, 6 H).

2,2,4,4-Tetramethyl-1-oxa-2-silacyclopentane[1,14] was obtained from the reaction of dimethyldichlorosilane, 3,3-dimethyloxetane, and sodium in toluene: 47% yield; NMR δ 3.35 (s, 2 H) 1.04 (s, 6 H), 0.67 (s, 2 H), 0.21 (s, 6 H).

Reaction of Oxetane and Dimethyldichlorosilane. Oxetane (2.9 g, 50 mmol) and freshly distilled dimethyldichlorosilane (7.1 g, 55 mmol) were placed in a 25-mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar. The mixture was stirred at reflux for 2.5 h. The reaction mixture was cooled and subjected to fractional distillation through a 15-cm Vigreux distillation column. There was obtained (3-chloroproxy)dimethylchlorosilane: 8.9 g (47.6 mmol, 95.2%); bp 190–194 °C [lit.[3] bp 72 °C (16 mm)]; NMR δ 3.90 (2 H, t, J = 5.5 Hz), 3.61 (2 H, t, J = 6 Hz), 2.01 (2 H, q, J = 6 Hz), 0.48 (6 H, s).

Reaction of (3-Chloropropoxy)dimethylchlorosilane and Sodium Metal. (3-Chloropropoxy)dimethylchlorosilane (8.9 g, 47.6 mmol), 50 mL of *n*-decane, and sodium metal (1.2 g, 52 mmol) were placed into a 100-mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar. The mixture was stirred at reflux for 10 h. The reaction mixture was cooled. Ethanol (10 mL) was added into the mixture slowly to destroy excess sodium metal. The mixture was washed with two portions of 10 mL of water. The organic layer was dried and subjected to fractional distillation through a 15-cm Vigreux distillation column to give 2,2-dimethyl-1-oxa-2-silacyclopentane: 2.58 g (22.2 mmol, 47%); bp 93–95 °C (lit.[3] bp 95 °C).

Reaction of Oxetanes with Trimethylchlorosilane and Sodium. A typical reaction of trimethylchlorosilane, oxetane, and sodium is described below. Oxetane (0.05 mol), sodium (2.3 g, 0.1 mol), and 20 mL of toluene or *n*-decane were placed in a 100-mL, three-necked round-bottomed flask equipped with a pressure-equalizing funnel, reflux condenser, and a Teflon-covered magnetic stirrer. Freshly distilled trimethylchlorosilane (0.11 mol) in 20 mL of toluene or *n*-decane was added dropwise to the refluxing, stirred solution. After the addition was complete, the solution was refluxed for 3 h. The reaction mixture was cooled to room temperature. Ethanol was added to destroy residual sodium metal. The reaction mixture was washed with water, dried over Na_2SO_4, and filtered. The filtrate was subjected to GLPC analysis.

[3-(Trimethylsiloxy)propyl]trimethylsilane[12] was isolated from the reaction trimethylchlorosilane, oxetane, and sodium in *n*-decane as above: 55% yield; NMR δ 3.50 (t, 2 H, J = 7 Hz), 1.72–1.36 (m, 2 H), 0.55–0.34 (m, 2 H), 0.10 (s, 9 H), –0.03 (s, 9 H); IR $\bar{\nu}$ 1094 (Si–O–C), 1248 and 840 cm^{-1} ($Si(CH_3)_2$).

(3-Chloropropoxy)trimethylsilane[13] was found in 8% yield: NMR δ 3.76 (t, 2 H, J = 6 Hz), 3.68 (t, 2 H, J = 6 Hz), 1.96 (q, 2 H, J = 6 Hz), 0.12 (s, 9 H); IR $\bar{\nu}$ 1250 (Si–O–C), 1100 and 848 cm^{-1} ($Si(CH_3)_2$).

[2,2-Dimethyl-3-(trimethylsiloxy)propyl]trimethylsilane was obtained from the reaction of trimethylchlorosilane, 3,3-dimethyloxetane, and sodium in toluene as above: 48% yield; NMR δ 3.15 (s, 2 H), 0.88 (s, 6 H), 0.59 (s, 2 H), 0.07 (s, 9 H), 0.02 (s, 9 H); IR $\bar{\nu}$ 1078 (Si–O–C), 1250 and 840 cm^{-1} ($Si(CH_3)_2$). Anal. Calcd for $C_{11}H_{28}OSi$: C, 56.82, H, 12.14. Found: C, 56.75, H, 12.11.

[3-Methyl-3-(trimethylsiloxy)propyl]trimethylsilane was obtained from the reaction of trimethylchlorosilane, 2-methyloxetane, and sodium in toluene: 52% yield; NMR δ 3.70–3.42 (m, 1 H), 1.54–1.22 (m, 2 H), 1.13 (d, 3 H, J = 6 Hz), 0.54–0.33 (m, 2 H), 0.11 (s, 9 H), –0.03 (s, 9 H). Anal. Calcd for $C_{10}H_{26}OSi_2$: C, 54.97, H, 11.99. Found: C, 54.74, H 12.37.

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Reactions of 2,6-Di-*tert*-butylpyridine Derivatives with Methyl Fluorosulfate under High Pressure

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Introduction of alkyl groups into the 2- and 6-positions of pyridine results in a decrease in the rate of reaction with alkyl halides which becomes more and more pronounced as the size of the alkyl group increases.[1] The most highly

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