Journal of Organometallic Chemistry, 222 (1981) 201—209
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MECHANISTIC STUDIES OF THE REACTION OF OXETANES WITH METHYLTHIOTRIMETHYLSILANE

HEINRICH A. FIRGO and WILLIAM P. WEBER

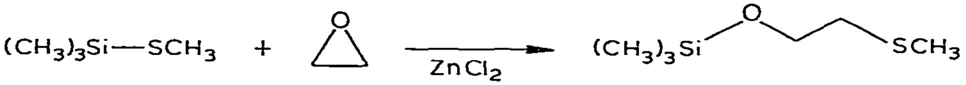
Department of Chemistry, University of Southern California, Los Angeles, California 90007 (U.S.A.)

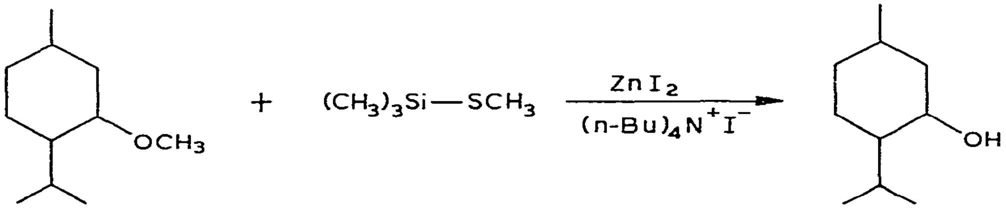
(Received July 6th, 1981)

Summary

The zinc chloride-catalyzed reaction of oxetane with methylthiotrimethylsilane yields (3-chloropropoxy)trimethylsilane (minor) and (3-methylthiopropoxy)trimethylsilane (major). Similar results have been obtained with 2-methyloxetane, 3,3-dimethyloxetane and 2,2-dimethyloxetane. These results have been interpreted in terms of competing S_N1 and S_N2 processes.

Organosilicon compounds have increasingly been utilized as reagents in organic synthesis. The zinc chloride-catalyzed reaction of methylthiotrimethylsilane with ethylene oxide and oxetane yields (2-methylthioethoxy)trimethylsilane and (3-methylthiopropoxy)trimethylsilane, respectively [1]. Closely related synthetically useful reactions have recently been reported. Specifically, the combination of methylthiotrimethylsilane, zinc iodide and tetra-n-butylammonium iodide has proved valuable for the cleavage of methyl ethers to yield alkoxytrimethylsilanes and dimethyl sulfide [2]. Unlike trimethylsilyl iodide, this combination of reagents neither results in the competitive formation of alkyl iodides nor the cleavage of esters [3]. The regiospecific reaction of S-trimethyl-



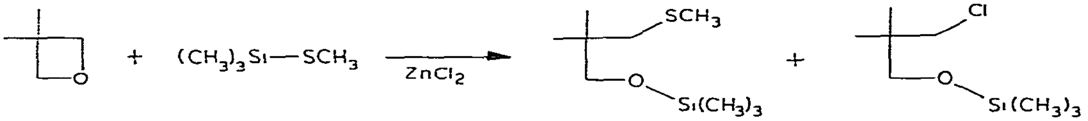


0022-328X/81/0000—0000/$02.50

silyl derivative of glutathione dimethyl ester *N*-trifluoroacetamide with methyl-*E*,5,6-epoxy-*E*,*E*,*Z*,*Z*-7,9,11,14-eicosatetraenoate is a key step in the synthesis of A-Leukotriene [4].

With the goal of understanding the mechanism of this ether cleavage reaction, we have studied the zinc chloride-catalyzed reactions of methylthiotrimethylsilane with oxetane, 2-methyloxetane, 3,3-dimethyloxetane and 2,2-dimethyloxetane.

We have found that oxetane reacts with methylthiotrimethylsilane and dry zinc chloride at 80°C to give (3-methylthiopropoxy)trimethylsilane (58%) and (3-chloropropoxy)trimethylsilane (4%). The formation of (3-chloropropoxy)-trimethylsilane in this reaction has not been previously observed [1]. This is not an isolated observation, but rather the formation of (3-chloroalkoxy)trimethylsilanes is observed with all the oxetanes we have studied with the exception of 2,2-dimethyloxetane. Therefore, 3,3-dimethyloxetane undergoes zinc chloride-catalyzed reaction with methylthiotrimethylsilane to yield (3-methylthio-2,2-dimethylpropoxy)trimethylsilane (66%) and (3-chloro-2,2-dimethylpropoxy)-trimethylsilane (16%).

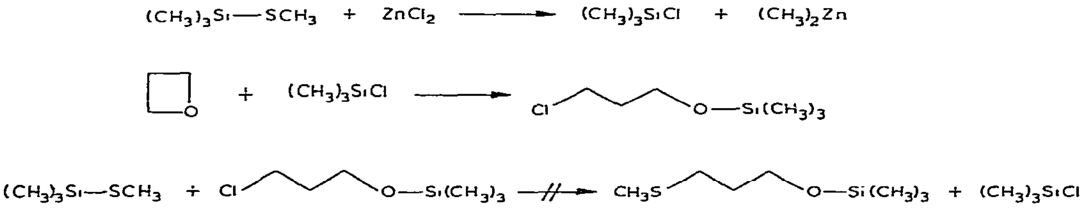


Before attempting to interpret these experiments, there are several additional pieces of information which we have obtained which should be considered. First, methylthiotrimethylsilane does not react with oxetane in the absence of zinc chloride. Second, methylthiotrimethylsilane reacts with zinc chloride to yield trimethylchlorosilane and bis(methylthio)zinc. Third, bis(methylthio)zinc does not react with (3-chloro-2,2-dimethylpropoxy)trimethylsilane.

$$2\ (CH_3)_3Si{-}SCH_3 + ZnCl_2 \rightarrow 2\ (CH_3)_3SiCl + (CH_3S)_2Zn$$

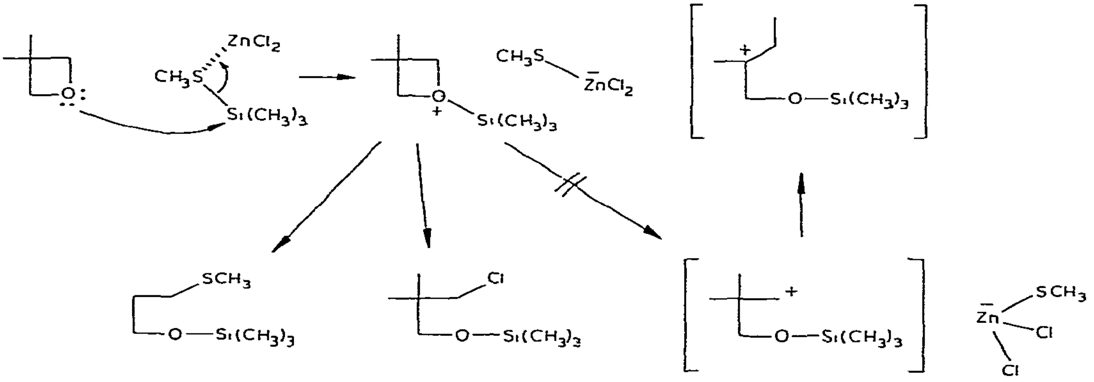
Fourth, bis(methylthio)zinc, which is only slightly soluble under the reaction conditions, is a catalyst for the reaction of methylthiotrimethylsilane and oxetanes.

On the basis of this data, one might suggest the following sequence of events. Zinc chloride first reacts with methylthiotrimethylsilane to yield trimethylchlorosilane and bis(methylthio)zinc. The trimethylchlorosilane thus formed reacts with oxetane to yield (3-chloropropoxy)trimethylsilane. There are numerous examples of the cleavage of epoxides and oxetanes by chlorosilanes [5—8]. Finally, the (3-chloropropoxy)trimethylsilane might react with methylthiotrimethylsilane to yield (3-methylthiopropoxy)trimethylsilane and regenerate the trimethylchlorosilane. Unfortunately, control experiments with (3-chlo-



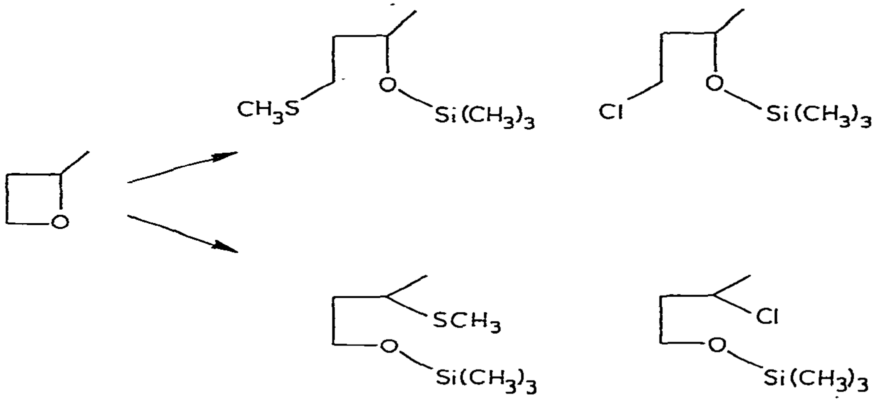
ro-1-methylpropoxy)trimethylsilane have shown that this final step does not occur. Therefore, the formation of (3-methylthiopropoxy)trimethylsilane does not involve prior formation of (3-chloropropoxy)trimethylsilane. While a small amount of (3-chloropropoxy)trimethylsilane is undoubtedly formed by reaction of trimethylchlorosilane and oxetane, this process can not be important since only a catalytic amount of zinc chloride is used.

Given this information, a possible alternative mechanism for zinc chloride or bis(methylthio)zinc catalysis might involve coordination of zinc chloride, a borderline hard-soft Lewis acid [9], to the sulfur atom of methylthiotrimethylsilane. Nucleophilic attack by a lone pair of electrons of the oxygen of oxetane on this complex would yield a trimethylsilyl-substituted oxonium cation—methylthiozinc dichloride anion pair. Nucleophilic attack by the zinc-coordinated methylthio anion on an α-carbon of the trimethylsilyl-substituted oxonium cation would lead to (3-methylthiopropoxy)trimethylsilane, while nucleophilic attack by zinc-coordinated chloride anion would form (3-chloropropoxy)-trimethylsilane. The fact that 3,3-dimethyloxetane leads cleanly to (3-methylthio-2,2-dimethylpropoxy)trimethylsilane and (3-chloro-2,2-dimethylpropoxy)-trimethylsilane is consistent with this interpretation since any S_N1-type opening of the trimethylsilyl-substituted oxonium cation would lead to an unstable primary carbonium ion which would be expected to rapidly undergo a neopentyl-type rearrangement to form a stable tertiary carbonium ion by way of 1,2-Wagner-Meerwein shift of a methyl group [10]. No neopentyl-type rearrangement products are observed.

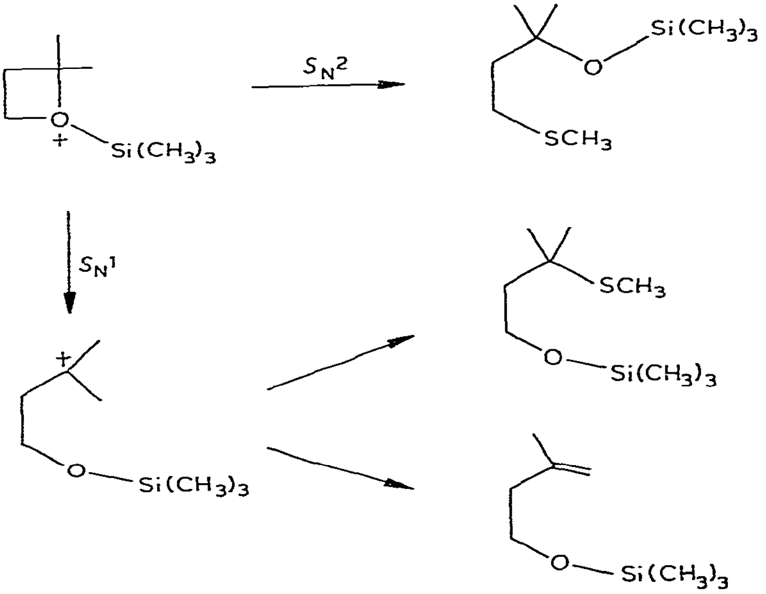


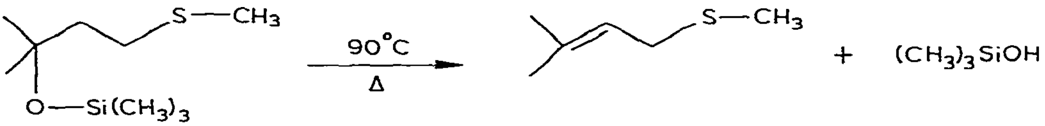
2-Methyloxetane undergoes zinc chloride-catalyzed reaction with methylthiotrimethylsilane to yield (4-methylthio-2-butoxy)trimethylsilane (59%), (3-methylthiobutoxy)trimethylsilane (8.4%) as well as (3-chlorobutoxy)trimethylsilane (6%) and (4-chloro-2-butoxy)trimethylsilane (3%). These results are consistent with the above mechanistic interpretation if the zinc-coordinated methylthio anion has a greater selectivity for nucleophilic attack at a primary α-carbon compared to a secondary α-carbon of the trimethylsilyl-substituted oxonium cation than does the zinc-coordinated chloride anion.

Alternatively, the secondary sulfide and secondary chloride products may result from competitive S_N1 cleavage of the trimethylsilyl-substituted oxonium cation to yield secondary carbonium ion. This pathway may be favored for the chloride anion which is a weaker nucleophile than methylthio anion [11].



The reaction of 2,2-dimethyloxetane with methylthiotrimethylsilane and zinc chloride at 70°C yields (3-methylbut-3-en-1-oxy)trimethylsilane (29%), (4-methylthio-2-methyl-2-butoxy)trimethylsilane (13%), and (3-methylthio-3-methylbutoxy)trimethylsilane (16%). Similar results were obtained at 50°C. These results are consistent with competitive S_N1 and S_N2 processes. (4-Methylthio-2-methyl-2-butoxy)trimethylsilane results from S_N2 nucleophilic attack by the zinc-coordinated methylthio anion on the primary α-carbon of the trimethylsilyl-substituted oxonium cation. An S_N1 cleavage of the trimethylsilyl-substituted oxonium cation yields a tertiary carbonium ion which reacts with the zinc-coordinated methylthio anion to yield (3-trimethylthio-3-methylbutoxy)-trimethylsilane. Loss of methyl thiol under the reaction conditions from this latter product yields (3-methylbut-3-en-1-oxy)trimethylsilane. At higher temperature (4-methylthio-2-methyl-2-butoxy)trimethylsilane loses trimethylsilanol, isolated as hexamethyldisiloxane, to yield 2-methylthio-3-methyl-2-butene. We believe our results are consistent with the hypothesis that these oxetane cleavage





reactions occur by way of trimethylsilyl-substituted oxonium cation-methylthiozinc dichloride anion pairs. These concepts may prove useful in predicting the regiospecificity of such reactions.

Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen. NMR spectra were obtained on a Varian XL-100 spectrometer using 1% solutions in deuterochloroform. Chloroform was used as an internal standard. IR spectra were obtained on a Perkin—Elmer 281 instrument. IR bands were calibrated against known bands of a polystyrene film. Mass spectra were obtained on a Hewlett—Packard 5985 GC-MS instrument. A 6′ × 1/4″ 5% OV-101 column was used in the gas chromatograph. GLPC analysis was performed on a Hewlett—Packard F&M 700 using a 28′ × 1/4″ 20% SE-30 on 60/80 mesh Chromosorb W column. Yields were calculated by GLPC using n-decane or n-hexadecane as internal standards. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. Starting materials and some products are known compounds. They had spectra in complete agreement with literature values. In those cases where spectral properties are not known, we have reported these values.

Methylthiotrimethylsilane was prepared by the method of Allred [12]. Oxetane, 2-methyloxetane and 3,3-dimethyloxetane were obtained from Aldrich. 2,2-Dimethyloxetane was prepared from 4-bromo-2-methyl-2-butanol [13] and tributylmethoxytin [14].

Reaction of oxetane with methylthiotrimethylsilane and zinc chloride

The general procedure described below was used for all of the reactions. A few crystals of zinc chloride (anhydrous) were placed in a glass tube of approximately 2 ml volume and heated to 120°C under vacuum for 3 h. After this, the tube was filled with nitrogen, oxetane (58 mg, 1.0 mmol), methylthiotrimethylsilane (177 mg, 1.5 mmol), n-dodecane (68 mg) and 1 ml of 1,2-dichloroethane were added. The mixture was degassed by three "freeze and thaw" cycles. The tube was sealed and then heated to 80°C for 20 h. After the mixture had cooled to room temperature, the finely divided precipitate was separated by centrifugation. GLPC analysis of the liquid indicated the formation of (3-methylthiopropoxy)trimethylsilane [1] (58%) and (3-chloropropoxy)trimethylsilane (4%).

(3-Chloropropoxy)trimethylsilane had the following spectral properties: NMR: δ 3.64 (t, 2H, $J = 6$ Hz), 3.56 (t, 2H, $J = 6$ Hz), 1.88 (qint, 2H, $J = 6$ Hz), 0.11 (s, 9H). IR ν(Si—O—C) 1110 cm^{-1}. MS $M^+ - 15$, 151 (30.2%), 153 (10.9%); $Cl(CH_3)_2SiOCH_2^+$ 123 (68.8%), 125 (24.8%), $(CH_3)_2Si^+$ $OCH{=}CH_2$ 115 (33.4%), $(CH_3)_3Si\overset{+}{O}CH_2$ 103 (10.7%), $(CH_3)_2Si^+Cl$ 93 (100.0%), 95 (38.0%), $(CH_3)_2Si^+OH$ 75 (5.7%), $(CH_3)_3Si^+$ 73 (25.2%). These mass spectral results are consistent with those reported by McCloskey [15]. An authentic sample prepared by reaction of 3-chloropropanol (Aldrich) with trimethylchlorosilane in pyridine had identical spectral and GLPC properties.

The reaction of 3,3-dimethyloxetane with methylthiotrimethylsilane and zinc chloride

A mixture of 1 ml 1,2-dichloroethane, 158 mg (1.3 mmol) methylthiotrimethylsilane, 114 mg (1.3 mmol) 3,3-dimethyloxetane, 39 mg n-hexadecane and a few crystals of zinc chloride was heated to 90°C for 16.5 h in a sealed tube. GLPC analysis showed the production of (3-methylthio-2,2-dimethylpropoxy)trimethylsilane and (3-chloro-2,2-dimethylpropoxy)trimethylsilane in 66% and 16% yields respectively.

(3-Methylthio-2,2-dimethylpropoxy)trimethylsilane had the following spectral properties: NMR δ 3.30 (s, 2H), 2.47 (s, 2H), 2.11 (s, 3H), 0.91 (s, 6H), 0.09 (s, 9H). IR ν(Si—O—C) = 1100 cm^{-1}. MS M^+ 205 (7.6%), $M^+ - 15$ 191 (4.9%), $M^+ - 15 - CH_3SH$ 143 (41%), $CH_3SCH_2(CH_3)_2C{=}CH^+$ 116 (21.6%), $CH_3SSi(CH_3)_2^+$ 105 (20.1%), $(CH_3)_3SiOCH_2^+$ 103 (33.2%), $CH_3SCH_2(CH_3)_2C{=}CH^+ - 15$ 101 (24.6%), $(CH_3)_2Si^+OH$ 75 (61.5%), $(CH_3)_3Si^+$ 73 (100%). Anal. found: C, 52.29; H, 10.66. calcd. for $C_9H_{22}OSSi$: C, 52.37; H, 10.74%.

(3-Chloro-2,2-dimethylpropoxy)trimethylsilane had the following spectral properties. NMR δ 3.40 (s, 2H), 3.32 (s, 2H), 0.91 (s, 6H), 0.08 (s, 9H) MS $M^+ - 15$ 179 (13.3%), 181 (4.4%), $Cl(CH_3)_2SiOCH_2CH_2^+$ 137 (24.0%), 139 (8.7%), $Cl(CH_3)_2SiO^+{=}CH_2$ 123 (20.9%), 125 (7.6%), $(CH_3)_3SiOCH_2^+$ 103 (55.6%), $(CH_3)_2Si^+Cl$ 93 (46.7%), 95 (19.8%), $(CH_3)_2Si^+OH$ 75 (23.8%), $(CH_3)_3Si^+$ 73 (100.0%). IR ν(Si—O—C) 1103 cm^{-1}. An authentic sample was prepared by reaction of 3-chloro-2,2-dimethyl-1-propanol [16] and trimethylchlorosilane in the presence of pyridine. It had identical spectral properties and GLPC retention time.

Reaction of 2-methyloxetane with methylthiotrimethylsilane and zinc chloride

A mixture of 1 ml 1,2-dichloroethane, 101 mg (1.4 mmol) 2-methyloxetane, 169 mg (1.4 mmol) methylthiotrimethylsilane, 75 mg n-hexadecane and a few crystals of zinc chloride was heated to 90°C for 21 hours in a sealed tube. GLPC analysis of the reaction mixture showed the formation of a 7 : 1 mixture of (4-methylthio-2-butoxy)trimethylsilane and (3-methylthiobutoxy)trimethylsilane in 67% combined yield and a 2 : 1 mixture of (3-chlorobutoxy)trimethylsilane and (4-chloro-2-butoxy)trimethylsilane in 9% combined yield. These isomers could not be separated by GLPC, but were analyzed by NMR.

(4-Methylthio-2-butoxy)trimethylsilane. NMR δ 3.87 (m, 1H, $J = 6$ Hz), 2.49 (t, 2H, $J = 7$ Hz), 2.07 (s, 3H), 1.81—1.53 (m, 2H), 1.13 (d, 3H, $J = 3.6$ Hz, 0.09 (s, 9H).

(3-Methylthiobutoxy)trimethylsilane. NMR δ 3.66 (t, 2H, $J = 6$ Hz), 2.50 (m, 1H), 1.80 (s, 3H), 1.81—1.53 (m, 2H), 1.26 (d, 3H, $J = 7$ Hz), 0.08 (s, 9H). The 7 : 1 mixture of (4-methylthio-2-butoxy)trimethylsilane and (3-methylthiobutoxy)trimethylsilane had the following properties: MS: M^+ 192 (8.2%), 194 (0.6%); $M^+ - 15$ 177 (15.7%), 179 (1.4%), $CH_3S(CH_3)_2SiO(CH_3)CH^+$ 149 (5.3%), 151 (0.5%), $M^+ - CH_3SH$ 144 (25.3%), $(CH_3)_3SiO(CH_3)CHCH_2^+$ 129 (31.4%), $(CH_3)_3SiO(CH_3)CH^+$ 117 (25.5%), $CH_3S(CH_3)_2Si^+$ 105 (34.6%), 107 (3.1%), $(M^+ - 15) - (CH_3)_2Si^+OH$ 102 (76.3%), 104 (5.1%), $(M^+ - 15) -$

$(CH_3)_2SiOH)$ — 15 87 (48.4%), 89 (3.9%), $(CH_3)_2Si^+OH$ 75 (64.2%), $(CH_3)_3Si^+$ 73 (100.0%), IR ν(Si—O—C) 1080 cm^{-1}. Anal. found: C, 49.68; H, 10.54; calcd. for $C_8H_{20}OSSi$: C, 49.94; H, 10.48%.

(4-Chloro-2-butoxy)trimethylsilane. NMR δ 3.97 (sext. 1H, J = 6 Hz), 3.54 (t, 2H, J = 6 Hz), 1.80 (quart, 2H, J = 6 Hz), 1.15 (d, 3H, J = 6 Hz), 0.13 (s, 9H).

(3-Chlorobutoxy)trimethylsilane. NMR δ 4.10 (sext, 1H, J = 6 Hz), 3.71 (t, 2H, J = 6 Hz), 1.80 (quart, 2H, 6 Hz), 1.52 (d, 3H, J = 6 Hz), 0.11 (s, 9H). The 1 : 2 mixture of (4-chlorobutoxy)trimethylsilane and (3-chlorobutoxy)trimethylsilane had the following properties: MS M^+ — 15 165 (18.7%), 167 (2.7%), $(CH_3)_2ClSiOCH_2CH_2^+$ and $(CH_3)_2ClSiO(CH_3)CH^+$ 137 (38.3%), 139 (10.3%), $(CH_3)_2ClSiOCH_2^+$ 123 (66.3%), 125 (24.7%), $(CH_3)_2ClSi^+$ 93 (100%), 95 (41.3%), $(CH_3)_2Si^+OH$ 75 (34%), $(CH_3)_3Si^+$ 73 (86.1%). IR ν(Si—O—C) 1090 cm^{-1}. An authentic sample of (4-chloro-2-butoxy)trimethylsilane was prepared by reaction of 4-chloro-2-butanol and trimethylchlorosilane in pyridine, it had spectral properties in agreement with the above values.

4-Chloro-2-butanol was prepared by reduction of 4-chloro-2-butanone with $NaBH_4$ in MeOH [17].

Reactions of 2,2-dimethyloxetane with methylthiotrimethylsilane and zinc chloride

A) A mixture of 1 ml 1,2-dichloroethane, 170 mg (1.4 mmol) methylthiotrimethylsilane, 120 mg (1.4 mmol) 2,2-dimethyloxetane, 36 mg n-decane and a few crystals of zinc chloride was heated to 90°C for 24 h in a sealed tube. GLPC analysis of the reaction mixture showed the formation of 2-methylthio-3-methyl-2-butene in 36% yield [18] and hexamethyldisiloxane in 28% yield.

B) A mixture of 0.7 ml 1,2-dichloromethane, 116 mg (1 mmol) methylthiotrimethylsilane, 83 mg (1 mmol) 2,2-dimethyloxetane, 33 mg n-decane and a few crystals of zinc chloride was heated to 70°C for 21 h in a sealed tube. GLPC analysis indicated the formation of (3-methylbut-3-en-1-oxy)trimethylsilane (29% yield), (4-methylthio-2-methyl-2-butoxy)trimethylsilane (13% yield) and (3-methylthio-3-methylbutoxy)trimethylsilane (16% yield) and methyl mercaptan. Due to its volatility the yield of methylthiol was not determined.

(4-Methylthio-2-methyl-2-butoxy)trimethylsilane and 3-methylthio-2-butoxy)trimethylsilane could not be separated by preparative GLPC but were analyzed by NMR spectroscopy and GC-MS.

(4-Methylthio-2-methyl-2-butoxy)trimethylsilane. NMR δ 2.53 (m, 2H, $[J(AX) + J(AX')]/2$ = 8 Hz), 2.11 (s, 3H), 1.63 (t, 2H, J = 8 Hz), 1.23 (s, 6H), 0.12 (s, 9H).

(3-Methylthio-3-methylbutoxy)trimethylsilane. NMR δ 3.72 (t, 2H, J = 8 Hz), 2.00 (s, 3H), 1.79 (t, 2H, J = 7 Hz), 1.29 (s, 6H), 0.12 (s, 9H). The mass spectrum of the mixture of the above isomers: M^+ 206 (4.7%), 208 (0.4%), M^+ — 15 191 (3.5%), 193 (0.2%), M^+ — 48 158 (12.3%), (M^+ — 48) — 15 143 (47.1%), (M^+ — 48) — 27 131 (16.3%), (M^+ — 48 — 15) — 27 116 (16.9%), $(CH_3)_2Si^+SCH_3$ 105 (13.0%), 107 (1.4%), M^+ — 103 103 (47.6%), M^+ — 105 101 (18.3%), $(CH_3)_2Si^+OH$ 75 (53.7%), $(CH_3)_3Si$ 73 (100.0%).

The IR spectrum of the mixture had ν(Si—O—C) = 1080 cm^{-1}. Anal. found: C, 57.47; H, 10.06; calcd. for $C_9H_{22}OSSi$: C, 52.37; H, 10.74%.

(3-Methylbut-3-en-1-oxy)trimethylsilane. NMR δ 4.70 (m, 2H), 3.66 (t, 2H,

$J = 7$ Hz), 2.24 (t, 2H, $J = 6$ Hz), 1.73 (s, 3H), 0.10 (s, 9H). MS: M^+ 158 (1.0%), $M^+ - 15$ 143 (12.5%), $M^+ - 55$ 103 (74.5%), $(M^+ - 15) - 42$ 101 (23.4%), $(CH_3)_2SiOH$ 73 (18.4%), $(CH_3)_3Si^+$ 73 (100.0%). IR ν(C=C) 1662 cm^{-1}. ν(Si—O—C) = 1103 cm^{-1}. These spectroscopic data were in agreement with an authentic sample prepared from 3-methylbut-3-en-1-ol (Aldrich) and trimethylchlorosilane.

C) A mixture of 1.1 ml 1,2-dichloroethane, 179 mg (1.5 mmol) methylthiotrimethylsilane, 136 mg (1.5 mmol), 2,2-dimethyloxetane, 45 mg n-decane and a few crystals of zinc chloride were heated to 50°C for 20 h in a sealed tube. After this time GLC analysis indicated the formation of (3-methylbut-3-en-1-oxy)trimethylsilane (24% yield) and a 2 : 1 mixture (determined by NMR) of (3-methylthio-3-methylbutoxy)trimethylsilane and (4-methylthio-2-methyl-2-butoxy)trimethylsilane (28% combined yield).

Reaction of methylthiotrimethylsilane and zinc chloride

A mixture of 9 g (0.065 mol) zinc chloride (heated to 110°C in vacuo overnight prior to use), 6 g methylthiotrimethylsilane (0.05 mol) and 15 ml 1,2-dichloroethane was refluxed for 24 h. After this time, the formerly crystalline zinc chloride had disappeared and a white, very finely divided precipitate had formed. 10 ml of 1,2-dichloroethane were added to the mixture, which was then filtered under an atmosphere of dry nitrogen. Distillation of the filtrate gave 1 g of pure trimethylchlorosilane (yield 14%). The white precipitate was washed with water and dried at 60°C in vacuo. The yield was 2 g. Anal. found: S, 38.53; Cl 2.16. calcd. for $ZnS_2C_2H_6$: S, 40.19; Cl, 0.00%.

Reaction between oxetane and methylthiotrimethylsilane without solvent

A mixture of 0.4 g (6.9 mmol) oxetane, 0.75 g (6.3 mmol) methylthiotrimethylsilane 0.13 g (1 mmol) and 0.2 g n-decane and a few crystals of zinc chloride was heated to 70°C for 22 h in a sealed tube. After this time, GLPC analysis showed the formation of (3-methylthiopropoxy)trimethylsilane (26% yield) and (3-chloropropoxy), trimethylsilane (4% yield).

Reaction of oxetane and methylthiotrimethylsilane in the presence of bis(methylthio)zinc

A mixture of 16.1 mg (1.34 mmol) methylthiotrimethylsilane, oxetane (58 mg, 1 mmol), 65 mg n-decane, 1 ml 1,2-dichloroethane and a few crystals of bis(methylthio)zinc was heated to 85°C for 22 h in a sealed tube. GLPC analysis indicated the formation of (3-methylthiopropoxy)trimethylsilane in 57% yield. No (3-chloropropoxy)trimethylsilane was formed.

Attempted reaction between (3-chloro-2,2-dimethylpropoxy)trimethylsilane and bis(methylthio)zinc

A mixture of 257 mg (1.32 mmol) (3-chloro-2,2-dimethylpropoxy)trimethylsilane, 105 mg bis(methylthio)zinc (0.66 mmol), 50 mg n-hexadecane and 1 ml 1,2-dichloroethane was heated in a sealed tube for 20 h to 90°C. After this time, no reaction had occurred as determined by GLPC.

Attempted reaction between (4-chloro-2-butoxy)trimethylsilane and methylthiotrimethylsilane

A mixture of 190 mg (1.05 mmol) (4-chloro-2-butoxy)trimethylsilane, 171 mg (1.4 mmol) methylthiotrimethylsilane, 1 ml 1,2-dichloroethane and a few crystals of zinc chloride was heated to 85°C for 24 h in a sealed tube. GLPC analysis only showed unchanged starting materials.

Acknowledgement

This work was supported by the Air Force Office of Scientific Research, Grant number 80-0006.

References

1 E.W. Abel and D.J. Walker, J. Chem. Soc. A, (1968) 2338.
2 S. Haniessan and Y. Guindon, Tetrahedron Lett., (1980) 2305.
3 M.E. Jung and T.A. Blumekopf, Tetrahedron Lett., (1978) 3657.
4 J. Rokach, Y. Girard, Y. Guindon, J.G. Atkinson, M. Larue, R.N. Young, P. Masson and G. Holme, Tetrahedron Lett., (1980) 1485.
5 N.I. Shuikin, I.E. Grushko and I.F. Bel'skii, Dokl. Akad. Nauk SSSR, 141 (1961) 649.
6 I.M. Gverdtsiteli, R.Y. Papava and E.S. Gelashvili, Zhur. Obsh. Khim., 36 (1966) 112.
7 R.C. Mehrotra and P. Bajaj, J. Organometal. Chem., 22 (1970) 41.
8 K.A. Andrianov, G.A. Kurakov and M. Khananashvili, Zhur. Obsh. Khim., 35 (1965) 328.
9 M. Misono and Y. Saito, Bull. Japan Chem. Soc., 43 (1970) 3680.
10 J. Marsh, Advanced Organic Chemistry Reaction Mechanism and Structures, McGraw-Hill, New York, N.Y., 1977, p. 964—969.
11 C.G. Swaim and C.B. Scott, J. Amer. Chem. Soc., 75 (1953) 141.
12 K. Hooton and A.L. Allred, J. Inorg. Chem., 4 (1965) 471.
13 B. Delmond, J.C. Pommier and J. Valade, J. Organometal. Chem., 47 (1973) 337.
14 D.L. Aileston and A.G. Davies, J. Chem. Soc., (1962) 2050.
15 E. White V, and J.A. McCloskey, J. Org. Chem., 35 (1970) 4241.
16 W.H. Richardson, C.M. Golino, R.H. Wachs and M.B. Yelvington, J. Org. Chem., 36 (1971) 943.
17 F. Sondheimer and R.B. Woodward, J. Am. Chem. Soc., 75 (1953) 5438.
18 A.A. Oswald, K. Griesbaum, W.A. Thaler, B.E. Hudson, Jr., J. Amer. Chem. Soc., 84 (1962) 3897.