to suggest a five-membered cyclic activated complex (**3** or **6**) for the bicyclic system.[53]

3, **4**, **5**, or **6** would require the large negative entropies of activation (−23.5 to −42.7 eu) tabulated in Table V. $\Delta S^{\ddagger}$ values of this magnitude have been observed for reactions, *e.g.*, epoxidation, 1,3-dipolar cycloadditions, with rigid orientation requirements in the activated complex.

We conclude from the kinetic studies and the comparative rate data that the activated complex for the chromyl chloride oxidation of cycloalkenes can be represented by the partially charged unsymmetrical structure **4**.[56] **4** is consistent with the rapid rate of oxidation in solvents of low polarity and with the ρ^* of approximately −2.0. In this postulated mechanism, which is similar to the one proposed by Bartlett[57–59] for epoxidation, oxygen transfer from chromyl chloride occurs by a concerted process. That is, as the two new σ bonds are being formed, the oxygen–chromium bond is being broken.[60] After the rate-determining step, this mechanism could lead to a product-determining epoxide intermediate (Scheme II). Activated complexes similar to **4** and **5** have also been proposed for the chromic acid[44] and chromyl acetate[42] oxidation of carbon–carbon double bonds.[40,56]

The limited comparative rate data suggest that the activated complex for the chromyl chloride oxidation of bicyclo[2.2.1]hept-2-ene *probably* has a close resemblance to **3** or **6**. Additional studies on more bicyclic systems are in process in order to fully elucidate the mechanism.

Registry No.—Chromyl chloride, 7791-14-2.

Acknowledgment.—We express our thanks to the donors of the Petroleum Research Fund administered by the American Chemical Society and the Long Beach California State College Foundation for support of this work.

[56] The symmetrical species **5** and **6** could have sufficient carbonium ion character to satisfy $\rho^* \cong -2.0$. It is also recognized that the oxidation is a process in which there is a net flow of electrons from the substrate through the oxidant. This results in the inevitable development of a partial positive charge either on the carbon atoms of the double bond or on the oxygen atom, and of a partial negative charge on the chromium atom undergoing a valency change or on its ligands.

[57] P. D. Barteltt, *Rec. Chem. Progr.*, **11**, 47 (1950).

[58] A $\rho = -1.20$ has been obtained for the epoxidation of stilbenes with peroxybenzoic acid: B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); Y. Ogata and I. Tabushi, *J. Amer. Chem. Soc.*, **83**, 3440 (1961).

[59] D. Swern, "Organic Peroxides," Vol. II, Wiley, New York, N. Y., 1971, p 355.

[60] Concerted closure of the two incipient σ bonds does not necessarily mean that the development of the bonds has proceeded to the same degree in the activated complex. Any difference between the bond-making rates during the activation process would lead to a partial charge at the more substituted carbon atom.

Silation of Dichloromethyllithium in the Presence of Excess *n*-Butyllithium

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The silation of a −100° solution of 2 equiv of *n*-butyllithium and 1 equiv of methylene chloride in THF–hexane with trimethylchlorosilane leads to a complex product mixture of butyltrimethylsilane (**3**), dichloro(trimethylsilyl)methane (**1**), bis(trimethylsilyl)chloromethane (**4**), bis(trimethylsilyl)dichloromethane (**2**), tris(trimethylsilyl)methane (**5**), 1,1-di(trimethylsilyl)-1-chloropentane (**6**), and tris(trimethylsilyl)chlorosilane (**7**). Experimental evidence is presented that indicates that successive silation of monolithio intermediates is occurring rather than production of dilithiodichloromethane.

It has been reported[1] that additions of *n*-butyllithium to cold (−100°) solutions of methylene chloride and trimethylchlorosilane in tetrahydrofuran (THF) give respectable yields of dichloro(trimethylsilyl)methane (**1**) and bis(trimethylsilyl)dichloromethane (**2**), depending on the quantity of reagents used (eq 1 and 2). In repeating this second reaction, we found it

$$1Me_3SiCl + 1CH_2Cl_2 + 1BuLi \xrightarrow[51\%]{THF,\ -100^\circ} \underset{\mathbf{1}}{Me_3SiCHCl_2} \quad (1)$$

$$2Me_3SiCl + 1CH_2Cl_2 + 2BuLi \xrightarrow[40\%]{THF,\ -100^\circ} \underset{\mathbf{2}}{Me_3SiCCl_2SiMe_3} \quad (2)$$

to be quite complex, regardless of whether the reaction was done *in situ* as Bamford and Pant describe or if the intermediate, dichloromethyllithium ($LiCHCl_2$), was preformed prior to addition of trimethylchlorosilane.

When trimethylchlorosilane was added last to a cold solution of 2 equiv of *n*-butyllithium to 1 equiv of methylene chloride in THF as the solvent, compound **2** was formed in approximately 50% yield (based on vpc). The other 50% of the reaction products was composed of compounds **1** and **3**–**7**. The silated products were isolated by preparative gas chromatography and characterized by infrared, nmr, and mass spectra,[2] elemental analysis, and comparisons to previously reported properties[1,3–7] (see Experimental Section for details and relative amounts). Additional structure proof of compound **2** was provided by its hydride reduction to a mixture of **4** and bis(trimethylsilyl)methane (**8**).[3] (Compound **4**, unlike **2**, reduces only very slowly with lithium aluminum hydride.)

Me_3SiBu **3** $(Me_3Si)_2CHCl$ **4** $(Me_3Si)_3CH$ **5** $(Me_3Si)_2CClBu$ **6**

$(Me_3Si)_3CCl$ **7** $(Me_3Si)_2CH_2$ **8** $(Me_3Si)_4C$ **9**

[1] W. R. Bamford and B. C. Pant, *J. Chem. Soc. C*, 1470 (1967).

[2] D. R. Dimmel, C. A. Wilkie, and F. Ramon, *J. Org. Chem.*, **37**, 2665 (1972).

[3] R. L. Merker and M. J. Scott, *J. Organometal. Chem.*, **4**, 98 (1965).

[4] R. Müller and G. Seitz, *Chem. Ber.*, **91**, 22 (1958).

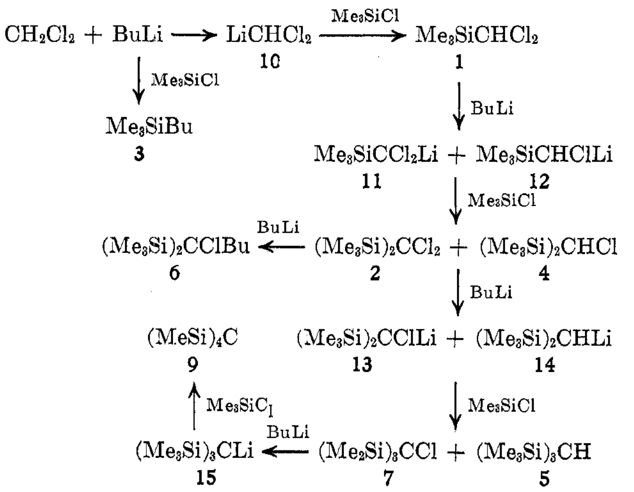
[5] R. Mueller and S. Reichel, *ibid.*, **99**, 793 (1966).

[6] G. Fritz and J. Grobe, *Z. Anorg. Allg. Chem.*, **309**, 77 (1961).

[7] V. F. Mironov and N. A. Pogonkina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 182 (1955); *Chem. Abstr.*, **50**, 1574*d* (1956).

A probable mechanism which might account for the variety of products found when methylene chloride is silated is presented in Scheme I. The evidence supporting Scheme I is the following.

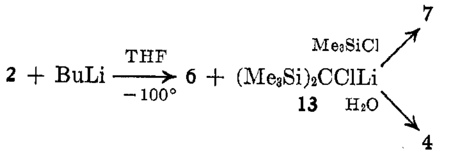
SCHEME I



(1) Silyl groups are known to enhance the reactivity of an α carbon toward further reactions with base[8] and, consequently, polysilation can occur. The reaction of methylene chloride with varying amounts of *n*-butyllithium supports this premise. With 1 equiv of *n*-butyllithium, the major product was the monosilated compound **1**, with 2 equiv it was **2**, with 3 equiv it was the trisilated compound **7**, and with 4.5 equiv it was the tetrasilated product **9**. The consecutive silations could be lessened to some extent by the inverse addition of the cold CH_2Cl_2/BuLi solutions to cold Me_3SiCl; here the product composition was 74% **2**, 14% **7**, 10% **4**, and 2% **6**.

(2) An equal molar mixture of bis(trimethylsilyl)dichloromethane (**2**) and trimethylchlorosilane in THF was treated with 1 equiv of BuLi at −100° to afford products **7** and **3** in a 15:1 ratio. Thus, at these low temperatures, the reaction between *n*-butyllithium and trimethylchlorosilane is quite slow relative to reaction of the base with a silyl activated methylene, an observation also made by Bamford and Pant.[1]

(3) Verification that halogen exchange reactions,[9] such as **1** → **12**, **2** → **13**, etc., are plausible steps in these transformations was provided by the observation that a sample of **2** could be converted, *via* its lithium derivative **13**, to either **7** or **4** (eq 3). The results (eq 3) also



(3)

indicate that **2** is the likely precursor of **6** and that hydrolysis (or proton abstraction) of lithio intermediates **11**, **13**, and **15** could account for some or all of the observed products **1**, **4**, and **5**.

(4) If the reaction described by eq 2 was performed on a vacuum line, 1 equiv of butane was collected prior to silation and 0.5 equiv was collected after silation [in this case ineffective mixing led to more than the usual amount of butyltrimethylsilane (**3**)]. Butyl chloride was also detected as a by-product. In like manner, only 1 equiv of isobutane was collected when 2 equiv of *tert*-butyllithium was treated with 1 equiv of methylene chloride (eq 4). These results rule out dichloromethyllithium (Li_2CCl_2) as an intermediate in these reactions since its formation would lead to 2 equiv of butane prior to silation.

$$\mathrm{CH_2Cl_2 + 2\ \textit{t}\text{-}BuLi \xrightarrow[-100^\circ]{THF} LiCHCl_2 + (CH_3)_3CH + \textit{t}\text{-}BuLi} \qquad (4)$$

If the silations were done according to the procedure of Bamford and Pant,[2] namely, the *n*-butyllithium added last to a cold solution of trimethylchlorosilane and CH_2Cl_2 in solvent, a mixture of products was also obtained. Using an excess of Me_3SiCl and THF as the solvent, the predominant product was the trisilated compound **7** and not **2** (eq 5). With a solvent mixture

$$\mathrm{3Me_3SiCl + 1CH_2Cl_2 + 2BuLi \xrightarrow[-100^\circ]{THF}} \underset{27\%}{\mathbf{2}} + \underset{12\%}{\mathbf{4}} + \underset{9\%}{\mathbf{6}} + \underset{52\%}{\mathbf{7}} \qquad (5)$$

of 5 parts THF/5 parts hexane/1 part ether and a stoichiometric amount of Me_3SiCl, a 65% yield (vpc) of **2** was obtained (eq 6).

$$\mathrm{2Me_3SiCl + 1CH_2Cl_2 + 2BuLi \xrightarrow[-100^\circ]{THF/hexane/ether}} \underset{65\%}{\mathbf{2}} + \underset{19\%}{\mathbf{4}} + \underset{9\%}{\mathbf{6}} + \underset{7\%}{\mathbf{7}} \qquad (6)$$

To summarize, the silation of methylene chloride in the presence of excess *n*-butyllithium, no matter how the reaction is done, gives several products. These products apparently result because the reaction of trimethylchlorosilane with *n*-butyllithium is quite slow at −100° relative to *n*-butyllithium reacting with silyl-activated α protons or chlorines. The reaction does not appear to be a useful preparative reaction unless one has a very good fractionating column or preparative gas chromatograph. The exceptions to this generalized statement are **7** and **9**, which can be sublimed from the reaction mixtures and obtained in fairly pure states and decent quantities.

Experimental Section

All the *n*-butyllithium reactions were conducted in flame-dried 500-ml four-neck round-bottom flasks fitted with a dropping funnel, tru-bore stirrer, thermometer, and drying tube. The reactions were done under an atmosphere of nitrogen; temperature control was achieved using liquid nitrogen. The methylene chloride and THF were freshly distilled prior to use, the former from P_2O_5, the latter from sodium–potassium alloy. The *n*-butyllithium and *tert*-butyllithium in hexane solvent were purchased from Alfa Inorganics.

Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer, using TMS as the internal standard and CCl_4 as the solvent. Infrared spectra were recorded on a Beckman IR-12 spectrometer. Mass spectra were obtained using a CEC 21-104 mass spectrometer. Gas chromatographic analyses were performed on a 6 ft × 0.25 in. aluminum column packed with SE-30 on 60–80 mesh Chromosorb W using a F & M Model 700 gas chromatograph. Preparative work was done on 8 ft × 0.75 in. stainless steel columns packed with SE-30 on Chromosorb W using a F & M Model 770 preparative gas chromatograph.

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[8] R. West and G. A. Gornowicz, *J. Organometal Chem.*, **28**, 25 (1971), and references cited therein.

[9] G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry," Methuen, London, 1968, p 47.

Boiling points were determined by the capillary method. All boiling points and melting points are uncorrected.

Silation of Methylene Chloride.—To a stirred solution of 8.85 g (0.104 mol) of methylene chloride in about 200 ml of THF, cooled to about −90°, was slowly added 90 ml (0.214 mol) of 2.37 *M* *n*-butyllithium in hexane. After complete addition and additional stirring for 3 hr, 24.7 g (0.229 mol) of trimethylchlorosilane in 50 ml of THF was added over a 2-hr period. The reaction was then allowed to gradually warm to room temperature. Much of the THF was distilled off; then water and ether were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with fresh ether. The combined ether extracts were washed with water, dried ($MgSO_4$), and distilled. Four fractions ranging in boiling points of 35–145° were collected at atmospheric pressure using a Vigreux column. Another five fractions, bp 50–170° (15 mm), were collected using a short-path distillation column.

The various fractions were analyzed by gas chromatography (SE-30) and percentages of each component were calculated by the triangle method. From the percentages and quantities of each, the rough composition of product mixture was determined to be 20% **1**, 48% **2**, 12% **3**, 5% **4**, 9% **5**, 1% **6**, and 4% **7**. The various components were then separated by preparative gas chromatography (SE-30). The properties of the collected compounds (listed in increasing retention time) were the following.

Butyltrimethylsilane (**3**) was identical with a sample prepared by the reaction of *n*-butyllithium with trimethylchlorosilane, bp 115–116° (lit.[10] bp 116.0–116.5°).

Dichloro(trimethylsilyl)methane (**1**) had bp 134° (lit.[1] bp 132–134°); nmr (CCl_4) δ 0.22 (s, 9, Me_3Si) and 5.24 (s, 1, CH); ir (neat) 850 (s) and 1258 (s) (CSi), 633, 690, 717 (s), 763, 781, and 872 cm^{-1} (s); mass spectrum (70 eV) molecular ion at *m/e* 156, 158, and 160 (two chlorines).[11]

Anal. Calcd for $C_4H_{10}SiCl_2$: C, 30.58; H, 6.42. Found: C, 30.80; H, 6.31.

Bis(trimethylsilyl)chloromethane (**4**) had bp 175° [lit.[7] bp 177–8.5°]; nmr (CCl_4) δ 0.12 (s, 18, Me_3Si) and 2.35 (s, 1, CH); ir (neat) 850 (s) and 1260 (s) (CSi), 619, 632, 698, 713, 770, and 1145 cm^{-1} (s); mass spectrum (70 eV) molecular ion at *m/e* 194 and 196 (3:1 patterns, weak, monochloro).[11]

Anal. Calcd for $C_7H_{19}Si_2Cl$: C, 43.15; H, 9.83; Cl, 18.19. Found: C, 42.27; H, 9.59; Cl, 18.19.

Bis(trimethylsilyl)dichloromethane (**2**) had bp 204° [lit.[1] bp 125–127° (60 mm)]; nmr (CCl_4) δ 0.23 (s, Me_3Si); ir (neat) 851 (s) and 1266 (s) (CSi), 632, 649, 703 (s), 747, 768, 810 (s), and 878 cm^{-1} (s); mass spectrum (70 eV) molecular ion at *m/e* 228, 230, and 232 (weak, dichloro).[11]

Anal. Calcd for $C_7H_{18}Si_2Cl_2$: C, 36.67; H, 7.91; Cl, 30.92. Found: C, 36.82; H, 7.61; C, 30.79.

Tris(trimethylsilyl)methane (**5**) had nmr (CCl_4) δ 0.10 (s, 27, Me_3Si) and −0.78 (s, 1, CH) [lit.[11] nmr (CCl_4) δ 0.11 (Me_3Si–) and −0.79 (CH)]; ir (neat) 850 (s) and 1256 (s) (CSi), 680, 690, and 1010 cm^{-1} (s); mass spectrum (70 eV) no molecular ion, base peak at *m/e* 217 (M − 15).[11]

Anal. Calcd for $C_{10}H_{28}Si_3$: C, 51.64; H, 12.13. Found: C, 51.50; H, 12.08.

1,1-Di(trimethylsilyl)-1-chloropentane (**6**) had nmr (CCl_4) δ 0.13 (s, 18, Me_3Si), 0.95 (t, 3, CH_3), and 1.1–2.0 [m, 6, $-(CH_2)_3-$]; ir (neat) 850 (s) and 1254 (s) (CSi), 625, 695, and 765 cm^{-1}; mass spectrum (70 eV) no molecular ion, base peak at *m/e* 73 (Me_3Si^+).[11] A satisfactory analysis could not be obtained due to a small impurity of **7** which was difficult to remove. The primary basis of the structural assignment relied heavily on the nmr spectrum.

Tris(trimethylsilyl)chloromethane (**7**) had mp 125–126°; nmr (CCl_4) δ 0.19 (s, Me_3Si); ir (Nujol mull) 865 (s), 1259 (s) and 1267 (s) (CSi), 690 and 705 cm^{-1}; mass spectrum (70 eV), molecular ions at *m/e* 266 and 268 (3:1 ratio, weak, monochloro).[11]

Anal. Calcd for $C_{10}H_{27}Si_3Cl$: C, 44.98; H, 10.19; Cl, 13.28. Found: C, 44.83; H, 9.89; Cl, 13.23.

The experiment was repeated in the exact same manner except that trimethylchlorosilane was added to the reaction mixture very rapidly. The product distribution is this case was 2% **1**, 52% **2**, 9% **3**, 4% **4**, 0.5% **5**, 2% **6**, and 21% **7**.

The experiment was repeated a third time using 4.0 g (0.0486 mol) of methylene chloride and 100 ml (0.23 mol) of 2.3 *M* *n*-butyllithium and quenching with 40 ml (0.321 mol) of trimethylchlorosilane. Distillation removed the solvent and low-boiling products, leaving a solid mass. The latter was added to pentane and filtered to remove the inorganic salts. Removal of the pentane by distillation and sublimation of the residue gave 5.3 g (36%) of tetrakis(trimethylsilyl)methane (**9**): mp > 300° (lit.[12] mp 408–410°); nmr (CCl_4) δ 0.23 (s, Me_3Si) (lit.[3] single peak at δ 0.2]; ir (Nujol) 840 (s), 865 (s), and 1265 (s) (CSi), 330, 621, 678 (s), and 730 cm^{-1}; mass spectrum (70 eV), no molecular ion, base peak at *m/e* 289 (M − 15).[11]

Hydride Reduction of Bis(trimethylsilyl)dichloromethane (**2**).—To a stirred suspension of 0.6 g (16 mmol) of lithium aluminum hydride in about 40 ml of anhydrous ether was added, over a 10-min period, 2.3 g (10 mmol) of a sample containing (vpc) 80% **2**, 14% tris(trimethylsilyl)methane (**5**), 3% bis(trimethylsilyl)chloromethane (**4**), and 3% tris(trimethylsilyl)chloromethane (**7**) dissolved in 20 ml of ether. The reaction mixture was stirred at reflux for 3 hr and at room temperature for 21 hr. The reaction was quenched by adding 0.5 ml of saturated Na_2SO_4 solution. The salts were filtered and washed several times with ether. The combined ether washings were dried ($MgSO_4$) and distilled to remove the solvent. Analysis of the crude residue by vpc indicated incomplete reaction.

The residue was then placed in anhydrous ether, refluxed overnight with a large excess of lithium aluminum hydride, and worked up as before. Analysis of the crude product by vpc (SE-30, 120°) showed 20% **5**, 50% **4**, and 30% of a new low retention time component. The main starting material, **2**, was completely gone. The three components of the mixture were isolated by preparative vpc; compounds **4** and **5** were identical with previously characterized samples. The third, low retention time, component was bis(trimethylsilyl)methane (**8**): nmr (CCl_4) δ 0.02 (s, 18, Me_3Si) and −0.29 (s, 2, CH_2) [lit.[3] nmr (CCl_4) δ 0.02 (Me_3Si–) and −0.28 (CH_2)]; ir (neat) 845 (s) and 1257 (s) (CSi), 692 and 1058 cm^{-1} (lit.[13] identical match); mass spectrum (70 eV) molecular ion at *m/e* 160, base peak at *m/e* 145.[11]

Hydrolysis of Bis(trimethylsilyl)dichloromethane (**2**) *via* **Its Lithium Derivative.**—A sample (2.1 g, 9.2 mmol) which was known (by vpc) to contain 80% **2**, 14% tris(trimethylsilyl)methane (**5**), 3% bis(trimethylsilyl)chloromethane (**4**), and 3% tris(trimethylsilyl)chloromethane (**7**) was dissolved in 20 ml of THF and cooled to −100°. To this stirred solution was slowly added 5 ml (11.5 mmol) of 2.3 *M* *n*-butyllithium in hexane. After the solution was stirred for 1 hr, 5 ml of water in 25 ml of THF was added and the solution was allowed to warm to room temperature. The reaction mixture was distilled to remove much of the THF. Ether was added, the water was separated, and the organic phase was dried ($MgSO_4$) and concentrated. Analysis of the crude product by vpc (SE-30, 150°) showed the following composition: 70% **4**, 13% **5**, and 17% 1,1-di(trimethylsilyl)-1-chloropentane (**6**). Besides vpc comparisons, the compounds were collected by preparative vpc and compared (ir and nmr) to previously characterized samples.

Silation of Bis(trimethylsilyl)dichloromethane (**2**) *via* **Its Lithium Derivative.**—A sample (1 g, 0.0436 mol) which was known (by vpc) to contain 80% **2**, 9% bis(trimethylsilyl)chloromethane (**4**), and 11% tris(trimethylsilyl)chloromethane (**7**), was dissolved in 40 ml of THF and cooled to −100°. To this stirred solution was slowly added 2 ml (0.046 mmol) of 2.3 *M* *n*-butyllithium. After the solution was stirred for 1 hr, 2 ml (excess) of trimethylchlorosilane was added and the solution was allowed to warm to room temperature. Water was added and the organic layer was separated. The aqueous phase was extracted with fresh ether and the combined organic extracts were dried over $MgSO_4$. Distillation at 1-atm pressure and under water aspirator pressure removed the low-boiling solvents and compounds, leaving a solid residue (0.3 g). Spectral and vpc analysis indicated that the solid mass was 77% **7**, 15% tetrakis(trimethylsilyl)methane (**9**), 3% 1,1-di(trimethylsilyl)-1-chloropentane (**6**), 2.5% tris(trimethylsilyl)methane (**5**), 2% **4**, and 0.5% **2**.

Inverse Silation of Methylene Chloride.—The procedure was as before except that the reaction mixture of CH_2Cl_2/BuLi in 200 ml at −100° was rapidly transferred under nitrogen to a tenfold excess of trimethylchlorosilane dissolved in THF cooled to −100°. Work-up as before and analysis by vpc (SE-30,

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(10) D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 618 (1961).

(11) Refer to ref 2 for additional details.

(12) G. Köbrich and R. V. Nagel, *Tetrahedron Lett.*, 4693 (1970).

(13) C. C. Cerato, J. L. Lauer, and H. C. Beachell, *J. Chem. Phys.*, **22**, 1 (1954).

135°) gave a product composition of 74% **2**, 14% **7**, 10% **4**, and 2% **6**.

Competitive Silation of 2 and Trimethylchlorosilane.—To a cooled (−100°), stirred solution of 0.57 g (2.5 mmol) of bis(trimethylsilyl)dichloromethane (**2**) and 0.269 g (2.5 mmol) of trimethylchlorosilane in 40 ml of THF was slowly added 1 ml (2.3 mmol) of 2.3 *M* *n*-butyllithium in hexane. After stirring for 1 hr, the solution was allowed to warm to room temperature. Most of the solvent was then distilled off. The crude sample was then analyzed by vpc (SE-30, programmed from 60° to 135°), showing that most of the starting material, **2**, had reacted and that the ratio of tris(trimethylsilyl)chloromethane (**7**) to trimethylbutylsilane (**3**) was approximately 15:1. In the absence of **2**, the reaction between *n*-butyllithium and trimethylchlorosilane was shown to proceed cleanly at −100° to give **3**.

Vacuum Line Metalation of Methylene Chloride.—Five milliliters (11 mmol) of 2.3 *M* *n*-butyllithium was placed in a 100-ml round-bottom flask and pumped on to remove the hydrocarbon solvent. Methylene chloride (0.46 g, 5.5 mmol) and 20 ml of THF were condensed into the flask, and the solution was warmed to −100 (methanol slush) and allowed to stand for 3 hr in a closed system. Butane is volatile at −100° and was removed by pumping through a −100° bath to liquid nitrogen. After repeated pumping, 0.35 g of butane (1 equiv = 0.32 g) was collected in the liquid nitrogen trap; THF was in the −100° trap. These were both identified by infrared and mass spectral analysis. There was a trace of THF mixed with the butane.

While still cold, 10 ml of trimethylchlorosilane was distilled in the reaction flask. The mixture was allowed to slowly warm to room temperature overnight. Pumping through −78°, −100°, and liquid nitrogen, as before, afforded about 0.15 g (0.5 equiv) of butane. The black reaction mixture was worked up similarly to the other silation reactions. Analysis of the crude product by vpc (SE-30, 100°) showed the same products as previous silations of methylene chloride except that there was a larger amount of monosilated products; *i.e.*, trimethylsilyldichloromethane (**1**) and butyltrimethylsilane (**3**). The changes in product composition may be a result of changes in this particular reaction, namely less solvent, pure THF solvent, no mechanical mixing, and the apparent decomposition. The reaction was repeated to give the same overall results: 1 equiv of butane prior to silane, 0.5 equiv after silation and, relatively, the same product mixture.

The reaction as described was repeated except that 10 ml (23 mmol) of 2.3 *M* *tert*-butyllithium was combined with 0.8 g (10 mmol) of methylene chloride and 25 ml of THF. No silation was performed; however, 0.54 g (0.93 equiv) of isobutane was collected. The isobutane was analyzed by infrared spectroscopy. If the *tert*-butyllithium reaction was done as described except that no methylene chloride was present, isobutane was not observed in the 3-hr reaction time.

Registry No.—**1**, 5926-38-5; **2**, 15951-41-4; **4**, 5926-35-2; **5**, 1068-69-5; **6**, 27484-06-6; **7**, 27484-03-3; **9**, 1066-64-4; methylene chloride, 75-09-2; dichloromethyllithium, 2146-67-0.

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Mass Spectra of Silanes. Multiple Rearrangements and Bonding to Silicon[1]

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The mass spectra of mono-, bis-, tris-, and tetrakis(trimethylsilyl)methanes and chloromethanes have been compared. All of the major ions in the spectra, except possibly *m/e* 43, appear to be siliconium ions. The spectra of the silanes show little or no molecular ion and a base peak corresponding to loss of a methyl group. The α-chlorinated silanes all exhibit a base peak of the *m/e* 73 (Me_3Si), in addition to fragments which contain Cl–Si bonds. A rearrangement process involving a chlorine migration from carbon to silicon and a methyl migration from silicon to carbon is proposed. Three such rearrangements occur in the fragmentation of trichloro(trimethylsilyl)methane (**11**). Several allyl type siliconium ions appear to be present. Mechanisms are proposed for the various fragmentation reactions.

In connection with our studies on the silation of lithiodichloromethane,[2] we have had the opportunity to obtain the mass spectra of a variety of silanes and α-chlorosilanes. Molecular weight determination was our primary interest; however, many of the compounds did not display a molecular ion and, consequently, fragmentation ions had to be relied upon for structural information. Mass spectral studies on methylsilanes,[3] alkylsilanes,[4] bis(trimethylsilyl)methanes,[5] and other di- and trisilanes (alicyclic and cyclic)[5,6] have been reported, but the interpretations in most cases are either brief or ambiguous and, therefore, of little help. This paper reports our observations concerning the mass spectra of some selected silanes. The spectra of tris- and tetrakis(trimethylsilyl)methane and the α-chlorosilanes have not been previously described.

Interpretation of the elemental composition of fragment ions was generally quite simple since the compounds studied were composed of only C, H, Si, and possibly Cl. For example, the *m/e* 73 peak must be C_3H_9Si, since C_6H_{13} is an impossible composition. In some cases, the isotope pattern of chlorine was clearly evident.[7] It should be pointed out, however, that there is a certain element of risk involved with assigning compositions without high-resolution spectra to corroborate the findings. Unfortunately, we did not have a high-resolution instrument at our disposal. All our spectra were obtained with a CEC 21-103 mass spectrometer, at an ionizing voltage of 70 eV, with an inlet temperature of about 180° and a source temperature of 250°.

Compounds.—Most of the compounds studied were

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(2) D. R. Dimmel, C. A. Wilkie, and F. Ramon, *J. Org. Chem.*, **37**, 2662 (1972).

(3) G. P. van der Kelen, O. Volders, H. van Onckelen, and Z. Eeckhaut, *Z. Anorg. Allg. Chem.*, **338**, 106 (1965).

(4) N. Ya. Chernyak, R. A. Khmelńitskii, T. V. Dýakova, and V. M. Vdovin, *Zh. Obshch. Khim.*, **36**, 89 (1966); *J. Gen. Chem. USSR*, **36**, 93 (1966).

(5) (a) G. Fritz, H. Buhl, J. Grobe, F. Aulinger, and W. Reering, *Z. Anorg. Allg. Chem.*, **312**, 201 (1961); (b) F. Aulinger and W. Reering, *Z. Anal. Chem.*, **197**, 24 (1963); (c) F. Aulinger and W. Reering, *Collog. Spectrosc. Int., 9th, 1961*, **3**, 556 (1962); (d) G. Fritz, J. Grobe, and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, **7**, 348 (1965).

(6) N. Ya. Chernyah, R. A. Khmelńitskii, T. V. Dýakova, K. S. Pushchevaya, and V. M. Vdovin, *Zh. Obshch. Khim.*, **37**, 917 (1967); *J. Gen. Chem. USSR*, **37**, 867 (1967).

(7) The normal isotope ratio of ^{35}Cl to ^{37}Cl is 3:1 and, consequently, a monochloro fragment should show a 3:1 pattern, a dichloro fragment a 1:0.67:0.1 pattern, and a trichloro fragment a 1:1:0.33:0.03 pattern.