

PREPARATION OF ETHYNYLSILANES FROM POLYCHLOROETHYLENES*

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SUMMARY

General methods for the preparation of organosilylacetylenes from chloroethylenes are described. Symmetrical bis(trialkylsilyl)acetylenes are obtained in good yield from tetrachloroethylene, lithium and trialkylhalosilanes at -80° in tetrahydrofuran. When lithium and tetrachloroethylene are similarly allowed to react at -80° and then quenched with organosilicon halides, (chloroethynyl)triorganosilanes, $R_3SiC\equiv CCl$, are produced. These can be coupled with lithium and chlorosilanes to give unsymmetrically substituted bis(organosilyl)acetylenes. Trichloroethylene, lithium and trialkylchlorosilanes give fair yields of ethynyltrialkylsilanes, $R_3SiC\equiv CH$. Symmetrical bis(organosilyl)acetylenes can also be prepared from *cis*- or *trans*-1,2-dichloroethylene, alkyllithium compounds and chlorosilanes.

The reaction between tetrachloroethylene, lithium and organochlorosilanes appears to take place through chloroethynyllithium as an intermediate.

INTRODUCTION

Several workers have recently studied systems containing polyhalogen compounds with magnesium or organolithium compounds as synthetic intermediates¹⁻⁴. Viehe⁵⁻¹¹ has prepared chloroacetylides of Li, Na, K, or Ca from dichloroacetylene or dichloroethylenes. Using lithium chloroacetylide produced in the reaction of phenyllithium with dichloroacetylene, he prepared tetrakis(chloroethynyl)silane and chloroethynyltrimethylsilane⁵. These metal haloacetylides also react in liquid ammonia with halides (or organohalides) of Al, Sn, Pb, As, Sb, or Bi to form organometallic chloroacetylides⁸.

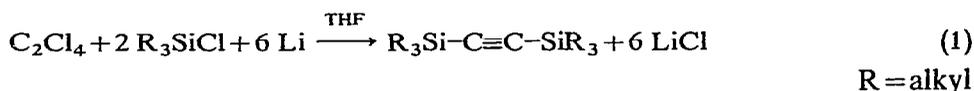
In 1963, Merker and Scott¹² reported the preparation of bis(trimethylsilyl)acetylene in 60% yield by an *in situ* Grignard and concurrent coupling reaction of tetrabromoethylene with trimethylchlorosilane. Because of the relative unavailability of tetrabromoethylene, we attempted this *in situ* Grignard coupling with tetrachloroethylene, but only a very low yield of bis(trimethylsilyl)acetylene was obtained even under forcing conditions. However, it was found that tetrachloroethylene when reacted *in situ* with lithium metal and trimethylchlorosilane yielded bis(trimethylsilyl)-

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acetylene in excellent yield*. The convenience of this procedure prompted us to investigate the scope and limitations of the synthesis of organosilylacetylenes from di- and polychloroethylenes and lithium metal, using both *in situ*¹³ and sequential coupling with chlorosilanes**.

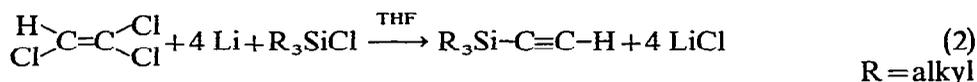
RESULTS AND DISCUSSION

The low temperature procedure of Köbrich for forming organolithium compounds¹⁷ proved essential for the successful utilization of polyhaloethylenes in silylacetylene syntheses. Recently, this method has been used to obtain polychloroorganolithium compounds from several polychlorocarbons^{16,18}. The reaction of lithium with tetrachloroethylene at room temperature leads only to a black insoluble carbonaceous material¹⁹. At -78° in tetrahydrofuran, we find that lithium chloroacetylide is formed. However, when the reaction of tetrachloroethylene and lithium is carried out with trialkylchlorosilane present at -78° , bis(trialkylsilyl)acetylenes are produced according to eqn. (1).



The results of these experiments are summarized in Table 1. The *in situ* reaction of tetrachloroethylene, lithium, and chlorosilanes is limited to the preparation of bis(trialkylsilyl)acetylenes. When the reaction was attempted using phenyldimethylchlorosilane, diphenylmethylchlorosilane, and triphenylchlorosilane, only trace amounts of the desired bis(silyl)acetylenes were obtained due to side reactions. Gilman and Aoki²⁰ have investigated the reaction of triphenylsilyllithium with trichloroethylene, and from the observed products have described the side reactions that are apparently occurring.

The *in situ* reaction of trichloroethylene, lithium, and a trialkylchlorosilane, eqn. (2), to yield an ethynyltrialkylsilane in moderate yields is presented in Table 2. The course of the reaction probably parallels that of tetrachloroethylene (see below)



since dichlorovinylolithium⁶ is more unstable than trichlorovinylolithium. The reaction is also limited to trialkylchlorosilanes, extensive side reactions being observed with arylchlorosilanes.

As mentioned above lithium chloroacetylide can be produced from tetrachloroethylene and lithium at -78° ; precipitation of this lithium compound apparently prevents further reaction with lithium. $\text{LiC}\equiv\text{CCl}$ can also be made from *cis*- or *trans*-1,2-dichloroethylene and methyllithium. Subsequent coupling with chlorosilanes gives good to excellent yields of chloroethynylsilanes, eqn. (3), Tables 1 and 2. The reaction appears to be general with successful results being obtained with tetrachloro-

* This preparation is also mentioned in a recent publication by Ballard and Gilman^{12a}.

** Two recent reviews^{14,15} describe other syntheses and chemical properties of organosilyl and other organometallic acetylenes.

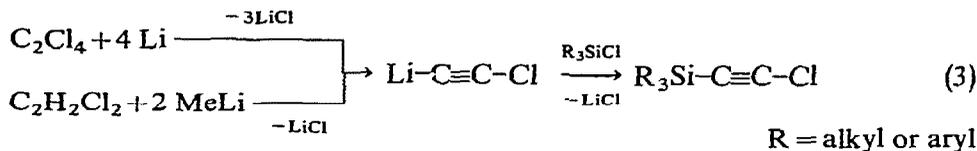
TABLE I

ETHYNYLSILANES FROM C₂Cl₄, R₃SiCl AND LITHIUM METAL IN THF

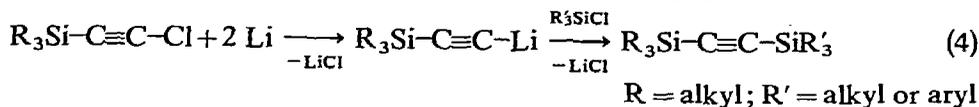
R ₃ SiCl	C ₂ Cl ₄ /R ₃ SiCl/Li	Temp. (°C)	Time (h)	Product(s) (% yield)
Me ₃ SiCl	1/4/8	RT + reflux	14 + 8	(Me ₃ Si) ₂ C ₂ (46)
Me ₃ SiCl	1/3/7	RT	24	(Me ₃ Si) ₂ C ₂ (56)
Me ₃ SiCl ^a	1/3/7	RT	24	(Me ₃ Si) ₂ C ₂ (0)
Me ₃ SiCl	1/3/7	RT	72	(Me ₃ Si) ₂ C ₂ (45)
Me ₃ SiCl	1/3/4	RT	24	(Me ₃ Si) ₂ C ₂ (13)
Me ₃ SiCl ^b	1/6/4	Reflux	4	Me ₃ Si-C≡C-Cl (20)
				(Me ₃ Si) ₂ C ₂ (9)
				Me ₃ Si-C≡C-Cl (5)
				Me ₃ Si-CCl=CCl ₂ (11)
Me ₃ SiCl ^b	1/6/4	Reflux	48	(Me ₃ Si) ₂ C ₂ (24)
				Me ₃ Si-CCl=CCl ₂ (7)
Me ₃ SiCl	1/3/7	-80°	6	(Me ₃ Si) ₂ C ₂ (34)
Me ₃ SiCl	1/3/7	-80°	12	(Me ₃ Si) ₂ C ₂ (52)
Me ₃ SiCl	1/3/7	-80°	24	(Me ₃ Si) ₂ C ₂ (63)
Me ₃ SiCl	1/3/7	-80°	48	(Me ₃ Si) ₂ C ₂ (74)
				Me ₃ Si-C≡C-Cl (6)
Me ₃ SiCl	1/3/2	-80°	48	(Me ₃ Si) ₂ C ₂ (31) ^d
Me ₃ SiCl	1/3/7	-110°	48	(Me ₃ Si) ₂ C ₂ (8)
				Me ₃ Si-C≡C-Cl (17)
				Me ₃ Si-C≡C-Cl (79)
Me ₃ SiCl ^c	1/3/7	-80°	48	Me ₃ Si-C≡C-Cl (60)
Ph ₂ MeSiCl ^c	1/1/5	-80°	48	Ph ₂ MeSi-C≡C-Cl (60)
Et ₃ SiCl	1/2.5/7	RT	24	(Et ₃ Si) ₂ C ₂ (47)
				Et ₃ Si-C≡C-Cl (13)
n-Bu ₃ SiCl	1/2.5/7	-78° + RT	24 + 48	(n-Bu ₃ Si) ₂ C ₂ (30)
EtMe ₂ SiCl	1/2.5/7	-78° + RT	24 + 24	(EtMe ₂ Si) ₂ C ₂ (57)
tert-BuMe ₂ SiCl	1/2.5/7	RT	24	(tert-BuMe ₂ Si) ₂ C ₂ (65)
Me ₃ Si-SiMe ₂ Cl	1/2.5/7	-78°	48	(Me ₃ Si-SiMe ₂) ₂ C ₂ (58)
				Me ₃ Si-SiMe ₂ -C≡C-Cl (8)

^a Diethyl ether as solvent. ^b Magnesium turnings were used. ^c Reaction mixture from C₂Cl₄ and Li added to chlorosilane. ^d 93% based on Li.

silane⁵, trimethylchlorosilane, and diphenylmethylchlorosilane.



With the ready availability of the (chloroethynyl)silanes, a convenient route to unsymmetrical bis(silyl)acetylenes was available by reaction with lithium and a chlorosilane, eqn. (4). The results of the reaction of (chloroethynyl)silanes with lithium



and a chlorosilane are presented in Table 2. Excellent yields were obtained with (chloroethynyl)trialkylsilanes, but with (chloroethynyl)phenyldimethylsilane, side reactions occurred and the desired coupling product was obtained only in low yield. How-

TABLE 2

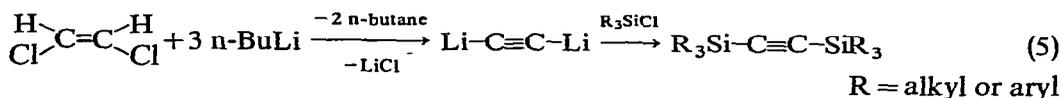
ETHYNYLSILANES FROM CHLOROCARBONS OTHER THAN C₂Cl₄

Chlorocarbon (mole)	Li compd. (mole)	R ₃ SiCl (mole)	Temp. (°C)	Time (h)	Product(s) (% yield)
CCl ₂ =CClH (0.10)	Li (0.60)	Me ₃ SiCl (0.30)	-78°	24	Me ₃ Si-C≡C-H (44) (Me ₃ Si) ₂ C ₂ (15)
CCl ₂ =CClH (0.10)	Li (0.60)	Et ₃ SiCl (0.20)	-78°	48	Et ₃ Si-C≡C-H (44) (Et ₃ Si) ₂ C ₂ (15)
CCl ₂ =CClH (0.10)	Li (0.50)	EtMe ₂ SiCl (0.20)	-78°	36	(EtMe ₂ Si) ₂ C ₂ (28) EtMe ₂ Si-C≡C-H (54)
Me ₃ Si-CCl=CCl ₂ (0.10)	Li (0.50)	Me ₃ SiCl (0.20)	-78°	48	(Me ₃ Si) ₂ C ₂ (70)
Me ₃ Si-CCl=CCl ₂ (0.05) ^a	Li (0.15)	PhMe ₂ SiCl (0.075)	-78°	48	PhMe ₂ Si-C≡C-Cl (43) Me ₃ Si-C≡C-SiMe ₂ Ph (27)
Me ₃ Si-CCl=CCl ₂ (0.05)	Li (0.15)	n-Bu ₃ SiCl (0.05)	-78°	48	n-Bu ₃ Si-C≡C-H (29) Me ₃ Si-C≡C-Si-n-Bu ₃ (33)
Me ₃ Si-C≡C-Cl (0.05)	Li (0.15)	Et ₃ SiCl (0.10)	-78°	48	Me ₃ Si-C≡C-SiEt ₃ (82)
Me ₃ Si-C≡C-Cl (0.09) ^a	Li (0.27)	Ph ₂ MeSiCl (0.136)	-78°	48	Me ₃ Si-C≡C-SiMePh ₂ (86)
Ph ₂ MeSi-C≡C-Cl (0.075) ^a	Li (0.225)	Me ₃ SiCl (0.15)	-78°	48	Me ₃ Si-C≡C-SiMePh ₂ (21)
<i>trans</i> -CHCl=CHCl (0.10) ^b	MeLi (0.22)	Me ₃ SiCl (0.20)	RT	3	Me ₃ Si-C≡C-Cl (96)
<i>cis</i> -CHCl=CHCl (0.10) ^b	n-BuLi (0.30)	Me ₃ SiCl (0.30)	RT	3	(Me ₃ Si) ₂ C ₂ (77) Me ₃ Si-C≡C-Cl (7)
<i>cis</i> -CHCl=CHCl (0.05) ^b	n-BuLi (0.15)	PhMe ₂ SiCl (0.15)	RT	3	(PhMe ₂ Si) ₂ C ₂ (64)

^a Reaction mixture from chlorocarbon and lithium added to chlorosilane. ^b See Experimental.

ever, phenylchlorosilanes undergo coupling with (lithioethynyl)trialkylsilanes. By proper choice of reaction sequence, good over-all yields can be obtained except for unsymmetrical bis(silyl)acetylenes containing a phenyl substituent on *both* silicon atoms. Two papers have appeared recently on the preparation of unsymmetrical acetylenes of the general formula R_nM(C≡CM'R₃)_{4-n}²¹⁻²² where M and M' are different group IV elements. The preparation of these mixed types from lithium chloroacetylide also seems feasible.

The reaction of *cis*-1,2-dichloroethylene with three moles of n-butyllithium results in the formation of dilithium acetylide⁷. The dilithium acetylide thus formed* couples readily with chlorosilanes to give good yields of bis(silyl)acetylenes, eqn. (5). The results of this reaction are given in Table 2. This procedure allows the preparation



of bis(silyl)acetylenes from phenylchlorosilanes, making all symmetrical bis(silyl)acetylenes readily available using polychloroethylenes as starting materials.

Table 3 presents the physical properties, analyses, and spectral characteristics of the new ethynylsilanes prepared in this study. The acetylenic infrared absorption in the unsymmetrical bis(silyl)acetylenes was too weak to be observed, probably due to the almost symmetrical nature of the compounds.

* A commercial sample of "dilithiumacetylide" (Alfa Inorganics, Inc.) in three attempts would not react with trimethylchlorosilane even at reflux in THF.

TABLE 3

PHYSICAL PROPERTIES, ANALYSES AND SPECTRAL CHARACTERISTICS OF NEW ETHYNYLSILANES

Compound	B.p. [$^{\circ}$ C (mm)] or m.p. ($^{\circ}$ C)	n_D^{20}	Analysis (%)		$\nu(\text{C}\equiv\text{C})^a$	$\tau(\text{SiMe})^b$
			Calcd.	Found		
$(\text{EtMe}_2\text{Si})_2\text{C}_2$	100–103 $^{\circ}$ (35)	1.4387	C	60.51	60.41	9.88
			H	11.17	11.27	
			Si	28.30	28.21	
$(\text{tert-BuMe}_2\text{Si})_2\text{C}_2$	103–107 $^{\circ}$ (10) 82–83 $^{\circ}$		C	66.05	65.90	9.90 ^d
			H	11.88	11.69	
			Si	22.07	22.20	
$(\text{Me}_3\text{Si-SiMe}_2)_2\text{C}_2$	106–108 $^{\circ}$ (13)	1.4690	C	50.26	50.55	9.90 (18) 9.83 (12)
			H	10.55	10.56	
			Si	39.19	38.98	
$(\text{PhMe}_2\text{Si})_2\text{C}_2$	125–130 $^{\circ}$ (0.2) 43.0–43.5 $^{\circ}$		C	73.40	73.24	9.59
			H	7.53	7.64	
			Si	19.07	19.02	
$\text{Me}_3\text{Si-C}\equiv\text{C-SiMe}_2\text{Ph}$		1.4994	C	67.16	67.24	9.80 (9) 9.61 (6)
			H	8.67	8.83	
			Si	24.17	23.79	
$\text{Me}_3\text{Si-C}\equiv\text{C-Si-n-Bu}_3$	138–140 $^{\circ}$ (10)	1.4522	C	68.83	68.07	9.84
			H	12.23	11.97	
			Si	18.94	18.61	
$\text{Me}_3\text{Si-C}\equiv\text{C-SiEt}_3$	93–95 $^{\circ}$ (23)	1.4437	C	62.18	62.39	9.84
			H	11.38	11.47	
			Si	26.44	26.54	
$\text{Me}_3\text{Si-C}\equiv\text{C-SiMePh}_2$	117–120 $^{\circ}$ (0.25)	1.5496	C	73.40	73.20	9.78 (9) 9.34 (3)
			H	7.53	7.44	
			Si	19.07	19.21	
$\text{n-Bu}_3\text{Si-C}\equiv\text{C-H}$	122–125 $^{\circ}$ (10)	1.4476	C	74.91	75.12	2030 (s) ^e
			H	12.57	12.46	
			Si	12.52	12.53	
$\text{Ph}_2\text{MeSi-C}\equiv\text{C-Cl}$	110–113 $^{\circ}$ (0.2)	1.5857	C	70.15	70.04	2100 (s)
			H	5.10	5.12	
			Si	10.94	10.99	
			Cl	13.81	13.80	
$\text{Et}_3\text{Si-C}\equiv\text{C-Cl}$		1.4587	C	54.98	55.15	2150 (s)
			H	8.65	8.69	
			Si	16.08	16.33	
			Cl	20.29	20.04	
$\text{Me}_3\text{Si-SiMe}_2\text{-C}\equiv\text{C-Cl}$	75–80 $^{\circ}$ (13)	1.4640	C	44.05	44.25	2140 (s)
			H	7.92	8.04	
			Si	29.44	29.23	
			Cl	18.58	18.29	
$\text{PhMe}_2\text{Si-C}\equiv\text{C-Cl}$		1.5278	C	61.67	61.69	2140 (s)
			H	5.69	5.74	
			Si	14.42	14.51	
			Cl	18.21	18.30	

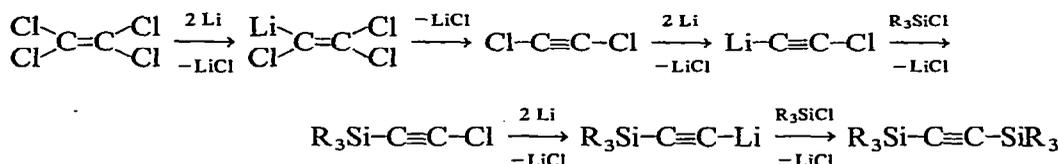
^a Infrared absorptions of neat films (in cm^{-1}). ^b PMR signals of approximately 15% solution in CCl_4 ; TMS at 10 ppm; relative integrated areas in parentheses. ^c $\nu(\text{C-H})$ 3295 (s) cm^{-1} . ^d $\tau(\text{tert-Bu})$ 9.06 ppm. ^e $\tau(\text{CH})$ 7.79 ppm.

Nature of the lithiation-coupling reaction

In the reaction of tetrachloroethylene with lithium and trialkylchlorosilanes, the first step is almost certainly metalation to form trichlorovinyl lithium¹⁶. Following this, several divergent pathways can be imagined of which those designated *I* and *II* below seem most probable.

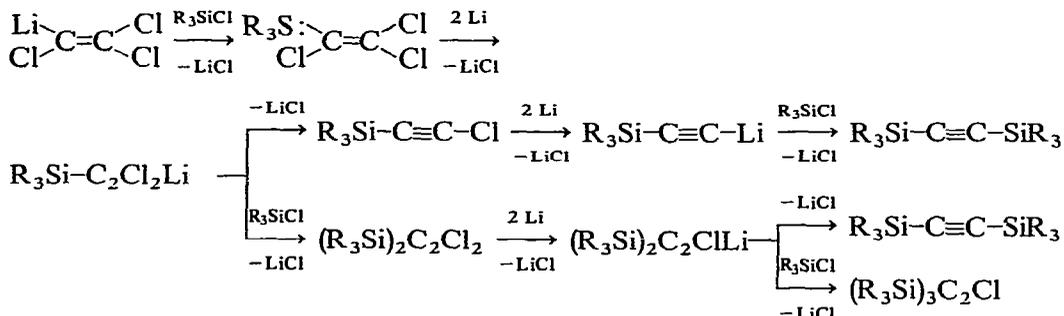
I. The trichlorovinyl lithium undergoes LiCl elimination to yield dichloroacetylene, which is further metalated to lithiochloroacetylene. The latter undergoes successively coupling, metalation and coupling to give the bis(silyl)acetylene product as shown in Scheme 1.

SCHEME 1



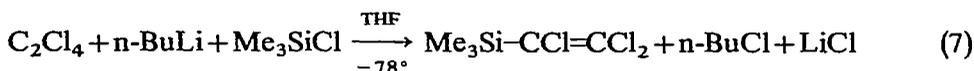
II. The trichlorovinyl lithium couples with the trialkylchlorosilane to give a (trichlorovinyl)trialkylsilane which then reacts with lithium to form a silyldichlorovinyl lithium intermediate. The latter could either eliminate lithium chloride or couple with excess trialkylchlorosilane, the process continuing as shown in Scheme 2.

SCHEME 2



Several variations for each of the major pathways are possible. However, the course of the reaction is entirely different depending on whether or not coupling with trimethylchlorosilane takes place prior to elimination to form an acetylene.

Some experimental observations are at least consistent with Scheme 2. The key intermediate in Scheme 2, (trichlorovinyl)trimethylsilane, can be isolated in related reactions. It is produced in the *in situ* reaction of tetrachloroethylene and trimethylchlorosilane with *magnesium* (eqn. 6, Table 1), and also, in low yield, when tetrachloroethylene and trimethylchlorosilane are treated with *n*-butyllithium at -78° (eqn. 7). Moreover, (trichlorovinyl)trimethylsilane itself undergoes reaction with



lithium and trimethylchlorosilane to produce bis(trimethylsilyl)acetylene (Table 2).

The following observations, however, lead us to believe that the formation of bis(silyl)acetylenes from tetrachloroethylene and lithium probably proceeds by Scheme 1, involving the formation of dichloroacetylene and lithium chloroacetylide as the intermediates:

- (1) No (trichlorovinyl)trialkylsilanes were ever detected in the products of the reaction, under the wide range of conditions employed.
- (2) Results of a competition experiment, summarized in Table 4, show that *tetrachloroethylene reacts more rapidly with lithium than does (trichlorovinyl)trimethylsilane*.

TABLE 4

MOLE RATIO OF STARTING MATERIALS IN COMPETITION REACTION OF LITHIUM WITH TETRACHLOROETHYLENE AND (TRICHLOROVINYL)TRIMETHYLSILANE

Time (h)	Me ₃ Si-C ₂ Cl ₃ /C ₂ Cl ₄ ^a	Time (h)	Me ₃ Si-C ₂ Cl ₃ /C ₂ Cl ₄ ^a
0	1.00	20	1.38
2	1.06	24	1.86
4	1.03	28	2.03
6	1.06	36	1.92
8	1.00	40	1.97
12	1.25	44	1.48
16	1.20		

^a Results are estimated to be good to within about ± 0.05 .

These two observations taken together eliminate (trichlorovinyl)trimethylsilane as a reaction intermediate. Indirect evidence also indicates that dichloroacetylene and chloroethynyllithium are actual intermediates, as shown in Scheme 1. (1) When tetrachloroethylene is allowed to react with lithium at -78° and then quenched with a chlorosilane at the same temperature, good yields of (chloroethynyl)silanes are obtained (Table 1). (This observation also rules out dilithium acetylide as an intermediate in the reaction.) (2) When an excess of tetrachloroethylene is used, a 91% yield of the bis(silyl)acetylene is obtained, based on lithium (Table 1). This is consistent with a highly reactive intermediate such as dichloroacetylene.

If our conclusions are correct and the reaction proceeds by Scheme 1, it follows that the trichlorovinyl lithium intermediate from lithium metal is more reactive than trichlorovinyl lithium from tetrachloroethylene and lithium alkyls, since the latter lithium compound can be trapped to some extent by trimethylchlorosilane. Two possible explanations for the difference in reactivity are: (1) elimination of LiCl from the trichlorovinyl lithium from lithium metal may be catalyzed by the metal surface or (2) trichlorovinyl lithium from n-butyllithium may be stabilized by complex formation with residual n-butyllithium.

EXPERIMENTAL

All reactions with lithium were carried out in an atmosphere of prepurified argon. Reactions with alkyl lithium compounds were carried out in an atmosphere of

prepurified nitrogen. Except for lithium which was cleaned and cut in an argon stream, all reactants were added by syringe directly into apparatus which had been flamed and cooled under a stream of either argon or nitrogen. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. IR and NMR spectra were obtained using Perkin-Elmer Model 457 and Varian A-60A spectrometers, respectively. Tetramethylsilane was used as an internal standard for all NMR spectra. Boiling points and melting points are uncorrected with melting points being obtained on a Thomas-Hoover melting point apparatus. Gas-chromatographic separations were made on a Varian/Aerograph Model 705 using columns packed with either SE-30 (20%) or Apiezon L (25%) on 40-60 Chromosorb W. Pure samples of all ethynylsilanes were obtained by preparative gas chromatography for characterization. IR and NMR spectra of all ethynylsilanes which were known compounds were consistent with proposed structures.

The polychloroethylenes are commercially available and were used as obtained. Ethyldimethylchlorosilane and tert-butyldimethylchlorosilane were prepared from dimethyldichlorosilane by standard procedures. All the other chlorosilanes are commercially available products. The alkyllithium solutions were purchased from Foote Mineral Co. and concentrations were checked by titration before using. Tetrahydrofuran was dried with lithium aluminum hydride and distilled under nitrogen immediately before each use.

I. Preparation of ethynylsilanes from tetrachloroethylene

A. The in situ reaction of tetrachloroethylene with lithium and a chlorosilane

1. *Reaction with trimethylchlorosilane.* A series of experiments were carried out after the preliminary experiment to determine the course of the reaction and optimum conditions for this reaction as presented in Table 1. In an optimal run, 200 ml of THF and trimethylchlorosilane (32.60 g, 0.30 mole) were added to finely-cut lithium wire (4.86 g, 0.70 g-atom) in a 500-ml flask. The flask was cooled in a dry ice/acetone bath to -78° . Tetrachloroethylene (16.58 g, 0.10 mole) in 20 ml of THF was added and the reaction mixture was stirred rapidly for 48 h at -78° . The mixture was filtered to remove unreacted lithium and salts. The filtrate was distilled through a short Vigreux column. The fraction that distilled from $80-145^{\circ}$ was collected, leaving negligible residue. Distillation of the $80-145^{\circ}$ fraction on a spinning-band column gave bis(trimethylsilyl)acetylene (12.55 g, 74%), b.p. $134-136^{\circ}$, n_D^{20} 1.4255 (lit.²³ n_D^{25} 1.4259); and (chloroethynyl)trimethylsilane (0.71 g, 6%), b.p. $100-101^{\circ}$, n_D^{23} 1.4323 (lit.⁷ n_D^{25} 1.4312).

2. *Reaction with triethylchlorosilane.* Triethylchlorosilane (37.67 g, 0.25 mole) was added to finely-cut lithium wire (4.86 g, 0.70 g-atom) in THF (100 ml). Tetrachloroethylene (16.58 g, 0.10 mole) was added slowly over 1 h. The reaction mixture was stirred at room temperature for 24 h and filtered to remove unreacted lithium. The golden yellow filtrate was hydrolyzed with a saturated sodium bicarbonate solution and extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and distilled to give bis(triethylsilyl)acetylene (11.89 g, 47%), b.p. $121-123^{\circ}/10$ mm, n_D^{20} 1.4575 (lit.²⁴ n_D^{20} 1.4268) (Found: C, 66.18; H, 11.69; Si, 22.14. $C_{14}H_{30}Si_2$ calcd.: C, 66.05; H, 11.88; Si, 22.07%); and (chloroethynyl)triethylsilane (Table 3).

3. *Reaction with tri-n-butylchlorosilane.* Tri-n-butylchlorosilane (23.49 g,

0.10 mole) was added to finely-cut lithium wire (1.94 g, 0.28 g-atom) in THF (100 ml). The reaction flask was cooled in a dry ice/acetone bath to -78° . Tetrachloroethylene (6.63 g, 0.04 mole) was added and the reaction mixture was stirred rapidly for 24 h at -78° , allowed to warm to room temperature, and stirred at room temperature for 48 h. The mixture was filtered to remove excess lithium and salts and distilled to give bis(tri-*n*-butylsilyl)acetylene (4.96 g, 30%), b.p. 120–123 $^{\circ}$ /0.1 mm, n_D^{20} 1.4628 (lit.²⁵ n_D^{20} 1.4597). (Found: C, 73.81; H, 12.77; Si, 13.18. $C_{26}H_{54}Si_2$ calcd.: C, 73.84; H, 12.87; Si, 13.29%.)

4. *Reaction with ethyldimethylchlorosilane.* Ethyldimethylchlorosilane (15.34 g, 0.125 mole) was added to finely-cut lithium wire (2.43 g, 0.35 g-atom) in THF (50 ml). The flask was cooled in a dry ice/acetone bath to -78° and tetrachloroethylene (8.29 g, 0.05 mol) was added. The reaction was stirred rapidly for 24 h at -78° , allowed to warm to room temperature, and stirred at room temperature for 24 h. The mixture was filtered and distilled to give bis(ethyldimethylsilyl)acetylene (4.64 g, 57%) (Table 3).

5. *Reaction with tert-butyldimethylchlorosilane.* Tetrachloroethylene (8.29 g, 0.05 mole) was added dropwise to a suspension of finely-cut lithium wire (2.43 g, 0.35 mole) and tert-butyldimethylchlorosilane in THF (50 ml) at room temperature. The reaction mixture was stirred at room temperature for 24 h, filtered to remove excess lithium, hydrolyzed with a saturated sodium bicarbonate solution, and extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and distilled to give bis(tert-butyldimethylsilyl)acetylene (8.22 g, 65%) (Table 3).

6. *Reaction with pentamethylchlorodisilane.* Using the procedure described for optimal yields with trimethylchlorosilane, chloroethynylpentamethyldisilane (1.52 g, 8%) (Table 3) and bis(pentamethyldisilyl)acetylene (16.52 g, 58%) (Table 3) were prepared from pentamethylchlorodisilane (41.7 g, 0.25 mole), finely-cut lithium wire (4.86 g, 0.70 g-atom), and tetrachloroethylene (16.58 g, 0.10 mole) in THF (200 ml).

B. Lithium chloroacetylide from tetrachloroethylene and lithium at low temperatures

1. *Reaction with trimethylchlorosilane.* Tetrachloroethylene (16.58 g, 0.10 mole) was added to a suspension of finely-cut lithium wire (4.86 g, 0.70 mole) in THF (200 ml) at -78° . The reaction mixture was stirred at -78° for 48 h and removed with a syringe equipped with a No. 13 needle, allowing effective removal of all salts present and leaving unreacted lithium behind. The cold reaction mixture was then added rapidly to a solution of trimethylchlorosilane (32.60 g, 0.30 mole) in THF (100 ml) cooled in a dry ice/acetone bath. After addition was completed the reaction mixture was stirred for 2 h at -78° , allowed to warm to room temperature, filtered to remove salts, and distilled to give (chloroethynyl)trimethylsilane (10.51 g, 79%), b.p. 100–101 $^{\circ}$, n_D^{23} 1.4321 (lit.⁷ n_D^{25} 1.4321).

2. *Reaction with diphenylmethylchlorosilane.* Using the procedure described above, (chloroethynyl)diphenylmethylsilane (30.36 g, 60%) (Table 3) was prepared from diphenylmethylchlorosilane (46.56 g, 0.20 mole), lithium wire (6.94 g, 1.0 g-atom) and tetrachloroethylene (33.17 g, 0.20 mole) in THF (300 ml).

C. The *in situ* Grignard reaction of tetrachloroethylene and trimethylchlorosilane

Two attempts were made to use an *in situ* Grignard procedure, but even under the forcing conditions described here only poor yields were obtained. A suspension of

magnesium turnings (9.73 g, 0.40 g-atom) in THF (150 ml) and trimethylchlorosilane (65.20 g, 0.60 mole) was brought to reflux and maintained at reflux by the application of external heat. To the refluxing reaction mixture a solution of tetrachloroethylene (16.58 g, 0.10 mole) in THF (50 ml) was added slowly over 3 h. The reaction mixture was maintained at reflux for an additional 48 h, poured over crushed ice, and the unreacted magnesium was filtered off. The hydrolyzed mixture was extracted with ether and the organic phase was washed several times with water and dried over anhydrous magnesium sulfate. Distillation on the spinning-band column yielded bis(trimethylsilyl)acetylene (4.21 g, 24%) and (trichlorovinyl)trimethylsilane (1.44 g, 7%), b.p. 81–82°/33 mm, n_D^{23} 1.4874 (lit.^{26a} n_D^{20} 1.4890 and lit.^{26b} n_D^{25} 1.4869).

II. Preparation of ethynylsilanes from trichloroethylene

A. Reaction with trimethylchlorosilane. A suspension of lithium wire (4.16 g, 0.60 g-atom) in THF (200 ml) and trimethylchlorosilane (32.60 g, 0.30 mole) was cooled in a dry ice/acetone bath to -78° . Trichloroethylene (13.14 g, 0.10 mole) was added and the reaction was stirred at -78° for 24 h, filtered to remove excess lithium, and hydrolyzed. The organic layer was washed twice with water, dried over anhydrous magnesium sulfate, and distilled on the spinning-band column to give ethynyltrimethylsilane (4.31 g, 44%), b.p. 51–53°, n_D^{20} 1.3865 (lit.²⁷ n_D^{25} 1.3870) and bis(trimethylsilyl)acetylene (2.55 g, 15%).

The same products in approximately the same yields were produced when the reaction mixture was worked up without hydrolysis. Therefore the acetylenic proton is not produced by hydrolysis of a $\text{Me}_3\text{SiC}\equiv\text{CLi}$ intermediate.

B. Reaction with triethylchlorosilane. A suspension of lithium wire (4.16 g, 0.60 g-atom) in THF (200 ml) and triethylchlorosilane (30.14 g, 0.20 mol) was cooled in a dry ice/acetone bath to -78° . Trichloroethylene (13.14 g, 0.10 mole) was added and the reaction mixture was stirred at -78° for 48 h. The work-up proceeded as above and distillation resulted in ethynyltriethylsilane (6.15 g, 44%), b.p. 136–137°, n_D^{20} 1.4310 (lit.²⁸ n_D^{20} 1.4302) and bis(triethylsilyl)acetylene (3.75 g, 15%).

C. Reaction with ethyldimethylchlorosilane. Trichloroethylene (13.14 g, 0.10 mole) was added to lithium wire (3.97 g, 0.50 g-atom), THF (200 ml), and ethyldimethylchlorosilane (24.54 g, 0.20 mole) cooled in a dry ice/acetone bath to -78° . The reaction mixture was stirred for 36 h at -78° , worked-up as above, and distilled on a spinning-band column to give ethynylethyldimethylsilane (6.10 g, 54%), b.p. 82–83°, n_D^{20} 1.4080 (lit.²⁹ n_D^{20} 1.4082); and bis(ethyldimethylsilyl)acetylene (4.67 g, 28%) (Table 3).

III. Preparation and reactions of (trichlorovinyl)trimethylsilane

A. Preparation of (trichlorovinyl)trimethylsilane. THF (200 ml), trimethylchlorosilane (21.74 g, 0.20 mole), and tetrachloroethylene (16.58 g, 0.10 mole) were added to a 500-ml flask and cooled in a carbon disulfide/liquid nitrogen bath to -110° . During a 90-min period, n-butyllithium (62.5 ml of a 1.6 M soln. in hexane, 0.10 mole) was added slowly. The reaction mixture was stirred at -110° for an additional 3 h, allowed to warm to room temperature, hydrolyzed, and extracted with ether. The ether layer was washed four times with water, dried over anhydrous magnesium sulfate, and distilled to give (trichlorovinyl)trimethylsilane (13.68 g, 68%), b.p. 84–85°, n_D^{23} 1.4874 (lit.²⁶ n_D^{20} 1.4890). In two repeat reactions this product was isolated in yields of 90% and

37%. When the reaction was carried out at -78° a 33% yield of the product was obtained.

B. In situ reaction with lithium and trimethylchlorosilane. A suspension of finely-cut lithium wire (3.47 g, 0.50 g-atom) in THF (200 ml) and trimethylchlorosilane (21.74 g, 0.20 mole) was cooled in a dry ice/acetone bath to -78° . (Trichlorovinyl)trimethylsilane (20.40 g, 0.10 mole) was added and the reaction mixture was stirred at -78° for 48 h, filtered, hydrolyzed with a saturated solution of sodium bicarbonate, and extracted with ether. The organic layer was washed three times with water and dried over anhydrous magnesium sulfate. Distillation resulted in bis(trimethylsilyl)acetylene (11.53 g, 70%, 80% based on unrecovered starting material) and recovery of 3.10 g of (trichlorovinyl)trimethylsilane.

C. In situ reaction with lithium and tri-n-butylchlorosilane. Using the procedure described above, ethynyltri-n-butylsilane (3.24 g, 29%) (Table 3) and (trimethylsilyl)-(tri-n-butylsilyl)acetylene (4.86 g, 33%) (Table 3) were obtained from tri-n-butylchlorosilane (11.74 g, 0.05 mole), lithium wire (1.04 g, 0.15 g-atom) and (trichlorovinyl)trimethylsilane (10.18 g, 0.05 mole) in THF (100 ml).

D. Reaction with lithium followed by quenching with phenyldimethylchlorosilane. A suspension of finely-cut lithium wire (1.04 g, 0.15 g-atom) in THF (100 ml) was cooled in a dry ice/acetone bath to -78° and (trichlorovinyl)trimethylsilane (10.18 g, 0.05 mole) was added. The reaction mixture was stirred at -78° for 48 h, removed by a syringe equipped with a No. 13 needle leaving excess lithium behind, and injected into a solution of phenyldimethylchlorosilane (12.80 g, 0.075 mole) in THF (50 ml) at -78° . The mixture was stirred for 2 h at -78° and then warmed to room temperature. Work-up proceeded as above and distillation yielded (chloroethynyl)phenyldimethylsilane (4.11 g, 43%) (Table 3) and (phenyldimethylsilyl)(trimethylsilyl)acetylene (3.12 g, 27%) (Table 3).

IV. Preparation of bis(silyl)acetylenes from chloroethynylsilanes

A. In situ reaction of (chloroethynyl)trimethylsilane with lithium and triethylchlorosilane. A suspension of finely-cut lithium wire (1.04 g, 0.15 g-atom) in THF (100 ml) and triethylchlorosilane (15.07 g, 0.10 mole) was cooled in a dry ice/acetone bath to -78° and (chloroethynyl)trimethylsilane (6.63 g, 0.05 mole) was added. The reaction mixture was stirred at -78° for 48 h, worked-up as in IIIA, and distilled to give (triethylsilyl)(trimethylsilyl)acetylene (8.70 g, 82%) (Table 3).

B. Reaction of (chloroethynyl)trimethylsilane with lithium followed by quenching with diphenylmethylchlorosilane. To a suspension of finely-cut lithium wire (1.87 g, 0.27 g-atom) in THF (200 ml) cooled in a dry ice/acetone bath to -78° was added (chloroethynyl)trimethylsilane (12.0 g, 0.0904 mole). The reaction mixture was stirred at -78° for 48 h, removed by syringe, and injected into a solution of diphenylmethylchlorosilane (31.66 g, 0.136 mole) in THF (50 ml) at -78° , again stirred for 2 h at -78° , and warmed to room temperature. Work-up proceeded as above and distillation resulted in (trimethylsilyl)(diphenylmethylsilyl)acetylene (22.83 g, 86%) (Table 3).

C. Reaction of (chloroethynyl)diphenylmethylsilane with lithium followed by quenching with trimethylchlorosilane. Using the procedure described above, (trimethylsilyl)(diphenylmethylsilyl)acetylene (4.66 g, 21%) (Table 3) was prepared from (chloroethynyl)diphenylmethylsilane (19.26 g, 0.075 mole), lithium wire (1.56 g, 0.225 g-atom), and trimethylchlorosilane (16.30 g, 0.15 mole) in THF (250 ml).

V. Preparation of ethynylsilanes from 1,2-dichloroethylenes and alkyllithiums

A. Preparation of (chloroethynyl)trimethylsilane. Methylolithium (142 ml of a 1.55 M soln. in ether, 0.22 mole) was diluted with 100 ml of ether and cooled in an ice bath. A solution of *trans*-dichloroethylene (9.70 g, 0.10 mole) in ether (25 ml) was added slowly over 1 h. The ice bath was removed and the reaction mixture was stirred for 2 h at room temperature and then cooled in a dry ice/acetone bath to -78° . A solution of trimethylchlorosilane (21.74 g, 0.20 mole) in ether (25 ml) and THF (25 ml) was added slowly over 45 min. The reaction mixture was allowed to warm to room temperature, stirred at room temperature for 9 h, and filtered. The filtrate was distilled on a spinning-band column to yield (chloroethynyl)trimethylsilane (12.70 g, 96%).

B. Preparation of dilithium acetylide and derivatization with trimethylchlorosilane.

Using the procedure described above, *cis*-dichloroethylene (9.70 g, 0.10 mole) diluted with ether (75 ml) was allowed to react with *n*-butyllithium (193.5 ml of a 1.55 M soln. in hexane, 0.30 mole) diluted with ether (300 ml) followed by reaction with a solution of trimethylchlorosilane (32.60 g, 0.30 mole) in THF (100 ml) to give bis(trimethylsilyl)acetylene (13.08 g, 77%) and (chloroethynyl)trimethylsilane (1.00 g, 7%).

C. Preparation of dilithium acetylide and derivatization with phenyldimethylchlorosilane. Using the procedure described above, bis(phenyldimethylsilyl)acetylene (9.36 g, 64%) (Table 3) was prepared from *cis*-dichloroethylene (4.85 g, 0.05 mole) diluted with ether (50 ml), *n*-butyllithium (97 ml of a 1.55 M soln. in hexane, 0.15 mole) diluted with ether (150 ml), and phenyldimethylchlorosilane (25.60 g, 0.15 mole) in THF (100 ml).

VI. Competition reaction between tetrachloroethylene and (trichlorovinyl)trimethylsilane.

THF (200 ml), trimethylchlorosilane (32.60 g, 0.30 mole), tetrachloroethylene (8.29 g, 0.05 mole), and (trichlorovinyl)trimethylsilane (10.18 g, 0.05 mole) were added to a 500-ml flask and cooled in a dry ice/acetone bath to -78° . Finely-cut lithium wire (4.86 g, 0.70 g-atom) was added and the reaction mixture was stirred at -78° for 48 h. Samples (0.20 ml) were withdrawn at the times indicated in Table 4 and analyzed by VPC using thermal conductivity correction factors and standard procedures. The results are presented in Table 4.

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