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THE FORMATION AND ALKYLATION OF (TRIMETHYLSILYL)-, (PHENYLDIMETHYLSILYL)-, AND (DIPHENYLMETHYLSILYL)-DICHLOROMETHYLLITHIUM. PREPARATION OF α,α -DICHLOROALKYLSILANES AND ((Z)-1-CHLORO-1-ALKENYL)-SILANES

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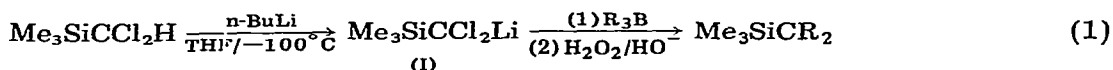
(Received August 1st, 1978)

Summary

(Dichloromethyl)trimethylsilane, $\text{Me}_3\text{SiCCl}_2\text{H}$, (dichloromethyl)phenyldimethylsilane, $\text{PhMe}_2\text{SiCCl}_2\text{H}$, and (dichloromethyl)diphenylmethylsilane, $\text{Ph}_2\text{MeSiCCl}_2\text{H}$, readily react with lithium diisopropylamide in THF at -78°C to form the corresponding α -silyldichloromethyl lithium reagents. The relative stability of the lithium reagents at -78°C is $\text{Ph}_2\text{MeSiCCl}_2\text{Li} \sim \text{PhMe}_2\text{SiCCl}_2\text{Li} \gg \text{Me}_3\text{SiCCl}_2\text{Li}$. All three of the lithium reagents are readily silylated with chlorosilanes or alkylated with primary bromides and iodides. The α,α -dichloroalkylsilanes formed from the alkylation are stereoselectively dehydrochlorinated in refluxing dimethylformamide to ((Z)-1-chloro-alkenyl)silanes.

Introduction

In our research on the preparation of carbo-functional organosilanes via organoboranes [1], we prepared trimethylsilyldichloromethyl lithium (I) according to Seyferth [2] and treated it with trialkylboranes at temperatures between -100° and -78°C (eq. 1). Reagent I has been shown to be unstable above -78°C and is best used at -100°C [3].



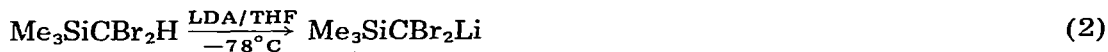
The low temperatures necessary resulted in slow or poor reactions of reagent I with organoboranes and this prompted us to investigate (phenyldimethylsilyl)-

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dichloromethylithium (II) and (diphenylmethylsilyl)dichloromethylithium (III) as possible alternatives to I.



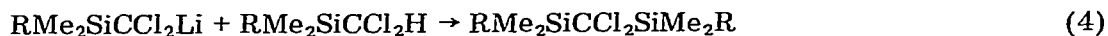
Villieras et al. [4] have formed (trimethylsilyl)dibromomethylithium (IV) by treatment of (dibromomethyl)trimethylsilane with lithium diisopropylamine (LDA) (eq. 2). We decided to employ this approach to reagents I, II, and III and to investigate their relative stabilities (eq. 3).



Results and discussion

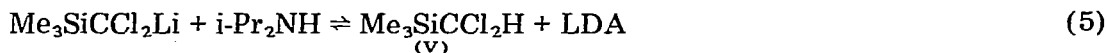
Thermal stability of Me₃SiCCl₂Li, PhMe₂SiCCl₂Li and Ph₂MeSiCCl₂Li

In our studies it was found that a principal mode of decomposition of these reagents is the self-coupling reaction illustrated in eq. 4. This type of coupling has also been noted in other work [2,3]. For example when I was formed at



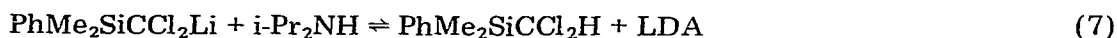
R = Ph, Me

-78°C and quenched within two minutes with triethylchlorosilane at that temperature, a 93% yield (by NMR) of (trimethylsilyl)(triethylsilyl)dichloromethane was obtained indicating a high yield of I. When the reagent was not quenched within two minutes, the solution turned dark brown and eventually black and the yield decreased. This is consistent with the observations of Seyferth and coworkers [2,3]. When the solution of I was allowed to warm slowly to room temperature and was quenched with water (or triethylchlorosilane), the only isolated product was bis(trimethylsilyl)dichloromethane. This is best explained by an equilibrium involving the lithium reagent (I) and diisopropylamine to form (dichloromethyl)trimethylsilane (V) and LDA. Lithium reagent I then reacts with V to give the observed product (eq. 5 and 6). In order to rule out the formation of trimethylsilylchlorocarbene as an intermedi-



ate in the reaction, a 1 M solution of I in THF was formed in the presence of a 5-fold excess of cyclohexene and allowed to warm to room temperature. Again the only isolated product was the self-coupled product, bis(trimethylsilyl)dichloromethane, with no evidence for 7-chloro-7-(trimethylsilyl)norcarane. This is consistent with the results of Olofson et al. [5] who have observed trimethylsilylchlorocarbene in hexane solvent, but not in THF.

It was felt that the use of the phenyldimethylsilyl or diphenylmethylsilyl group rather than the trimethylsilyl group might add to the stability of the lithium reagent and at the same time decrease the rate of displacement of CHCl_2^- . Reagent II was readily formed upon treatment of (dichloromethyl)phenyldimethylsilane with LDA in THF for 1 h at -78°C . II was formed considerably more slowly than I, as evidenced by the presence of 40% of the starting material after 10 min at -78°C (trimethylchlorosilane quench). When the solution of II was quenched with trimethylchlorosilane after 1 h a 95% yield (by NMR) of (phenyldimethyl)(trimethylsilyl)dichloromethane was observed. Though formed more slowly than I, reagent II is much more stable, surviving several hours at -78°C without noticeable decomposition or loss of activity. The reagent II also is much more stable at temperature above -78°C . However, it retained only 70% of its activity at -50°C . Reagent II also undergoes the self-coupling reaction as its principal mode of decomposition (eq. 7 and 8). Thus, when II was formed at -78°C and allowed to warm to room temperature, a



40% yield of bis(phenyldimethylsilyl)dichloromethane was isolated. Strong evidence for the equilibrium illustrated in eq. 7 comes from the fact that when a 2-fold excess of LDA was employed in the formation of the lithium reagent II and the solution quenched with trimethylchlorosilane at -30°C , a quantitative yield (by NMR) of (phenyldimethylsilyl)(trimethylsilyl)dichloromethane was observed. If this solution was allowed to warm to 25°C before adding the trimethylchlorosilane, only the self-coupling product (eq. 8) was observed.

Reagent III was formed quantitatively from (dichloromethyl)diphenylmethylsilane and LDA at -78°C in 1 h and is very stable at that temperature. Quenching of III with trimethylchlorosilane at -78°C gave (diphenylmethylsilyl)(trimethylsilyl)dichloromethane in 95% yield (by NMR). A similar quench at -60°C gave a 72% yield of $\text{Ph}_2\text{MeSiCCl}_2\text{SiMe}_3$ and 31% yield of (dichloromethyl)diphenylmethylsilane. When the quench was carried out at 25°C , a 40% yield of the starting silane was obtained with none of the self-coupling or the desired product observed. Thus, the addition of one or two phenyl groups to the silyl function increases considerably the stability of the silyldichloromethyl-lithium reagent and the presence of two phenyl groups eliminates the self-coupling reaction.

Alkylations of $\text{Me}_3\text{SiCCl}_2\text{Li}$, $\text{PhMe}_2\text{SiCCl}_2\text{Li}$ and $\text{Ph}_2\text{MeSiCCl}_2\text{Li}$

All of these reagents (I, II, and III) generated according to eq. 3, could be silylated with chlorosilanes (eq. 9) or alkylated with primary bromides or iodides (eq. 10) at -78°C in good to excellent yield. The lithium reagent (I) failed to react with benzyl chloride, the self-condensation reaction being faster than the alkylation. Reagent I, however, reacted quite nicely with benzyl bromide to give the desired alkylated product in 48% yield. Attempts to alkylate I, II or III with secondary halides such as 2-bromopropane or bromocyclohexane, even in the presence of potassium iodide and HMPA, or with added TMEDA, resulted in no alkylation and observed instead were the formation of self-

condensation products in the case of reagents I and II and the recovery of starting material in the case of reagent III. A rigorous check by GLC for cyclohexene in the reactions of II or III with bromocyclohexane showed that elimination is not a side-reaction, at least in this secondary system. Table 1 gives the results of the alkylations and silylations of I, II and III. These reactions present excellent entries into the bis-silyldichloromethane derivatives and α,α -dichloroalkylsilanes, both of which are capable of further elaboration.



(VI)

The preparation of ((Z)-1-chloro-1-alkenyl)silanes

In view of the continued interest in the chemistry of α -halovinylsilanes [6,7] we decided to investigate the dehydrochlorination of the α,α -dichloroalkylsilanes (VI). A wide variety of bases including LDA, n-BuLi, t-BuOK, KOH and pyridine gave mixed results, leading to partial elimination, attack on silicon

(continued on p. 19)

TABLE 1

SILYLATION AND ALKYLATION OF α -SILYLDICHLOROMETHYLLITHIUM REAGENTS

R ₃ SiCCl ₂ Li ^a	RX (mmol)	Product	Yield	
			NMR ^b	Isolated
I	Me ₃ SiCl (11)	(Me ₃ Si) ₂ CCl ₂	70	69
I	Et ₃ SiCl (11)	Me ₃ SiCCl ₂ SiEt ₃	93	85
I	CH ₃ I (50)	Me ₃ SiCCl ₂ CH ₃	93	80
I	CH ₃ CH ₂ Br (11)	Me ₃ SiCCl ₂ CH ₂ CH ₃	98	84
I	CH ₃ CH ₂ CH ₂ CH ₂ Br (11)	Me ₃ SiCCl ₂ CH ₂ CH ₂ CH ₂ CH ₃	93	75
I	PhCH ₂ Br (11)	Me ₂ SiCCl ₂ CH ₂ Ph	—	48
I	PhCH ₂ Cl (11)	^c	—	— ^c
II	Me ₃ SiCl (35)	PhMe ₂ SiCCl ₂ SiMe ₃	—	78
II	PhMe ₂ SiCl (20)	(PhMe ₂ Si) ₂ CCl ₂	—	77
II	CH ₃ I (20)	PhMe ₂ SiCCl ₂ CH ₃	—	81
II	CH ₃ CH ₂ Br (11)	PhMe ₂ SiCCl ₂ CH ₂ CH ₃	—	64
II	CH ₃ CH ₂ CH ₂ CH ₂ Br (20)	PhMe ₂ SiCCl ₂ CH ₂ CH ₂ CH ₂ CH ₃	—	78
II	CH ₂ =CHCH ₂ Br (20)	PhMe ₂ SiCCl ₂ CH ₂ CH=CH ₂	—	78
II	PhCH ₂ Cl (20)	PhMe ₂ SiCCl ₂ CH ₂ Ph	—	69
II	C-C ₆ H ₁₁ Br (20)	^d	—	— ^d
III	Me ₃ SiCl (20)	Ph ₂ MeSiCCl ₂ SiMe ₃	95	87
III	CH ₃ I (20)	Ph ₂ MeSiCCl ₂ CH ₃	92	85
III	CH ₃ CH ₂ Br (20)	Ph ₂ MeSiCCl ₂ CH ₂ CH ₃	93	90
III	CH ₃ CH ₂ CH ₂ CH ₂ Br (20)	Ph ₂ MeSiCCl ₂ CH ₂ CH ₂ CH ₂ CH ₃	—	67
III	PhCH ₂ Cl (20)	Ph ₂ MeSiCCl ₂ CH ₂ Ph	63	58
III	CH ₃ CH ₂ CH ₂ Cl (20)	none ^e		
III	C-C ₆ H ₁₁ Br (20)	none ^e		
III	(CH ₃) ₂ CHBr	none ^e		

^a 10 mmol of lithium reagent. ^b Determined by adding CH₂Br₂ or CH₂Cl₂ as an internal standard to crude reaction residue. ^c Only (Me₃Si)₂CCl₂ isolated. ^d Only (PhMe₂Si)₂CCl₂ isolated. ^e Only Ph₂MeSiCHCl₂ isolated.

TABLE 2
CHARACTERIZATION OF α,α -DICHLOROSILANES

Product	B.p. (°C/mmHg)	$n_D(T)$	NMR ^a (δ , ppm)
Me ₃ SiCCl ₂ SiMe ₃	90—95/80	1.4646(22) ^b	0.23 (s)
Me ₃ SiCCl ₂ SiEt ₃	101—107/10	1.4848(22)	0.24 (s, 9H); 1.38—0.44 (m, 15H)
Me ₃ SiCCl ₂ CH ₃	m.p. 115.5—117°C ^c	—	0.23 (s, 9H); 2.03 (s, 3H)
Me ₃ SiCCl ₂ CH ₂ CH ₃	68—73/73	1.4553(22)	0.25 (s, 9H); 1.22 (t, 3H, <i>J</i> 7 Hz); 2.08 (q, 2H, <i>J</i> 7 Hz)
Me ₃ SiCCl ₂ CH ₂ CH ₂ CH ₂ CH ₃	97—99/20	1.4585(21)	0.24 (s, 9H); 2.28—0.73 (m, 9H)
Me ₃ SiCCl ₂ CH ₂ Ph	m.p. 55—56°C	—	0.36 (s, 9H); 3.48 (s, 2H); 7.30 (s, 5H)
PhMe ₂ SiCCl ₂ SiMe ₃	99—101/0.1	1.5266(24)	—0.01 (s, 9H); 0.54 (s, 6H); 7.63—7.97 (m, 5H)
PhMe ₂ SiCCl ₂ SiMe ₂ Ph	165—180/0.15 m.p. 58.5—59°C	—	0.23 (s, 12H); 7.65—7.03 (m, 10H)
PhMe ₂ SiCCl ₂ CH ₃	81—85/0.1	1.5345(22)	0.52 (s, 6H); 1.93 (s, 3H); 7.70—7.05 (m, 5H)
PhMe ₂ SiCCl ₂ CH ₂ CH ₃	100—110/0.4	1.5330(21)	0.56 (s, 6H); 1.12 (t, 3H, <i>J</i> 7.5 Hz); 2.0 (q, 2H, <i>J</i> 7.5 Hz); 7.60—7.00 (m, 5H)
PhMe ₂ SiCCl ₂ CH ₂ CH ₂ CH ₂ CH ₂	125—130/1.25	1.5239(22)	0.54 (s, 6H); 2.15—0.69 (m, 9H); 7.71—7.10 (m, 5H)
PhMe ₂ SiCCl ₂ CH ₂ Ph	150—160/0.10 m.p. 81—82	1.5715(25)	0.49 (s, 6H); 3.22 (s, 2H); 7.73—6.92 (m, 10H)
PhMe ₂ SiCCl ₂ CH ₂ CH=CH ₂	112—115/0.20	1.5357(22)	0.59 (s, 6H); 2.75 (d, 2H, <i>J</i> 6.5 Hz); 6.25—5.58 (m, 3H) 7.72—7.00 (m, 5H)
Ph ₂ MeSiCCl ₂ SiMe ₃	159—160/0.12	1.5697(21)	—0.03 (s, 9H); 0.77 (s, 3H); 7.83—7.04 (m, 10H)
Ph ₂ MeSiCCl ₂ CH ₃	148—150/0.15	1.5870(20)	0.78 (s, 3H); 2.03 (s, 3H); 7.73—6.88 (m, 10H)
Ph ₂ MeSiCCl ₂ CH ₂ CH ₃	144—146/0.04	1.5851(21)	0.79 (s, 3H); 1.15 (s, 3H, <i>J</i> 6.5 Hz); 2.11 (q, 2H, <i>J</i> 6.5 Hz) 7.70—7.00 (m, 10H)
Ph ₂ MeSiCCl ₂ CH ₂ CH ₂ CH ₂ CH ₃	148—150/0.02	1.5720(21)	0.79 (s, 3H); 2.25—0.70 (m, 9H); 7.68—7.01 (m, 10H)
Ph ₂ MeSiCCl ₂ CH ₂ Ph	m.p. 71.5—73°C	—	0.69 (s, 3H); 3.32 (s, 2H); 7.73—6.95 (m, 15H)

^a In CCl₄, with respect to internal TMS. ^b Lit. n_D^{25} 1.4667; ref. 2,3. ^c Lit. m.p. 117—119°C; ref. 2,3.

TABLE 3
 YIELDS AND PROPERTIES OF (Z)-1-CHLORO-1-ALKYL-SILANES

Silane	% Yield ^a	B.p. (°C/mmHg) (m.p. (°C))	<i>n</i> _D (T)	NMR
PhMe ₂ SiClCl=CH ₂	73	71-73/1.5	1.5235(22)	7.53-7.07 (m, 5H), 5.90 (s, 1H), 5.54 (s, 1H), 0.48 (s, 6H)
PhMe ₂ SiClCl=CHCH ₃	80	91-93/1.5	1.5339(21)	7.47-6.95 (m, 5H), 5.77 (t, 1H), J 6 Hz), 1.74 (d, 3H, J 6 Hz), 0.42 (s, 6H)
PhMe ₂ SiClCl=CHCH ₂ CH ₃	77	114-120/2.0	1.5183(22)	7.48-6.95 (m, 5H), 5.77 (t, 1H, J 7 Hz), 2.17 (q, 2H, J 7 Hz), 1.8-0.7 (m, 5H), 0.43 (s, 6H)
PhMe ₂ SiClCl=CHPh	85	146-148/0.3	1.5832(21)	7.90-7.70 (m, 5H), 6.65 (s, 1H), 0.53 (s, 6H)
Ph ₂ MeSiClCl=CH ₂	60	130-135/0.05	1.5819(21)	7.53-6.95 (m, 10H), 6.00 (s, 1H, J 6 Hz), 1.78 (d, 3H, J 6 Hz), 0.67 (s, 3H)
Ph ₂ MeSiClCl=CHCH ₃	83	(72-73)	—	7.50-6.95 (m, 10H), 5.86 (q, 1H, J 6 Hz), 1.78 (d, 3H, J 6 Hz), 0.67 (s, 3H)
Ph ₂ MeSiClCl=CHCH ₂ CH ₃	78	137-138/0.05	1.5675(21)	7.53-6.97 (m, 10H), 5.81 (t, 1H, J 6.5 Hz), 2.28 (q, 2H, J 7 Hz), 1.81-0.57 (m, 7H), 0.69 (s, 3H)
Ph ₂ MeSiClCl=CHPh	79	^b	1.5704(21)	7.66-6.82 (m, 15H), 6.73 (s, 1H), 0.77 (s, 3H)

^a Isolated yields. ^b Final purification by GLC.

final purification using preparative gas-liquid chromatography was employed in most cases. All compounds show IR, NMR, and mass spectral data in complete accord with the assigned structures.

Infrared spectra were recorded on a Perkin—Elmer 237 spectrophotometer, NMR spectra on a Varian T-60 or a Perkin—Elmer R-24 spectrophotometer and mass spectra on a Varian Mat CH-7. Tetrahydrofuran was donated by Pfizer of Puerto Rico and was distilled from sodium-benzophenone prior to use. (Dichloromethyl)dimethylchlorosilane was purchased from Petrarch Systems and converted to (dichloromethyl)trimethylsilane [9] and (dichloromethyl)phenyldimethylsilane by treatment with methylmagnesium iodide (76%) and phenylmagnesium bromide (85%), respectively. In a like manner, (dichloromethyl)methyldichlorosilane (Petrarch) was converted to (dichloromethyl)diphenylmethylsilane with two equivalents of phenylmagnesium bromide (58%). Trimethylchlorosilane, a gift from Bristol of Puerto Rico, was distilled prior to use. Phenyldimethylchlorosilane was prepared according to Bamford and Pant [10]. All other compounds were commercially available and were distilled prior to use.

Characterizing physical and spectral data for the compounds reported here are given in Table 2.

Preparation of α,α -dichlorosilanes. General procedure

The standard apparatus (100 ml capacity) was charged with 20 ml of THF and 1.11 g (11 mmol) of diisopropylamine. This solution was cooled to 0°C and 11 mmol of n-butyllithium in hexane added over 1 min. After it had been stirred for 15 min at 0°C, the solution was cooled to -78°C (Dry Ice acetone) and 10 mmol of the appropriate dichloromethylsilane in THF added. The lithium reagent was allowed to form over an appropriate length of time (2 min for I, 1 h for II and III) and then from 11–50 mmol of the chlorosilane or alkyl halide added. After it had been stirred at -78°C for 30 min, the solution was hydrolyzed by the addition of 20 ml of 1.5 N HCl, saturated with sodium chloride and extracted with ether (3 × 20 ml). The organic layer was dried (Na₂SO₄) and concentrated by fractional distillation and the product distilled at reduced pressure.

Preparation of ((Z)-1-chloro-1-alkenyl)silanes. General procedure

A 25 ml, round-bottomed flask was charged with from 4–8 mmol of the α,α -dichloroalkylsilane and ca. 15 ml of dry dimethylformamide. The solution was refluxed with stirring for 16 h, cooled and diluted with 50 ml of pentane. This solution was washed with 1.5 N HCl (3 × 25 ml) and water (3 × 25 ml). After the organic layer was dried (Na₂SO₄), filtered and concentrated, the residue was distilled through a micro-distillation apparatus.

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