Reactions of polyhalides with lithium and trimethylchlorosilane

Earlier investigations in this laboratory[1,2] of *in situ* Grignard reactions of polyhalocarbons with trimethylchlorosilane to yield (trimethylsilyl)methanes and the application by Gilman and Smith[3] of these techniques to a lithium reaction of silicon tetrachloride and trimethylchlorosilane to yield tetrakis(trimethylsilyl)silane stimulated our interest in the analogous lithium reactions between polyhalocarbons and organochlorosilanes. Here reported are successful syntheses for the trimethylsilyl derivatives of carbon tetrabromide, carbon tetrachloride, chloroform, and methylene chloride carried out with lithium metal in the presence of trimethylchlorosilane and tetrahydrofuran. The results are summarized in Table 1.

TABLE 1

In situ LITHIUM REACTIONS OF CARBON POLYHALIDES AND TRIMETHYLCHLOROSILANE

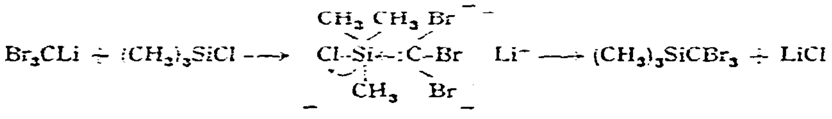
No.	*Polyhalide*	*Products*	
		Structure	*Yield (%*)*
1	CBr_4	$[(CH_3)_3Si]_4C$	28.3
		$[(CH_3)_3Si]_3CH$	46.8
		$[(CH_3)_3Si]_2CH_2$	7.7
		Total	82.8
2	CCl_4	$[(CH_3)_3Si]_4C$	66.5
		$[(CH_3)_3Si]_3CH$	10.6
		Total	77.1
3	$CHCl_3$	$[(CH_3)_3Si]_3CH$	66.7
		$[(CH_3)_3Si]_2CH_2$	Trace
		Total	66.7
4	CH_2Cl_2	$[(CH_3)_3Si]_2CH_2$	64.5

* Based on polyhalide.

As was true for the Grignard reactions[2], the lithium reaction of carbon tetrabromide yielded tris- and bis(trimethylsilyl)methanes as well as the expected tetrakis(trimethylsilyl)methane. Present evidence indicates that the hydrogen atoms are abstracted from the tetrahydrofuran[4]. However, in contrast to the *in situ* Grignard method where little or no reaction occurred with carbon tetrachloride[2], the reaction of lithium with this polyhalide gave an excellent yield of tetrakis(trimethylsilyl)methane, together with a small amount of tris(trimethylsilyl)methane.

It is tentatively suggested that these reactions proceed through a series of nucleophilic displacements as illustrated in (1)–(4) since earlier work of this laboratory

$$CBr_4 + 2Li \longrightarrow Br_3CLi + LiBr \qquad (1)$$



$$Br_3CLi + (CH_3)_3SiCl \longrightarrow \left[Cl{-}\overset{CH_3\ CH_3}{\underset{CH_3}{Si}}{\leftarrow}{:}\overset{Br}{\underset{Br}{C}}{-}Br \right]^- Li^+ \longrightarrow (CH_3)_3SiCBr_3 + LiCl \qquad (2)$$

$$(CH_3)_3SiCBr_3 + 2Li \longrightarrow (CH_3)_3SiCBr_2Li + LiBr \qquad (3)$$

$$(CH_3)_3SiCBr_2Li + (CH_3)_3SiCl \longrightarrow [(CH_3)_3Si]_2CBr_2 + LiCl \text{ etc.} \qquad (4)$$

has shown that carbon tetrabromide and magnesium in the presence of excess trimethylchlorosilane react in this stepwise fashion[4]. Hine and others[5] have found evidence for a CCl_3^- intermediate in kinetic studies of the base-catalyzed deuterium exchange of chloroform in aqueous solution at 35°. That α-chloro alkali metal compounds in aprotic solvents such as tetrahydrofuran can act as nucleophiles has been previously established[6]. The findings of this present work are, therefore, consistent in suggesting a trihalomethyl nucleophile stable at temperatures to 60°. The feasibility of preparing lithium trihalomethanes, etc., directly from lithium metal and the respective polyhalocarbon rather than from lithium alkyls and the polyhalocarbon is clearly demonstrated.

Experimental

Materials. Trimethylchlorosilane was supplied by Dow Corning Corporation. Foote Mineral Company lithium suspension was used. Carbon tetrabromide was from Eastman Organic Chemicals; other halides were Baker reagent grades. Eastman tetrahydrofuran was used without further purification.

Carbon tetrabromide (*Table 1, No. 1*). A solution of 21.6 g (0.065 mole) of carbon tetrabromide in 50 ml of tetrahydrofuran was added dropwise to a refluxing mixture of 67.9 g of trimethylchlorosilane, 200 ml of tetrahydrofuran, and 7.2 g of a 50/50 by weight suspension of finely divided lithium metal in hexane. After an additional hour at reflux temperature the mixture was held at room temperature for three days. The liquid was decanted from the solids which were washed twice with tetrahydrofuran and the washings added to the decantate. After washing with water, the organic layer was dried over sodium sulfate. Solvents and lower boiling constituents were distilled to a head temperature of 100°. The remainder was then diluted with 100 ml methanol and chilled in a dry ice/acetone bath. The precipitate which formed was removed by filtration. The filtrate was washed with water and the organic phase was distilled yielding the following products: (1) 0.8 g of bis(trimethylsilyl)methane; b.p. 133° at atmospheric pressure; n_D^{25} 1.4145, lit.[7] n_D^{20} 1.4170; d_4^{25} 0.746, lit.[7] d_4^{20} 0.752; R_D calcd. 0.3347, found 0.3354. The ^1H NMR spectrum consists of a methyl peak at $\tau = 9.98$ ppm and CH_2 peak at $\tau = 10.28$ run in carbon tetrachloride using cyclohexane as the internal reference; (2) 7.05 g tris(trimethylsilyl)methane; b.p. 104° at 20 mm; n_D^{25} 1.4604. lit.[8] n_D^{20} 1.4630; d_4^{25} 0.832, lit.[8] d_4^{20} 0.836; R_D calcd. 0.3320, found 0.3294. The ^1H NMR spectrum in carbon tetrachloride solution consists of a methyl peak at $\tau = 9.89$ ppm and CH peak at $\tau = 10.79$ ppm using cyclohexane as the internal reference.

The distillation residue was extracted with benzene and the benzene solubles were combined with the precipitate earlier filtered from the chilled methanol solution of products. These solids were recrystallized from 50/50 by volume ethanol/*n*-propanol, yielding 5.6 g tetrakis(trimethylsilyl)methane; sealed tube m.p. 305–307°. (Found*: C, 51.46; H, 11.72; Si, 37.04, mol. wt., 310. $C_{13}H_{36}Si_4$ calcd.: C, 51.20; H, 11.90; Si, 36.86 %, mol. wt., 304.8.) The ^1H NMR spectrum consists of a single peak at $\tau = 9.8$ ppm using cyclohexane as the internal reference.

Carbon tetrachloride (*Table 1, No. 2*). A solution of 10 g (0.065 mole) carbon tetrachloride in 50 ml of tetrahydrofuran was added dropwise to 67.9 g of trimethylchlorosilane, 200 ml of tetrahydrofuran, and 7.2 g of a 50/50 by weight suspension of

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* Analysis performed by Galbraith Laboratories, Knoxville, Tennessee.

finely divided lithium metal in hexane. The reaction products were treated as described above yielding 13.1 g tetrakis(trimethylsilyl)methane and 1.6 g tris(trimethylsilyl)-methane.

Chloroform (*Table 1, No. 3*). After heating 67.9 g of trimethylchlorosilane, 200 ml of tetrahydrofuran, and 7.2 g of 50/50 by weight suspension of finely divided lithium metal in hexane to reflux, 10.3 g (0.0866 mole) of chloroform in 50 ml tetrahydrofuran was added dropwise. The mixture was refluxed one additional hour, then held at room temperature for two days. The liquid products were decanted from the solids, washed with water, dried, and distilled yielding 13.3 g of tris(trimethylsilyl)methane and a trace amount of bis(trimethylsilyl)methane.

Methylene chloride (*Table 1, No. 4*). To 67.9 g of trimethylchlorosilane, 200 ml of tetrahydrofuran and 7.2 g of 50/50 by weight suspension of finely divided lithium in hexane heated to reflux was added 11 g. (0.13 mole) of methylene chloride in 50 ml of tetrahydrofuran. After one hour at reflux and four days at room temperature the liquid was decanted from the solid, washed with water, dried, and distilled yielding 13.4 g bis(trimethylsilyl)methane.

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