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THE CLEAVAGE OF (PERHALOARYL)DIMETHYLSILANES BY ORGANOLITHIUM COMPOUNDS

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SUMMARY

(Perhaloaryl)dimethylsilanes undergo a cleavage reaction with organolithium compounds, using very moderate conditions, to produce (perhaloaryl)lithium derivatives in good yield.

$$Ar_XSiMe_2H + RLi \rightarrow Ar_XLi + RSiMe_2H$$

The corresponding trimethylsilyl compounds [except for 2,5-bis(trimethylsilyl)dichlorothiophene] and phenyldimethylsilane were not cleaved significantly.

INTRODUCTION

We observed, some years ago[1], that phenyllithium was formed in a cleavage reaction when n-butyllithium was allowed to react with triphenylsilanol or with hexaphenyldisiloxane. The cleavage of carbon–silicon bonds by an organolithium reagent has been shown to take place with a variety of cyclic silanes[2]. Methyllithium effects some cleavage of a series of the $Ph_{4-n}SiMe_n$ type (but not with $PhSiMe_3$) to give PhLi[3,*].

More pertinent to our present studies was the cleavage of the pentachlorophenyl–silicon bond by methyllithium (and by phenyllithium), as in the following illustration[4]:

$$C_6Cl_5SiPh_2H + MeLi \rightarrow C_6Cl_5Li + MeSiPh_2H$$

Then we observed[5] the cleavage of the C_6F_5–Si linkage by MeLi (and by BuLi) to yield C_6F_5Li:

$$C_6F_5SiPh_2H + BuLi \rightarrow C_6F_5Li + BuSiPh_2H$$

In all these four cases, the (perhalophenyl)lithium was characterized by reaction with $ClSiMe_3$ to yield $C_6X_5SiMe_3$.

It was a short step to using $ClSiMe_2H$ in place of the less accessible $ClSiPh_2H$ to give $C_6X_5SiMe_2H$ types. These, as well as other (perhaloaryl)dimethylsilanes, were

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[*] The compounds were unreactive to filtered MeMgI, but were later shown to be cleaved to a small extent by Mg/RMgX combinations[3b].

TABLE 1

REACTION OF ARYL- AND (POLYHALOARYL)DIMETHYL- AND -TRIMETHYLSILANES WITH ALKYL METALLIC REAGENTS IN ETHER

Silane (Mole)	*RM (Mole)*	*Max. (°C)*	*Time*	*Derivatizing reagent*	*Product*[a] *and yield*[b]
2-$C_4Cl_3SSiMe_2H$ (0.025)	BuLi (0.025)	−70	10 min	CO_2	2-C_4Cl_2SCOOH 5.2 g, 90%
2-$C_4Cl_3SSiMe_2H$ (0.02)	BuMgBr (0.02)	60[c]	48 h		2-$C_4Cl_3SSiMe_2H$ 4.05 g, 83%
2-$(Me_2SiH)C_4Cl_2S$- (Me_2SiH)-5 (0.02)	BuLi (0.02)	−70	2 h[d]	CO_2	2-$C_4Cl_2HSCOOH$ 3.0 g, 72%
2-$(Me_2SiH)C_4Cl_2S$- (Me_2SiH)-5 (0.02)	BuLi (0.04)	0	4.5 h	CO_2	2-$(COOH)C_4Cl_2S(COOH)$-5 4.2 g, 87%
2-$(Me_2SiH)C_4Cl_2S$- (Me_2SiH)-5 (0.02)	PhLi (0.04)	0	6 h	Me_3SiCl	2-$(Me_3Si)C_4Cl_2S(SiMe_3)$-5 45%[e]
2-$(Me_2SiH)C_4Cl_2S$- (Me_2SiH)-5 (0.02)	EtMgBr (0.04)	30	80 h		2-$(Me_2SiH)C_4Cl_2S$- (Me_2SiH)-5[f]
$C_6F_5SiMe_2H$ (0.02)	BuLi (0.02)	−70	1 h	CO_2	C_6F_5COOH 3.3 g, 80%
4-$C_5Cl_4NSiMe_2H$ (0.02)	BuLi (0.02)	−70	40 min	CO_2	4-C_5Cl_4NCOOH 5.2 g, 86%[g]
$C_6Cl_5SiMe_2H$ (0.02)	BuLi (0.02)	−15	3.5 h	CO_2	Mixtures of tars and some acid products
$C_6Cl_5SiMe_2H$ (0.02)	BuLi (0.04)	25	2 h	Me_2HSiCl	Mixture of tars. IR shows only weak Si−H stretch.
$C_6Cl_5SiMe_2H$ (0.02)	BuLi (0.02)	0	5 h	Me_3SiCl	Mixture of $C_6Cl_5SiMe_3$ 62% p-$Me_3SiC_6Cl_4SiMe_2H$-p 27% 5.8 g[h]
$C_6Cl_5SiMe_2H$ (0.02)	MeLi (0.02)	−70	2 h	Me_3SiCl	$C_6Cl_5SiMe_3$ 4.9 g, 76%
$C_6H_5SiMe_2H$ (0.04)	BuLi (0.04)	10	16 h		$C_6H_5SiMe_2Bu$ 6.6 g, 86%[i]
$C_6H_5SiMe_2Bu$ (0.02)	BuLi (0.02)	30	24 h		No reaction
2-$C_4Cl_3SSiMe_3$ (0.025)	BuLi (0.025)	−78	1 min	CO_2	2-$(SiMe_3)C_4Cl_2S(COOH)$-5 6.0 g, 91%[j]
2-$C_4Cl_3SSiMe_3$ (0.02)	BuLi (0.04)	25	87 h	CO_2	2-$(SiMe_3)C_4Cl_2S(COOH)$-5 2.6 g, 48%
2-$C_4Cl_3SSiMe_3$ (0.02)	BuMgBr (0.02)	60[c]	20 h		2-$C_4Cl_3SSiMe_3$ 4.7 g, 91%
2-$(Me_3Si)C_4Cl_2S$- $(SiMe_3)$-5 (0.02)	BuLi (0.04)	10	4 h	H_2O	2,5-$C_4Cl_2H_2S$ 5%[k] 2-$HC_4Cl_2SSiMe_3$-5 2%
2-$(Me_3Si)C_4Cl_2S$- $(SiMe_3)$-5 (0.02)	BuLi (0.04)	−70	48 h	H_2O	2,5-$C_4Cl_2H_2S$ 15%[c,k] 2-$HC_4Cl_2SSiMe_3$-5 8%

(*For Footnotes see p.* 37)

cleaved very smoothly and in high yields by BuLi. A similar cleavage has been reported recently[6] by Pinkerton and Thames of the C–$SiMe_3$ linkage, particularly in some non-halogenated heterocycles.

RESULTS AND DISCUSSION

The cleavage of the carbon–silicon bond in the (perhaloaryl)dimethylsilanes proceeded smoothly and cleanly under very moderate conditions (−70°), and in relatively short reaction times (see Table 1). The products were [except for (pentachlorophenyl)dimethylsilane] the (polyhaloaryl)lithium compound and the alkyl- (usually n-butyl-) dimethylsilane or phenyldimethylsilane. All reactions proceeded with little or no apparent decomposition. The resulting perhaloaryllithium reagents were colorless.

This appears to be the first preparation of isomer-free tetrachloro-4-pyridyllithium in ether. Previous studies[7] have produced mixtures of 3- and 4-lithio derivatives in low yields when ether was employed as the solvent. Furthermore, an extremely clean colorless solution is produced in contrast to the formerly observed "clean but colored" solutions.

There seemed to be some differences in the ease of cleavage of the bonds in the several compounds. Of the (perhaloaryl)dimethylsilanes, (trichloro-2-thienyl)dimethylsilane appeared to be cleaved most easily (less than 10 min). Similarly, the first dimethylhydrosilyl group was cleaved from 2,5-bis(dimethylsilyl)dichlorothiophene in less than 20 min. The second of these did not react until the temperature reached about 0°, at which time the reaction proceeded smoothly. The first of these cleavages takes place under conditions which fail to effect Cl–Li exchange in tetrachlorothiophene[8], whereas the second $-SiMe_2H$ group appears to be cleaved under essentially the same conditions required for the preparation of 2,5-dilithiodichlorothiophene[9]. The trimethylsilyl group can be cleaved from 2,5-bis(trimethylsilyl)dichlorothiophene, but not so readily nor in such good yields as is the $SiMe_2H$ moiety. With trimethylsilyl derivatives examined, the reaction takes an alternate path[5,10] (Table 1).

In the case of (pentachlorophenyl)dimethylsilane, a competing metal–halogen exchange reaction at the *p*-carbon atom was observed. When the reaction was re-run using methyllithium, which is known to be a poor reagent for the halogen–metal exchange reaction[11], the reaction proceeded "normally" to give (pentachlorophenyl)lithium in good yield.

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[a] Products were identified by comparison with authentic samples (mixed m.p. and IR spectra).

[b] Based on mole of starting silane.

[c] Solvent was THF.

[d] Reaction was complete in 20 min (VPC). The second $SiMe_2H$ was cleaved by hydrolysis during work-up.

[e] The yield was determined by VPC. Also present was 35% of 2-$(Me_3Si)C_4Cl_2S(SiMe_2H)$-5. From the mixture was isolated 1.12 g (21%) of $PhSiMe_2H$.

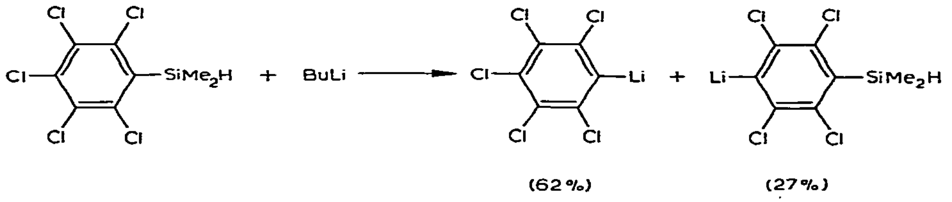
[f] Product had other materials present. These were of longer retention time in the VPC and may have been the ethylated silanes.

[g] No evidence of other isomers.

[h] Percentages determined by VPC.

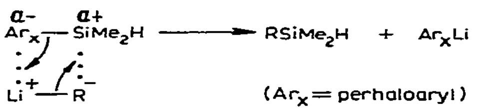
[i] n_D^{20} 1.4920; cited[14] n_D^{20} 1.4920. Identical retention time with material prepared on a small scale from $PhMe_2SiCl$ and BuLi.

[j] Analysis found: Cl 26.40%, Calcd. for $C_8Cl_2H_{10}O_2SSi$: Cl 26.34%.



Even with the easily cleaved (trichloro-2-thienyl)dimethylsilane, no significant cleavage by a Grignard reagent was observed. In the case of ethylmagnesium bromide a product (ca. 05%) of longer retention time in the VPC may have been (trichloro-2-thienyl)ethyldimethylsilane. This is consistent with the lesser reactivity of most Grignard reagents, and also with known reactions of Grignard reagents and the Si–H bond[12,13].

The mechanism of the cleavage reaction can be visualized as a nucleophilic attack on the silicon atom, *viz.*:



Such a mechanism would be favored by electron-withdrawing groups (Cl, F) on the aryl nucleus which would increase the positive nature of the silicon atom. The absence of a cleavage reaction with $PhMe_2SiH$ may be attributed largely to a lack of the strongly electron-withdrawing halogens. The reaction proceeded instead to give the known $PhBuMe_2Si$ in 86% yield[14]. The fact that $C_6Cl_5SiMe_2H$ is only partially cleaved by BuLi is probably due largely to the ease of the halogen–metal exchange reaction with the *p*-chlorine atom. We were unable to cleave a trimethylsilyl group from the trichlorothiophene nucleus. Instead there was a rapid (1 min) chlorine–lithium exchange reaction to give 2-lithio-5-(trimethylsilyl)dichlorothiophene in 91% yield at −78°. The difference in behavior of the trimethylsilyl *vs.* the dimethylhydrosilyl types may be steric in origin. The use of more severe conditions might result in cleavage of $(2\text{-}C_4Cl_3S)SiMe_3$ by a second mole of alkyllithium reagent. However, the first mole of alkyllithium would still probably follow the reaction path of least resistance, *i.e.* the halogen–metal exchange on the α-position. The above exchange reaction did not take place when BuMgBr was used. It has been previously reported that 2-thienyltriphenylsilane in a similar reaction underwent metalation at the α-position of the thiophene nucleus[1].

We will report later on applications of this conversion or cleavage reaction for syntheses leading to R_FM and $M(CF_2)_nM$ types.

EXPERIMENTAL

All reactions were effected under an atmosphere of dry nitrogen in a three-necked round-bottomed flask equipped with a nitrogen inlet tube, dropping funnel and sealed stirrer. The equipment was dried at 120°, assembled while hot and flushed with dry nitrogen prior to charging the flask with the reactants. n-Butyllithium (1.6 *N* in hexane) phenyllithium and methyllithium (1.7 *N* in ether/benzene) were from the Foote Mineral Co.. Ether was distilled from sodium benzophenone ketyl. All other solvents were used without further purification. (Pentachlorophenyl)-[15], (tetrachloro-4-pyridyl)-[16], (pentafluorophenyl)-[17], phenyl-[18], (trichloro-2-thienyl)dimethylsilanes[8], 2,5-bis(dimethylsilyl)dichlorothiophene[9], 2,5-bis(trimethylsilyl)dichlorothiophene[9], and (trichloro-2-thienyl)trimethylsilane[8] were prepared by standard procedures.

General procedure

The reaction flask was charged with ca. 80 ml of dry ether and the appropriate silane and cooled to ca. −70° with a Dry Ice/acetone bath. To this solution, with vigorous stirring, was added an equivalent quantity of the organolithium compound. The reactions were monitored by inspection of VPC curves ($4\frac{1}{2}$ ft. Silicone Gum Rubber, 15% on Chromosorb W) of small aliquots after either hydrolysis and/or treatment with Me_3SiCl. When the particular reaction appeared complete, the products were derivatized. Details of the various reactions are contained in Table 1.

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