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LITHIATION OF TRIS(TRIMETHYLSILYL)METHANE AND TETRAKIS(TRIMETHYLSILYL)METHANE*

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SUMMARY

Lithiation of $(Me_3Si)_3CH$ by methyllithium (ether–THF) yields $(Me_3Si)_3CLi$ and by t-butyllithium (C_5H_{12}–TMEDA) yields $(Me_3Si)_2CHSiMe_2CH_2Li$. Only starting material is recovered when $(Me_3Si)_3CH$ is allowed to react with n-butyllithium (ether–THF and C_5H_{12}–TMEDA) and t-butyllithium (C_5H_{12} and C_5H_{12}–THF). $(Me_3Si)_4C$ is lithiated by t-butyllithium (C_5H_{12}–TMEDA) to give $(Me_3Si)_3CSiMe_2CH_2Li$, but not by methyllithium (ether–THF and ether–THF–TMEDA). The structures of the lithiated compounds are based on the carbonation products. The above results are explained in terms of carbanion stability and steric effects. Spectral data are reported on the α-silylacetic acids.

INTRODUCTION

It has been observed that organosilicon compounds containing an α-hydrogen can be lithiated by organolithium reagents under a variety of conditions depending on the structure of the compound**. The importance of potentiating catalysts for lithiation, such as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), has been stressed[1-4].

The preparation of tris(trimethylsilyl)methyllithium by the reaction of tris(trimethylsilyl)methane (I) with methyllithium in ether–THF has been reported by Cook *et al.*[5]. Concurrently, we observed that I was not lithiated by n-butyllithium in ether and THF.

In order to discern the requirements for lithiating I and tetrakis(trimethylsilyl)methane (II), we have treated these compounds with a variety of organolithium reagents in several solvent systems. When hydrocarbon solvents were employed, the potentiating catalyst, TMEDA, was usually added. The position and extent of lithiation are explained in terms of carbanion stability and steric effects.

EXPERIMENTAL

General

Molecular weights were determined at 70 eV with a LKB-9000 combined gas

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** For a review article, *cf.* ref. 1.

chromatograph–mass spectrometer. Analyses were performed by Alfred Bernhardt Microanalytical Laboratories, West Germany. All melting points are corrected.

n-Butyllithium, 1.6 *M* in hexane, was supplied by Foote Mineral Co; methyllithium, 1.66 *M* in ether, and t-butyllithium, 2.26 *M* in pentane, were supplied by Alfa Products, Ventron Corp. TMEDA, technical grade, Eastman, was distilled from calcium hydride, b.p. 119.5°. All solvents used in the lithiation reactions were distilled from calcium hydride. Tris(trimethylsilyl)methane (I), b.p. 101°/20 mm, and tetrakis(trimethylsilyl)methane (II), m.p. 302–305° were prepared by the methods of Merker and Scott[6].

Procedure for the reaction of the alkyllithium reagents with tris(trimethylsilyl)methane (I) and tetrakis(trimethylsilyl)methane (II)

The alkyllithium reagent, solvent, and TMEDA, if present, were injected into a three-necked flask, equipped with a magnetic stirrer, condenser, and rubber septum, containing the silane dissolved in the solvent. The flask was cooled, if indicated, before the injection of the alkyllithium reagent, and the reaction was carried out under a nitrogen atmosphere. The conditions for each reaction are given in Tables 1 and 2.

TABLE I

REAGENTS AND CONDITIONS WHERE LITHIATION OF $(Me_3Si)_3CH$ (I) AND $(Me_3Si)_4C$ (II) OCCURS

Silane	*RLi*	$\frac{[RLi]}{[Silane]}$	*Solvent*	*Temp.* (°*C*)	*Time* (*h*)	*Carbonation product* (*% Yield*)
$(Me_3Si)_3CH$	MeLi	6	ether–THF^a	reflux	8	$(Me_3Si)_3CCO_2H$ (59)
$(Me_3Si)_3CH$	MeLi	10	ether–THF^a	reflux	7	$(Me_3Si)_2CHCO_2H$ (79)^b
$(Me_3Si)_3CH$	t-BuLi	6	C_5H_{12}–TMEDA^c	25	59	$(Me_3Si)_2CHSiMe_2CH_2Li$ (51)^d
$(Me_3Si)_4C$	t-BuLi	5	C_5H_{12}–TMEDA^c	25	40	$(Me_3Si)_3CSiMe_2CH_2Li$ (57)

[a] 50 Vol-%. [b] Acid isolated by basic extraction. [c] [t-BuLi]/[TMEDA]=2. [d] Starting material, 34% recovered.

TABLE 2

REAGENTS AND CONDITIONS WHERE LITTLE OR NO LITHIATION OF $(Me_3Si)_3CH$ (I) AND $(Me_3Si)_4C$ (II) OCCURS

Silane	*RLi*	$\frac{[RLi]}{[Silane]}$	*Solvent*	*Temp.* (°*C*)	*Time* (*h*)	*Silane recovered* (*%*)
$(Me_3Si)_3CH$	n-BuLi	2	ether	0	8.5	77
$(Me_3Si)_3CH$	n-BuLi	2	THF	−50	6.5	76
$(Me_3Si)_3CH$	n-BuLi	1.4	C_5H_{12}–TMEDA^a	25	49	89
$(Me_3Si)_3CH$	t-BuLi	2	C_5H_{12}	25	49	86
$(Me_3Si)_3CH$	t-BuLi	2	C_5H_{12}–THF^b	−78	2	83
$(Me_3Si)_4C$	MeLi	6	ether–THF^c	25	48	94
$(Me_3Si)_4C$	MeLi	6	ether–THF^c	reflux	48	93
$(Me_3Si)_4C$	MeLi	6	ether–THF–TMEDA^{a,c}	reflux	23	92

[a] [RLi]/[TMEDA]=4. [b] 50 vol-%. [c] 25 vol-% ether.

Procedures for the carbonation of the organolithium reagents and the isolation of the carboxylic acids

After the reaction mixture had been stirred for the time indicated, it was poured onto powdered Dry Ice. The resulting slurry was poured directly into a 5% hydrochloric acid solution. This mixture was extracted several times with ether, and the combined ethereal solution was dried. In addition to the isolation of the carboxylic acids resulting from the carbonation of the lithiating reagents, the α-silylacetic acids were isolated as indicated below:

(a) Bis(trimethylsilyl)acetic acid (III) and tris(trimethylsilyl)acetic acid (IV). These acids were isolated as previously reported[7].

(b) 4-Trimethylsilyl-3,3,5,5-tetramethyl-3,5-disilahexanoic acid (V). Removal of the ether under pressure gave an oily residue (NMR analysis, 60% V and 40% I). Fractional sublimation of the above material gave a sample of V of high purity, m.p., 51–53° (Found: C, 47.69; H, 10.10; *m/e*, 276. $C_{11}H_{28}O_2Si_3$ calcd.: C, 47.76; H, 10.21; *m/e*, 276).

(c) 4,4-Bis(trimethylsilyl)-3,3,5,5-tetramethyl-3,5-disilahexanoic acid (VI). Removal of the ether under reduced pressure gave a waxy solid. Sublimation of the solid followed by several crystallizations from ethanol gave a sample of VI, m.p., 225–230° (Found: C, 48.42; H, 10.24; *m/e*, 348. $C_{14}H_{36}O_2Si_4$ calcd.: C, 48.21; H, 10.41; *m/e*, 349).

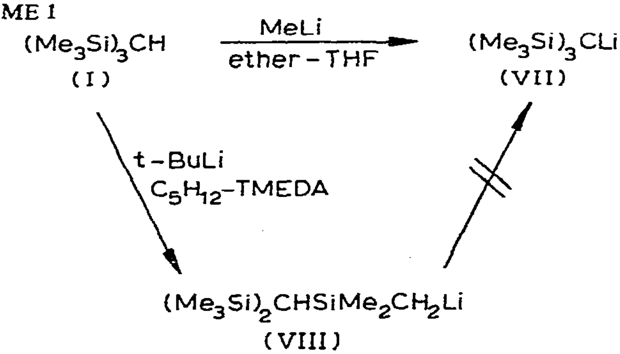
Yields (%) and properties of the above α-silylacetic acids are given in Tables 1 and 3.

RESULTS AND DISCUSSION

The reagents and conditions used in the lithiation experiments are given in Tables 1 and 2. The position and extent of lithiation are based on the structure and yield of the carbonation product*.

Of the organolithium reagents studied, only methyllithium (ether–THF) is capable of lithiating the central carbon atom of I[5] (see Scheme 1). Since both n-butyllithium and t-butyllithium are stronger lithiating reagents than methyllithium[1,8], only steric effects can explain adequately the observed order of reactivity of the organolithium reagents toward I.

SCHEME 1



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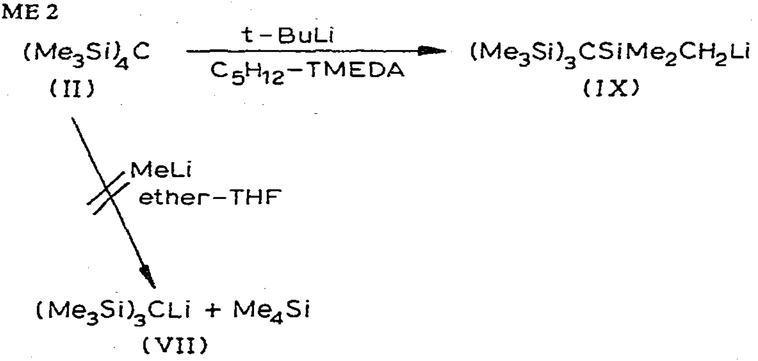
* The actual extent of lithiation is as high or higher than the carbonation value.

Only t-butyllithium (C_5H_{12}–TMEDA) of the reagents studied is effective in lithiating a methyl group of I (Scheme 1). t-Butyllithium (C_5H_{12} and C_5H_{12}–THF) and n-butyllithium (ether, THF and C_5H_{12}–TMEDA) are not effective reagents for lithiating I in either position due to insufficient reactivity and steric effects.

The lithiation experiments indicate that the thermodynamically favored organolithium derivative of I is $(Me_3Si)_3CLi$ (VII) rather than $(Me_3Si)_2CHSiMe_2CH_2Li$ (VIII). The observation that VIII does not rearrange to VII in C_5H_{12}–TMEDA (Scheme 1) by an intramolecular or intermolecular process again emphasizes the importance of steric effects on this system[5].

The observation that II is lithiated by t-butyllithium (C_5H_{12}–TMEDA) and not by methyllithium (ether–THF and ether–THF–TMEDA), see Scheme 2, is in accord with the data on lithiation of I. Carbon–silicon bond cleavage by methyllithium (ether–THF), which would yield VII and tetramethylsilane, does not occur with II. In contrast, silicon–silicon and silicon–germanium bond cleavage occurs when $(Me_3Si)_4M$, where M = Si and Ge, are allowed to react with methyllithium (ether–THF)[9,10].

SCHEME 2



PMR and IR data for the carbonation products are given in Table 3. Bis(trimethylsilyl)acetic acid (III) arises from the base-catalyzed rearrangement and/or cleavage of tris(trimethylsilyl)acetic acid (IV)[7]. The PMR chemical shifts are consis-

TABLE 3

PMR AND IR DATA ON THE α-SILYACETIC ACIDS

Acid	$\delta^{a,b}$					*ν(C=O)*[c,d] (*cm*$^{-1}$)
	H^a	*H*^{b}	*H*^{c}	*H*^{d}	*H*^{e}	
$[(CH^b_3)_3Si]_2CH^eSi(CH^c_3)_2CH^d_2CO_2H^a$	11.84(1)	0.14(17)	0.25(6)	1.95(2)	−0.62(1)	1689
$[(CH^b_3)_3Si]_3CSi(CH^c_3)_2CH^d_2CO_2H^a$	10.90(1)	0.27(26)	0.35(6)	2.07(2)		1690
$[(CH^b_3)_3Si]_2CH^dCO_2H^a$	12.08(1)	0.17(19)		1.57(1)		1668
$[(CH^b_3)_3Si]_3CCO_2H^a$	11.95(1)	0.27(27)				1645

[a] Spectra determined in CCl_4 with internal standard, TMS, at 60 MHz. [b] Relative peak area in parentheses. [c] CCl_4 solutions. [d] Acetic acid, ν(C=O), 1711 cm^{-1} in CCl_4.

tent with the proposed structures. The substitution of a trimethylsilyl group for hydrogen on the central carbon leads to a downfield shift of ~0.1 ppm for δ(C–H). The carbonyl stretching absorption of the α-silylacetic acids is observed at a lower energy than acetic acid with $\Delta\nu$ 0.22 ± 0.01 cm^{-1} for each α-trimethylsilyl group (see Table 3)*.

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REFERENCES

1 D. J. Peterson, *Organometal. Chem. Rev. A*, 7 (1972) 295.
2 D. J. Peterson, *J. Organometal. Chem.*, 9 (1967) 373.
3 G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, 90 (1968) 4478.
4 R. West and G. A. Gornowicz, *J. Organometal. Chem.*, 28 (1971) 25.
5 M. A. Cook, C. Eaborn, A. E. Jukes and D. R. M. Walton, *J. Organometal. Chem.*, 24 (1970) 529.
6 R. L. Merker and M. J. Scott, *J. Amer. Chem. Soc.*, 85 (1963) 2243; *J. Org. Chem.*, 28 (1963) 2717; *J. Org. Chem.*, 29 (1964) 953; *J. Organometal. Chem.*, 4 (1965) 98.
7 O. W. Steward, J. S. Johnson and C. Eaborn, *J. Organometal. Chem.*, 46 (1972) 97.
8 P. West in H. J. Emeleus and B. J. Aylett (Eds.), *MTP International Review of Science, Organometallic Derivatives of the Main Group Elements, Series* 1, *Vol.* 4, Butterworth, London, 1972, pp. 1–40.
9 H. Gilman and C. L. Smith, *J. Organometal. Chem.*, 14 (1968) 91.
10 O. W. Steward and J. S. Johnson, unpublished studies.
11 A. G. Brook, J. M. Duff and D. G. Anderson, *Can. J. Chem.*, 48 (1970) 561.
12 W. K. Musker and G. L. Larson, *J. Organometal. Chem.*, 6 (1966) 627.
13 O. W. Steward, J. E. Dziedzic and J. S. Johnson, *J. Org. Chem.*, 36 (1971) 3475.

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* Such shifts to lower energy have been reported previously[11–13].