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[TRIS(TRIMETHYLSILYL)METHYL]LITHIUM: AN ALKYLLITHIUM COMPOUND OF UNUSUAL STABILITY

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SUMMARY

Tris(trimethylsilyl)methane readily undergoes metallation when treated with methyllithium in a mixture of tetrahydrofuran and diethyl ether, and the [tris(trimethylsilyl)methyl]lithium produced is remarkably stable in tetrahydrofuran. The ease of formation and the stability of the organolithium compound may be associated with stabilization of the carbanion $(Me_3Si)_3C^-$ by delocalization of the lone pair of electrons into the *d*-orbitals of the silicon atom.

The organolithium compound can also be obtained by treatment of tris(trimethylsilyl)methyl chloride with lithium, methyllithium, or the n-butyllithium–*N,N,N',N'*-tetramethylethylenediamine complex. It couples normally with the halides MeI, Me_3SiCl, Me_2HSiCl, Me_3GeBr, and Me_3SnCl, and gives the new acid $(Me_3Si)_3CCO_2H$ on carbonation.

INTRODUCTION

In the course of our studies of the substituent effects of trimethylsilyl groups[1], we have examined the preparation and behaviour of [tris(trimethylsilyl)methyl]-lithium. We have found it to be readily formed and to be unusually stable in solution.

RESULTS

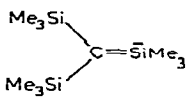
Tris(trimethylsilyl)methane[2] is readily metallated by methyllithium in a 10/3 vol/vol mixture of tetrahydrofuran (THF) and diethyl ether. Reaction is complete in about 6 h at the reflux temperature or about 20 h at room temperature (ca. 20°), and the yield of [tris(trimethylsilyl)methyl]lithium is at least 80–85%, as indicated by the yield of tetrakis(trimethylsilyl)methane obtained on treatment with chlorotrimethylsilane. The new organolithium reagent is unusually stable, the half-life of an 0.15 *M* solution in THF being about 70 h at the reflux temperature (see Table 1). Only 20% decomposition occurs in one week in a similar solution at room temperature. It is thus markedly more stable than methyl- or n-butyllithium; about 30% of the former disappeared during 3 h under the reflux conditions we used, while the latter is reported to decompose completely in 2 h at room temperature in THF[3]. tert-Butyllithium is very much less stable[4].

[Tris(trimethylsilyl)methyl]lithium can also be readily prepared from tris-(trimethylsilyl)methyl chloride by treatment with lithium in THF/ether, with methyllithium in THF/ether, or with n-butyllithium–*N,N,N',N'*-tetramethylethylenediamine (TMEDA) in ether/hexane. Metallation of tris(trimethylsilyl)methane is the most convenient method because this starting material is more readily available than the chloride.

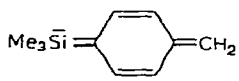
[Tris(trimethylsilyl)methyl]lithium couples normally with the halides Me_3SiCl, Me_2HSiCl, Me_3GeBr, Me_3SnCl, and MeI to give the compounds $(Me_3Si)_4C$, $(Me_3Si)_3CSiMe_2H$, $(Me_3Si)_3CGeMe_3$, $(Me_3Si)_3CSnMe_3$, and $(Me_3Si)_3CMe$, respectively, in satisfactory yields. Carbonation gives the new acid $(Me_3Si)_3CCO_2H$ in 76% yield.

DISCUSSION

The ready metallation of tris(trimethylsilyl)methane and the stability of [tris(trimethylsilyl)methyl]lithium towards tetrahydrofuran can reasonably be attributed mainly to stabilization of the carbanion $(Me_3Si)_3C^-$ by delocalisation involving interaction of the lone-pair with the vacant *d*-orbitals of silicon, represented by contributions from structures such as (I)*; this delocalisation clearly outweighs the influence of the inductive release of electrons to carbon by the Me_3Si group, which



(I)



(II)

would be expected to lower the stability of the carbanion. [A similar, but less directly applied, effect of the Me_3Si group on a carbanion, was suggested as long ago as 1955 to account for the ease of base cleavage of the benzyl–silicon bond in the compound p-$Me_3SiC_6H_4CH_2SiMe_3$[6]; in the latter case the delocalization, represented by (II), is more extended.] Steric hindrance may also contribute, however, to the low reactivity of [tris(trimethylsilyl)methyl]lithium towards the solvent THF**. As would be expected, the stabilization of the carbanions $(Me_3Si)_xH_{(3-x)}C^-$ falls as the value of x is decreased. Bis(trimethylsilyl)methane can be metallated with methyllithium in THF/ether, but markedly more slowly than tris(trimethylsilyl)methane, and the yield is low, probably because of decomposition of both the methyllithium and the [bis-(trimethylsilyl)methyl]lithium in the time needed for metallation. Metallation of tetramethylsilane requires use of the much stronger metallating agent, n-BuLi–TMEDA[8].

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* The reagent $(Me_3Si)_3CLi$ should also be more thermally stable than simple alkyllithium compounds because loss of a β-hydrogen atom to form an olefin, as for example in the formation of isobutylene and lithium hydride from tert-butyllithium[5], is not possible.

** It is noteworthy that the free radical $(Me_3Si)_3C^{\cdot}$ is also unusually stable in solution[7]. Electron delocalization into the *d*-orbitals of silicon is thought to contribute to the stability in that case also, but steric hindrance to formation of the compound $(Me_3Si)_3CC(SiMe_3)_3$ by radical dimerization is probably of considerable importance.

In spite of the ease of metallation of tris(trimethylsilyl)methane, a trimethylsilyl group is not cleaved from the compound $(Me_3Si)_4C$ by methyllithium. (Although $>C-SiMe_3$ bonds are usually broken by alcoholic alkali much more readily than the corresponding $>C-H$ bonds[9,10], the reverse order of reactivity normally applies to reactions with organolithium reagents, although cleavages of $>C-SiMe_3$ bonds by these reagents are known[10].) In view of this, it seemed surprising to us that the Grignard reagent $(Me_3Si)_3CMgBr$ was thought, on the basis of indirect evidence, to be formed from tetrakis(trimethylsilyl)methane and methylmagnesium bromide[11], and we have found that no reaction occurs between these compounds in ether. The formation of this Grignard reagent from the bromide $(Me_3Si)_3CBr$ and phenylmagnesium bromide[12], on the other hand, is consistent with our observations.

The ease of metallation of RH compounds normally runs parallel with the ease of base cleavage of the corresponding $R-SiMe_3$ compounds, but we found that the tetrakis-compound, $(Me_3Si)_4C$, was not affected by ca. 1.4 *M* sodium methoxide in methanol even during 22 h at the reflux temperature; a similar result was obtained by Merker and Scott using a rather lower alkali concentration[13]. By contrast, Merker and Scott observed the extensive cleavage of the central C–Si bonds accompanied replacement of the Si–H by Si–OMe bonds during treatment of the compound $(Me_2HSi)_4C$ with a much weaker solution of sodium methoxide in methanol[13].

EXPERIMENTAL

General

The NMR spectra were recorded on a Varian A60 spectrometer with 10% solutions in carbon tetrachloride. Tetramethylsilane was normally used as internal standard for the τ values, but integrated spectra were run in absence of an internal standard. Chloroform was used as internal standard for 1,1,1-tris(trimethylsilyl)-ethane.

For the GLC analysis a 2 m column of 5% SE 30 on 100–120 mesh silanized, acid-washed Chromosorb G was used in conjunction with a Pye Series 104 Model 64 dual flame ionisation gas chromatograph. For following progress of the metallation of tris(trimethylsilyl)methane a column temperature of 220° was used.

Melting points

The $(Me_3Si)_3CMMe_3$ compounds all gradually took on a glassy appearance above about 300° when heated in sealed tubes; the compound with M = Sn melted with decomposition at 354–356°, but the other two did not melt below 360°. All sublimed readily in tubes open to the air.

Metallation of tris(trimethylsilyl)methane

Tris(trimethylsilyl)methane (11.5 g, 0.050 mole) in THF (100 ml) was added to a solution of methyllithium (0.060 mole) prepared from bromomethane and lithium in ether (30 ml), and the reaction mixture was boiled under reflux. The progress of the metallation was followed by measurement of the amount of methane evolved, and also by withdrawing aliquots (0.5 ml), treating them first with chlorotrimethylsilane (0.5 ml) then with water, and measuring the relative peak heights in GLC for the compounds $(Me_3Si)_4C$ and $(Me_3Si)_3CH$. Metallation had ceased after 6 h. In another

reaction, in which the reactants were mixed and allowed to stand at room temperature, metallation had ceased after 20 h.

Stability of [tris(trimethylsilyl)methyl]lithium

A mixture of tris(trimethylsilyl)methane (9.28 g, 0.040 mole), methyllithium (20 ml of 1.8 *M* solution in ether), and THF (80 ml) was boiled under reflux for 3.5 h. During a further 30 min the ether was slowly fractionated out of the reaction mixture until the boiling point of distillate reached 66–67°. More THF (100 ml) was added to the reaction mixture which was then divided into two portions. One of these was maintained at room temperature, while the other was boiled under reflux by immersion of the container in an oil bath at 90°. Samples were withdrawn from each at appropriate intervals and were analysed for organolithium content by the double titration procedure using 1,2-dibromoethane[14]. The concentrations of the organolithium reagent derived in this way are given in Table 1*.

TABLE 1

STABILITY OF [TRIS(TRIMETHYLSILYL)METHYL]LITHIUM IN THF

Time	$[(Me_3Si)_3CLi]^a$	
(h)	At reflux	At 20°
0[b]	0.154	0.154
19	0.125	0.152
41	0.104	
72	0.070	0.149
92	0.043	0.145
171	0.017	0.131

[a] Molar concentration of $(Me_3Si)_3CLi$ in solution, as determined by the double titration method[14].
[b] This first determination was made after the preparation had been completed and the ether had been distilled from the mixture (ca. 4 h after the start of the preparation).

Syntheses with [tris(trimethylsilyl)methyl]lithium

Tetrakis(trimethylsilyl)methane. Chlorotrimethylsilane (7.0 g, 0.060 mole) was added to [tris(trimethylsilyl)methyl]lithium, prepared from tris(trimethylsilyl)-methane (11.5 g, 0.050 mole) and methyllithium (0.060 mole) as described above. The mixture was boiled under reflux for 10 min, then added to a mixture of ice and solid ammonium chloride. Organic products were extracted with ether, the ethereal layer was dried (Na_2SO_4), and solvent was evaporated off to leave a solid which was recrystallised from methanol to give tetrakis(trimethylsilyl)methane (12 g, 79%), m.p. >360° (*cf.* ref. 2). (Found: C, 51.4; H, 11.8. $C_{13}H_{36}Si_4$ calcd.: C, 51.2; H, 11.9%.) The NMR spectrum showed a singlet at τ 9.77 (Me_3Si).

[Tris(trimethylsilyl)methyl]dimethylsilane. Chlorodimethylsilane (3.0 g, 0.032 mole) was added to a solution of the organolithium reagent prepared from tris(tri-

* The concentration of the organolithium compound at the time of the first analysis corresponds with a yield of only about 60%. To some extent this may reflect the inaccuracy of the absolute values given by the titration method, but it is mainly to be attributed to the use of only one molar proportion of methyllithium in the preparation.

methylsilyl)methane (5.5 g, 0.024 mole) and methyllithium (0.03 mole) in THF/ether (70 ml). The mixture was boiled under reflux then worked up as described for tetrakis-(trimethylsilyl)methane, to give, after crystallisation from ethanol, [tris(trimethylsilyl)methyl]dimethylsilane (nc) (6.0 g, 87%), m.p. >320° (sealed tube). (Found: C, 49.9; H, 11.6. $C_{12}H_{34}Si_4$ calcd.: C, 49.6; H, 11.8%.) The NMR spectrum showed singlets at τ 9.90 (Me_3Si) and τ 9.80 (Me_2Si), and a septet at τ 5.93 (Si–H).

[Tris(trimethylsilyl)methyl]trimethylgermane and -stannane. Bromotrimethylgermane (10 g, 0.050 mole) was added to [tris(trimethylsilyl)methyl]lithium prepared from tris(trimethylsilyl)methane (11.5 g, 0.050 mole) and methyllithium (0.060 mole) in THF/ether (100 ml). The mixture was boiled under reflux for 30 min then added to a mixture of ice and ammonium chloride. The organic layer was separated, dried, and evaporated to dryness, and the solid obtained was recrystallised from ethanol to give [tris(trimethylsilyl)methyl]trimethylgermane (nc) (13.0 g, 75%), m.p. >360° (Found: C, 44.5; H, 10.7. $C_{13}H_{36}GeSi_3$calcd.: C, 44.7, H, 10.4%.) The NMR spectrum showed singlets at τ 9.87 (Me_3Si) and τ 9.63 (Me_3Ge).

A similar reaction on a 0.025 molar scale with bromotrimethylstannane, involving 1 h of boiling under reflux, gave crude material which was recrystallised from ethanol and sublimed in vacuum to give [tris(trimethylsilyl)methyl]trimethylstannane (nc) (6.1 g, 62%), m.p. 354–356° (decompn.). (Found: C, 39.6; H, 9.0. $C_{13}H_{36}Si_3Sn$ calcd.: C, 39.5; H, 9.2%.) The NMR spectrum showed singlets at τ 9.82 (Me_3Si) and τ 9.75 (Me_3Sn).

Tris(trimethylsilyl)acetic acid. A solution of [tris(trimethylsilyl)methyl]-lithium made from tris(trimethylsilyl)methane (5.5 g, 0.024 mole) and methyllithium (0.030 mole) in THF/ether (70 ml) was added to an excess of ether-washed solid carbon dioxide. The mixture was set aside at room temperature for 12 h, and then acidified with dilute sulphuric acid (20 ml). Organic products were taken up in light petroleum and the organic acid was extracted from the petroleum with 10% aqueous sodium hydroxide. The combined aqueous extracts were washed with light petroleum (2 × 50 ml), and traces of petroleum and other organic solvents were removed from the aqueous layer by brief rotary evaporation. This layer was then acidified, and the precipitate was filtered off and recrystallised twice from ethanol to give tris(trimethylsilyl)acetic acid (nc) (5.3 g, 81%), m.p. 105°. (Found: C, 47.85; H, 10.4. $C_{11}H_{28}O_2Si_3$ calcd.: C, 47.8; H, 10.2%.) The NMR spectrum showed singlets at τ 9.86 (Me_3Si) and τ 8.43 (CO_2H).

1,1,1-Tris(trimethylsilyl)ethane. Iodomethane (3.1 g, 0.022 mole) was added to a solution of [tris(trimethylsilyl)methyl]lithium, made from tris(trimethylsilyl)-methane (0.020 mole) and methyllithium (0.025 mole) in THF (50 ml) and ether (12 ml). The mixture was stirred at room temperature for 12 h then added to a mixture of crushed ice and 2 *N* hydrochloric acid. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layers were dried. Ether and THF were distilled off, and the residue (3.1 g) was recrystallised from methanol to give material of m.p. 140–144°, which contained a small amount of tris(trimethylsilyl)methane. Recrystallisation from methanol, followed by drying under vacuum (80°/100 mm), gave 1,1,1-tris(trimethylsilyl)ethane (2.45 g, 50%), m.p. 155–157° (lit.[2], m.p. 115°). (Found: C, 53.1; H, 12.5. $C_{11}H_{30}Si_3$ calcd.: C, 53.6; H, 12.2%.) The NMR spectrum had the correct integration pattern, and showed singlets at τ 8.93 (CH_3) and τ 9.94 (Me_3Si).

Chlorotris(trimethylsilyl)methane [tris(trimethylsilyl)methyl chloride]

A solution of bis(trimethylsilyl)dichloromethane[15] (50 g, 0.22 mole) in THF (200 ml), ether (25 ml), and light petr. (10 ml, b.p. 40–60°) mixture was cooled to −110° in a nitrogen slush bath, and n-butyllithium (150 ml of a 1.6 *M* solution in hexane), precooled to −80°, was added dropwise during 1 h. Chlorotrimethylsilane (35 g, 0.30 mole) was then added, and the reaction mixture was allowed to warm to room temperature during 12 h. It was then added to a mixture of ice and ammonium chloride, and the organic layer was separated, dried, and distilled until a semi-solid appeared in the still head. The residue in the distillation flask was then recrystallised several times from methanol, and finally from light petroleum (b.p. 40–60°), to give chlorotris(trimethylsilyl)methane (nc) (40 g, 69%), m.p. 139–141°. (Found: C, 45.3; H, 9.9. $C_{10}H_{27}ClSi_3$ calcd.: C, 45.0; H, 10.2%.) The NMR spectrum showed a singlet at τ 9.83 (Me_3Si).

Formation of [tris(trimethylsilyl)methyl]lithium from tris(trimethylsilyl)methyl chloride

(*a*). *With lithium metal.* A solution of tris(trimethylsilyl)methyl chloride (2.7 g, 0.010 mole) in THF (20 ml) was added to lithium chippings (0.7 g, 0.1 g-atom) in THF (20 ml) and ether (8 ml). The reaction mixture was boiled under reflux for 6 h, then added to water. The organic layer was separated, dried, and analysed by GLC, which revealed that much tris(trimethylsilyl)methane had been formed and that no unchanged tris(trimethylsilyl)methyl chloride remained.

(*b*). *With n-butyllithium/TMEDA.* n-Butyllithium (9 ml of a 1.5 *M* solution in hexane) was added at 0° to a cooled solution of tris(trimethylsilyl)methyl chloride (2.7 g, 0.010 mole) in ether (20 ml) and TMEDA (1 ml). The mixture was stirred at room temperature for 3 h, then added to water. The organic layer was separated, dried, and analysed by GLC, which revealed that much tris(trimethylsilyl)methane had been formed and that no tris(trimethylsilyl)methyl chloride remained. No products of side reactions were detected.

(*c*). *With methyllithium.* A solution of methyllithium (0.015 mole) in THF/ether (9 ml) was added to tris(trimethylsilyl)methyl chloride (2.7 g, 0.010 mole) in THF (10 ml) and the reaction mixture was stirred at −10° for 3 h. Work up and GLC analysis gave results as under (b).

Treatment of tetrakis(trimethylsilyl)methane with methylmagnesium bromide

The compound $(Me_3Si)_4C$ (2.0 g) was added to a large excess of methylmagnesium bromide (ca. 0.10 mole) in ether (80 ml) and the mixture was refluxed for 20 h. A portion was treated with water, and subsequent GLC analysis showed that no tris(trimethylsilyl)methane had been formed. Unchanged tetrakis(trimethylsilyl)methane (1.9 g, 95%) was recovered.

Treatment of tetrakis(trimethylsilyl)methane with methanolic sodium methoxide

Sodium (1.1 g) was dissolved in anhydrous methanol (35 ml) and tetrakis(trimethylsilyl)methane (1.06 g) was added. The mixture was refluxed for 22 h, then cooled and diluted with water. Filtration and drying gave unchanged tetrakis(trimethylsilyl)methane (1.03 g, 97%).

Metallation of bis(trimethylsilyl)methane

A mixture of bis(trimethylsilyl)methane[2] (3.00 g), n-decane (1.01 g, included as internal standard), methyllithium (10 ml of 1.8 *M* solution in ether), and THF (50 ml) was refluxed for 20 h. To the resulting pale yellow solution was added chlorotrimethylsilane (5 ml), and the mixture was stirred for 3 h then treated with ice/water containing ammonium chloride. Extraction with ether, followed by drying (Na_2SO_4) of the extract, removal of the ether through a short fractional distillation column, and GLC analysis of the residue showed that tris(trimethylsilyl)methane had been formed in $21 \pm 1\%$ yield, and that $79 \pm 2\%$ of the bis(trimethylsilyl)methane remained unchanged.

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