

The preparation and analysis of the phenyldimethylsilyllithium reagent and its reaction with silyl enol ethers

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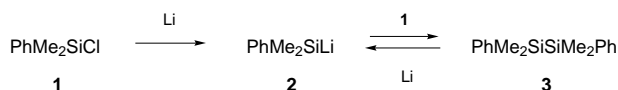
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Phenyldimethylsilyllithium is formed from lithium and phenyldimethylsilyl chloride by slow cleavage of the Si–Si bond of 1,1,2,2-tetramethyl-1,2-diphenyldisilane after the rapid formation of the disilane. 1,1,2,2-Tetramethyl-1,2-diphenyldisiloxane, produced from the silyl chloride by reaction with oxides and hydroxides on the lithium metal surface, is cleaved by dimethyl(phenyl)silyllithium to give lithium dimethyl(phenyl)silanoxide. Dimethyl(phenyl)silyllithium reacts with 1,2-dibromoethane to give dimethyl(phenyl)silyl bromide, which is so rapidly consumed by excess silyllithium reagent that it does not interfere with the double titration used to measure its concentration. Dimethyl(phenyl)silane, produced by protonation of the silyllithium reagent, is also consumed by the silyllithium reagent to give 1,1,2,2-tetramethyl-1,2-diphenyldisilane, which regenerates the silyllithium reagent, as long as lithium is still present. By-products in the preparation of dimethyl(phenyl)silyllithium include 1,3-diphenyl-1,1,2,2,3,3-hexamethyltrisilane, dimethyldiphenylsilane and 1,4-bis[dimethyl(phenyl)silyl]benzene. Dimethyl(phenyl)silyllithium displaces the silyl group from the *tert*-butyldimethylsilyl enol ether of cyclohexanone to give the lithium enolate under relatively mild conditions.

Introduction

For many years we, and countless others, have used the lithium bis(phenyldimethylsilyl)cuprate reagent,¹ and its precursor phenyldimethylsilyllithium **2**,² as nucleophiles for introducing a silyl group into a wide range of organic structures. For all our experience with the phenyldimethylsilyllithium reagent,^{1,3} there remained some uncertain features in its preparation and analysis. Gilman established that phenyldimethylsilyllithium **2** could be prepared by stirring phenyldimethylsilyl chloride **1** with lithium in THF (Scheme 1). He also showed that silyl



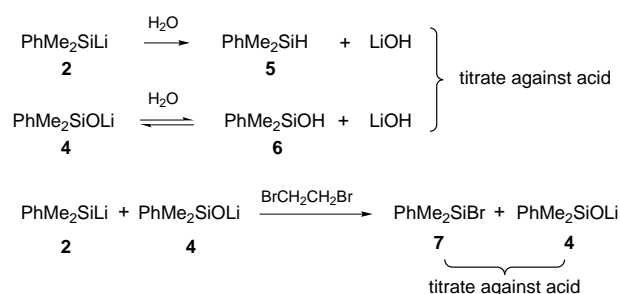
Scheme 1

chlorides in general react with lithium in THF to give initially a silyllithium reagent, but these react with more of the silyl chloride to give disilanes. The disilane can then be cleaved with more lithium to give the silyllithium reagent, but only when there is a phenyl group attached to the silicon, as in the conversion of the disilane **3** to the silyllithium reagent **2**. We have shown that the cleavage is remarkably sensitive to the presence of substituents on the phenyl ring,⁴ with *p*-tolyl dimethylsilyl chloride giving a disilane, which is not cleaved by lithium.

We were aware of six uncertainties in the chemistry of phenyldimethylsilyllithium.

(i) It had not been firmly established whether Gilman's preparation of the phenyldimethylsilyllithium reagent **2** was successful *only* because the disilane **3** could be cleaved, as seemed probable, or whether it was easy to make because the rate of formation of the silyllithium reagent from the silyl chloride **1** was faster than its reaction with the silyl chloride to give the disilane **3**. It is known that tris(*o*-tolyl)silyl chloride² and mesityldimethylsilyl chloride⁵ give silyllithium reagents when stirred with lithium, and it seemed possible that this success with a substituted phenyl ring might be because the coupling of the silyllithium reagent with the silyl chloride was slow.

(ii) Secondly, there was an anomaly in the analytical method⁶ most commonly used for measuring the concentration of the



Scheme 2

silyllithium reagent. Typically, we carry out a double titration for organometallic compounds (Scheme 2), quenching one aliquot with water and one with 1,2-dibromoethane followed by water, and titrating each against acid, with the difference giving the concentration of the silyllithium reagent **2**. Although the reaction of an *alkyl* lithium reagent with dibromoethane gives an inoffensive *alkyl* bromide,⁷ the product in our case is presumably phenyldimethylsilyl bromide **7**, which would hydrolyse in the water to create an equivalent of hydrobromic acid. Any acid created in this way would cause us to underestimate the concentration of residual base and to overestimate the concentration of silyllithium reagent. Furthermore, the formation of acid after the addition of the dibromoethane should have been obvious—there is always more silyllithium reagent than residual base, and we should have obtained an acidic solution. This never happened.

(iii) Our estimates of the concentration of silyllithium reagent showed a rapid increase over the first 1–4 hours of stirring with lithium, but the time taken to reach a maximum concentration varied between 5 hours and several days. It was not obvious what was happening during the long stirring, following the first surge of silyllithium formation.

(iv) The silyllithium solutions appeared to maintain their titre for silyllithium over many weeks and even months, although using old solutions rarely gave good yields in whatever reaction we were trying. The titre of old solutions merely revealed an increase in residual base, which presumably interfered with our reactions in some way.

Table 1 ^1H NMR chemical shifts δ (using C_6D_6 as internal lock for spectra in THF) for the SiMe signals of the various silicon species

Compound	$\delta_{\text{H}}(\text{CDCl}_3)$	$\delta_{\text{H}}(\text{THF})^b$
1 PhMe_2SiCl	—	0.75
2 PhMe_2SiLi	—	0.23
3 $(\text{PhMe}_2\text{Si})_2$	0.32	0.42
4 $\text{PhMe}_2\text{SiOLi}$	—	0.32
5 PhMe_2SiH	0.37 ^a	0.46 ^a
6 PhMe_2SiOH	0.42	0.38 ^c
7 PhMe_2SiBr	0.92	—
8 $(\text{PhMe}_2\text{Si})\text{O}$	0.33	0.43
9 $(\text{PhMe}_2\text{Si})_2\text{Me}_2\text{Si}$	0.30, 0.10	—
10 Ph_2SiMe_2	0.57	—
11 $\text{PhMe}_2\text{Si-}p\text{-C}_6\text{H}_4\text{-SiMe}_2\text{Ph}$	0.55	—

^a Doublet, J 3.9 Hz. ^b Referenced to the THF signal as δ 1.85. ^c Doublet, J 0.5 Hz.

(v) When we add aqueous ammonium chloride to quench our reaction mixtures, which often use an excess of silyllithium reagent (or a cuprate or zincate derived from it), we rarely detect phenyldimethylsilane **5**, which has a characteristic septet (J 3.9 Hz) at δ 4.62 (in THF solution). Instead we obtain non-polar material, which appears to be a mixture of diphenyltetramethyldisilane and diphenyltetramethyldisiloxane.

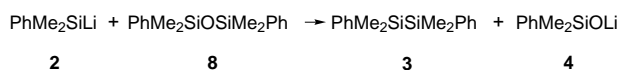
(vi) The colour of phenyldimethylsilyllithium solutions is red or reddish brown when derived from the silyl chloride and greenish when derived by cleavage of the disilane. It is known that the colour is not that of the silyllithium reagent itself, since it can be quenched with a trace of oxygen without affecting the ^1H and ^7Li NMR signals of the silyllithium reagent.⁸ The colour is associated with a quintet pattern in the EPR spectrum, assigned to the radical anion of a 1,4-disilylated benzene.^{8,9} Is this a correct assignment and where did such a by-product come from?

Having published some of our work in preliminary form,¹⁰ we report here our answers, as far as they go, in full, together with the useful corollary that the silyllithium reagent generates a lithium enolate from a silyl enol ether more rapidly than methylithium does.

Results and discussion

The phenyldimethylsilyllithium reagent

We monitored the reaction in THF by ^1H NMR spectroscopy, following the growth and diminution of the SiMe signals from the various species present (Table 1). The signal from phenyldimethylsilyl chloride **1** disappeared over a few minutes at 0 °C, and the signal from diphenyltetramethyldisilane **3** grew at an equal rate. Clearly the slow step in the formation of the silyllithium reagent **2** is the cleavage of the disilane, as expected. We also see the appearance of the signal from the disiloxane **8**, some of it derived from the more or less unavoidable hydrolysis of the silyl chloride before we made up the reaction mixture, and some of it derived, as soon as we mixed the reagents, from the coat of oxides and/or hydroxides on the lithium. We then see its disappearance, starting to take place as soon as the silyl chloride has been consumed, to be replaced by the signal from lithium phenyldimethylsilyloxide **4** (Scheme 3). This reaction takes place as fast as the silyllithium



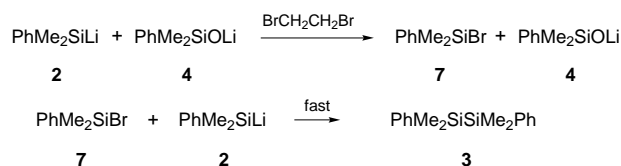
Scheme 3

is being formed, and is typically complete within 30 minutes. During these two phases, wisps of red colour flow off the lithium, rapidly to be quenched as disilane forms. The full red

colour typical of the reagent then develops more slowly, usually starting 30 minutes into the reaction, and approaching maximum intensity after 4–6 hours. During this period, we saw the gradual development of the ^1H NMR signal from the silyllithium reagent and the disappearance of the signal from the disilane.

Lithium fresh from the bottle does not always cleave the disilane, presumably because of the protective coat of oxides and/or hydroxides. The fast initial reaction with the silyl chloride, on the other hand, cleans the surface, causing the appearance in the NMR spectrum of the signal from diphenyltetramethyldisiloxane. We find that the reaction between diphenyltetramethyldisilane and lithium fresh from a bottle can be initiated by adding a little silyl chloride, either phenyldimethylsilyl chloride or trimethylsilyl chloride, to clean the surface of the lithium. *We add our experience to that of others,¹¹ in urging that this is a simple way to prepare active metals for the organometallic chemistry of common main-group metals like lithium, zinc and magnesium.* Whereas traditional activation¹² of these metals, by sonication, or by treatment with alkyl halides or iodine, probably works because reaction with the underlying metal mechanically dislodges the oxide film, a silyl halide will combine with it chemically and remove it completely.

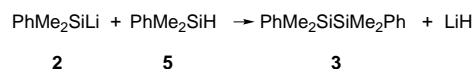
The rapidity of the reaction between the silyllithium reagent and the silyl chloride answered our second question too—as dibromoethane is added to the silyllithium reagent **2**, and silyl bromide **7** is formed, we can now expect it to be quenched rapidly by more of the silyllithium reagent. When we followed the reaction by ^1H NMR spectroscopy, no signal from the silyl bromide **7** appeared on addition of dibromoethane, but we did see the immediate appearance of the signal from the disilane **3** (Scheme 4).



Scheme 4

The slow continuous development of silyllithium reagent over hours, is not so easily explained. One possibility is that lithium phenyldimethylsilyloxide **4** reacts very slowly with the silyllithium reagent to give silane **5** and lithium oxide, but we were unable to demonstrate that this reaction is taking place. We made up a mixture of these reagents, but saw the signals in the ^1H NMR spectra simply grow broader, making a definitive statement risky. Thus it is likely that the variable slow rise in the titre reflects only the different rates of stirring and the variable quality of the lithium used over the years.

The answer to our fourth question is that any proton source reacts with the silyllithium reagent to give phenyldimethylsilane **5**, which then reacts with the silyllithium reagent to give the disilane **3** and lithium hydride (Scheme 5). The disilane in turn



Scheme 5

is cleaved by lithium (Scheme 1) to regenerate the silyllithium reagent, and all that happens to the titre, as long as there is an excess of lithium present, is an increase in residual base. We confirmed the reasonableness of this pathway by adding the silyllithium reagent to phenyldimethylsilane, and observing the formation of disilane within 15 minutes at room temperature.

However, water is not the only potential contaminant—

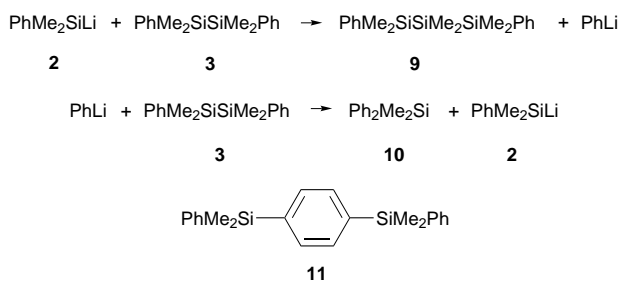
oxygen can be expected to give successively silyl peroxide anion and silanoxide, which will remove silyllithium and contribute to residual base. We do not know why this is not a conspicuous problem, but there is some evidence that the reaction with oxygen is not straightforward. We quenched the silyllithium reagent **2** with oxygen, and observed the formation of the silanol **6** in 26% yield, the silane **5** in 3% yield and disilane **3** in 38% yield, similar to Gilman's results with triphenylsilyllithium and oxygen.¹³ Since disilane is formed, it will regenerate the silyllithium reagent in the presence of lithium, and the incursion of oxygen is not as serious as one might at first suppose.

The observation that silane **5** is easily cleaved by the silyllithium reagent also provides the answer to our fifth question. The phenyldimethylsilane that is presumably formed in an aqueous quench is itself unstable, both towards any residual silyllithium reagent not yet quenched, and towards reaction with hydroxide ion in the alkaline solution, giving silanoxide and hence the disiloxane to a greater or lesser extent, depending upon the precise conditions of the workup. The reaction with hydroxide ion is known to be too fast in aqueous media to follow the kinetics.¹⁴

We checked that the development in intensity of the signals assigned to the silyllithium reagent **2** and to the silanoxide **4** corresponded to the concentration of the lithium reagent and of residual base that we were measuring by titration. We carried out three runs with, successively, a good sample of the silyl chloride **1**, a 2:1 mixture of the silyl chloride **1** with the disiloxane **8**, and a 1:2 mixture. The agreement between the two methods of estimating concentration was moderately good, with the concentration of the silyllithium reagent measured by NMR spectroscopy consistently about 10–15% lower than the value from titration, but the concentration of lithium phenyldimethylsilanoxide measured by NMR spectroscopy and of residual base measured by titration agreed rather better ($\pm 5\%$).

By-products in the formation of the phenyldimethylsilyllithium reagent

We also saw weak SiMe signals not assignable to any of the species mentioned so far. Accordingly, we kept a mixture of the silyllithium reagent **2** and the disilane **3** at 4 °C for 7 days, and examined the mixture of products by GC–MS. One of the products was 1,3-diphenyl-1,1,2,2,3,3-hexamethyltrisilane **9**, a plausible product if the silyllithium reagent attacks diphenyltetramethyldisilane at silicon,¹⁵ and displaces phenyllithium (Scheme 6). Phenyllithium will react in turn with disilane **3** to



Scheme 6

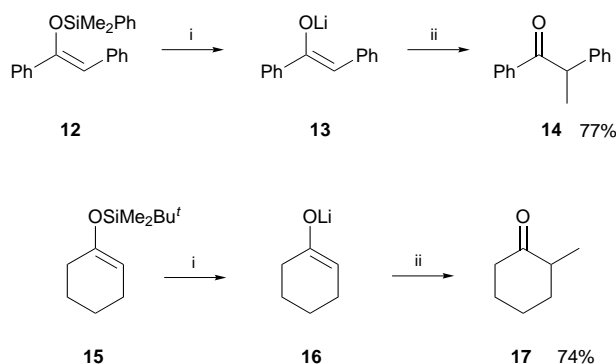
give dimethyldiphenylsilane **10**, and we do indeed observe the presence of this compound both in the ¹H NMR spectrum and by GC–MS. An alternative route to the silane **10** is by attack of the phenyllithium on the trisilane **9**, this time displacing 1-lithio-2-phenyl-1,1,2,2-tetramethyldisilane. However, the signals from the trisilane and the silane **10** were always present in constant proportions, suggesting that the latter pathway is not important. Pathways like these are almost certainly responsible for the unexpected formation of pentamethyldisilanyl lithium when hexamethyldisilane is treated with methyl lithium on a large scale.¹⁶ Methyl lithium will first displace trimethylsilyllithium,¹⁷ but on a large scale this reagent will have time to attack the

disilane to give octamethyltrisilane and regenerate methyl lithium, which will attack at silicon in the trisilane to displace pentamethyldisilanyl lithium.

We also detected by GC–MS a significant quantity of 1,4-bis[dimethyl(phenyl)silyl]benzene **11**, identified by comparison with an authentic sample prepared from the silyllithium reagent and 1,4-dibromobenzene. Although we have no evidence for how this substance is formed, it adds support to the assignment^{8,9} of its radical anion as the source of the colour in solutions of the phenyldimethylsilyllithium reagent. Our finding dimethyl(diphenyl)silane **10** in the reaction mixture also provides for the first time a substrate for *para*-coupling¹⁸ with the silyllithium reagent that could lead to this compound.

Cleavage of silyl enol ethers using the phenyldimethylsilyllithium reagent

The speed with which the disiloxane **8** was cleaved by the silyllithium reagent **2** suggested that other ethers might also be cleaved easily, just as triphenylsilyl ethers are cleaved by triphenylsilyllithium.¹⁹ We find that the trimethylsilyl ether of benzyl alcohol is cleaved in THF solution even at –78 °C, with a 30% yield of pentamethyl(phenyl)disilane formed after four hours. More significantly, the silyl enol ether **12** was cleaved within 10 minutes at –78 °C in THF to give the lithium enolate **13**, identified by methylation giving the ketone **14** (Scheme 7).



Scheme 7

Stork and Hudrlik, in their pioneering work on the use of silyl enol ethers as precursors to lithium enolates,²⁰ typically cleaved comparable trimethylsilyl enol ethers with methyl lithium at 0 °C in 1 hour in diethyl ether and in a few minutes in glyme.

Although our reagent works faster, there is little difficulty cleaving trimethylsilyl enol ethers, so we turned to the *tert*-butyldimethylsilyl enol ether **15**. In a comparable case, Stork and Hudrlik found that methyl lithium took 20 h at room temperature, and the reaction had to be carried out in glyme. We find that phenyldimethylsilyllithium cleaves this silyl enol ether in THF within two hours at 20 °C to give the lithium enolate **16**, identified in the ¹H NMR spectrum and by methylation giving 2-methylcyclohexanone **17** in 74% yield together with 1-*tert*-butyl-1,1,2,2-tetramethyl-2-phenyldisilane, in 99% yield. The silyllithium reagent even cleaves the silyl enol ether **15** with a half-life of about eight hours in a 1:4 mixture of THF and diethyl ether. Clearly *phenyldimethylsilyllithium is a powerful reagent for preparing lithium enolates from silyl enol ethers*, avoiding long reaction times and special solvents.

Experimental

Unless otherwise stated, light petroleum refers to the fraction bp 40–60 °C. Ether refers to diethyl ether.

Dimethyl(phenyl)silyllithium **2**

Typically, lithium shot (0.5 g in mineral oil, 70 mmol) was stirred rapidly for 15 min in dry hexane (20 cm³) under argon.

The hexane was removed and the lithium suspended in dry THF (20 cm³). The mixture was stirred rapidly with chlorodimethyl(phenyl)silane (5.0 cm³, 29.8 mmol) at 0 °C for 6 h to give a deep red solution; δ_{H} (270 MHz; THF-[²H₆]benzene, 85:15) 7.45 (2 H, d, *J* 7, *o*-H), 7.06 (2 H, t, *J* 7, *m*-H), 6.87 (1 H, t, *J* 7, *p*-H) and 0.23 (6 H, s, SiMe₂); δ_{C} (THF-[²H₆]benzene, 85:15) 165.3, 133.0, 125.7, 121.9 and 6.9.

1,1,2,2-Tetramethyl-1,2-diphenyldisilane 3

Chlorodimethyl(phenyl)silane **1** (20 cm³, 117 mmol) was stirred with a suspension of hexane-washed lithium shot (0.90 g in mineral oil, 128 mmol) in dry THF (80 cm³) at 0 °C under argon for 4 h. 1,2-Dibromoethane (1 cm³) and water (100 cm³) were added, and the aqueous layer was extracted with ether-hexane (1:1, 2 × 50 cm³). The combined organic layers were washed with brine (50 cm³), dried (MgSO₄) and the solvent evaporated. Distillation (Kugelrohr, oven temperature 120 °C at 1 mmHg) gave the disilane (9.4 g, 59%) as needles, mp 31–35 °C (from hexane at low temperature) (lit.,²¹ mp 35 °C, bp 130–133 °C at 2 mmHg); *R_f* (hexane) 0.40; ν_{max} (Nujol)/cm⁻¹ 1586 (Ph), 1245 (SiMe₂) and 830 (SiMe₂); δ_{H} (250 MHz; CDCl₃) 7.4–7.2 (10 H, m, Ph) and 0.32 (12 H, s, SiMe₂); δ_{C} (CDCl₃) 139.1, 134.0, 128.5, 127.8 and –3.8; *m/z* (CI, NH₄⁺) 288 (20%, M + NH₄⁺); (EI) 270 (15%, M⁺), 197 (20) and 135 (100).

Lithium dimethyl(phenyl)silanoxide 4

Dimethyl(phenyl)silanol **6** (8 mg, 0.05 mmol), (2,2-dimethylpropyl)benzene (0.1 cm³, 0.06 mmol), [²H₆]benzene (0.05 cm³), *n*-butyllithium (2.5 mol dm⁻³ in hexane, 0.02 cm³, 0.05 mmol) and dry THF (0.6 cm³) were mixed in a dry NMR tube under argon. The doublet of silanol **6** at δ_{H} 0.38 (1 H, d, *J* 1.5, SiMe₂) was replaced by the singlet of silanoxide **4**; δ_{H} (270 MHz; THF-[²H₆]benzene 85:15) (partial) 0.32 (6 H, s, SiMe₂).

Dimethyl(phenyl)silanol 6

Sodium hydroxide (0.8 g, 20 mmol), methanol (3 cm³), propan-2-ol (7 cm³) and 1,1,2,2-tetramethyl-1,2-diphenyldisiloxane **8** (2.85 g, 10 mmol) were heated, initially at 50 °C and then at 120 °C to evaporate the solvents. Methanol (15 cm³) was added and the solvents were distilled (bath temperature 120 °C at 15 mmHg). This was repeated three times, the final distillation giving a crude solid on cooling. The solid was dissolved in boiling light petroleum (bp 80–100 °C), hot filtered and evaporated under reduced pressure. Ether (30 cm³) was added and the mixture poured into glacial acetic acid (1.8 cm³), water (30 cm³) and ether (15 cm³). The organic layer was washed with water, dried (MgSO₄) and evaporated under reduced pressure. Distillation (Kugelrohr, oven temperature 115 °C at 15 mmHg) (bp lit.,²² 101–101.5 °C at 14 mmHg) gave the silanol (1.30 g, 43%); *R_f* (EtOAc-hexane, 20:80) 0.26; ν_{max} (film)/cm⁻¹ 3286 (OH), 1253 (SiMe₂), 1119 (SiPh), 866 (SiO) and 829 (SiMe₂); δ_{H} (270 MHz; CDCl₃) 7.6 (2 H, m, *o*-H), 7.4 (3 H, m, *m*- and *p*-H), 1.9 (1 H, br s, OH) and 0.42 (6 H, s, SiMe₂).

1,1,2,2-Tetramethyl-1,2-diphenyldisiloxane 8

Chlorodimethyl(phenyl)silane **1** (10 cm³, 59 mmol) was stirred in water (0.5 cm³), acetone (25 cm³) and saturated sodium hydrogen carbonate solution (40 cm³) for 1 h at 0 °C. An aqueous work-up and distillation (Kugelrohr, oven temperature 170 °C at 5 mmHg) (bp lit.,²³ 135 °C at 2 mmHg) gave the disiloxane (7.5 g, 89%); *R_f* (hexane) 0.40; ν_{max} (film)/cm⁻¹ 1590 (Ph), 1254 (SiMe₂), 1119 (SiPh) and 831 (SiMe₂); δ_{H} (270 MHz; CDCl₃) 7.46 (4 H, m, *o*-H), 7.3 (6 H, m, *m*- and *p*-H) and 0.33 (12 H, s, SiMe₂); δ_{C} (CDCl₃) 139.9, 133.1, 129.3, 127.8 and 0.9; *m/z* (EI) 286 (35%, M⁺), 271 (85), 193 (100) and 89 (25).

1,4-Bis[dimethyl(phenyl)silyl]benzene 11

1,4-Dibromobenzene (1.2 g, 5 mmol), tetrakis(triphenylphosphine)palladium (0.5 g, 0.4 mmol) and dry toluene (40 cm³) were refluxed for 30 min under argon. Dimethyl(phenyl)-

silyllithium (1.0 mol dm⁻³ in THF, 10 cm³, 10.0 mmol) in toluene (20 cm³) was added and the mixture refluxed for 2.5 h. The mixture was cooled to room temperature, quenched with dilute hydrochloric acid (0.3 mol dm⁻³, 50 cm³), extracted with ether (3 × 100 cm³), the organic layers washed with brine (100 cm³), dried (MgSO₄) and evaporated under reduced pressure. Light petroleum (60 cm³) was added precipitating a solid, which was filtered off, and the solution evaporated under reduced pressure. Chromatography (SiO₂, light petroleum) gave the bis-silane **11** (0.59 g, 34%) as needles, mp 56–60 °C (from hexane at low temperature) (lit.,²⁴ 59 °C); *R_f* (light petroleum) 0.18; ν_{max} (Nujol)/cm⁻¹ 1587 (Ph), 1250 (SiMe₂), 1134 (SiPh) and 1115 (SiPh); δ_{H} (250 MHz; CDCl₃) 7.6 (4 H, m, *o*-H), 7.53 (4 H, s, SiC₆H₄Si), 7.3 (6 H, *m*- and *p*-H) and 0.55 (12 H, s, SiMe₂); δ_{C} (CDCl₃) 139.1, 138.1, 134.2, 133.5, 129.1, 127.8 and –2.5; *m/z* (EI) 346 (25%, M⁺), 331 (100), 193 (25) and 143 (30) (Found: M⁺, 346.1583. C₂₂H₂₆Si₂ requires *M*, 346.1573).

Titration of silyllithiums

Following the method of Gilman,⁶ an aliquot of silyllithium solution (typically 1 cm³) was quenched in water (5 cm³) and the basic solution titrated against standardised hydrochloric acid (0.1 mol dm⁻³) using phenolphthalein. A second aliquot was quenched in 1,2-dibromoethane (5 cm³), shaken vigorously with water (5 cm³) and the mixture titrated against hydrochloric acid (0.1 mol dm⁻³). The silyllithium reagent was typically 1 mol dm⁻³.

Reaction of silyl chloride 1 with lithium observed by ¹H NMR spectroscopy

Hexane-washed lithium shot (30 mg, 5 mmol), silyl chloride **1** (0.1 cm³, 0.6 mmol), (2,2-dimethylpropyl)benzene (0.1 cm³, 0.6 mmol), dry THF (1 cm³) and [²H₆]benzene (0.05 cm³) were sonicated in an NMR tube under argon, maintaining the sonicator bath below 10 °C, and recording the ¹H NMR spectra at intervals (Table 1).

Comparison of molarities of silyllithium 2 measured by titration and ¹H NMR spectroscopy

Hexane-washed lithium shot (three molar equivalents based on silicon content), silyl chloride **1**, disiloxane **8**, (2,2-dimethylpropyl)benzene (1.51 g, 10.2 mmol) and dry THF (10 cm³) were stirred rapidly for 6 h at 0 °C under argon. Aliquots (1 cm³) of the silyllithium solution were titrated against hydrochloric acid (0.1 mol dm⁻³). The ¹H NMR spectra were acquired from another aliquot (0.6 cm³) added to [²H₆]benzene (0.05 cm³). Two samples were kept for 90 d at –20 °C. The molarities of the silyllithium reagent and residual base were calculated from the integrals of the peaks for **2** at δ 0.26 (6 H, s, SiMe₂), for **4** at δ 0.38 (6 H, s, SiMe₂) and for (2,2-dimethylpropyl)benzene at δ 1.00 (Table 2).

Reaction of silyllithium 2 with 1,2-dibromoethane

Method A. Hexane-washed lithium shot (0.5 g, 83 mmol), silyl chloride **1** (1.5 cm³, 8.86 mmol), disiloxane **8** (2.0 cm³, 6.66 mmol), (2,2-dimethylpropyl)benzene 1.2 cm³, 9.70 mmol) and dry THF (14 cm³) were stirred for 6 h at 0 °C under argon. The ¹H NMR spectra of aliquots (0.6 cm³) in [²H₆]benzene (0.05 cm³) were acquired after 0.5 and 6 h. 1,2-Dibromoethane (0.04 cm³, 0.46 mmol) was added to the NMR tube and the spectrum reacquired. The signal from the silyl chloride **1** had disappeared after 0.5 h, the signal from the disilane **3** disappeared after 6 h, the signal from the silanoxide **4** remained constant throughout, the signal from the silyllithium reagent **2** grew between 0.5 and 6 h, and disappeared after the treatment with dibromoethane, and signals for the disilane **3** and ethane (δ 5.10) appeared.

Method B. 1,2-Dibromoethane (1 cm³) was added to silyllithium **2** (0.75 mol dm⁻³ solution in THF, 7.5 cm³, 5.6 mmol) under argon. Ether (20 cm³) was added at 0 °C, and the mixture filtered through Florisil. The solvent was evaporated under

Table 2 Comparison of the concentration of silyllithium reagent by double titration and by integration in the ^1H NMR spectra

Reagents	Conc. silyllithium (mol dm^{-3})		Conc. residual base (mol dm^{-3})		Conc. after 90 days ^a	
	By titration	By ^1H NMR	By titration	By ^1H NMR	Silyllithium	Res. base
Silyl chloride 1 (2.50 cm^3 , 14.7 mmol) and no disiloxane	0.76	0.71	0.01	0.02	0.99	0.59
Silyl chloride 1 (1.25 cm^3 , 7.3 mmol) and disiloxane 8 (1.6 g, 3.5 mmol)	0.77	0.62	0.41	0.42	0.81	1.66
Silyl chloride 1 (1.25 cm^3 , 7.3 mmol) and disiloxane 8 (4.27 g, 14.9 mmol)	0.65	0.50	0.58	0.62	—	—

^a Measured by titration in mol dm^{-3} .

reduced pressure, and the residue chromatographed (SiO_2 , hexane) to give a mixture of disilane **3** (45%, ^1H NMR), identical (TLC, ^1H NMR, GC) to an authentic sample, and 1,3-diphenyl-1,1,2,2,3,3-hexamethyltrisilane²⁵ **9** (8%, ^1H NMR); R_f (hexane) 0.32; δ_{H} (250 MHz; CDCl_3) 7.6–7.0 (10 H, m, Ph), 0.30 (12 H, s, SiMe_2Ph) and 0.10 (6 H, s, SiSiMe_2Si); m/z (EI) 328 (5%, M^+), 313 (10), 193 (30), 135 (100), 116 (60) and 73 (20).

The reaction of silane **5** and silyllithium **2**

Dimethyl(phenyl)silyllithium (1.06 mol dm^{-3} in THF, 0.31 cm^3 , 0.33 mmol) was added to dimethyl(phenyl)silane (0.05 cm^3 , 0.33 mmol), (2,2-dimethylpropyl)benzene (0.05 cm^3) and [$^2\text{H}_6$]-benzene (0.05 cm^3) in dry THF (0.5 cm^3) under argon in a dry NMR tube. The ^1H NMR spectrum was acquired after 15 min at room temperature and after standing for 16 h, when a white precipitate (probably lithium hydride) had precipitated. Quantitative conversion to disilane **3** was observed [^1H NMR, by comparison with the integral of the peak at δ 1.00 from (2,2-dimethylpropyl)benzene] after 16 h, with most of the reaction (*ca.* 80%) complete within 15 min. Carbon dioxide was bubbled through the mixture for 1 min, the mixture washed with sodium hydroxide (5%, 1 cm^3), the organic layer was dried (MgSO_4) and evaporated under reduced pressure to give the disilane **3** (65 mg, 74%) as an oil, identical (IR, ^1H NMR, GC) to an authentic sample.

The reaction of silyllithium **2** with disilane **3**

Dimethyl(phenyl)silyllithium (0.95 mol dm^{-3} in THF, 3.2 cm^3 , 3.0 mmol) and disilane **3** (0.27 g, 1.0 mmol) were kept for 8 d at 4°C . Carbon dioxide was bubbled through the mixture for 1 min, ether (15 cm^3) was added, the solution washed with sodium hydroxide (5% in H_2O , $3 \times 10 \text{ cm}^3$) and the organic layer dried (MgSO_4) and evaporated under reduced pressure. ^1H NMR and GC analysis of the residue showed the presence of the following compounds (yields in mmol by ^1H NMR spectroscopy, based on total silicon content): 1,2-diphenyltetramethyldisilane **3** (2.2 mmol, 55%), identical (^1H NMR, GC, MS) to an authentic sample, 1,3-diphenyl-1,1,2,2,3,3-hexamethyltrisilane **9** (0.4 mmol, 10%), identical (^1H NMR, GC) with another sample, dimethyl(diphenyl)silane²⁶ **10** (0.4 mmol, 10%); R_f (hexane) 0.32; δ_{H} (250 MHz; CDCl_3) 7.6–7.0 (10 H, m, Ph), 0.57 (6 H, s, SiMe_2); m/z (EI) 212 (15%, M^+), 197 (100), 135 (15), 105 (20) and 77 (10), and 1,4-bis[dimethyl(phenyl)silyl]benzene **11** (1 mmol, 25%), identical (δ_{H} 0.55, δ_{C} -2.5, and MS) to an authentic sample, and no trace of benzoic acid.

The reaction of silyllithium **2** with oxygen

Oxygen was bubbled through a solution of silyllithium **2** (1.04 mol dm^{-3} in THF, 0.50 cm^3 , 0.52 mmol) and (2,2-dimethylpropyl)benzene (0.05 cm^3 , 0.29 mmol) at 0°C for 1 min, the red colour rapidly disappearing. Water (5 cm^3) was added, the mixture extracted with ethyl acetate (5 cm^3), the organic layer dried (MgSO_4) and evaporated under reduced pressure. GC analysis

showed the presence of [yields based on the (2,2-dimethylpropyl)benzene]: dimethyl(phenyl)silane **5** (2.5%), dimethyl(phenyl)silanol **6** (26%), dimethyl(diphenyl)silane **10** (6%, unstandardised), 1,1,2,2-tetramethyl-1,2-diphenyldisilane **3** (38%) and 1,1,2,2-tetramethyl-1,2-diphenyldisiloxane **8** (0.3%).

1,2-Diphenyl-1-[dimethyl(phenyl)silyloxy]ethene **12**

1,2-Diphenylethanone (0.42 g, 2.2 mmol) in dry THF (4 cm^3) was refluxed with hexane-washed sodium hydride (60% dispersion in oil, 0.20 g, 5 mmol) in dry THF (6 cm^3) under argon for 3 h. Dry triethylamine (0.46 cm^3 , 3.2 mmol) and chlorodimethyl(phenyl)silane **1** (0.55 cm^3 , 3.2 mmol) were added at room temperature, and the mixture was stirred for 15 min, diluted with ether (30 cm^3), washed with cold saturated sodium hydrogen carbonate solution ($3 \times 20 \text{ cm}^3$), brine (20 cm^3), dried (MgSO_4) and evaporated under reduced pressure. Rapid chromatography (SiO_2 , EtOAc–light petroleum, 2:98) gave the *silyl enol ether* **12** (0.44 g, 60%) (*Z*-**12**:*E*-**12**, >99:1) as an oil; R_f (EtOAc–light petroleum, 2:98) 0.33; ν_{max} (film)/ cm^{-1} 1630 ($\text{C}=\text{C}$), 1600 (Ph) and 1592 (Ph); δ_{H} (250 MHz; CDCl_3) 7.7–7.2 (15 H, m, Ph and SiPh), 6.16 (1 H, s, =CH) and 0.34 (6 H, s, SiMe_2); δ_{C} (CDCl_3) 151.0, 139.6, 136.9, 136.6, 133.6, 129.9, 128.9, 128.2, 128.2, 128.1, 127.8, 126.5, 126.2, 111.0 and -0.7; m/z (EI) 330 (90%, M^+), 135 (100) (Found: M^+ , 330.1438. $\text{C}_{22}\text{H}_{22}\text{OSi}$ requires M , 330.1440).

Reaction of silyllithium **2** with silyl enol ether **12**

Dimethyl(phenyl)silyllithium (0.90 mol dm^{-3} in THF, 3.55 cm^3 , 3.2 mmol) was stirred with the silyl enol ether **12** (96 mg, 0.29 mmol) in dry THF (1 cm^3) under argon at -78°C for 10 min. Iodomethane (0.20 cm^3 , 3.2 mmol) was added, the mixture warmed to room temperature, methanol (3 cm^3) and dilute hydrochloric acid (3 mol dm^{-3} , 2 drops) were added and the mixture kept overnight. An aqueous work-up and chromatography (SiO_2 , EtOAc–light petroleum, 8:92) gave the ketone **14** (47 mg, 77%) as a solid, mp 52 – 54°C (from MeOH – H_2O) (lit.,²⁷ 53 – 54°C); R_f (Et_2O –light petroleum, 12:88) 0.33; ν_{max} (film)/ cm^{-1} 1682 ($\text{C}=\text{O}$), 1597 (Ph) and 1582 (Ph); δ_{H} (250 MHz; CDCl_3) 7.97 (2 H, dd, J 7.5 and 1, PhCO *o*-H), 7.5–7.1 (8 H, m, other Ph), 4.70 (1 H, q, J 7.5, *CHMe*) and 1.55 (3 H, d, J 7.5, Me).

1-*tert*-Butyl-1,1,2,2-tetramethyl-2-phenyldisilane

Dimethyl(phenyl)silyllithium (1.1 mol dm^{-3} in THF, 3.0 cm^3 , 3.3 mmol) and *tert*-butylchloro(dimethyl)silane (0.5 g, 3.3 mmol) were kept in dry THF (5 cm^3) under argon at 0°C for 4 h. 1,2-Dibromoethane (0.5 cm^3) was added and the solvents evaporated under reduced pressure. The residue was taken up in hexane (20 cm^3), filtered and the solution evaporated under reduced pressure. Distillation (Kugelrohr, oven temperature 135°C at 21 mmHg) gave the *silane* (485 mg, 59%); R_f (light petroleum) 0.32; ν_{max} (film)/ cm^{-1} 1245 (SiMe_2), 1106 (SiPh) and 831 (SiMe_2); δ_{H} (250 MHz; CDCl_3) 7.52 (2 H, m, *o*-H), 7.36 (3

H, m, *m*- and *p*-H), 0.90 (9 H, s, CMe₃), 0.45 (6 H, s, SiMe₂Ph) and 0.05 (6 H, s, SiMe₂CMe₃); δ_C(CDCl₃) 140.3, 133.8, 128.2, 127.7, 27.6, 17.9, -2.4 and -6.1; *m/z* (EI) 250 (85%, M⁺), 193 (100), 135 (90) and 73 (45) (Found: M⁺, 250.1573. C₁₄H₂₆Si₂ requires *M*, 250.1573).

Reaction of silyllithium 2 with benzyloxy(trimethyl)silane

Dimethyl(phenyl)silyllithium 2 (1.28 mol dm⁻³ in THF, 0.13 cm³, 1.67 mmol), benzyloxy(trimethyl)silane²⁸ (0.03 cm³, 0.15 mmol) and 2,2-dimethyl(phenyl)propane (0.026 cm³, 0.15 mmol) in dry THF (0.5 cm³) were kept under argon at -78 °C for 4 h with occasional shaking. 1,2-Dibromoethane (0.2 cm³, excess) was added, the mixture shaken with water (0.3 cm³), diluted with ether (1 cm³) and the organic layer dried (MgSO₄). GC analysis showed the presence of 1-phenyl-1,1,2,2-pentamethyldisilane (30%, calibrated against 2,2-dimethyl(phenyl)propane).

Reaction of silyllithium 2 with silyl enol ether 15

Dimethyl(phenyl)silyllithium (0.90 mol dm⁻³ in THF, 0.33 cm³, 0.30 mmol) was added to silyl enol ether 15²⁹ (41 mg, 0.19 mmol), [²H₆]benzene (0.1 cm³) and dry [²H₆]THF (0.75 cm³) under argon in a dry NMR tube at room temperature. The ¹H NMR spectra were recorded at intervals, measuring the relative integrals of the peaks at δ 4.95 (1 H, m, 15 =CH) and δ 4.37 (1 H, m, 16 =CH), until none of the starting material was visible (approx. 2.5 h with a half-life of ca. 20 min). Iodomethane (0.2 cm³, excess) was added, the sample diluted with ether (20 cm³), the organic layer washed with sodium metabisulfite solution (10%, 10 cm³) and dried (MgSO₄). GC (a known amount of benzyl alcohol standard) showed 2-methylcyclohexanone (74%) and 2-*tert*-butyl-1-phenyl-1,1,2,2-tetramethyldisilane (99%). Enolate 16; δ_H(250 MHz; [²H₆]THF-[²H₆]benzene, 85:15) 4.37 (1 H, m, =CH) and 2.2–1.5 (8 H, m, cyclohexyl CH₂). The disilane was identical (GC, ¹H NMR spectroscopy) to an authentic sample.

Acknowledgements

We thank the EPSRC and Zeneca Agrochemicals for a CASE award (R. S. R.).

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Paper 7/09111G
Received 22nd December 1997
Accepted 5th February 1998