

The Phenyl dimethylsilyllithium Reagent

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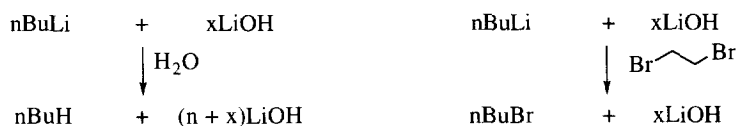
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Abstract The phenyl dimethylsilyllithium reagent can be titrated using the double titration for organolithium reagents, in spite of the formation of silyl bromide on adding dibromoethane; the reagent is different from alkylolithiums in maintaining its titre over a long period even as traces of water seep in.

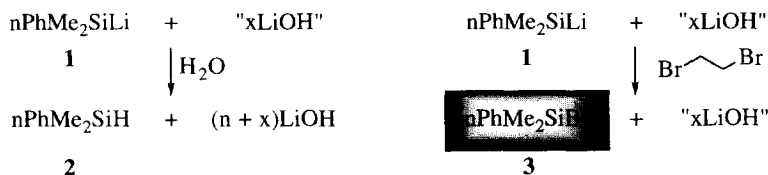
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We, and countless others, have used the phenyl dimethylsilyllithium reagent¹ for many purposes—it is easy to make, simply by stirring the silyl chloride with lithium in THF for a few hours, it reacts efficiently with a wide variety of electrophiles, and it is the basis for making our silylcuprate² and zincate reagents.³ Its preparation, however, does present two puzzles, which have not been commented upon before. The first is about the method of estimating its concentration. Each time we have prepared it, we, and no doubt others, have assessed its concentration by double titration, hitherto adapted uncritically⁴ from one of the standard methods for assessing the concentration of butyllithium.⁵ Typically (Scheme 1), one aliquot of butyllithium is quenched with water to give the total base, expressed as $(n+x)\text{LiOH}$, while another aliquot is quenched first with 1,2-



Scheme 1

dibromoethane, to destroy only the butyllithium, and then with water to give the residual base, expressed as xLiOH . The difference between the two titres, $(n+x) - x$, against acid then gives the concentration of butyllithium. However, when applied to the silyllithium reagent **1** (Scheme 2), this procedure creates the benign



Scheme 2

silane **2** in the quench with water, but the reactive silyl bromide **3** from the quench with dibromoethane. *When this mixture is added to water, it ought to give immediately an acidic solution* by the rapid hydrolysis of the excess (when $n > x$) of silyl bromide. In practice it does not, but this possibility calls into question the accuracy of our double titration. The double titration for alkylolithiums does not run into this problem, because the product from the quench with dibromoethane is an alkyl bromide inert to the conditions of the titration, and the older double titration for silyllithium reagents using butyl bromide⁶ is also safe because the byproduct is a butylsilane.

All is well, however—we find that when we add the silyllithium reagent to an excess of dibromoethane, and analyse the mixture by GC, there is no trace of the silyl bromide **3**. Instead, what we detect is tetramethyldiphenyldisilane **4**, which must have been produced by a rapid reaction of the silyllithium reagent **1**

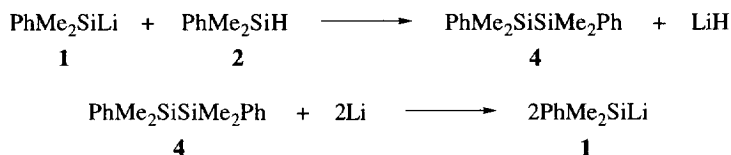
with the silyl bromide **3** (Scheme 3). We see the same result when we examine the $^1\text{H-NMR}$ spectrum immediately after adding dibromoethane to the silyllithium solution. The silyl bromide is therefore removed from the reaction mixture before it has any opportunity to interfere with the titration—the disilane **4** is, of



Scheme 3

course, inoffensive. Although we show the residual base as “LiOH” in Scheme 2, we actually detect lithium phenyldimethylsilanoxide as the form that it takes before hydrolysis. This must have been formed by the reaction of lithium oxide or hydroxide with the silyl chloride giving tetramethyldiphenyldisiloxane, which must then have been cleaved by the silyllithium reagent, a reaction that was also essentially instantaneous when we carried it out deliberately at 0 °C.

A second problem is less serious but was rather puzzling. Normally, after making a fresh solution of the silyllithium reagent by stirring the silyl chloride with lithium for a few hours, we keep it refrigerated for a week or two, taking aliquots as we need them. Occasionally, when using older solutions, we have had reactions fail, and so we rarely keep them for much more than a couple of weeks. Nevertheless, the double titration has indicated that *even after three months there is virtually no drop in the concentration of the silyllithium reagent*—all that happens is that the titre for residual base increases steadily with time. Clearly the accumulation of base interferes with some of our reactions, but how does the titre remain high when water is clearly getting into our flasks? We find that the answer to this puzzle is that the silane **2** is also rapidly consumed (confirmed by $^1\text{H-NMR}$) by the silyllithium reagent **1**, and the disilane **4** so produced is then cleaved (Scheme 4) by the lithium



Scheme 4

that we have simply left in our flasks. The cleavage of tetramethyldiphenyldisilane by lithium is known,^{1,7} and is indeed the reason that the formation of the silyllithium reagent takes several hours. By following the reaction ($^1\text{H-NMR}$), we see the disappearance of the silyl chloride within a few minutes of starting the stir with lithium, and the concurrent formation of the disilane. This is followed by the slow disappearance of both the disilane and the disiloxane produced by the reaction of lithium hydroxide and the silyl chloride. Thus all the silicon-containing material, except the initially formed silanoxide, is kept topped up as silyllithium reagent by the susceptibility of the silane **2** to displacement of the hydride ion. Naturally the corresponding reaction does not occur with alkylolithium reagents, which give a hydrocarbon when any water gets into the mixture.

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

REFERENCES

- George, M. V.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 403-406.
- Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520-2526.
- Crump, R. A. N. C.; Fleming, I.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 701-706.
- Fleming, I. in *Organocopper Reagents: A Practical Approach*, ed. Taylor, R. J. K., OUP, Oxford, **1995**, Chapter 12, pp. 260-261. Fleming, I. Lithium bis[dimethyl(phenyl)silyl]cuprate, in *Encyclopaedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, Wiley, Chichester, **1995**, p. 3037-3040. Fleming, I. Dimethyl(phenyl)silyllithium, in *Synthetic Methods of Organometallic and Inorganic Chemistry (Hermann/Brauer)*, ed. Herrman, W. A., Georg Thieme, Stuttgart, Vol. 2, ed. Auner, N.; Klingebiel, U. **1996**, pp. 167-168.
- Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447-454.
- Gilman, H.; Klein, R. A.; Winkler, H. J. S. *J. Org. Chem.* **1961**, *26*, 2474-2478.
- Sharma, S.; Oehlschlager, A. C. *Tetrahedron* **1989**, *45*, 557-568.