

SYNLETT Spotlight 22

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Phenyldimethylsilyllithium

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Mark Betson graduated from the University of Manchester in 1998, after which he moved to Cambridge where he is studying towards his PhD under the guidance of Professor Ian Fleming.

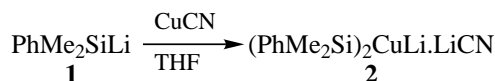


The phenyldimethylsilyl group is commonly used in organic synthesis, partly because it forms a lithium reagent more easily than trialkylsilyl groups. It is easily introduced into a molecule, either from a direct reaction with phenyldimethylsilyllithium¹ (PhMe₂SiLi, **1**), or from the addition of the silylcuprate² **2** (or zincate) to α,β -unsaturated carbonyl compounds (1,4-addition), to acid chlorides (to give acylsilanes), or to acetylenes (to give vinylsilanes).^{1c} After the phenyldimethylsilyl group has performed its task in the synthesis it can be easily removed, either as an electrofugal group in an elimination or, and most notably, via the silyl-to-hydroxyl conversion, which proceeds with retention of stereochemical configuration.³

Phenyldimethylsilyllithium has been shown to react directly with iminium salts, esters, amides and aldehydes/ketones, to give α -silyl amines,^{4a} disilyl alcohols,^{4b} acylsilanes^{4b} and

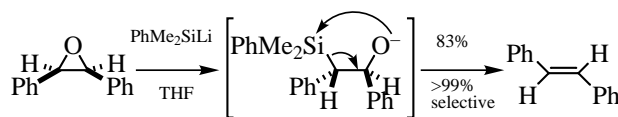
α -silyl alcohols.^{4c} α -Silyl alcohols can be converted, by way of the α -silyl iodides, to the α -metallated silanes which react with aldehydes or acid chlorides to set up, stereospecifically, the components of the Peterson elimination.^{4d} In addition, esters, ketones^{5a} and epoxides^{5b} can be converted to alkenes by the use of PhMe₂SiLi, and α -siloxy ketones can be converted to ketones, the mechanism of which involves a Brook rearrangement to reveal a regiodefined silyl enol ether.⁶

Preparation: Phenyldimethylsilyl chloride is stirred with lithium shot at 0 °C in THF for 6 h.¹ The dark red, moisture-sensitive solution can be stored for several days at -20 °C. The strength of the solution can be determined by double titration.^{1b}

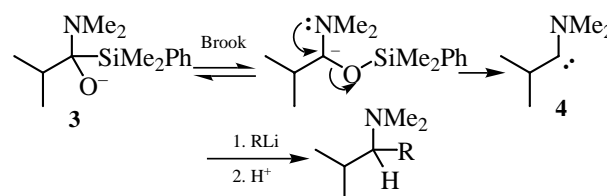


Abstracts

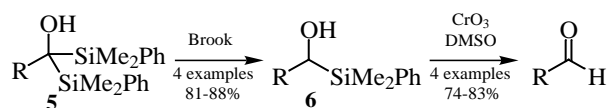
The reaction of PhMe₂SiLi with epoxides gives alkenes, formed by opening of the epoxide ring, a bond rotation and then a Peterson elimination.^{5b} This results in the overall reversal of stereochemistry, as exemplified for the conversion of the *cis*-stilbene oxide to *trans*-stilbene.



The reaction of PhMe₂SiLi with carbonyl compounds sets up the components of a Brook rearrangement, which can be utilised or suppressed. Treatment of amides with one equivalent of PhMe₂SiLi can be used to synthesise acylsilanes,^{4b} whereas the reaction of tertiary amides with PhMe₂SiLi, when quenched at -20 °C, gives enediamines.⁷ These are formed from carbenes such as **4**, a result of the Brook rearrangement of intermediate **3**. Trapping of this carbene is possible (R = SiMe₂Ph, Ph, Buⁿ or Bu₃Sn).



Treatment of esters with an excess of PhMe₂SiLi gives disilyl alcohols **5**, which undergo a Brook rearrangement to give the α -hydroxysilanes **6**. Oxidation of **6** provides a hydride free route for the conversion of esters to aldehydes.^{4b}



References and Notes

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