



From Mixed Li/K Metal TMP Amides to Trimethylsilanes

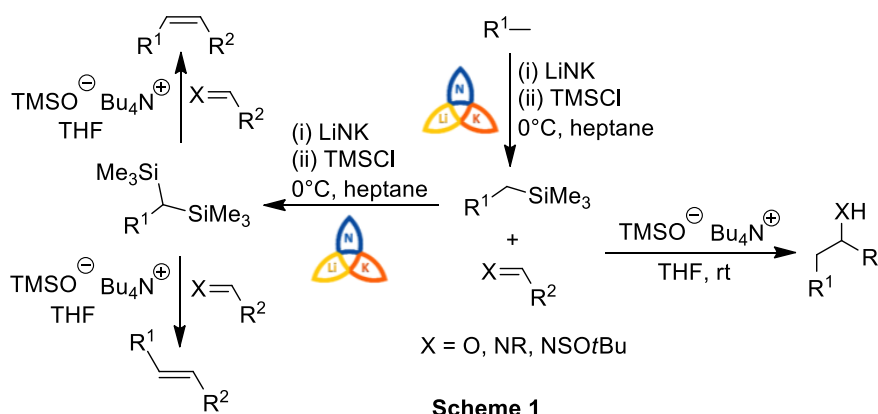
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Abstract:

The development of new general organometallic synthetic methods which are accessible to the non-specialist user remains an important challenge. In this presentation the rt or 0 °C use of mixed Li/K metal amides derived from BuLi, KO t Bu and TMP(H) (LINK conditions) for selective benzylic metalations will be discussed.¹ The reaction protocol is operationally straightforward removing the need for typical cryogenic conditions and found to be applicable to a broad range of substrates. Using this protocol access to benzyltrimethylsilane and α,α -bis(trimethylsilyl)toluene reagents, which are bench-stable surrogates of benzyl anions and α -silyl carbanions, was obtainable. The use of TMSO⁻/Bu₄N⁺ as a silicon activator for organotrimethylsilanes in addition and olefination reactions with carbonyls, imines and sulfinyl imines will be described. The key to unlocking the carbanionic reactivity of the silanes lies in the use of a Bu₄N⁻ cation.²



The broad scope of this method offers trimethylsilanes including acetate, allyl, propargyl, benzyl, dithiane, heteroaryl and aryl derivatives as bench-stable organometallics which can be readily utilized as carbanion equivalents for synthesis. Reactions are achieved with no specialised precautions required other than anhydrous conditions. Using this approach the addition of numerous trimethylsilanes to chiral *N*- t butanesulfinyl imines was achievable with excellent diastereoselectivity in nearly all cases.³ Evidence that the diastereoselective additions occur via an open transition state was obtained.

Highly stereoselective aza-Peterson olefinations from α,α -bis(trimethylsilyl) toluene reagents and *N*-substituted imines have been achieved using TMSO-/Bu₄N- as Lewis base activator in THF.⁴ Remarkably, and for the first time, *N*-*t*-butanesulfinyl imines were utilized for the synthesis of *Z*-stilbenes with excellent selectivities while *N*-aryl imines generated *E*-stilbenes under identical reaction conditions. Rationales for the origins of the *E*- and *Z*-selectivity will be proposed.

References:

1. (a) Manvar, A.; Fleming, P.; O'Shea, D.F. *J. Org. Chem.* **2015**, *80*, 8727. (b) Fleming, P.; O'Shea, D.F. *J. Am. Chem. Soc.* **2011**, *113*, 1698.
2. Das, M.; O'Shea, D.F. *J. Org. Chem.* **2014**, *79*, 5595.
3. (a) Das, M.; O'Shea, D.F. *Org. Lett.* **2015**, *17*, 1962. (b) Das, M.; O'Shea, D.F. *Chem. Eur. J.* **2015**, *21*, 18723.
4. (a) Das, M.; O'Shea, D.F. *Org. Lett.* **2016**, *18*, 336. (b) Das, M.; Manvar, A.; Jacolot, M.; Blangetti, M.; Jones, R.; O'Shea, D.F. *Chem. Eur. J.* **2015**, *21*, 8737.