t-BuOK-Catalyzed addition of ketones and nitriles to vinylic silanes, phosphines and thio derivatives

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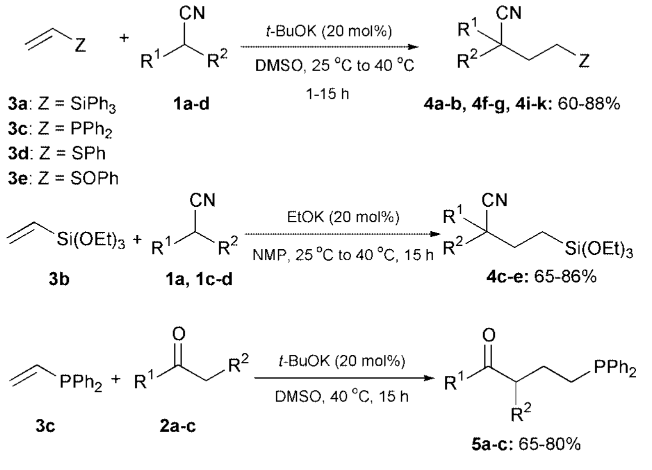
Catalytic amounts of *t*-BuOK in DMSO allow the smooth addition of nitriles and in some cases of ketones to vinylsilanes, phosphines or thio derivatives in good yields.

The conjugate addition of metalated nitriles **1** or ketones **2** to activated alkenes of type **3** (Z = electron-withdrawing group) is a well-known reaction (Michael addition).[1] Stabilized nucleophiles like enolates usually do not add to moderately activated vinylic derivatives of type **3** (Z = SiR$_3$, SR or PR$_2$).

Only highly reactive organolithiums add to these moderately active Michael-acceptors.[2] Recently, we have found that potassium enolates of ketones or nitriles generated catalytically using *t*-BuOK in DMSO or *N*-methylpyrrolidinone (NMP) have a high nucleophilicity in these solvents and add readily to various styrenes in good yields, allowing a unique catalytic phenylethylation reaction.[3] Herein, we wish to report that a range of nitriles add to vinylic silanes **3a** and **3b**, diphenylvinylphosphine (**3c**), phenyl vinyl thioether (**3d**) and phenyl vinyl sulfoxide (**3e**) in the presence of a catalytic amount of *t*-BuOK (20 mol%) in DMSO leading to the corresponding Michael-adducts **4a–g** and **4i–4k** in 60–88% yield (Scheme 1, Table 1). Thus, 2-phenylbutyronitrile **1a** (entry 1 of Table 1) adds to triphenylvinylsilane (**3a**) within 12 h at 40 °C in the presence of *t*-BuOK (20 mol%) in DMSO leading to the addition product **4a** in 60% yield. The related cyclohexanecarbonitrile (**1b**) adds to **3a** even at rt (12 h) affording the adduct **4b** in 76% yield (entry 2). Triethoxyvinylsilane (**3b**) adds similarly valeronitrile (**1d**), secondary nitriles **1a** and α-tetralone (**2a**) at 40 °C. In this case potassium ethoxide (20 mol%) is used as a catalyst in NMP. This avoids alkoxide exchanges at silicon and leads to the functionalized alkyltriethoxysilanes **4c–e** and **5d** in 65–86% yield (entries 3–5 and entry 15). These products may be interesting precursors for the preparation of functionalized silicones. This result shows that a variety of potassium alkoxides can certainly be used in this catalytic addition reaction. Vinylic phosphines only reluctantly undergo the addition of nucleophiles[2g] and, usually, efficient additions only are observed to vinylic phosphine oxide derivatives or alkenylphosphonium salts.[4] Under our reaction conditions, various nitriles add to diphenylvinylphosphine (**3c**) very smoothly (25 °C, 1 h) leading to the expected products **4f–g** in 81–88% yield and the double addition product **4h** in 80% yield. Interestingly, ketones like α-tetralone (**2a**), camphor (**2b**) and cyclohexanone (**2c**) also undergo an efficient Michael addition at 40 °C (12 h) leading to the ketophosphines **5a**, **5b** and **5c** in respectively 80, 72 and 65% yields (entries 12, 13 and 14). In the case of **5b** only the *endo*-isomer is produced.[5] Finally, nitriles like **1a** or **1b** add also to phenyl vinyl thioether (**3d**) affording the Michael-adducts **4i–j** (entries 9 and 10) in 75–78% yield. The corresponding sulfoxide (**3e**) adds nitrile **1a** under similar conditions (40 °C, 1 h) furnishing the sulfoxide **4k** in 82% yield (entry 11).



Scheme 1

In summary, we have described a new *t*-BuOK-catalyzed addition of nitriles to various moderately active Michael-acceptors allowing the preparation of new functionalized silanes, phosphines and thioethers. In the case of diphenylvinylphosphine (**3c**) the addition of ketones also proceeds well. We are currently exploring the application of this reaction for the preparation of new chiral ligands for metal catalysis.[6]

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Notes and references

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4 R. M. Cory, D. M. T. Chan, Y. M. A. Naguib, M. H. Rastall and R. M. Renneboog, *J. Org. Chem.*, 1980, **45**, 1852.

5 The relative stereochemistry of the *endo*-configuration has been established by NOESY experiment.

6 Typical procedure: preparation of 2-ethyl-2-phenyl-4-diphenylphosphinobutanenitrile (**4f**): To a stirred solution of *tert*-butoxide (45 mg, 0.4 mmol) in DMSO (2 mL) was successively added, under argon, 2-phenylbutyronitrile (**1a**; 290 mg, 2 mmol) and diphenylvinylphosphine (**3c**, 420 mg, 2 mmol). The reaction was stirred for 1 h at rt. Water (3 mL) and CH$_2$Cl$_2$ (25 mL) were added, and the resulting solution was washed with brine, dried (MgSO$_4$) and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, 5% ether–pentane) to give the desired product **4f** (630 mg, 88% yield).

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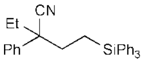
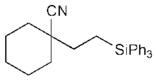
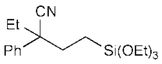
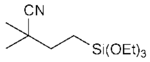
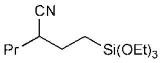
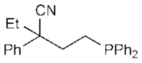
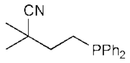
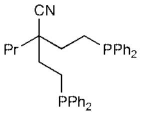
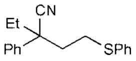
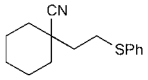
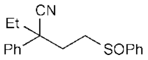
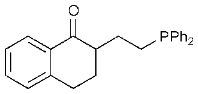
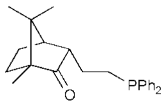
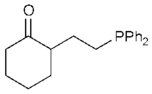
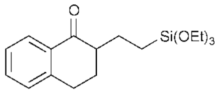
Table 1 Nitriles **4a**–**k** and ketones **5a**–**d** obtained by the *t*-BuOK-catalyzed addition of nitriles and ketones to the vinylic silanes, phosphines, thioethers and sulfoxides **3a**–**e** in DMSO

Entry	Carbonyl compound	Activated alkene	Product of type **4** or **5**	Yield (%)[a]
1	**1a**	**3a**	 **4a**	60
2	**1b**	**3a**	 **4b**	76
3	**1a**	**3b**	 **4c**	86[b]
4	**1c**	**3b**	 **4d**	85[b]
5	**1d**	**3b**	 **4e**	65[b]
6	**1a**	**3c**	 **4f**	88
7	**1c**	**3c**	 **4g**	81
8	**1d**	**3c**	 **4h**	80
9	**1a**	**3d**	 **4i**	78
10	**1b**	**3d**	 **4j**	75
11	**1a**	**3e**	 **4k**	82
12	**2a**	**3c**	 **5a**	80
13	**2b**	**3c**	 **5b**	72
14	**2c**	**3c**	 **5c**	65
15	**2a**	**3b**	 **5d**	65[b]

[a] Yield of analytically pure products; [b] EtOK (20 mol%) in NMP was used.