A new synthetic route to allylsilanes: the reaction of silyllithium reagents with aromatic carbonyl compounds and aluminium tris(2,6-diphenylphenoxide) (ATPH)

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Conjugate 1,6-addition of silyllithium reagents to aromatic carbonyl substrates in the presence of the carbonyl protector aluminium tris(2,6-diphenylphenoxide) (ATPH) gives allylsilanes.

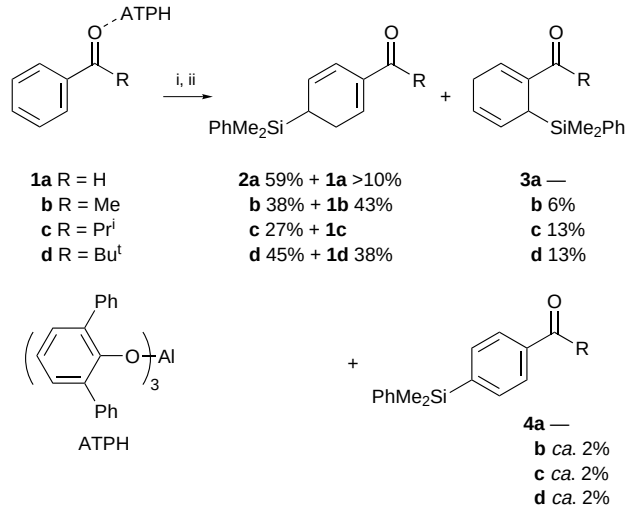
Allylsilanes are versatile synthetic intermediates,[1] and several methods are available to prepare these reagents.[2] We recently described the conjugate addition of several alkyllithiums to aromatic carbonyl compounds complexed with aluminium tris(2,6-diphenylphenoxide) (ATPH),[3] in which the Lewis acid effectively blocks carbonyl carbons from nucleophilic attack. This result led us to explore the possibility of using this strategy for the synthesis of allylsilanes using silyllithium reagents[4,5] in place of the alkyllithium reagents. We report here that the 1,6-addition of silyllithium reagents to the aromatic carbonyl compound–ATPH complex, and subsequent enolate capture with an appropriate electrophilic reagent, does provide a route to functionalised allylsilanes (Scheme 1).

Treatment of the precomplexed salt **1a** of benzaldehyde and ATPH with phenyldimethylsilyllithium ($PhMe_2SiLi$)[5] at −78 °C produced, after stirring for 30 min and quenching with concentrated hydrochloric acid at −78 °C, selective 1,6-addition to give allylsilane **2a** in 59% yield.‡ When a similar procedure was applied to aromatic ketones **1b**–**d**, 1,6-addition products **2b**–**d** were accompanied by small amounts of the 1,4-addition products **3b**–**d**§ and the aromatised silylated products **4b**–**d** (Scheme 1). These results suggest that the γ-carbon of the carbonyl substrate was selectively protonated by way of dienolate intermediates, which was confirmed by quenching the intermediates **5** in the acetophenone series at low-temperature with deuterated acid to give the monodeuterated products **6** (Scheme 2).

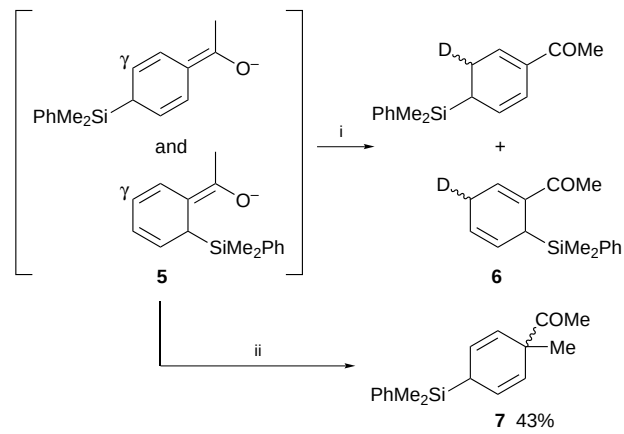
When the generation of dienolate **5** was followed by treatment with an excess of methyl trifluoromethanesulfonate (10 equiv.) at −78 °C for 1 h, the α-methylated product **7** was formed in 43% yield after the usual low-temperature acidic work-up. Methylation occurred predominantly at the α-carbon, in contrast to the exclusive γ-protonation with hydrochloric acid (Scheme 2).

Similarly, phenyldimethylsilyllithium underwent conjugate addition to methyl benzoate in the presence of ATPH with high 1,6-selectivity (1,6 : 1,4 = 87 : 13), but relatively low regioselectivity on protonation to give a mixture (52 : 35 : 13) of the regioisomeric pentadienyl silanes **9** (Scheme 3), including a stereoisomeric mixture (*cis* : *trans* = 1 : 3.1) in the case of the α-protonated product **9b**. The *cis* : *trans* ratio was determined by ^{1}H NMR spectroscopy and assigned by a NOESY measurement. In contrast, methylation of the dienolate intermediates **8** gave *cis*-**10** regio- and stereo-selectively, with the methyl group entering *anti* to the resident silyl group. This finding is similar to the alkylation of cyclic enolates having a silyl group adjacent to the nucleophilic centre, which are highly selective for attack by the incoming electrophile *anti* to the silyl group.[6] The relative stereochemistry of *cis*-**10** was assigned by a NOESY measurement by converting the mixture **10** into the alcohols **11** by reduction with diisobutylaluminium hydride (DIBAL-H).

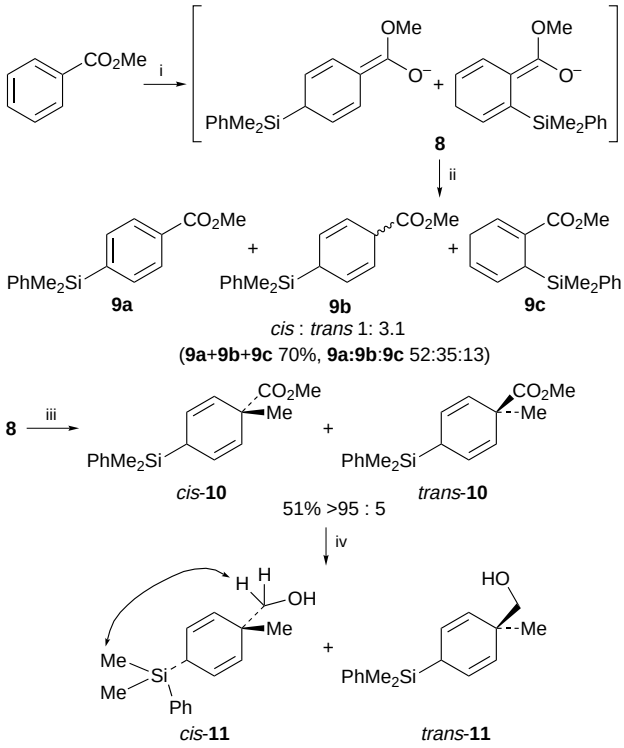
1,6-Addition also took place, in somewhat higher yield, with 1-naphthaldehyde **12a** and with 1-acetonaphthone **12b** to give the adducts **13** (Scheme 4). In an attempt to prepare the hydrate of an aromatic ring, we also carried out the reaction with the latter substrate using the more easily functionalised 2-methylbut-2-enyldiphenylsilyl group[7] to give the adduct **14**. Functionalisation of the silyl group was carried out using protodesilylation at the exocyclic allylsilane unit to give the



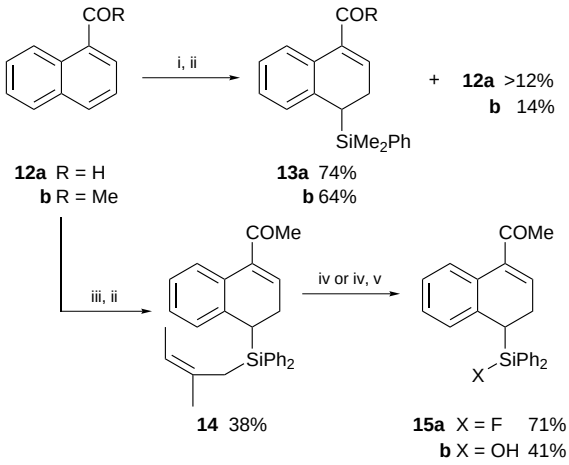
Scheme 1 *Reagents*: i, $PhMe_2SiLi$; ii, HCl, H_2O



Scheme 2 *Reagents*: i, DCl, D_2O; ii, $MeOSO_2CF_3$



Scheme 3 *Reagents and conditions*: i, ATPH, toluene, $PhMe_2SiLi$, −78 °C, 30 min; ii, conc. HCl, −78 °C to room temp.; iii, $MeOSO_2CF_3$ (10 equiv.), −78 °C, 1 h; iv, DIBAL-H, 0 °C



Scheme 4 *Reagents and conditions*: i, ATPH, toluene, $PhMe_2SiLi$, −78 °C; ii, conc. HCl, −78 °C to room temp.; iii, ATPH, toluene, 2-methylbut-2-enyldiphenylsilyllithium, −78 °C; iv, BF_3·AcOH, CH_2Cl_2, −10 °C; v, KF, H_2O_2, MeOH–THF, 0 °C

silyl fluoride **15a** in 71% yield. Subsequent treatment under Tamao's conditions[8] with potassium fluoride and hydrogen peroxide in THF–MeOH produced hydroxy silane **15b** in fair yield, but not the naphthalene hydrate (Scheme 4). A method for efficiently transforming the silyl group into a hydroxy group is still under investigation.

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Footnotes

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‡ *Typical experimental procedure*: benzaldehyde (51×10^{-3} cm³, 0.5 mmol) was added to a solution of ATPH (0.55 mmol) in toluene (4.0 cm³) at −78 °C under argon, and the resulting orange solution of the ATPH–benzaldehyde complex was stirred at this temperature for 10 min. A solution of phenyldimethylsilyllithium (0.35 mol dm⁻³ in THF, 2.86 cm³, 1.0 mmol) was added at −78 °C, and the reaction mixture was stirred at this temperature for 30 min. The reaction was quenched with concentrated hydrochloric acid (12 mol dm⁻³; 1.5 cm³) at −78 °C, stirred at room temperature for 15 min, diluted with water (4.5 cm³) and extracted with diethyl ether (3×15 cm³). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2–hexane to give the 1,6-adduct **2a** (59% isolated). *Selected data* for **2a**: R_f = 0.35 (CH_2Cl_2–hexane, 1 : 2); ν_{max} (film)/cm⁻¹ 1682, 1250, 1115. δ_H ($CDCl_3$, 300 MHz) 9.22 (1 H, s, CHO), 7.55–7.30 (5 H, m, SiCPh), 6.44 (1 H, t, *J* 5.6, SiCHCH$_2$C*H*), 6.28 (1 H, d, *J* 9.6, SiCHCHC*H*), 5.92 (1 H, dd, *J* 5.2 and 9.6, SiCHC*H*), 2.77 (1 H, ddd, *J* 3.9, 10.8 and 18.9, CH_AH$_B$), 2.48 (1 H, ddd, *J* 5.7, 5.7 and 18.9, CH$_A$$H_B$), 2.07 (1 H, m, SiCH), 0.32 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 190.7, 145.7, 138.2, 136.6, 133.8, 131.1, 129.3, 127.8, 116.6, 24.5, 23.9, −4.8 and −5.0 (Found: C, 74.2; H, 7.6. $C_{15}H_{18}OSi$ requires C, 74.3; H, 7.5%).

§ *Selected data* for **3b**: R_f = 0.28 (CH_2Cl_2–hexane, 4 : 1); ν_{max}(film)/cm⁻¹ 1671(C=O), 1612 (conjugated C=C) and 1239 (C–Si); δ_H($CDCl_3$, 250 MHz) 7.50–7.26 (5 H, m, SiPh), 6.63 (1 H, ddd, *J* 1.25, 2.5 and 5.7, CH=CCO), 5.75 (1 H, ddd, *J* 2.9, 5.2 and 9.6, C*H*=CHCHSi), 5.44 (1 H, br dd, *J* 4.6 and 9.6, CH=C*H*CHSi), 3.23 (1 H, dt, *J* 3.6 and 5.7, C*H*Si), 2.73 (1 H, dddd, *J* 4.5, 4.7, 4.7 and 23, CH$_A$$H_B$, equatorial), 2.39 (1 H, dddd, *J* 22.9, 8.8, 2.6 and 2.6, CH_AH$_B$, axial), 2.24 (3 H, s, MeCO), 0.24 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 198.2, 140.8, 135.4, 134.5, 134.2, 129.4, 128.2, 127.8, 119.7, 30.03, 29.5, 25.6, −3.2 and −4.2 (Found: M⁺, 256.1280. $C_{16}H_{20}OSi$ requires *M*, 256.1283).

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