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Supersilylating Agents from Chlorosilanes

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Abstract: The addition of R_3SiCl to $B(OTf)_3$ gives "supersilylating agents" formulated as $R_3SiB(OTf)_3Cl$. The catalytic properties of these species are similar to those of the previously-described (but less accessible) $R_3SiB(OTf)_4$.

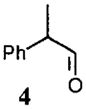
Electron-deficient organosilicon compounds have attracted widespread interest, on theoretical grounds[1] and as reagents for organic synthesis.[2] In the latter respect, the "supersilylating agents" $R_3SiB(OTf)_4$ **1** (Tf = SO_2CF_3), discovered in this laboratory,[3] are probably the most potent "R_3Si^+-equivalents" readily accessible to the synthetic chemist. However, while their preparation from R_3SiOTf and $B(OTf)_3$ (eq. 1) is straightforward, the required trialkylsilyl triflates may be less available (and are certainly less convenient to handle) than the corresponding chlorotrialkylsilanes **2**. We now report that treatment of $B(OTf)_3$ with **2** provides a new source of supersilylating species which facilitates access to this promising class of reagents.

$$B(OTf)_3 \quad + \quad R_3SiOTf \xrightarrow{CH_2Cl_2 \text{ or } CHCl_3} \underset{\mathbf{1}}{R_3SiB(OTf)_4} \qquad (1)$$

$$B(OTf)_3 \quad + \quad \underset{\mathbf{2}}{R_3SiCl} \longrightarrow \underset{\mathbf{3}}{R_3SiB(OTf)_3Cl} \qquad (2)$$

a R = Me **b** 'R_3Si' = Bu^tMe_2Si **c** R = Pr^i

Addition of **2a-c** in CH_2Cl_2 to freshly-prepared[4] $B(OTf)_3$ yielded a series of homogeneous pale yellow solutions with overall stoichiometry **3** (eq. 2). The catalytic properties of these solutions clearly indicated that supersilylating species were present. Previously demonstrated applications of the triflate-derived agents **1** had included (a) catalysis of the addition of allyltrimethylsilane to aldehydes by **1a**,[3a] and (b) the use of hindered analogues to catalyse the Mukaiyama aldol reaction with enhanced Cram-type diastereoselectivity.[3b] To a good approximation, solutions of **3** matched those of **1** for both reaction types. For example, **3a** at 1-2 mol% was a potent catalyst for the allylation of benzaldehyde and 2-phenylpropanal (**4**) with allyltrimethylsilane (CH_2Cl_2, room temperature, MeOH/HCl work-up). Homoallylic alcohols **5** and **6** (*syn*:*anti*::2:1) were formed in yields of 79% and 92% respectively, both reactions being complete within 15 minutes.



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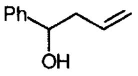

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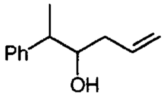

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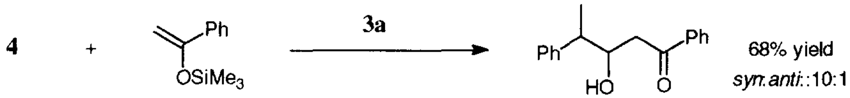
Similarly, **2a-c** catalysed the Mukaiyama additions shown in eq. 3-5 (general conditions; 5 mol% catalyst, 1 h at -80 °C in CH_2Cl_2, followed by $NaHCO_3/H_2O$ work-up). The yields and (especially) stereoselectivities recorded are closely similar to those achieved by the corresponding **1**.[3b] Although the solutions of **3** decomposed in a matter of days at room temperature, they retained their activity for several weeks provided they were stored at -18 °C.



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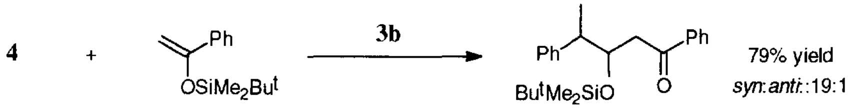

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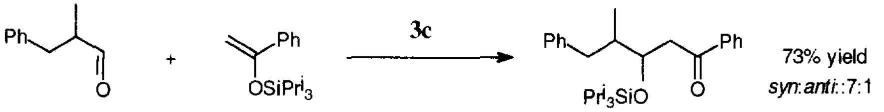

(5)

The nature of **3a** was explored using NMR in toluene-d_8 at -20 °C, conditions which appeared to maximise the stability of the reagent. The ^{11}B spectrum was dominated by a sharp singlet at δ -3.17 p.p.m. ($W_{1/2}$ = 7 Hz), consistent with a tetracoordinate boron atom with approximate (time-average) spherical symmetry.[5] The ^{29}Si signal at δ 45 p.p.m. appeared at somewhat higher field than that of **1a** (62 p.p.m. in CH_2Cl_2 at 20 °C), although the difference may be partly due to the change in conditions. In any case this relatively low chemical shift[6] leaves little doubt that the silicon is tetracoordinate, probably in rapid exchange between different points on the counterion. The Si-C one-bond coupling constant of 59 Hz, measured from the ^{13}C spectrum, also supports sp^3 hybridization at Si.[3a]

Aside from its practical advantages, the use of chlorosilanes increases the range of readily-accessible supersilylating agents. For example, while Bu^tPh_2SiCl (**7**) is commercially available, the corresponding triflate has seldom been prepared.[7] Treatment of **7** with $B(OTf)_3$ does indeed yield a supersilylating species, whose catalytic and stereodirecting properties will be described in a forthcoming paper.

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References and Footnotes

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4. From BBr_3 and TfOH. See Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Olah, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2560.
5. The similarity of this signal to that of $Me_3SiB(OTf)_4$ (see ref. 3a) raises the possibility of ligand exchange at boron.
6. *cf.* ref 1a; δ_{Si} = 115 p.p.m. has been recorded for the "silylium-like" silyl group in $Pr^i_3Si(Cl_6CB_{11}H_6)$.
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