Testing the functional tolerance of the Piers–Rubinsztajn reaction: a new strategy for functional silicones†

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The Piers–Rubinsztajn reaction, involving $B(C_6F_5)_3$-catalyzed siloxane formation from hydrosilanes + alkoxysilanes, is tolerant of a wide variety of functional groups, and provides a generic strategy for the preparation of structurally complex functional silicones.

The sensitivity of siloxane bonds to acid and base-catalyzed redistribution and other degradation reactions makes the synthesis of complex, well-defined silicone structures difficult.[1] Recently, we[2] and others[3–6] have examined the dehydrocarbonative condensation of alkoxysilanes with hydrosilanes ($R_3SiH + R'OSiR''_3 \rightarrow R_3SiOSiR''_3 + R'H$). The process, catalyzed by $B(C_6F_5)_3$—the Piers–Rubinsztajn reaction[7–10]—permits the rapid assembly of complex 3D silicone structures with high fidelity: degradation of the silicone framework does not normally occur.

Silicones are often conjugated with more polar species to yield a wide range of materials of significant industrial importance, such as surfactants, liquid crystals, foaming or anti-foaming agents, among others.[1,11] Thus, in order to be of practical importance, the ability of the Piers–Rubinsztajn reaction to perform in the presence of common organic functional groups needs to be addressed.

The mechanistic sequence (Fig. 1) involving the formation of siloxanes, with the concomitant production of alkanes, is thought to involve the complexation of hydrosilane with the Lewis acidic boron **1** (Fig. 1a–c). Displacement of hydride by alkoxysilane leads to the key intermediate **2** from which both metathetic processes (c)[12] and the desired reduction occur (b).

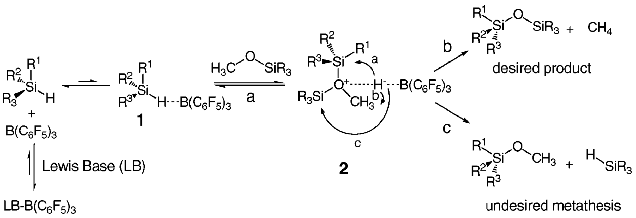

Fig. 1 Proposed mechanism for $B(C_6F_5)_3$-catalyzed siloxane formation.

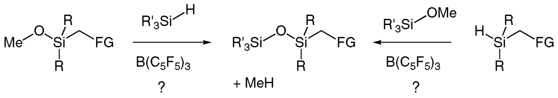

Fig. 2 Strategy for preparing organofunctional silicones.

Based on such a mechanism, it is expected—and can be inferred from Piers' pioneering studies of the use of the catalyst in synthetic organic transformations, such as the reduction of ketones by hydrosilylation[13]—that strong Lewis bases will complex effectively with $B(C_6F_5)_3$, suppressing reactions with weaker binding groups. We have undertaken a study of the functional tolerance of the Piers–Rubinsztajn reaction to establish the synthetic limitations imposed by organic functional groups on the process, whether present on the hydrosilane or alkoxysilane component (Fig. 2).§

Lewis bases. The presence of amino groups in the reaction mixture completely suppressed the Piers–Rubinsztajn reaction: there was no change in starting materials when 3-aminopropyltrimethoxysilane was combined with pentamethyldisiloxane **3** (Fig. 3A). As has been shown in examples from organic synthesis,[14] sufficiently strong Lewis bases complex the boron, essentially irreversibly, preventing the formation of **1**. However, useful reactions readily occurred with weaker Lewis bases.

Thiols cleanly react with hydrosilanes to produce both hydrogen and S–Si bonds,[15] as was confirmed by the reaction of dodecanethiol with **3**. The reaction, however, is slightly less explicit when both thiols and alkoxysilanes are present in the same reaction mixture, as in the case of the stoichiometric reaction of 3-mercaptotrimethoxysilane with pentamethyldisiloxane (Fig. 3B). When performed in dichloromethane, little reaction of any type appeared to occur. However, in hexane, complete disappearance of the thiol moiety was accompanied by partial loss of the alkoxysilane groups (about 10%). Lowering the temperature did not enhance the kinetic selectivity, as no reaction occurred. However, it is possible to convert all alkoxysilanes to siloxanes when excess hydrosilane (4.5 equivalents) is used. It should be possible to

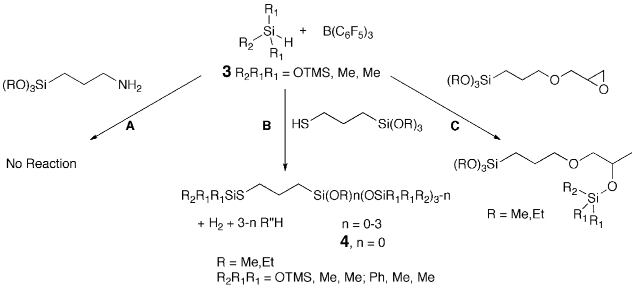

Fig. 3 Lewis basic functional groups in siloxane formation.

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† Electronic supplementary information (ESI) available: Preparative descriptions and spectroscopic data for the compounds in Table 1, and compounds **6–8**. See DOI: 10.1039/c0cc00369g

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selectively liberate the thiol from compound **4** ($n = 0$) by the facile hydrolysis of the S-silyl group.[16]

Epoxides are widely used as monomers, adhesion promoters and linkers. Ganachaud *et al.* demonstrated that, in the presence of water, $B(C_6F_5)_3$ will catalyze epoxide ring opening by carboxylic acids.[17] Under anhydrous conditions at room temperature, treatment of 3-(glycidoxy)propyltrimethoxysilane with pentamethyldisiloxane in the presence of catalytic amounts of $B(C_6F_5)_3$ led to selective reductive epoxide ring opening (Fig. 3C). Even in the presence of excess silane, however, there was no evidence of any reaction at the methoxysilane groups to give siloxanes.

Haloalkanes. Chloro- and iodoalkane-containing silicones were examined for their ability to participate in the Piers–Rubinsztajn reaction (Fig. 4A, Table 1, entries 1–2). For example, the reaction of phenyldimethylsilane with chloropropyltriethoxysilane in the presence of 0.15 mol% of $B(C_6F_5)_3$ occurred rapidly after an induction time of less than two minutes to give **5** in 93% isolated yield (Table 1, entry 1, Fig. 5). In all the examples described, the reaction proceeds after short induction times, and with no evidence of unwanted side reactions. The ability to further exploit such compounds was demonstrated using azide/alkyne click chemistry: the chloroalkylsilicone was treated with sodium azide at 90 °C to give **6**, which in turn underwent a facile 1,3-dipolar cycloaddition with diethyl acetylenedicarboxylate at room temperature to give **7**.[18]

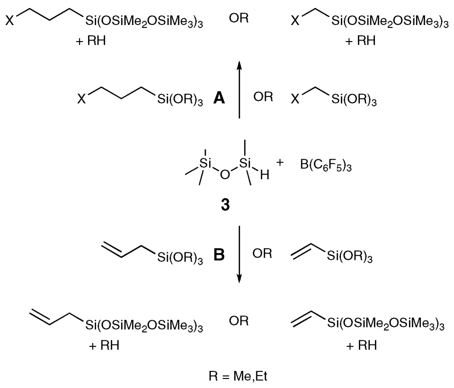
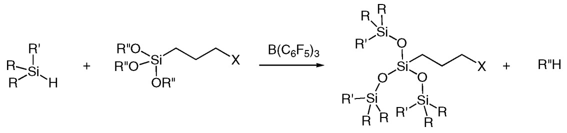
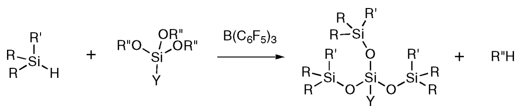


Fig. 4 Compatible functional groups.

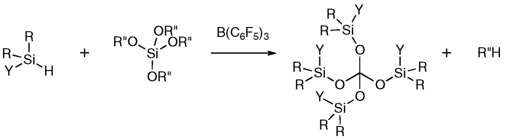
Table 1 Reaction of hydrosilanes with vinyl- or allyl-functionalized trialkoxysilanes



E	R, R	R′	R″	X	Time[a,d]	Yield
1	Me	Ph	Et	Cl	120	93
2	Me, Ph[c]	CH=CH$_2$	Me	I	60	73



E	R, R	R′	R″	Y	Time[a,d]	Yield
3	Me	OTMS[b]	Et	CH=CH$_2$	300	89
4	OTMS[b]	Me	Me		180	90
5	Me	OTMS	Et	CH$_2$CH=CH$_2$	180	87
6	OTMS	Me	Me		300	94



E	R, R	Y	R″	Time[a]	Yield
7	Me	OSi(CH$_3$)$_2$CH=CH$_2$	Et	120	75
8	Me. Ph[c]	CH=CH$_2$	Et	150	89

[a] Typical catalyst loadings of 0.05 mol%. [b] TMS = trimethylsilyl. [c] Three different ligands were used: R = Me, Ph. [d] Induction time in seconds.

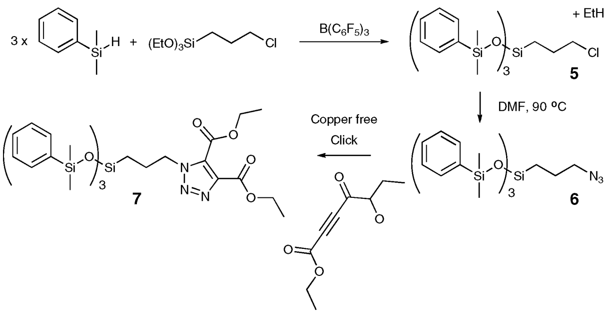


Fig. 5 Concise preparation of organofunctional silicones.

Hydrosilylation. Transition metal-catalyzed hydrosilylation is one of the key methods to make silicon–carbon bonds.[19] $B(C_6F_5)_3$ has also been reported to catalyze hydrosilylation reactions (*e.g.*, $R_3SiH + H_2C{=}CHR' \rightarrow R_3SiCH_2CH_2R'$), but only at catalyst concentrations that are relatively high ($\sim$5 mol%).[20] Siloxane formation from the Piers–Rubinsztajn reaction is not diverted by hydrosilylation processes irrespective of whether the SiH and alkenyl groups are on different (Fig. 4B, Table 1, entries 3–6) or the same (Table 1, entries 7, 8) silicon atoms. This provides an important synthetic opportunity because it is possible using dehydrocarbonative condensation to create complex alkenyl-modified silicones at exceptionally low boron catalyst loadings that can be subsequently modified in a platinum-catalyzed hydrosilylation reaction. With appropriate substituents the two reactions—hydrosilylation and the Piers–Rubinsztajn—are orthogonal, as shown in the preparation of compound **8** (Table 1, entry 3, Fig. 6).

With alkenyl- and haloalkylsilane starting materials, the Piers–Rubinsztajn process leads to complex, functional silicones in high yield, with no apparent by-products, and excellent fidelity. No evidence of metathesis during synthesis, or redistribution after or during silicone formation was observed. Complete displacement of all of the alkoxy groups on tri- (T) and tetrafunctional (Q) silanes occurred (Table 1). With the exception of highly hindered compounds, which have

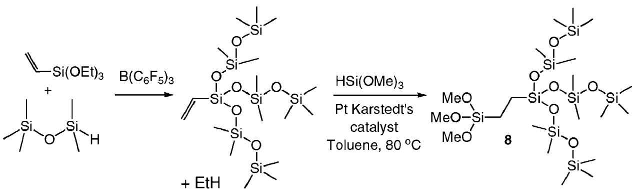


Fig. 6 Iterative silicone assembly.

not yet been tested, this protocol is suitable for the reaction of mono- (M) and difunctional (D) functional alkoxysilanes. Therefore, the assembly of complex silicone structures of various structural complexity (MDTQ¶[21] resins) is readily achieved. Moreover, silicone formation using this process can be complemented by subsequent organic reactions leading to yet more complex silicones by iterative use of the coupling reaction followed by hydrosilylation, nucleophilic substitution, or click chemistry. An examination of the degree to which these processes can be used to explicitly assemble large molecules will be the focus of future accounts.

In summary, the condensation of alkoxy- and hydrosilanes catalyzed by $B(C_6F_5)_3$ efficiently occurs to give functional siloxanes. While epoxides only underwent ring opening reduction, and thiols compete with condensation with alkoxysilanes, reactions with haloalkyl and alkenylsiloxanes led to the controlled assembly of complex functional silicones in a few steps.

Notes and references

§ An examination of the scope of this reaction will be the subject of a separate manuscript.

¶ General electric silicone nomenclature: M = Me_3Si, D = $Me_2SiO_{2/2}$, T = $MeSiO_{3/2}$ and Q = $SiO_{4/2}$. The subscript nomenclature is used to denote, for example with $SiO_{4/2}$, that there are four single bonds to oxygen from silicon, and that each oxygen bonds to another silicon through a single bond, *i.e.*, $Si(OSi)_4$ rather than SiO_2, which might imply Si=O double bonds.

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