Electronic and Steric Effects of Various Silyl Groups in Radical Addition Reactions

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Abstract: The ligands on a silicon atom in allylsilanes were found to influence the efficiency of their reaction with ketones in the presence of MnO_2. An electron-donating group on silicon provided a promoting effect, yet the steric effect of a bulky silyl group retarded the addition process. © 1998 Elsevier Science Ltd. All rights reserved.

Placement of a silyl group at an appropriate position in reactants allows chemists to control organic reactions involving carbocationic, carbanionic, and carboradical intermediates.[1–3] In addition to the steric congestion resulting from the silyl group with different spatial size, the electronic effect associated with a silicon atom also plays an essential role.[4] Recently, the synthetic applicability of oxidative additions of ketones to allylsilanes has been reported by use of ceric ammonium nitrate,[5,6] manganese(III) acetate,[5,6] and manganese(IV) dioxide.[4] In these reactions, the C–C bond formation is promoted by a silyl group; however, the effect resulting from different ligands attached to the silicon atom remains enigmatic.[7,8] Herein we report our findings on the electronic effect of various ligands on a silicon atom and the steric effect of silyl groups on the MnO_2-catalyzed addition of ketones to allylsilanes.

We treated allylsilanes **1a–h** with a ketone (i.e., acetone and cyclohexanone; 20 equiv), MnO_2 (2.0 equiv), and acetic acid (catalytic amount) at 140 °C for 14 h. The corresponding adducts **2a–h** were isolated in 51–81% yields (see Table 1). Use of **1i** bearing a bulky Si(*t*-Bu)Ph$_2$ group, however, did not lead to the adduct **2i** and only the starting materials were recovered.

In the mechanism shown in Scheme 1,[4] addition of an α-keto carboradical onto an olefin, in general, proceeds faster than hydrogen transfer between a carboradical and a ketone.[9] The latter step would be disturbed significantly by the size of the β silyl group. Bulk of the nine silyl groups in allylsilanes applied in our reactions follows the order $SiMe_3$ < $SiMe_2Ph$ < $SiMePh_2$ < $SiPh_3$ < $SiEt_3$ < $SiMe_2(t\text{-}Bu)$ < $Si(n\text{-}hexyl)_3$ < $Si(i\text{-}Pr)_3$ < $Si(t\text{-}Bu)Ph_2$.[10,11] The relative size of the corresponding allylsilanes is illustrated by the CPK space filling molecular model as shown in Figure 1. We found that the yields of the adducts generally decreased for the starting allylsilanes bearing a bulkier silyl group; the tertiary butyl group often exerted a strong steric effect. Nevertheless, the electronic effect resulting from the ligands on silicon atom also played a prominent part in the C–C bond formation.
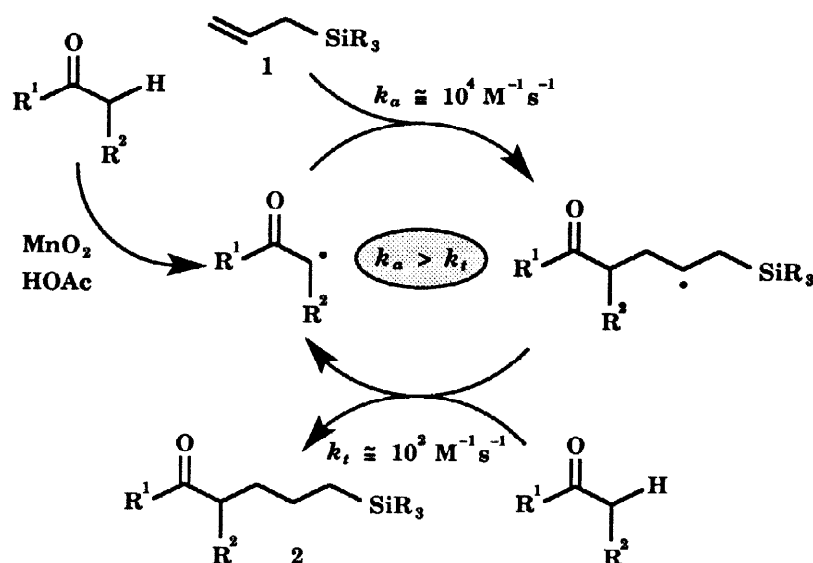
Scheme 1

Table 1. Reaction of allylsilanes with ketones in the presence of MnO_2 and a catalytic amount of HOAc to give the corresponding hydrogen atom transfer adducts at 140 °C

SiR_3	allylsilane	ketone	adduct[a]	% yield
$SiMe_3$	1a	acetone	2a	81
$SiMe_2Ph$	1b	acetone	2b	75
$SiMePh_2$	1c	acetone	2c	63
$SiPh_3$	1d	acetone	2d	56
$SiEt_3$	1e	acetone	2e	71
$SiMe_2(t\text{-}Bu)$	1f	acetone	2f	51
$Si(n\text{-}hexyl)_3$	1g	acetone	2g	62
$Si(i\text{-}Pr)_3$	1h	acetone	2h	60
$Si(t\text{-}Bu)Ph_2$	1i	acetone	2i	no reaction
$Si(OMe)_3$	1j	acetone	2j	no reaction
$SiMe_2Cl$	1k	acetone	2k	2
$SiCl_3$	1l	acetone	2l	no reaction
$SiMe_2Ph$	1b	cyclohexanone	2m	71
$SiMePh_2$	1c	cyclohexanone	2n	58
$SiPh_3$	1d	cyclohexanone	2o	54

[a] All compounds were fully characterized by spectroscopic methods, including IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

A silyl group can stabilize a β carboradical through "σ–π hyperconjugation"[1] (Figure 2(a)) or "p–d homoconjugation"[12,13] (Figure 2(b)) or both. We believe that an electron-donating group attached to the silicon atom could enhance the stabilization by the σ–π hyperconjugation through inductive effect. Thus a silyl group containing small alkyl

substituents with electron-donating character (e.g., Me and Et) in allylsilanes provided the products in good to excellent yields.
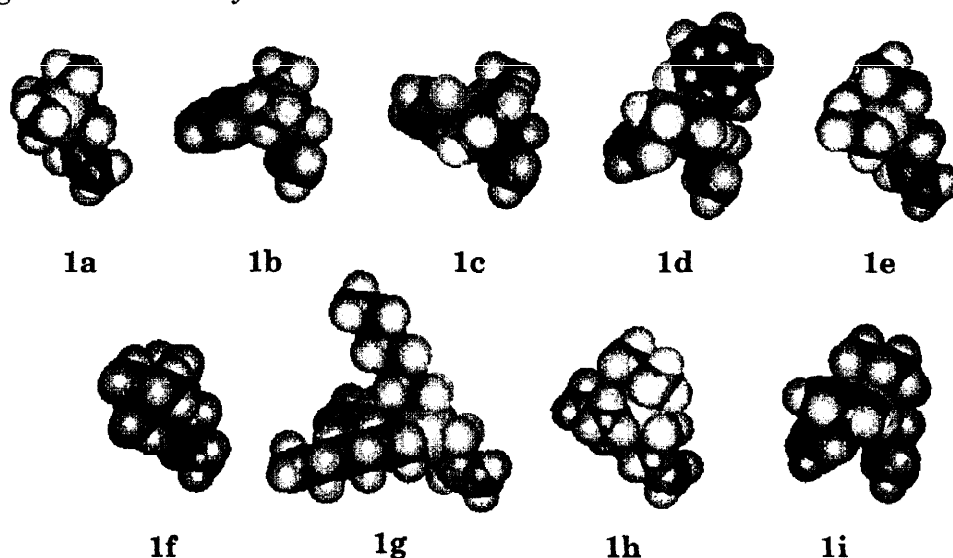

Figure 1. The CPK space filling molecular models exhibit the size of allylsilanes **1a–i**. The tail residing at the right bottom corner of each molecule represents the allyl moiety. Computations were performed on a Silicon Graphics IRIS CRIMSON/Elan workstation. The *Builder* and *Discover* modules of Insight II (Biosym Technologies, versions 2.3.5 and 2.95 individually) were used for model building and energy minimization, respectively. The energies for all conformations were minimized with the consistent valence forcefield (CVFF)[14] until the maximum derivative was less than 0.001 kcal/(mol Å).

To realize the ligand effect resulting from an electron-withdrawing group, we treated **1j–l**, respectively, with acetone, MnO_2, and a catalytic amount of acetic acid. These reactions failed to produce the adducts **2j–l** in a significant amount (see Table 1). Thus we conclude that an electron-withdrawing group, such as OMe and Cl, on a silicon atom retarded the addition process. Furthermore, in control experiments without MnO_2, allylsilanes did not react with acetone and we recovered the starting allylsilanes **1a** (>98%), **1d** (>98%), **1j** (>98%), **1k** (95%), and **1l** (87%). These results indicate the necessity of MnO_2.
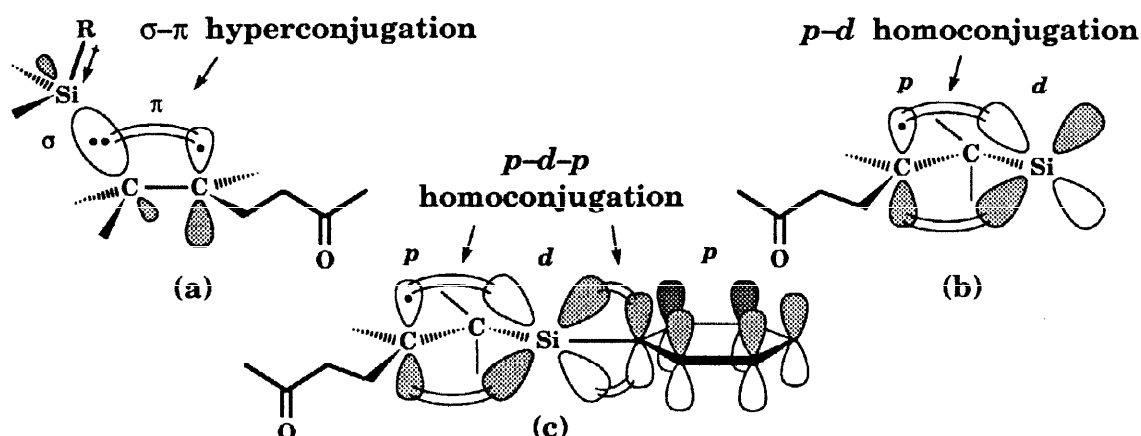

Figure 2. The role of a ligand on the silicon atom in the stabilization of a β carboradical

Being a low energy SOMO (singly occupied molecular orbital), α-keto carboradicals often react fast with molecules having a high-energy HOMO (highest occupied molecular orbital).[15] The C–C bond formation by addition of α-keto carboradicals to allylsilanes is considered irreversible; its efficiency would relate to the HOMO level of allylsilanes. A phenyl group possesses electron-withdrawing character and makes **1b–d** less electron-rich olefins than **1a**. In the studies on kinetics of the addition of allylsilanes with carbenium ions, Hagen and Mayr[8] also conclude that the change of a methyl to a phenyl group causes a decrease of addition rate by a factor of 5. On the other hand, the p orbitals in the phenyl group attached to the silicon atom could contribute to the "p–d homoconjugation" and thus may lead to the "p–d–p homoconjugation" for stabilization of the β carboradical (see Figure 2(c)). The net electronic effect of a silyl group is a combination that allowed **2b–d** generated in fair to good yields (56–75%). Given the same reason, we were able to obtain **2m–o** in 54–71% yields from **1b–d** and cyclohexanone (Table 1).

In conclusion, the electronic and the steric effects resulting from the ligands on a silicon atom have been investigated on the addition of a ketone to an allylsilane. Yields of the adducts are higher for allylsilanes containing a smaller electron-donating group, among which the trimethylsilyl group gave the best results. The addition process can be terminated by use of an electron-withdrawing group on the silicon atom.

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