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Synthesis of 2-Functionalized Allyl Tris(trimethylsilyl)silanes

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Abstract: Reactions of unsubstituted and 2-substituted allyl phenyl sulfides with tris(trimethylsilyl)silane provide the corresponding allyl tris(trimethylsilyl)silanes rapidly and in high yields while the related reactions with allyl phenyl sulfones occur more slowly and in moderate yields.

Over the last decade S_H2' type reactions (also called β-fragmentation reactions) have become an important radical method for the construction of functionalized molecules.[1] The key propagation steps for these radical chain reactions involve the attack of a radical on a double bond followed by β-cleavage of a radical from the allylic position. Radical allylations with allyl stannanes are among the most useful S_H2' reactions (eq 1)[2] and much attention has recently been focused on the application of 2-substituted allyl stannanes.[3] Allyl stannanes with C-2 substituents like Me,[3a,f,h,i] CO_2Et,[3b,f,i] CONHBu^t,[3b] CN,[3c] Cl,[3c] $SiMe_3$,[3d,h,i] SO_2Ph,[3e] and $SnMe_3$,[3g] have been synthesized and used in these reactions.

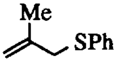
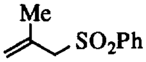
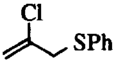
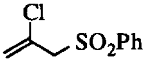
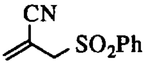
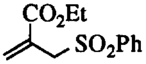
(1)

Based on the successful use of tris(trimethylsilyl)silane as an alternative to Bu_3SnH for the majority of its reactions,[4] it is reasonable to suggest that allyl tris(trimethylsilyl)silanes might be capable of sustaining radical chain reactions analogous to those of allyl stannanes.[5] In this paper, we describe the synthesis of allyl and 2-functionalized allyl tris(trimethylsilyl)silanes using the S_H2' methods (eq 2),[6] while in the following paper the use of these silanes as radical-based allylating agents is reported.[7] The choice of Y = PhS or $PhSO_2$ followed from the ease of the preparation of these compounds and the rapidity of β-elimination involving benzenethiyl and benzenesulfonyl radicals.[8] The choice of Z = H, Me, CO_2Et, CN, and Cl was based on the availability of the corresponding halides which are either commercial products (Me, CO_2Et) or readily prepared (CN, Cl).[2c]

(2)

The 2-substituted allyl phenyl sulfides were allowed to react with $(TMS)_3SiH$ under standard free radical conditions. In a typical experiment, the allylic substrate (0.2M), 1.0 - 1.5 equiv of $(TMS)_3SiH$ and α,α'-azo-

Table 1. Reaction of a variety of allylic sulfides and allylic sulfones with $(TMS)_3SiH$

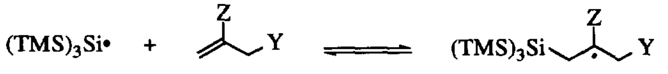
Reagent[a]	$(TMS)_3SiH$ / time[b]	Yield,[c] %	Reagent[d]	$(TMS)_3SiH$ / time[e]	Yield,[f] %
	1.5 equiv / 60 min	92 (98)		3.0 equiv /200 min	68
	1.5 equiv / 80 min	84 (90)		3.0 equiv /200 min	70
	1.5 equiv / 75 min	80 (93)		3.0 equiv /180 min	45
	1.0 equiv /15 min	82 (96)		3.0 equiv / 60 min	82
	1.0 equiv / 25 min	79 (97)		3.0 equiv / 60 min	77

[a] 0.2 M in benzene. [b] Conditions: AIBN (10 mol %) at 80 °C. [c] Isolated yields; In parenthesis NMR yields. [d] 0.2 M in benzene-d_6. [e] Conditions: Di-*tert*-butyl peroxide (10 mol %) at 140 °C. [f] NMR yields.

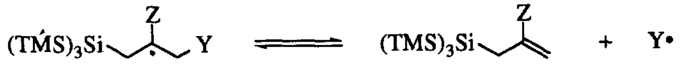
isobutyronitrile (AIBN; 10 mol %) were refluxed in benzene. The consumption of the starting materials as well as the appearance of products were followed by NMR or GC. The yields were first calculated on the crude mixture (^1H NMR using dibenzylether as internal standard), and workup with NaOH (1 N) followed by column chromatography on silica gel gave the desired isolated product. Table 1 reports the reaction conditions and product yields (NMR and isolated).[9] Reactions were rapid (15-80 min) and yields were high (80-98%). For Z = H, Me, and Cl, 1.5 equiv of silane was necessary for the disappearance of starting sulfides.

The reactions of 2-substituted allyl phenyl sulfones with $(TMS)_3SiH$ under similar conditions were sluggish. The consumption of sulfones was 55-75% after ca. 3h, whereas the yields were 40-70% (based on the conversion of starting materials). Longer reaction times did not improve the efficiency of these reactions. The results of the best of several conditions that we investigated for the reaction of sulfones are also summarized in Table 1 and correspond to 0.2 M of allylic substrate, 3.0 equiv of $(TMS)_3SiH$ and di-*tert*-butyl peroxide (10 mol %) at 140 °C. Under these conditions, however, a variety of by-products were formed (GC analysis) which rendered product isolation difficult. It has been shown that these by-products are derived from the reaction of the initially formed benzenesulfinic acid with $(TMS)_3SiH$ at 140 °C.[10]

The mechanism that we conceived for these reactions is outlined below (eqs 3-5). Tris(trimethylsilyl)silyl radicals, initially generated by small amounts of radical initiators, add to the double bond in a reversible manner giving rise to a radical intermediate that undergoes β-scission to form a sulfur-centered radical. Hydrogen abstraction from the silane completes the cycle of these chain reactions.[11]



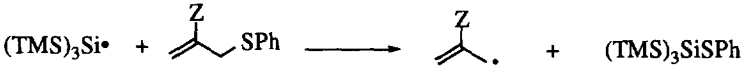
(3)



(4)

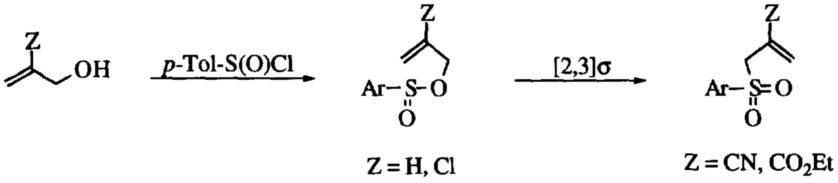
$$\mathrm{Y\bullet} + \mathrm{(TMS)_3SiH} \longrightarrow \mathrm{YH} + \mathrm{(TMS)_3Si\bullet} \qquad (5)$$

In the case of allyl phenyl sulfides, traces (1-2%) of $\mathrm{(TMS)_3SiSPh}$ were observed for Z = H or Me, whereas no such product was formed for Z = Cl, CN or $\mathrm{CO_2Et}$. We believe that these traces are significant and suggest a competitive path *via* homolytic substitution at the sulfur (eq 6). This explanation is in agreement with the behavior of silyl radicals[4] and suggests that for Z = H or Me the addition path is about two orders of magnitude higher than for the substitution at sulfur, and that for the other substituents the addition is even faster.



(6)

There is strong evidence from EPR experiments[12] that radicals of the type $\mathrm{RS(O)OCH_2CH_2^{\bullet}}$ undergo β-elimination of sulfonyl group, i.e. $\mathrm{RSO_2^{\bullet}}$ radical. Based on this finding, we tried to prepare a variety of 2-substituted allyl *p*-tolylsulfinates by coupling the sulfinyl chloride with the appropriate alcohol (eq 7). For Z = H, Cl the allylic alcohol gave the expected sulfinate in good yield. For Z = CN, $\mathrm{CO_2Et}$ the reaction of alcohols with *p*-methylbenzenesulfinyl chloride yielded sulfones instead of sulfinates. While [2,3]-sigmatropic rearrangement of allylic sulfinates to sulfones is fairly common when heating at ca. 100 °C,[13] this appears to be the first example to occur at ambient temperature and with electron withdrawing substituents at the C-2 position. However, the reactions of the two sulfinates with $\mathrm{(TMS)_3SiH}$ at 80 °C were unsuccessful, whereas at 140 °C all four allylic compounds behave similarly to the above reported 2-substituted allyl phenyl sulfones. It therefore seems probable that the thermal 2,3-sigmatropic shift precedes the radical substitution. The reaction is valuable because it allows the indirect radical substitution of an alcohol.



(7)

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5. (TMS)$_3$Si• radicals are known to add reversibly to a variety of double bonds and, therefore, to isomerize alkenes, see: Chatgilialoglu, C.; Ballestri, M.; Ferreri, C.; Vecchi, D. *J. Org. Chem.* **1995**, *60*, 3826.

6. Initial work on coupling reaction between (TMS)$_3$SiLi and CH$_2$=C(CO$_2$Et)CH$_2$Br gave an unseparable mixture of two isomer (1:1 ratio) and, therefore was abandoned.

7. The unsubstituted allylsilane has previously been used as an allylating agent with CCl$_4$, CHCl$_3$, CH$_3$CCl$_3$, (EtOCO)$_2$CHBr and NCCH$_2$Br under free radical conditions giving poor yields, see: Kosugi, M.; Kurata, H.; Kawata, K.; Migita, T. *Chem. Lett.* **1991**, 1327.

8. (a) The rate constants for the β-elimination of PhS• radical range from ca. 1x10^6 to 1x10^8 s^{-1} at room temperature, depending on the stabilizing effect of the Z group. For a review on thiyl radicals, see: Chatgilialoglu, C.; Guerra, M. In *Supplement S: The chemistry of sulphur-containing functional groups*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1993; pp 363-394. (b) For a review on sulfonyl radicals, see: Chatgilialoglu, C. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S.; Rappoport, Z.; Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; pp 1081-1113.

9. **CH$_2$=C(Z)CH$_2$Si(TMS)$_3$.** For Z = Me: ^{1}H NMR (CDCl$_3$): 0.18 (s, 27 H), 1.75 (broad s, J = 2 Hz, 3H), 1.77 (d, J = 2 Hz, 2H), 4.55 (m, 1H), 4.59 (m, 1H). ^{13}C NMR (CDCl$_3$): 1.2, 18.5, 24.8, 108.8, 146.1. GC/MS (m/e): 302 (M$^+$), 229, 174, 155, 113, 73, 59. For Z = Cl: ^{1}H NMR (CDCl$_3$): 0.20 (s, 27 H), 2.12 (d, J = 0.8 Hz, 2H), 4.93 (d, J = 1.08 Hz, 1H), 4.99 (m, 1H). ^{13}C NMR (CDCl$_3$): 1.0, 21.6, 109.4, 143.7. GC/MS (m/e): 322 (M$^+$), 247, 199, 173, 141, 73, 59. For Z = CN: ^{1}H NMR (CDCl$_3$): 0.21 (s, 27 H), 1.95 (d, J = 0.5 Hz, 2H), 5.54 (s, 1H), 5.62 (s, 1H). ^{13}C NMR (CDCl$_3$): 1.0, 16.5, 119.9, 123.8, 127.2. GC/MS (m/e): 298 (M$^+$- 15), 273, 240, 173, 159, 129, 73, 59. For Z = CO$_2$Et: ^{1}H NMR (CDCl$_3$): 0.22 (s, 27 H), 1.01 (t, J = 7.2 Hz, 3H), 2.19 (s, 2H), 4.04 (q, J =7.2 Hz, 2H), 5.34 (m, 1H), 6.03 (d, J = 4 Hz, 1H). ^{13}C NMR, (CDCl$_3$): 1.0, 11.7, 14.2, 60.6, 121.5, 141.5, 167.2. GC/MS (m/e): 360 (M$^+$), 345, 287, 259, 229, 191, 147, 73, 45.

10. Chatgilialoglu, C. unpublished results. Reactions of (TMS)$_3$SiH with S–O bonds will be reported separately.

11. Apparently (based on BDEs) the reaction 5 for Y = PhS is expected to be inefficient. For an explanation, see: Zavitsas, A. A.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645.

12. Chatgilialoglu, C.; Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1084.

13. For a review, see: Bravermann, S. In *The chemistry of Sulphones and Sulphoxides*; Patai, S.; Rappoport, Z.; Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; pp 665-716.

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