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Radical-Mediated Silyl- and Germyldesulfonylation of Vinyl and (α-Fluoro)vinyl Sulfones: Application of Tris(trimethylsilyl)silanes and Tris(trimethylsilyl)germanes in Pd-Catalyzed Couplings

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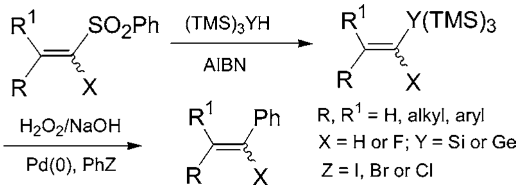
ABSTRACT



Radical-mediated silyl- and germyldesulfonylations of various vinyl and (α-fluoro)vinyl sulfones with tris(trimethylsilyl)silane and germanium hydrides provide access to vinyl and (α-fluoro)vinyl silanes and germanes. Upon oxidative treatment with hydrogen peroxide in basic aqueous solution, the vinyl tris(trimethylsilyl)silanes and -germanes undergo Pd-catalyzed cross-couplings with aryl halides.

Group 14 metals are employed as key elements in a number of cross-coupling[1] reactions between organometallics and organic halides. However, despite the wide application of Stille (Sn)[1,2] and the increasing attention to Hiyama (Si)[1,3] couplings, the coupling of organogermanes has received scant attention,[4] although germanium is located between silicon and tin in the periodic table. Complexity in the syntheses of vinyl germanyl derivatives in addition to their lower reactivity and the fact that they are usually prepared from acetylenic compounds has limited their development.[4,5] Moreover, since 1-fluoroalkynes are unstable and virtually unknown,[6] hydrosilylation and hydrogermylation approaches are inapplicable for the synthesis of (α-fluoro)vinyl silanes and germanes—classes of interesting fluoroalkenes which remain substantially unexplored. Herein, we report stereoselective radical-mediated silyl- and germyldesulfonylations[7] of vinyl

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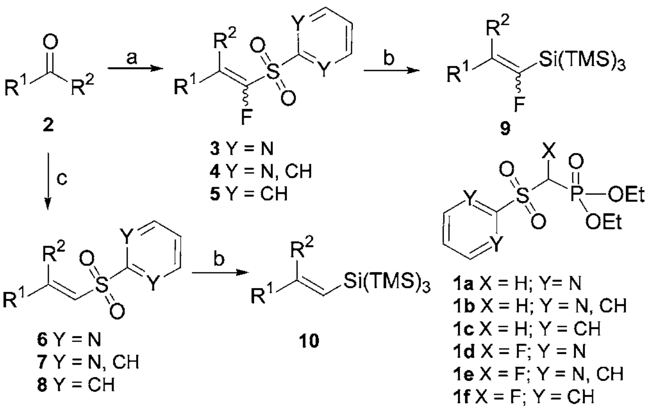
and (α-fluoro)vinyl sulfones with tris(trimethylsilyl)silane (TTMSS) and germanium hydrides to provide access to vinyl and (α-fluoro)vinyl silanes[8] and germanes. A general route (aliphatic/aromatic aldehydes/ketones → vinyl sulfones → vinyl silanes or germanes) offers convenient preparations of the alkenyl and 1-fluoroalkenyl tris(trimethylsilyl)silanes and -germanes, which we now have employed as substrates in Pd-catalyzed cross-coupling reactions with aryl halides.

Treatment of the sulfonyl-stabilized enolates generated from **1a−f** with various aromatic and aliphatic aldehydes and ketones **2a−f** gave selected *E/Z*-(α-fluoro)vinyl **3−5** (**a−f**) and *E*-vinyl **6−8** (**a−f**) sulfones in high yields (78−100%; Scheme 1). Treatment of the vinyl pyrimidin-2-yl sulfone **6a**(*E*) with TTMSS[9]/AIBN effected substitution of a sulfonyl group with a silyl group[10] (presumably via a radical addition−elimination mechanism[11]) to give vinyl silane **10a**(*E*) (50%). Such silyldesulfonylation provides a flexible alternative to the hydrosilylation of alkenes and alkynes with TTMSS under radical conditions.[12] Reaction of **3a** (*E/Z*, 19:1) with TTMSS produced (α-fluoro)vinyl silane **9a** (60%; *E/Z*, 24:1).

Scheme 1. Radical-Mediated Silyldesulfonylation



compds **2-10**	R1	R2
a	C_6H_5	H
b	$C_6H_5CH_2CH_2$	H
c	C_6H_{13}	H
d	C_6H_5	CH_3
e	-$(CH_2)_5$-	
f	$ClCH_2CH_2CH_2CH_2$	CH_3

[a] Reagents and conditions: (a) ArSO$_2$CHFPO(OEt)$_2$ (**1d−f**)/LHMDS/THF/−78 °C; (b) (TMS)$_3$SiH/AIBN/toluene (85 °C) or benzene (△); (c) ArSO$_2$CH$_2$PO(OEt)$_2$ (**1a−c**)/LHMDS/THF/−78 °C.

Phenyl sulfones **5** and **8** also underwent radical silyldesulfonylation with TTMSS to give **9** and **10**, respectively (Table 1). Treatment of pyridyl-2-yl sulfones **4b** and **7b** with TTMSS also affected silyldesulfonylation to give **9b** and **10b**. Nitrogen atom(s) in the ring did not have a significant effect on the time required or yields of the silyldesulfonylations. This is in contrast with radical removal of (*π*-deficient heterocyclic)sulfonyl groups from the saturated α-carbon atoms of carboxylic and phosphonic esters.[13] However, yields for silyldesufonylations of the α-fluoro sulfones in series **b** increased with increasing *π*-deficient character of the sulfonyl group [e.g., **3b**, **4b**, and **5b** gave **9b** in 83%, 66%, and 51% yields, respectively].

Table 1. Silyldesulfonylation of Vinyl Sulfones **3−8**

substrate (*E/Z*)[a]	product (*E/Z*)[a]	yield (%)[b]	substrate	product	yield (%)[b]
3a (95/5)	**9a** (96/4)	60	**5e**	**9e**	75
3b (65/35)	**9b** (96/4)	83	**6a**[d]	**10a**[d]	50
3d (96/4)	**9d** (100/0)	40	**6b**[d]	**10b**[d]	30
4b (67/33)	**9b** (94/6)	66	**7b**[d]	**10b**[d]	57
5a (97/3)	**9a** (99/1)	90	**8a**[d]	**10a**[d]	60
5b (71/29)	**9b** (100/0)	51	**8b**[d]	**10b**[d]	81
5b (0/100)	**9b** (100/0)	66[c]	**8c**[d]	**10c**[d]	83
5c (87/13)	**9c** (98/2)	42	**8e**	**10e**	68
5d (28/72)	**9d** (34/66)	73			

[a] Based on ^{1}H or ^{19}F NMR. [b] Isolated yields. [c] 4.5 equiv of TTMSS, 3.0 equiv of AIBN. [d] *E* isomer.

Silyldesulfonylation of the vinyl sulfones **3−8** occurred with retention or enrichment[11] of *E* stereochemistry. Treatment of **5b**(*Z*) with an excess of TTMSS (4.5 equiv, 5 h, AIBN) resulted in *cis−trans* isomerization of the starting vinyl sulfone to produce **5b**(*E*) in addition to product **9b**(*E*), with all **5b**(*Z*) being consumed. TTMSS is known to effectively isomerize alkenes by an addition−elimination process.[12b] Attempted silyldesulfonylation of **3−8** with other silanes [e.g., Ph$_3$SiH, Et$_3$SiH, or (EtO)$_3$SiH] under radical conditions did not produce the corresponding vinyl silanes.

Treatment of the vinyl phenyl sulfone **8a**(*E*) with (TMS)$_3$GeH/AIBN gave the vinyl germanes **15a**(*E*) stereo-

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(7) (a) For review on desulfonylation methods see: Najera, C.; Yus, M. *Tetrahedron* **1999**, *55*, 10547. (b) Vinyl sulfones react with tributyltin hydride/AIBN to afford vinyl stannanes (stannyldesulfonylation reaction): McCarthy, J. R.; Matthews, D. P.; Stemerick, D. M.; Bey, P.; Lippert, B. J.; Snyder, R. D.; Sunkara P. S. *J. Am. Chem. Soc.* **1991**, *113*, 7439. McCarthy, J. R.; Huber, E. W.; Le, T.-B.; Laskovics, F. M.; Matthews, D. P. *Tetrahedron* **1996**, *52*, 45.

(8) (a) Access to 1-(fluoroalkenyl)silanes based on the reaction of FC(SiMe$_3$)$_2$SnBu$_3$ (generated from CBr$_2$F$_2$/Me$_3$SiCl/Bu$_3$SnH)/BuLi with aromatic aldehydes was reported: Shimizu, M.; Hata, T.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1685. (b) Synthesis of (*E/Z*)-1,2-difluoro-(triethylsilyl)ethylene from bromotrifluoroethylene was reported: Xue, L.; Lu, L.; Pederson, S. D.; Liu, Q.; Narske, R. M.; Burton, D. J. *J. Org. Chem.* **1997**, *62*, 1064. (c) Waschbüsch, R.; Carran, J.; Savignac, P. *Tetrahedron* **1996**, *52*, 14199.

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(10) Treatment of (1-alkenyl)sulfones with Bu$_3$SnLi/Me$_3$SiCl effected “overall” silyldesulfonylation to give (1-alkenyl)silanes: Ochiai, M.; Ukita, T.; Fujita, E. *Chem. Lett*. **1983**, 1457.

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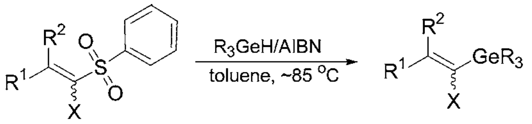
Scheme 2. Radical-Mediated Germyldesulfonylation (see Scheme 1 for description of R^1 and R^2)



5 X = F
8 X = H

11 R = Me$_3$Si, X = F
12 R = Bu, X = F
13 R = Ph, X = F
14 R = 2-furyl, X = F

15 R = Me$_3$Si, X = H
16 R = Bu, X = H
17 R = Ph, X = H
18 R = 2-furyl, X = H

selectively (Scheme 2). Analogous treatment of *E* vinyl sulfones **8** with Bu$_3$GeH, Ph$_3$GeH, and tri(2-furyl)germane produced the corresponding *E* germanes **16**, **17**, and **18**,[14] respectively (Table 2). Our radical germyldesulfonylation has also generally permitted synthesis of the previously unknown (α-fluoro)vinyl germanes **11**−**14** in high yields. Similarly to silyldesulfonylation, this novel substitution of a sulfonyl group with a germyl group occurred with retention or enhancement of *E* stereochemistry.

Table 2. Germyldesulfonylation of Vinyl Sulfones **5** and **8**

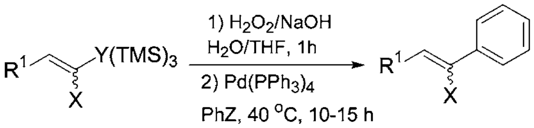
substrate (*E*/*Z*)^a	product (*E*/*Z*)^a	yield (%)^b	substrate	product	yield (%)^b
5a (100/0)	**11a** (100/0)	90	**5e**	**13e**	87
5a (97/3)	**12a** (100/0)	91	**8a**^{c}	**15a**^{c}	34 (80^a)
5a (97/3)	**13a** (100/0)	98	**8a**^{c}	**16a**^{c}	52 (90^a)
5a (97/3)	**14a** (100/0)	94	**8a**^{c}	**17a**^{c}	50 (95^a)
5b (100/0)	**12b** (100/0)	66	**8b**^{c}	**18b**^{c}	50
5b (71/29)	**13b** (99/1)	76	**8c**^{c}	**17c**^{c}	70
5b (100/0)	**14b** (100/0)	55	**8e**	**17e**	96
5c (87/13)	**13c** (98/2)	90			
5f (100/0)	**13f** (100/0)	98			

^{a} Based on ^{1}H or^{19}F NMR. ^{b} Isolated yields. ^{c} *E* isomer.

The germyldesulfonylation protocol tolerates functional groups vulnerable to radical hydrogenolysis with tributyltin hydride and TTMSS.[9] For example, treatment of **5f** with Ph$_3$GeH gave **13f** showing that a chloro substituent was not affected by the mild conditions required for germyldesulfonylation.[15]

We found that vinyl tris(trimethylsilyl)silanes and -germanes serve as good nucleophiles in coupling reactions. Thus, treatment of silanes **10a**(*E*) and **10b**(*E*), first with hydrogen peroxide in basic aqueous solution followed by addition of Pd(PPh$_3$)$_4$ and iodobenzene, gave the coupling products **19a** (*E*, 75%) and **19b** (*E*, 56%; Scheme 3). Similar coupling of **10a**(*Z*)[12a] with bromobenzene gave **19a**(*Z*) stereospecifically. Apparently, H$_2$O$_2$ cleaved Si−Si bond(s)[16] to generate siloxane intermediates, which are known to be good substrates for Hiyama coupling.[3]

Scheme 3. Pd-Catalyzed Cross-Coupling of the Vinyl TTMS Silanes and Germanes



substrate		product	yield
10a(*E*)	Y = Si, X = H, R^1 = Ph, Z = I	**19a**(*E*)	75%
10a(*Z*)	Y = Si, X = H, R^1 = Ph, Z = Br	**19a**(Z)	55%
10b(*E*)	Y = Si, X = H, R^1 = PhCH$_2$CH$_2$, Z = I	**19b**(*E*)	56%
11a(*E*)	Y = Ge, X = F, R^1 = Ph, Z = I	**20a**(Z)	63%
15a(*E*)	Y = Ge, X = H, R^1 = Ph, Z = I	**19a**(*E*)	50%
15a(*E*)	Y = Ge, X = H, R^1 = Ph, Z = Br	**19a**(*E*)	88%
15a(*E*)	Y = Ge, X = H, R^1 = Ph, Z = Cl	**19a**(*E*)	37%
15a(*Z*)	Y= Ge, X = H, R^1 = Ph, Z = I	**19a**(*E/Z*, 1/3)	60%

The oxidative treatment of germanes **11a**(*E*) (H$_2$O$_2$/NaOH) followed by addition of Pd(PPh$_3$)$_4$ and iodobenzene gave fluoro stilbene **20a** (*Z*, 63%).[17] Coupling of **15a**(*E*) with iodobenzene and bromobenzene produced stilbene **19a**(*E*). Even less reactive chlorobenzene[1b] yielded **19a**(*E*) when coupled with **15a**(*E*). Coupling of **15a**(*Z*), prepared by hydrogermylation of phenylacetylene with (TMS)$_3$GeH,[18] gave **19a** (*E/Z*, 1:3). H$_2$O$_2$ might cleave Ge−Si bond(s)[16d] to generate germanol(s)[4c] intermediates.

In summary, we have developed radical-mediated silyl- and germyldesulfonylations of various vinyl and (α-fluoro)-vinyl sulfones to provide access to vinyl and (α-fluoro)vinyl silanes and germanes. Vinyl tris(trimethylsilyl)silanes and -germanes successfully undergo Pd-catalyzed cross-couplings with aryl halides

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Supporting Information Available: Experimental procedures and characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Vinyl tri(2-furyl)germanes were recently employed in the Pd-catalyzed synthesis of biaryls.[4c]

[15] Treatment of **5f** with TTMSS/AIBN effected homolysis of the carbon−chlorine bond, and the 5-*exo*-trig cyclization product, 1-[fluoro-(phenylsulfonyl)methyl]-1-methylcyclopentane (31%), was produced.

[16] For the cleavage of the Si−Si bond under oxidative conditions see: (a) Razuvaev, G. A.; Semenov, V. V.; Brevnova, T. N.; Kornev, A. N. *J. Organomet. Chem.* **1985**, *287*, C31. (b) Naka, A.; Yoshida, K.; Ishikawa, M.; Miyahara, I.; Hirotsu, K.; Cha, S.-H.; Lee, K. K.; Kwak, Y.-W. *Organometallics* **2001**, *20*, 1204. (c) Ackerhans, C.; Roesky, H. W.; Labahan, T.; Magull, J. *Organometallics* **2002**, *21*, 3671. (d) Mochida, K.; Shimizu, H.; Kugita, T.; Nanjo, M. *J. Organomet. Chem.* **2003**, *673*, 84.

[17] (a) The (α-fluoro)vinylstannanes in combination with CuI are substrates for Stille coupling: Chen, C.; Wilcoxen, K.; Zhu, Y.-F.; Kim, K.-I.; McCarthy, J. R. *J. Org. Chem.* **1999**, *64*, 3476. (b) Coupling of (α-fluoro)vinylsilane **9a** with iodobenzene gave variable yields of **20a** (10−50%) in addition to the *Z*-*β*-fluorostyrene byproduct (30−70%). (c) CsF-assisted coupling of (1-fluorovinyl)methyldiphenylsilane has been reported: Hanamoto, T.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 6354.

[18] Bernardoni, S.; Lucarini, M.; Pedulli, G. F.; Valgimigli, L.; Gevorgyan, V.; Chatgilialoglu, C. *J. Org. Chem.* **1997**, *62*, 8009.