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An Efficient Synthesis of Vinylsilanes from Acylsilanes and Alkyl 1-Phenyl-1*H*-tetrazol-5-yl Sulfones. Brook vs Smiles Rearrangement

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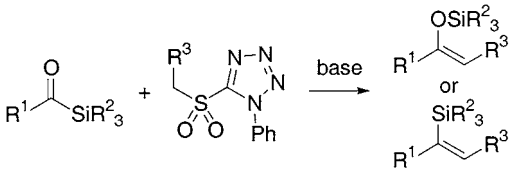
ABSTRACT



Vinylsilanes are formed in high yields in the reaction of representative acyl(trimethyl)silanes with anions generated from Kocienski's sulfones.

Vinylsilanes are important intermediates in stereocontrolled synthesis.[1,2] One of the most versatile methods for the synthesis of 1,2-dialkylvinylsilanes consists of the reaction of easily available acylsilanes[3] with ylides generated from alkyl(triphenyl)phosphonium halides.[4] However, applications of this method are hampered by moderate or low yields and ambiguity in establishing the ylide function in complex synthetic building blocks. It occurred to us that various types of vinylsilanes could be conveniently accessed by reaction of acylsilanes with anions generated from certain heterocyclic sulfones, provided that the intermediate adduct would undergo the Smiles rearrangement[5] rather that the Brook rearrangement.[6] Thus, reaction of acylsilane ***i*** (Scheme 1) with an anion generated from sulfone ***ii*** would give adduct ***iii***, which may rearrange via two routes. The Brook rearrangement, followed by elimination of the sulfonyl moiety from ***iv***, would lead (plain arrow, route a) to silyl enol ether ***v*** and, after hydrolysis, to the respective ketone. It is known that the reaction of α-lithioalkyl phenyl sulfones with acylsilanes is usually followed by Brook rearrangement and sulfonyl group elimination to afford the respective ketones.[7] On the other hand, due to the presence of an electrophilic C═N bond in the heterocyclic system, the intermediate ***iii*** could undergo the Smiles rearrangement (route b) affording sulfinic acid derivative ***vi***, which would then fragment to

(1) Oshima, K. In *Organometallics*: *Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds*; Fleming, I., Jacobsen, E. N., Ley, S. V., Noyori, R., Regitz, M., Reider, P. J., Schaumann, E., Shinkai, I., Thomas, E. J., Trost, B. M., Eds.; Georg Thieme Verlag: Stuttgart, New York, 2002; Vol. 4, pp 713−756.

(2) (a) Itami, K.; Nokami, T.; Yoshida, J. *Org. Lett.* **2000**, *2*, 1299−1302. (b) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726−12727. (c) Kwan, M. L.; Battiste, M. A. *Tetrahedron Lett.* **2002**, *43*, 8765−8768.

(3) Page, P. C. B.; McKenzie, M. J. In *Organometallics*: *Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds*; Fleming, I., Jacobsen, E. N., Ley, S. V., Noyori, R., Regitz, M., Reider, P. J., Schaumann, E., Shinkai, I., Thomas, E. J., Trost, B. M., Eds.; Georg Thieme Verlag: Stuttgart, New York, 2002; Vol. 4, pp 513−567.

(4) (a) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1988**, *29*, 2425−2428. (b) Anderson, C. L.; Soderquist, J. A.; Kabalka, G. W. *Tetrahedron Lett.* **1992**, *33*, 6915−6918.

(5) (a) Truce, W. E.; Kreider, E. M.; Brand, W. W. *Org. React. (N.Y.)* **1970**, *18*, 99. (b) Boschi, D.; Sorba, G.; Bertinaria, M.; Fruttero, R.; Calvino, R.; Gasco, A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1751−1757. (c) Izod, K.; O'Shaughnessy, P.; Clegg, W. *Organometallics* **2002**, *21*, 641−646. (d) Selvakumar, N.; Srinivas, D.; Azhagan, A. M. *Synthesis* **2002**, 2421−2425.

(6) (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77−84. (b) Moser, W. H. *Tetrahedron* **2001**, *57*, 2065−2084. (c) Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *J. Org. Chem.* **2002**, *67*, 8450−8456 and references cited.

(7) (a) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609−5617. (b) Zhang, J. H.; Corey, E. J. *Org. Lett.* **2001**, *3*, 3215−3216.

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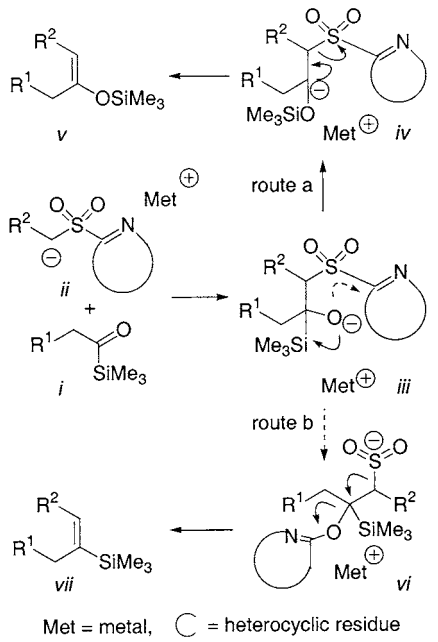
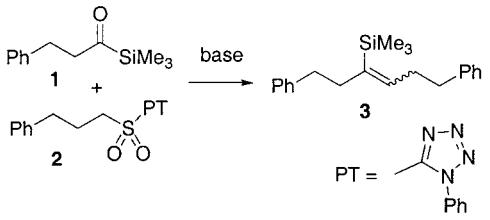
Scheme 1



vinylsilane ***vii***. Application of the Smiles rearrangement in olefin synthesis has been well documented.[8]

Scheme 2



For exploratory studies acylsilane **1** (Scheme 2) and 1-phenyl-1*H*-tetrazol-5-yl (PT) sulfone **2** were chosen, the latter representing a class of sulfones particularly useful in the Julia olefination reaction.[8b,9] Important results are summarized in Table 1.

Vinylsilane **3** was obtained in excellent yields with use of lithium hexamethyldisilazide (LiHMDS) as the base and by performing the reaction either with separate sulfonyl anion generation (Method A) or under "Barbier-type" conditions (Method B) (Table 1, entries 1 and 2, respectively). In both cases a mixture of *E*- and *Z*-isomers in a ratio of 64:36 was formed. The selectivity with respect to the *E*-isomer was improved by lowering the temperature (entries 3 and 4). The reaction was relatively fast; extending the reaction time

Table 1. Reaction of Acylsilane **1** with Sulfone **2** in THF Affording **3** (Scheme 2): Effects of the Addition Mode, Base, and Temperature

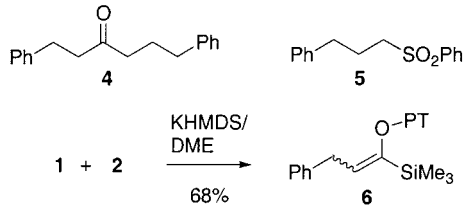
	base; method[a]	temp (°C)	time (min)	yield[b] (%)	*E*/*Z*[c]
1	LiHMDS;[d] A	−78	30	93	64:36
2	LiHMDS; B	−78	30	92	64:36
3	LiHMDS; A	−85	60	89	74:26
4	LiHMDS; B	−85	30	93	75:25
5	LiHMDS; B	−95	45	84	75:25
6	LiHMDS; B	−60	18 h	53	67:33
7	LDA; A	−78	90	61[e]	67:33
8	NaHMDS;[d] A	−78	40	50	59:41
9	KHMDS;[f] A	−78			

[a] Method A: The anion was generated from the sulfone (1.25 mol equiv) and the base at −60 to −78 °C. The mixture was brought to the indicated temperature and a solution of acylsilane (1 mol equiv) was added. Method B: To a solution of **1** (1 mol equiv) and sulfone **2** (1.25 mol equiv) in THF was added a solution of the base. [b] The product was isolated and purified by chromatography. [c] Determined by GC. [d] 1 M solutions in THF, purchased from Aldrich. [e] Acylsilane **1** (9%) was recovered; ketone **4** (20%) was isolated. [f] 0.5 M solution in toluene, purchased from Aldrich.

resulted in lower yield (entry 6). On replacement of LiHMDS with LDA, a somewhat lower yield was obtained but the isomer ratio was virtually the same (entry 7). With NaHMDS as the base, **3** was obtained in a lower yield and with poor stereoselectivity (Table 1, entry 8).

Analysis of the byproducts in the discussed reactions revealed the presence of a small amount of ketone **4** and (before aqueous workup) the respective trimethylsilyl enol ether (Scheme 3) formed via the Brook rearrangement. Accordingly, ketone **4** was obtained in 68% yield in the reaction of **1** with phenyl sulfone **5** and LiHMDS. Another minor side product was identified as the enol ether derivative **6**.

Scheme 3



Surprisingly, the use of KHMDS as the base in the reaction of **1** with **2** (in THF) generated **6** as the main product. When **1** was added to the anion generated from **2** and KHMDS in DME at −78 °C, crystalline PT enol ether **6** was isolated in 68% yield after chromatography.[10] Stable PT enol ethers have no precedent in the literature, to the best of our knowledge.

The effect of solvent on the product yield and the isomer ratio in the reaction of **1** and **2** with LiHMDS as the base

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(9) Blakemore, P. R.; Cole, W. J.; Kocienski, P. J.; Morley, A. *Synlett* **1998**, 26−28.

(10) Compound **6**: mp 61−62 °C (hexane); ^{1}H NMR δ (ppm) 1.18 (s, 9H), 3.50 (d, J = 7.1 Hz, 2H), 5.88 (t, J = 7.1 Hz, 1H), 7.17−7.34 (m, 5H), 7.43−7.60 (m, 3H), and 7.74−7.79 (m, 2H). ^{13}C NMR inter alia −1.55, 32; the structure was confirmed by elemental analysis.

was examined. As shown in Table 2, the use of DME at −60 °C gave **3** in a lower yield than THF; moreover, vinylsilane was accompanied by substantial amounts of ketone **4** (Table 2, entry 2). The reactions in diethyl ether

Table 2. Effect of Solvent in the Reaction of Acylsilane **1** (1 mol equiv) with Sulfone **2** (1.25 mol equiv) with Use of 1 M LiHMDS in THF[a]

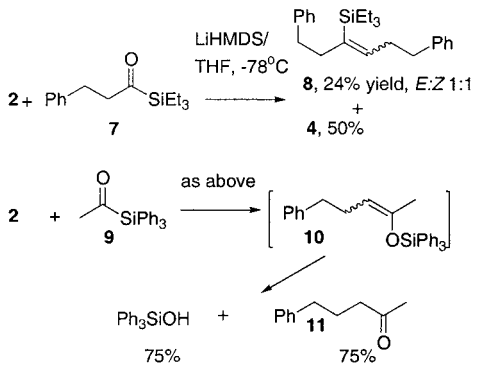
	solvent	temp (°C)	time (min)	yield[b](%)	*E*/*Z*
1	THF	−78	30	93	64:36
2	DME[c]	−70	40	49[d]	58:42
3	Et_2O[c]	−78	60	50	64:36
4	MeO^{t}Bu[c]	−78	150	47	54:46
5	DMF	−70	45	43	50:50
6	CH_2Cl_2	−78	30	59	55:45
7	PhMe	−78	30	77	47:53
8	PhMe[e]	−78	30	74	33:67

[a] A solution of 1 mmol of **1** and 1.2 mmol of **2** in 3 mL of the appropriate solvent was treated with 1.2 mL of 1 M LiHMDS in THF. [b] Yield refers to products purified by chromatography. [c] Metalated sulfone partly precipitated; method A was used (see footnote to Table 1). [d] Ketone **4** (32%) was also isolated. [e] LiHMDS was generated in situ from HMDS and BuLi/hexanes.

(entry 3) and *tert*-butyl methyl ether (entry 4) were complicated by low solubility of the lithiated sulfone. The reaction in DMF (entry 5) or dichloromethane (entry 6) afforded lower yields. In toluene as the solvent, vinylsilanes **3** were obtained in 77% yield as a mixture of isomers in a ratio of 47:53 (entry 7). Since stereochemical bias has been reversed in the latter case, an analogous experiment in which LiHMDS was generated from HMDS and BuLi (in hexanes) in situ was carried out. As expected, after exclusion of THF, the content of *Z*-isomer increased (isomer ratio 33:67, entry 8).

The effect of the silyl group was assessed in the reaction of triethylsilyl acylsilane **7** and sulfone **2** (Scheme 4). The

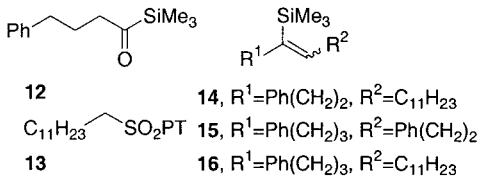
Scheme 4



reaction with the anion generated with LiHMDS under Barbier conditions afforded vinylsilane **8** and ketone **4**, the latter prevailing. The reaction of acyl(triphenyl)silane **9** with the anion generated from sulfone **2** led to labile silyl enol ether **10** and, after hydrolysis, ketone **11** and triphenylsilanol (each isolated in 75% yield).

The syntheses of some other vinylsilanes from the respective acylsilanes and PT sulfones are presented in Scheme 5

Scheme 5



and Table 3. In all cases high yields and significant stereoselectivities were attained. The solvent effect rendering the reversal of configuration of the main products was confirmed.

Table 3. Reaction of Acylsilanes with Sulfones Induced by LiHMDS under Barbier Conditions (Method B) at −78 °C

reactants	solvent	product	yield (%)	*E*/*Z*
1, **13**	THF	**14**	79	65:35
	PhMe[a]		69[b]	39:61
12, **2**	THF	**15**	78	62:38
	PhMe		76	32:68
12, **13**	THF	**16**	84	68:32
	PhMe[a]		61[b]	42:58

[a] Sulfone **13** is sparingly soluble in PhMe; method A was applied. [b] Starting acylsilane (ca. 15%) was recovered; a side product (ketone) was present.

Since hydrodesilylation of vinylsilanes occurs with retention of configuration,[11] our method may be extended to stereoselective synthesis of alkenes. Notably, a stereoselective approach to *E*-vinylsilanes contributes to the methodology of synthesis of *Z*-alkenes which is in demand.

The stereochemistry of the isomeric vinylsilanes was assigned on the grounds of established criteria[4a] and confirmed by nuclear Overhauser (NOE) effect measurements and comparison of $^{29}Si-^{1}H$ three-bond coupling constants[12] in the ^{1}H NMR spectra.[13]

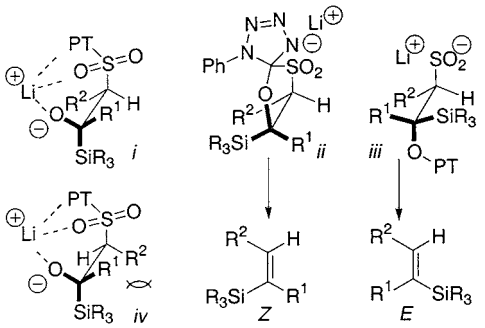
We reason that the steric course of the reaction is dominated by nonbonding interactions of the sterically bulky silyl and sulfonyl groups. In the intermediate adduct, these groups have a trans relationship (Scheme 6, ***i*** and ***iv***). Out of two diastereomeric adducts, ***i*** and ***iv*** (Scheme 6), the former, with fewer gauche interactions, is favored. As postulated by Julia and co-workers,[14] the countercation is bound to the heterocycle nitrogen and to the sulfonyl group

(11) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, *16*, 2825−2828.

(12) (a) Kupce, E.; Lukevics, E. In *Isotopes in the Physical and Biomedical Sciences*; Buncel, E., Jones, J. R., Eds.; Elsevier: Amsterdam, The Netherlands, 1991; Vol. 2, pp 213−295. We thank Professor Krystyna Kamieńska-Trela for bringing this reference to our attention. (b) Grignon-Dubois, M.; Laguerre, M. *Organometallics* **1988**, *7*, 1443−1446.

(13) $^{1}H-^{39}Si$ coupling constants for *E* and *Z* isomers, $J = 8$ or 13 Hz, respectively.

Scheme 6



oxygen atom. The Smiles rearrangement occurs via intermediate ***ii*** with coplanar arrangement of the involved centers (***ii***, for clarity of drawing no partial bonds are shown) and in THF is followed by rotation around of the central C−C bond to give intermediate ***iii***, which undergoes *anti*-periplanar elimination. By this route, the *E*-vinylsilane is formed. Increasing the bulkiness of the silyl group increases eclipsing interactions in ***ii***, which favors migration of the silyl group at the expense of heterocycle migration. It is of relevance that the triphenylsilyl group shows higher migratory aptitude in the Brook rearrangement,[15] presumably due to electronic factors. With regard to the solvent effect, it appears likely that after collapse of ***ii*** in toluene tighter binding of the Li cation to the heteroatoms restricts rotation to form ***iii***, in which case concerted fragmentation of intermediate ***ii*** provides a plausible alternative. Effects of the size of alkyl groups R^1 and R^2 and the nature of the heterocycle in the reaction are currently under investigation.

In conclusion, an efficient method for synthesis of vinylsilanes was developed.[16] *E*-Disubstituted vinylsilanes that are difficult to access on other routes were obtained as predominant products. It was demonstrated that reaction of acyl(trialkyl/aryl)silanes with metalated PT sulfones is followed either by a Smiles or by a Brook rearrangement to afford vinyl silanes or silyl enol ethers, respectively, depending on structural factors and the reaction conditions. Formation of stable and potentially useful PT enol ethers was observed.

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(15) Brook, A. G.; LeGrow, G. E.; MacRae, D. M. *Can. J. Chem.* **1967**, *45*, 239−253.

(16) **Typical procedure**: To a solution of acylsilane **1** (149 mg, 0.722 mmol) and sulfone **2** (307 mg, 0.935 mmol) in THF (5 mL), stirred under argon at −85 °C, was added LiHMDS (1 M in THF, 0.94 mL, 0.94 mmol) dropwise. Stirring at −85 °C was continued for 30 min and then the reaction was quenched with water (1 mL). The mixture was allowed to warm to room temperature and was partitioned between water (20 mL) and methylene chloride (20 mL). The water layer was extracted with methylene chloride (2 × 20 mL). Combined organic extracts were dried over Na_2SO_4 and the solvent was evaporated. The residue was chromatographed on silica gel to give vinylsilane **3** (208 mg, 93% yield, *E*:*Z* 75:25 by GC, Quadrex Q5-30W-0.5F column, programmed temperature, 80−250 °C, 15 °C/min, R_t 17.4 and 18.4 min, respectively).