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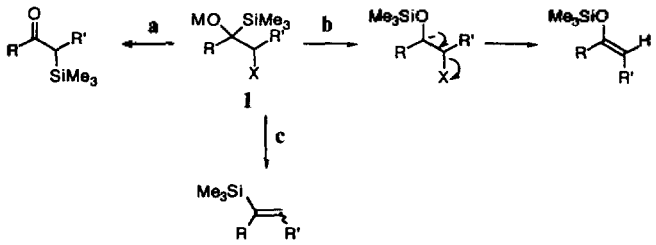
4. During the reaction compound **5c** is not precipitated out.



Scheme 1.

Reactions of Acylsilanes with Phenylthio(trimethylsilyl)methyllithium. A Competitive Peterson and Brook Rearrangement-Elimination Reactions in the β-Thiophenyl-α,β-disilylalkoxides

Kyung-Tae Kang*, Tae Myung Sung, Kyung-Ran Lee, Jong Gun Lee, and Kyung Kyu Jyung†

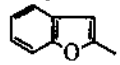
Department of Chemistry, and
†Department of Chemical Education,
Pusan National University, Pusan 609-735

Received July 6, 1993

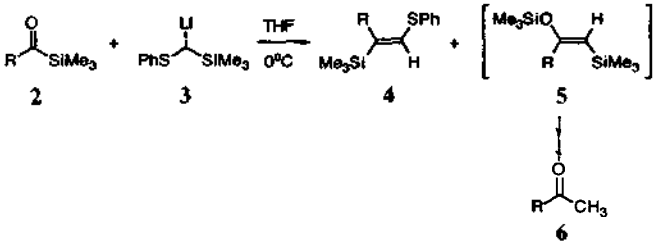
The intermediate α-trimethylsilyl-β-X-alkoxides **1** undergo different types of reactions depending on the nature of R and X groups. The intermediate **1** (X=Cl) formed in the reaction of (α-chloroacyl)silane with either Grignard reagents[1] or enolates[2] suffers silyl migration from C to C, giving β-ketoalkylsilane (path *a*, Scheme 1). The intermediate **1** with a suitable leaving group such as PhS, PhSO, $PhSO_2$, PhSe, CN, or OH affords silyl enol ether *via* Brook rearrangement-elimination sequence (path *b*).[3] The intermediate **1**(X=Ph_3P^+) generated from the reaction of acylsilanes with Wittig reagents undergoes alternative reactions depending on R group. When R is an alkyl group, only the Wittig product is formed (path *c*). On the other hand, if R is an aryl group silyl enol ether is produced through path *b*.[4] Thus, we examine α,β-disilylalkoxides with a phenylthio group (**1**, X=PhS, R'=$SiMe_3$) in order to distinguish among the existing competitive reaction pathways.

When phenylthio(trimethylsilyl)methyllithium (**3**)[5] prepared by the treatment of phenylthio(trimethylsilyl)methane with *n*-butyllithium in tetrahydrofuran (THF) reacted with acylsilanes **2** at 0℃, mixtues of (β-phenylthio)vinylsilanes **4** and methyl ketones **6** were produced after work-up and chromatography. All attempts to isolate silyl enol ethers **5** were failed. The results are shown in Table 1.

Table 1. Yields of **4** and **6**

Acylsilane **2**		Vinylsilane **4**		Ketone **6**
Compound	R	yield(%)*	isomeric purity of E**	yield(%)*
a	Ph	49	>99%	40
b	*p*-ClC_6H_4	47	>99%	51
c	*p*-BrC_6H_4	52	99%	47
d	*p*-$CH_3C_6H_4$	47	>99%	44
e	*p*-$CH_3OC_6H_4$	51	85%	25
f		42	98%	44
g		50	86%	36
h	$PhCH_2CH_2$	40	96%	21
i	$CH_3(CH_2)_9CH_2$	51	95%	24

*Isolated yields
**Determined by ^1H NMR and GC analysis



The structures of (β-phenylthio)vinylsilanes **4** were assigned by ^1H, ^{13}C and MS spectroscopy (Table 2). *E*-vinylsilanes were predominant over *Z*-isomers (>85%) in every cases

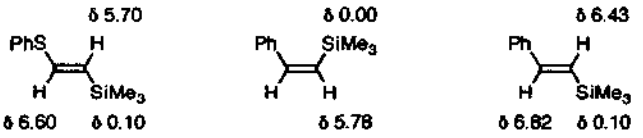
Table 2. Spectral Data of (β-phenylthio)vinylsilane **4**

Vinylsilane	^1H-NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C-NMR ($CDCl_3$) δ	MS m/z (rel. intensity, %)
(E)-4a	0.12 (s, 9H), 6.76 (s, 1H), 7.08-7.41 (m, 10)	−1.43, 126.30, 126.80, 127.46, 128.42, 129.05, 129.97, 135.12, 136.27, 141.64, 144.13	284 (M^+, 9), 269 (1), 167 (13), 84 (12), 73 (100)
(E)-4b	0.11 (s, 9H), 6.76 (s, 1H), 7.00-7.40 (m, 9H)	−1.48, 124.59, 126.02, 127.00, 128.71, 128.89, 129.13, 130.08, 132.14, 135.88, 135.98, 140.04, 142.79	320 (M+2, 2), 318 (M^+, 6), 167 (12) 84 (8), 73 (100)

(E)-4c	0.10 (s, 9H), 6.76 (s, 1H), 6.95−7.55 (m, 9H)	−1.47, 120.27, 127.03, 127.14, 129.26, 130.09, 131.65, 138.85, 135.95, 140.54, 142.75	364 (M+2, 5), 362 (M^+, 5), 167 (17), 73 (100)
(E)-4d	0.11 (s, 9H), 2.36 (s, 3H), 6.73 (s, 1H), 6.95-7.40 (m, 9H)	−1.39, 21.22, 126.73, 127.34, 129.02, 129.16, 129.92, 134.87, 135.84, 136.39, 138.54, 144.12	298 (M^+, 23), 283 (2), 167 (17), 84 (16), 73 (100)
(E)-4e	0.11 (s, 9H), 3.82 (s, 3H), 6.73 (s, 1H), 7.10-7.41 (m, 9H)	−1.35 ($SiMe_3$)	314 (M^+, 13), 167 (60), 84 (9), 73 (100)
(Z)-4e	0.26 (s, 9H), 3.79 (s, 3H), 7.10-7.41 (m, 10H)	0.16 ($SiMe_3$)	314 (M^+, 11), 167 (11), 84 (28), 73 (100)
(E)-4f	0.20 (s, 9H), 6.80 (s, 1H), 6.95-7.50 (m, 8H)	−0.94, 124.66, 125.59, 126.89, 127.22, 129.18, 130.34, 134.25, 136.11	290 (M^+, 12), 167 (13), 84 (26), 73 (100)
(E)-4g	0.30 (s, 9H), 6.88 (s, 1H), 6.90 (s, 1H), 7.18-7.60 (m, 9H)	−0.49, 105.52, 110.88, 120.85, 122.56, 124.04, 127.59, 127.71, 129.06, 129.23, 130.73, 136.14, 137.66, 153.86, 156.67	324 (M^+, 10), 86 (11), 73 (100)
(E)-4h	0.14 (s, 9H), 2.58-2.63 (m, 2H), 2.70-2.75 (m, 2H), 6.54 (s, 1H), 7.10-7.45 (m, 10H)	−1.35, 34.57, 35.02, 125.87, 126.64, 128.37, 129.07, 129.83, 133.18, 136.27, 142.26, 142.42	312 (M^+, 4), 86 (16), 84 (27), 73 (100)
(E)-4i	0.11 (s, 9H), 0.88 (t, 3H, J=6.4 Hz), 1.20-1.45 (m, 18H), 2.30 (t, 2H, J=6.4 Hz), 6.45 (s, 1H), 7.20-7.40 (m, 5H)	−1.22, 14.12, 22.69, 29.00, 29.36, 29.46, 29.64, 29.66, 29.96, 31.92, 32.45, 126.42, 128.99, 129.62, 131.93, 136.63, 143.80	362 (M^-, trace), 167 (3), 86 (2), 84 (3), 73 (100)

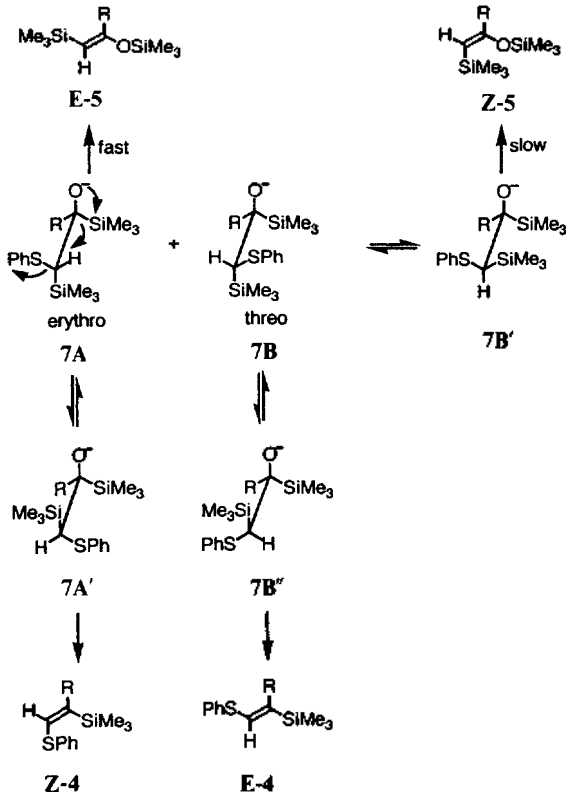
*The remaining signals could not be assigned.

(Table 1). The *E* and *Z* isomers of **4e** were separated by GC-MS; the ratio of *E/Z* isomers was 85 : 15 and both showed M^+ ion at m/z 314. In the ^1H NMR spectra of the mixture of isomers **4e** show only a singlet at δ 6.73 for the vinylic proton. This signal is assigned to the proton *cis* to the silyl group by comparing with the reported chemical shifts in *E* and *Z*-β-arylvinylsilanes[6] and (*E*)-β-(phenylthio)vinylsilane.[7] The vinylic proton of *Z* isomer of **4** seems to be overlapped with the aromatic proton signals. The silicon methyls absorbed at slightly higher field for the *E* than for *Z* isomer (*e.g.*, **4e**; δ 0.11 *vs* 0.26). This trend is consistent to the chemical shifts of the silicon methyls in the β-arylvinylsilanes.



The ratio of the products **4** and **6** has little effect on the nature of the para substituents on benzoyltrimethylsilanes (Table 1, entries **a-d**). Only *p*-methoxybenzoyltrimethylsilane (**2e**) which has a strong electron donating group, produced more **4e** a Peterson reaction product than **6e** a Brook rearrangement-elimination product. In aliphatic acylsilanes **2h** and **2i**, **4h** and **4i** were produced greater than **6h** and **6i**, respectively. However, the selectivity of the products is not so high (**4**/**6**≈ 2). The selectivity is very different from the result in the reaction of acylsilanes with phosphorus ylides; aliphatic acylsilanes undergo olefination while aromatic acylsilanes yield only silyl enol ethers *via* a Brook rearrangement-elimination.[4]

The formation of the two products **4** and **6**, and high ster-



Scheme 2.

eoselectivity of **4** could be explained as the decomposition by alternative pathways of the 1 : 1 adducts of the two dias-

tereomeric β-phenylthio-α,β-disilylalkoxides **7A** and **7B** generated from the reactions of acylsilanes **2** with phenylthio(trimethylsilyl)methyllithium (**3**) (Scheme 2). It is well established that α-silyl alkoxides having a β-leaving group undergoes rearrangement of silicon from carbon to oxygen (Brook rearrangement), and occurs simultaneously anti elimination of the leaving group.[3c,d] Thus, the C to O silyl migration in the erythro intermediate **7A**, the trimethylsilyl group must some point be eclipsed with a hydrogen at the second carbon. Meanwhile the threo intermediate **7B'**, conformer of **7B** properly arranged to be anti between the trimethylsilyl and phenylthio groups, the silyl migration must be eclipsed with the much bulkier trimethylsilyl group. As previously reported,[3d] the erythro intermediates **7A** is expected to occur Brook rearrangement-elimination much faster than **7B** to give silyl enol ethers **E-5**. In the reactions of *p*-methoxybenzoyltrimethylsilane (**4e**) and aliphatic acylsilanes **4h** and **4i** the Brook rearrangement would be somewhat retard, which caused the decrease of silyl enol ethers. Unfortunately, silyl enol ethers could not be isolated and spontaneously hydrolyzed to methyl ketones *via* α-silyl ketones during work up.[8]

It is well known base-induced elimination reactions of β-hydroxy silanes take place in highly stereospecific syn manner.[9] Thus, **Z-4** is expected from the erythro **7A'** and **E-4** from the threo **7B''**. The threo intermediate **7B** undergoes the silyl migration and elimination process much slower than the erythro **7A**, so that threo **7B** take place Peterson reaction *via* its conformer **7B''** to afford *E*-vinylsilanes **4**. For this reason, the preferential formation of *E*-vinyl silanes over *Z* isomers was resulted.

Experimental

All reactions were carried out under the argon atmosphere. ^{1}H NMR spectra were recorded on a Varian EM-360A (60 MHz) or a JEOL JSX 270 (270 MHz) spectrometer using tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained on a JEOL JSX 270 (58 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. GC-MS analyses were performed with a Hewlett-Packard 5971 A spectrometer using an HP-1 column (0.2 mm ID, 15 m). Acylsilanes were prepared in good yields by the reaction of acid chlorides with $LiAl(SiMe_3)_4$ or $LiMeAl(SiMe_3)_3$ in the presence of a catalytic amount of CuCN.[10]

General procedure for the reaction of acylsilane with phenylthio(trimethylsilyl)methyllithium. The reaction of **2a** with **3** is representative. *n*-Butyllithium (0.8 mL of a 1.5 M solution in hexane, 1.2 mmol) was added to the THF (2 mL) solution of phenylthio(trimethylsilyl)methane (235 mg, 1.20 mmol) at 0℃, and after being stirred for 1 hr, benzoyltrimethylsilane (**2a**) (206 mg, 1.15 mmol) in THF (2 mL) was added. The reaction mixture, after 20 min, was poured into 10 mL of saturated aqueous NH_4Cl, and extracted three times with 10 mL portions of ether. The combined organic extract was washed with water, dried over Na_2SO_4, concentrated. The residue was chromatographed on silica gel (hexane : ether = 3 : 1) to give **E-4a** (158 mg, 49%) and acetophenone (56 mg, 40%).

Aknowledgement. This work was supported by the Basic Science Research Institute Program, Ministry of Education (BSRI-92-308). We gratefully acknowledge Mr. Chi Hyo Park of Lucky Ltd., for GC-MS and NMR spectra.

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NMR Spectra of 4,4'-Bipyridyl, Pyrazine, and Ethylenediamine Coordinated to Undecatungstocobalto(III)silicate and -borate Anions. Identification of 1 : 1 and Dumbbell-Shaped 1 : 2 Complexes

Jeongmin Park, Moonhee Ko, and Hyunsoo So*

Department of Chemistry, Sogang University, Seoul 121-742

Received July 9, 1993

Some heteropolyanions contain more than two transition metal ions having replaceable water molecules.[1-3] We have been trying to prepare extended systems by connecting these heteropolyanions with bidentate ligands such as 4,4'-bipyridyl, pyrazine, and ethylenediamine. However, it has not been easy to characterize the reaction products. So we have turned to simpler systems containing heteropolyanions with one transition metal ion having a replaceable water molecule. For these systems one can expect to obtain 1 : 1 and dumbbell-shaped 1 : 2 complexes by replacing the water molecule with a bidentate ligand.

Recently our NMR study has shown that 4,4'-bipyridyl