is mainly responsible for the downshift in the amide I frequency on N-deuteration.[16] It is felt that an analogous process occurs in our deuteration studies of semicarbazones.

In conclusion, we have established the following. The IR frequencies for the carbonyl group of semicarbazones of variously substituted benzaldehydes and acetophenones often fall in an abnormally high frequency range. The origin of the high C=O frequencies could not be ascribed to the electronic effects of the substituents.[17] The high frequencies shift to normal values in the DMSO solution. This high C=O frequency phenomenon seems to be related to the solid-state structure of semicarbazones. The X-ray structures of two semicarbazones indicated a network of H-bonds in which each C=O is involved in a bifurcated bond with NH_2 and NH from two different molecules. If one assumes that other semicarbazones would form similar H-bond patterns, it is possible that the H-bonding in the solid state could be related to the observed carbonyl frequencies. The carbonyls of semicarbazones exhibit complex bands, which include NH bends. The H-bonding in the solid state could cause the N-H bend component to shift the higher band, the "C=O" one, toward higher frequencies. Theoretical studies of such systems are needed.

Acknowledgment. Thanks are expressed to Drs. B. R. Adams and T. W. Root for ^{13}C NMR studies and to Drs. S. R. Lowry and K. Kempfert for diffuse reflectance IR spectra.

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[17] It is interesting that a plot of $\nu_1-\nu_0$ in the solid state vs Hammett σ constants for the substituents in the ring gives a straight line.[14] A best fit was found when $\sigma > 0$. For para-substituted semicarbazones, the more positive σ, the lower the C=O. For meta-substituted semicarbazones, the greater σ, the higher the C=O.

Effect of Silica Gel on the Benzenesulfinic Acid Catalyzed Isomerization of Vinylsilanes. Formation of Silyl Benzenesulfinate

Masahito Ochiai,[*,†] Yoshikazu Takaoka,[†] Tatsuzo Ukita,[†] Yoshimitsu Nagao,[†] and Eiichi Fujita[‡]

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan, and Osaka University of Pharmaceutical Sciences, 10-65 Kawai 2-Chome, Matsubara 580, Japan

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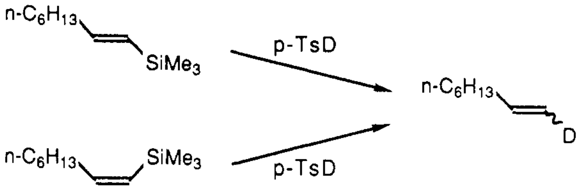
A new method for the isomerization of (*Z*)-vinylsilanes into the *E* isomers has been developed. In contrast to the facile protodesilylation of vinylsilanes with arenesulfinic acids, use of silica gel as an additive in the reaction of vinylsilanes with benzenesulfinic acid makes possible the selective isomerization of the double-bond geometry by decreasing the rate of the competing protodesilylation. On the basis of the finding that the isomerization proceeds on the surface of the silica gel activated with benzenesulfinic acid and that benzenesulfinic esters such as ethyl, tributylstannyl, and trimethylsilyl benzenesulfinates are also effective as catalysts for the isomerization, the selective isomerization of vinylsilanes was interpreted in terms of the in situ formation of silyl benzenesulfinate bound to a silanol group of the surface of silica gel.

The strong β-effect of trialkylsilyl groups makes possible the use of vinylsilanes as the most important vinyl anion equivalent species in modern organic synthesis.[1] Vinylsilanes react with a variety of electrophiles including halogens, acid chlorides, acetals, sulfenyl chlorides, and immonium salts in a stereo- and regiospecific manner, yielding substitution products.

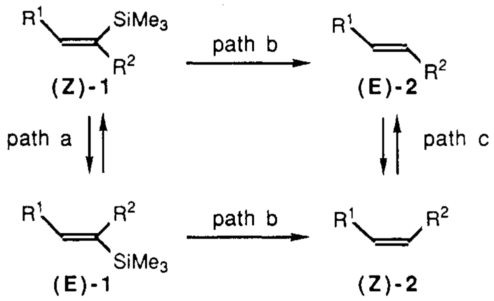
Recently, Büchi and Wüest reported that catalytic *p*-toluenesulfinic acid in wet refluxing acetonitrile is a reagent of choice for the protodesilylation of vinylsilanes, especially when acid-sensitive groups are present in the compound. Interestingly, the *p*-toluenesulfinic acid promoted cleavage of vinylsilanes lacks stereospecificity. Both *E* and *Z* isomers of 1-(trimethylsilyl)octene gave the same stereoisomeric mixture of deuterated olefins when cleaved with deuterio-*p*-toluenesulfinic acid (Scheme I).[2]

However, protodesilylation of vinylsilanes in the presence of strong acids such as hydriodic, hydrochloric, hydrobromic, and trifluoromethanesulfonic acids as well as weak acids such as acetic acid has been shown to proceed in a highly stereospecific manner with retention of configuration of double bonds.[3] To rationalize the retention of the alkene geometry on protodesilylation using protic acids, Koenig and Weber proposed that simultaneously

Scheme I



Scheme II



[†] Kyoto University.

[‡] Osaka University of Pharmaceutical Sciences.

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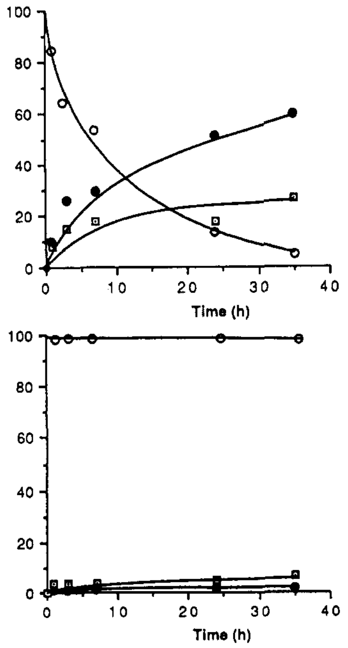

Figure 1. Time courses for the reaction of (*Z*)-**3a** with benzenesulfinic acid at 25 °C in chloroform: panel A, without SiO_2; panel B, with SiO_2 (Merck silica gel 60, 230–400 mesh). Symbols are % recovered **3a** (○), % *E* isomer of **3a** (□), and % 1-decene (●).

with proton addition to the double bond, rotation occurs about the developing carbon–carbon single bond in the direction to permit the trialkylsilyl group to continuously stabilize the incipient carbocation center by bridging or hyperconjugation of the Si–C bond.[3a]

On the basis of the fact described above, it seems reasonable to assume that the nonstereoselective protodesilylation of vinylsilanes 1 utilizing *p*-toluenesulfinic acid may involve the following three independent processes (Scheme II): (1) isomerization of the double-bond geometry of vinylsilanes (path a: (*E*)-**1** ⇄ (*Z*)-**1**), (2) stereospecific protodesilylation of vinylsilanes (path b: (*E*)-**1** → (*Z*)-**2** and (*Z*)-**1** → (*E*)-**2**), and (3) isomerization of the double-bond geometry of olefins (path c: (*E*)-**2** ⇄ (*Z*)-**2**). In fact, the path c is a known process and it has been reported that arenesulfinic acids catalyze the cis–trans equilibration of disubstituted olefins in high yield and without double-bond migration, as evidenced by studies of the reaction of various sulfinic acids with methyl 9-octadecenoate and 4-octene.[4] If the working hypothesis shown in Scheme II is valid, it seems possible to distinguish between these three reaction processes, path a, b, and c, in a logical sense. Furthermore, if it would be possible to decrease selectively the rate of the protodesilylation process (path b) compared to that of the isomerization of the double-bond geometry of vinylsilanes (path a) in the reaction of vinylsilanes with arenesulfinic acids, the reaction may offer a useful method for the isomerization of double-bond geometry of vinylsilanes.

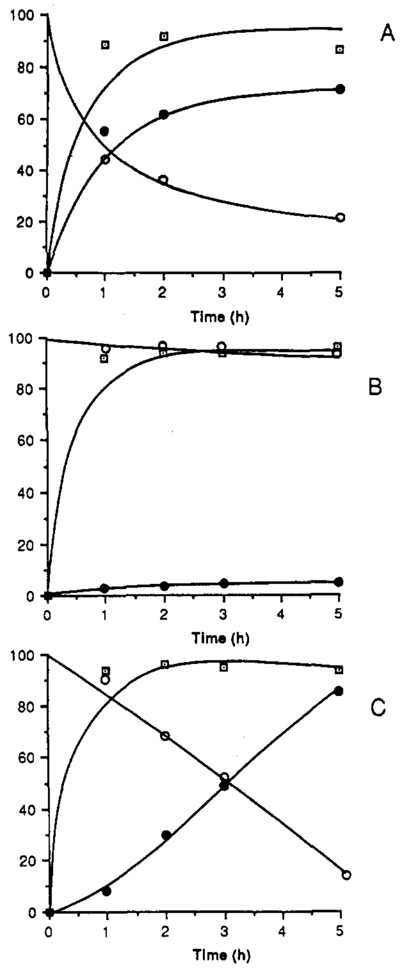

Figure 2. Time courses for the reaction of (*Z*)-**3a** with benzenesulfinic acid at 60 °C in chloroform: panel A, without SiO_2; panel B, with SiO_2 (Merck silica gel 60, 230–400 mesh); panel C, with SiO_2 (Merck silica gel 60, 70–230 mesh). Symbols are % recovered **3a** (○), % *E* isomer of **3a** (□), and % 1-decene (●).

In contrast to the extensive investigations on the protodesilylation of vinylsilanes, few methods are available for the isomerization of the double-bond geometry of vinylsilanes. Partial isomerization of (*E*)-β-styryltrimethylsilane by photochemical reaction in hexane solution afforded a mixture of both stereoisomers (*E*:*Z* = 63:37) in 96% yield.[5] Irradiation of an ethereal solution of (*Z*)-1-alkenylsilanes in the presence of pyridine and *N*-bromosuccinimide with an ultraviolet sunlamp results in the formation of the corresponding *E* isomers with high isomeric purity.[6] Recently, Oshima and Utimoto reported germyl radical induced isomerization of vinylsilanes and vinylgermanes utilizing a combination of triphenylgermane and triethylborane.[7]

We report herein an isomerization of (*Z*)-1-alkenylsilanes into the *E* isomers utilizing a combination of benzenesulfinic acid and silica gel, in which the use of silica gel plays an important role for decreasing selectively the rate

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(1) For reviews, see: (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Ager, D. *J. Chem. Soc. Rev.* **1982**, *11*, 493. (c) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. (d) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83. (e) Paquette, L. A. *Science* **1982**, *217*, 793. (f) Fleming, I. *Comprehensive Organic Chemistry*; Pergamon Press: Oxford, 1979; Vol. 3, Chapter 18. (g) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (h) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

(2) Büchi, G.; Wüest, H. *Tetrahedron Lett.* **1977**, 4305.

(3) (a) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416. (b) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825. (c) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Organomet. Chem.* **1976**, *107*, C1. (d) Hudrilik, P. F.; Schwartz, R. H.; Hogan, J. C. *J. Org. Chem.* **1979**, *44*, 155.

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(7) Ichinose, Y.; Nozaki, K.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *32*, 3709.

Table I. Isomerization of (*Z*)-Vinylsilanes 3a to the *E* Isomers

run	additive	(mol %)[b]	solvent	reactn temp, °C	yield (%) of **3a** (*E*:*Z*),[a] yield (%) of 1-decene[a]			
					1 h	2 h	3 h	5 h
1	$PhSO_2H$	(1), SiO_2	$CHCl_3$	60	97 (92:8), 3	96 (95:5), 4	95 (95:5), 5	95 (97:3), 5
2	$PhSO_2H$	(0.2), SiO_2	$CHCl_3$	60	>99 (3:97), <1		>99 (4:96), <1	>99 (5:95), <1
3	$PhSO_2H$	(1), SiO_2	CH_2Cl_2	40	99 (44:56), 1	97 (71:29), 3		94 (89:11), 6
4	$PhSO_2H$	(1), SiO_2	Et_2O	35		97 (30:70), 3	97 (44:56), 3	98 (72:28), 2
5	$PhSO_2H$	(1), SiO_2	*n*-C_5H_{12}	35	98 (83:17), 2	86 (89:11), 7	82 (90:10), 14	70 (92.8), 21
6	$PhSO_2H$	(1), SiO_2	CCl_4	77	90 (82:18), 10	88 (84:16), 12	87 (85:15), 13	
7	$PhSO_2H$	(1), SiO_2	$ClCH_2CHCl_2$	113	–, 68			
8	*p*-$MeOC_6H_4SO_2H$	(1), SiO_2	$CHCl_3$	60	77 (84:16), 21	48 (82:18), 39	40 (84:16), 59	21 (83:17), 75
9	*p*-$NO_2C_6H_4SO_2H$	(1), SiO_2	$CHCl_3$	60	86 (10:90), 14	77 (12:88), 23		49 (19:81), 45

[a] Yields were determined by GC. [b] Silica gel: 230–400 mesh.

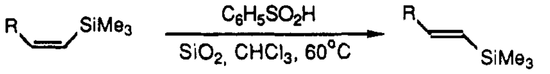
of the protodesilylation process (path b) catalyzed by benzenesulfinic acid.

Results and Discussion

Effect of Silica Gel. We have employed benzenesulfinic acid (BSA), prepared from the commercially available sodium salt by the reaction with hydrochloric acid,[2] as an acid catalyst instead of *p*-toluenesulfinic acid. Reaction of (*Z*)-1-(trimethylsilyl)decene ((*Z*)-**3a**) with 1 equiv of BSA was carried out at 25 °C in chloroform solution and monitored by GC. As shown in Figure 1 (panel A), both the protodesilylation yielding 1-decene and the isomerization of the double bond yielding the *E* isomer (*E*)-**3a** were found to compete with each other. After 35 h, a 60% yield of 1-decene was obtained and the recovered **3a** (5% yield) consisted of a 27:73 *E*/*Z* mixture. At 60 °C, both reaction processes are accelerated (Figure 2, panel A) and refluxing for 2 h produced a 62% yield of 1-decene and a 36% yield of isomerized (*E*)-**3a** with 92% isomeric purity. It is noted that the relative rate of isomerization to protodesilylation at 60 °C is much larger than that at 25 °C. The reason for the selective acceleration of the double-bond isomerization of (*Z*)-**3a** at 60 °C is not yet clear; however, the results clearly indicate that, in order to achieve the selective isomerization of vinylsilanes without leading to the desilylation product by utilizing BSA, a reaction temperature of 60 °C is more favorable than that of 25 °C.

We found that the use of silica gel as an additive decreased dramatically the rate of protodesilylation of vinylsilanes. As shown in Experimental Section, the reaction of (*Z*)-**3a** using silica gel was usually carried out after a mixture of BSA and silica gel was refluxed in chloroform for 1 h under nitrogen. The time course for the reaction of (*Z*)-**3a** with 1 equiv of BSA in a chloroform solution at 25 °C in the presence of silica gel (Merck Silica gel 60, 230–400 mesh) is shown in Figure 1 (panel B). After treatment of the reaction mixture for 35 h, 98% of **3a** was recovered and the yield of 1-decene was less than 2%. A marked tendency for the selective isomerization of the double-bond geometry and for the retardation of the competitive protodesilylation was observed at the reaction temperature of 60 °C (Figure 2, panel B and Table I, run 1). Thus, refluxing the reaction mixture for 5 h in the presence of silica gel afforded a 95% yield of (*E*)-**3a** with 97% isomeric purity.[8] Comparison of the time courses for the reactions of (*Z*)-**3a** at 60 °C (Figure 2, panel A and B) indicates that the presence of silica gel (230–400 mesh) has a negligible effect on the rate of double-bond isomerization; however, it decreases dramatically the rate of protodesilylation.[9]

Scheme III



		Yield (%)	E : Z
3b : R=$C_6H_5CH_2$	50h	86	93 : 7
3c : R=$C_6H_5(CH_2)_2$	5h	97	93 : 7

The size of silica gel as an additive plays a critical role in achieving the isomerization of (*Z*)-**3a**. As shown in Figure 2 (panel C), the use of 70–230 mesh silica gel (Merck Silica gel 60) slows down the rate of protodesilylation, especially at the beginning of the reaction (compare the results at reaction time of 1 h). The reaction, however, led to the formation of a large amount of 1-decene after 5 h.

As described above, catalytic amounts of *p*-toluenesulfinic acid have been reported to undergo desilylation of vinylsilanes.[2] The attempted isomerization of (*Z*)-**3a** utilizing a combination of 20 mol % of BSA and silica gel (230–400 mesh) in chloroform at 60 °C gave disappointing results. While the protodesilylation of (*Z*)-**3a** did not occur in this case, only less than 5% of isomerization was observed (Table I, run 2).

Silica gel itself has no effect on the isomerization as well as the protodesilylation of vinylsilanes: on refluxing the mixture of (*Z*)-**3a** and silica gel (70–230 mesh and 230–400 mesh) in chloroform for 7 h, both the isomerization and the protodesilylation were not observed and (*Z*)-**3a** was recovered unchanged in high yields.

Medium effect on the isomerization of (*Z*)-**3a** was then investigated. In refluxing dichloromethane, diethyl ether, or pentane, the rate of isomerization decreased considerably compared to that in refluxing chloroform, presumably because of the low boiling point of these solvents (run 3–5). On the other hand, an exclusive protodesilylation of (*Z*)-**3a** took place in a high boiling point solvent, 1,1,2-trichloroethane (run 7).

The influence of substituents attached to the aromatic ring of arenesulfinic acids on the isomerization was also studied. *p*-Methoxybenzenesulfinic acid led to the isom-

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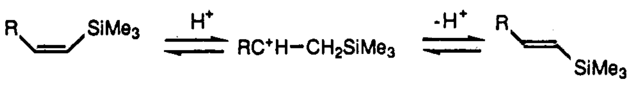
(8) Ochiai, M.; Ukita, T.; Fujita, E. *Chem. Lett.* **1983**, 1457.

(9) The reaction of (*Z*)-**3a** with BSA at 25 °C (Figure 1, panel A) apparently showed a higher degree of isomerization to the *E* isomer as compared to the reaction in the presence of silica gel (panel B). By assuming that the BSA-catalyzed protodesilylation of (*Z*)-**3a** probably proceeds much more rapidly than that of (*E*)-**3a**, these results can be reasonably explained.[10] Therefore, it appears that the addition of silica gel causes a negligible effect on the rate of isomerization of (*Z*)-**3a** at 25 °C.

(10) In the oxymercuration of disubstituted internal olefins, RCH=CHR′, (*Z*)-olefins have been shown to be considerably more reactive than the corresponding (*E*)-olefins, because of the higher ground-state energy of (*Z*)-olefins: (a) Asinger, F.; Fell, B.; Hadik, G.; Steffan, G. *Chem. Ber.* **1964**, *97*, 1568. (b) Brown, H. C.; Geoghegan, P. J. *J. Org. Chem.* **1972**, *37*, 1937.

Scheme IV



(Z)-3 4 (E)-3

erization of (*Z*)-**3a** to some extent, but with formation of significant amounts of the protodesilylation product (run 8). With *p*-nitrobenzenesulfinic acid, a low degree of the isomerization was observed, which may be interpreted in terms of the low solubility of the acid toward chloroform (run 9).

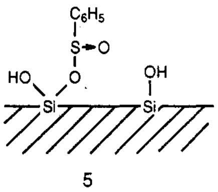
Treatment of (*Z*)-3-phenyl-1-(trimethylsilyl)propene ((*Z*)-**3b**) and (*Z*)-4-phenyl-1-(trimethylsilyl)butene ((*Z*)-**3c**) with BSA and silica gel in chloroform at 60 °C afforded the corresponding *E* isomers with high isomeric purity (Scheme III). The attempted isomerization of (*Z*)-β-(trimethylsilyl)styrene, however, resulted in extensive polymerization.

Reaction Mechanism. Use of silica gel as an additive in the reaction of vinylsilanes with BSA makes possible the selective isomerization of the double-bond geometry by decreasing the rate of the competing protodesilylation. As one of the possible reaction pathways, which is compatible with this observation, the following protonation–deprotonation sequence involving the formation of carbocation **4** stabilized by a β-trimethylsilyl moiety should be considered (Scheme IV).

Since nucleophiles such as BSA may be strongly adsorbed on the surface of silica gel, a low concentration of silicophiles in solution may explain the selective deprotonation of carbocation **4** yielding the isomerized vinylsilanes in preference to desilylation.[11] A similar mechanism involving addition of bromine atoms to double bonds was proposed in the light-induced isomerization of (α-halovinyl)silanes using bromine and pyridine.[6a] The observation that treatment of (*Z*)-**3a** with deuterio-BSA and deuterio-silica gel, prepared by repeated treatment with D_2O, in chloroform gave (*E*)-**3a** with high isomeric purity, but most importantly, that showed no deuterium incorporation at terminal vinylic protons clearly indicates that the isomerization of (*Z*)-**3a** does not involve the protonation–deprotonation process. Moreover, reaction of (*Z*)-**3a** with *p*-toluenesulfonic acid and silica gel in chloroform at 60 °C for 0.5 h afforded exclusively 1-decene in 98% yield.

To gain some insight into the mode of the isomerization, we have investigated whether the isomerization takes place in solution or on the surface of activated silica gel. The attempted isomerization of (*Z*)-**3a** in a filtered solution, obtained from a mixture of BSA and silica gel refluxed for 1 h in chloroform, showed no evidence for isomerization or protodesilylation. On the other hand, when (*Z*)-**3a** was treated with the filtered insoluble precipitate of the mixture, which was washed with chloroform repeatedly, in chloroform for 5 h, extensive isomerization was observed and (*E*)-**3a** of 96% isomeric purity was obtained in high yield. These results clearly indicate that the isomerization of (*Z*)-**3a** proceeds on the surface of silica gel activated with BSA.

Furthermore, we found that benzenesulfinic esters are also effective as catalysts for the isomerization of (*Z*)-**3a**, in contrast to the reported ineffectiveness of methyl *p*-toluenesulfinate in the isomerization of a simple olefin such as (*Z*)-4-octene.[4a] Thus, treatment of (*Z*)-**3a** with 0.2 equiv of ethyl benzenesulfinate or with 1 equiv of tributylstannyl benzenesulfinate in refluxing chloroform for 5 h gave quantitatively (*E*)-**3a** with 88–91% isomeric purity. Most importantly, the reaction with trimethylsilyl benzenesulfinate afforded (*E*)-**3a** (95% isomeric purity) in 80% yield and 1-decene in 20% yield (Scheme V).[12] On the basis of these observations and the fact that repeated washing of the BSA-activated silica gel with chloroform showed no effect on the catalytic activity, the selective isomerization reaction of (*Z*)-**3** with BSA in the presence of silica gel is probably attributed to the formation of benzenesulfinic ester bound to a silanol group of the surface of silica gel, namely, silyl benzenesulfinate **5**, in situ as reactive species (Figure 3).



5

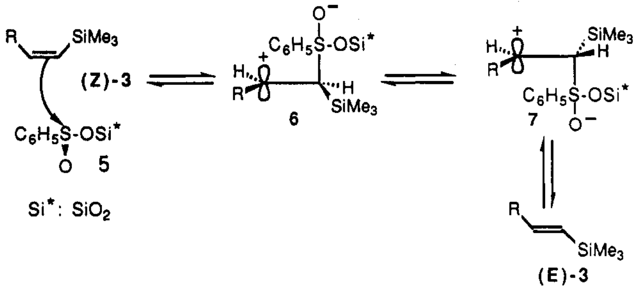
Figure 3.

Scheme V

$$(Z)\text{-}3a \xrightarrow[60^{\circ}C]{CHCl_3} (E)\text{-}3a$$

	Yield (%)	E : Z
$C_6H_5\overset{O}{S}OEt$	>99	88 : 12
$C_6H_5\overset{O}{S}OSnBu_3$	>99	91 : 9
$C_6H_5\overset{O}{S}OSiMe_3$	80	95 : 5

Scheme VI



The structure of the reactive species could not be fully characterized yet; however, we tentatively propose a reaction mechanism involving an addition–elimination reaction of **5** for the isomerization of (*Z*)-**3** (Scheme VI). Silicon-directed electrophilic addition and/or substitution of vinylsilanes has been proved to proceed in a regiospecific manner.[1] Electrophilic attack of **5** on the carbon attached to a trimethylsilyl group of (*Z*)-**3** yielding **6**, rotation about a newly formed carbon–carbon single bond, and then elimination of **5** may account for the isomerization. Protonation on the etheric oxygen atom of **5** by a neighboring silanol group of the surface of silica gel probably assists

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[11] Formation of α-chloro-α-trimethylsilyl sulfides by the reaction of α-trimethylsilyl sulfides with *N*-chlorosuccinimide has been reported. The facile deprotonation of α-trimethylsilyl sulfonium salt intermediate instead of the desilylation may account for the results: Ishibashi, H.; Nakatani, H.; Maruyama, K.; Minami, K.; Ikeda, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1443.

[12] Trialkylsilyl esters of BSA have been reported to be extremely labile toward moisture.[13] Thus, BSA produced by the hydrolysis of trimethylsilyl benzenesulfinate during the reaction presumably undergoes protodesilylation of **3a**, yielding 1-decene.

[13] Davis, F. A.; Rizvi, S. Q. A.; Ardecky, R.; Gosciniak, D. J.; Friedman, A. J.; Yocklovich, S. G. *J. Org. Chem.* **1980**, *45*, 1650.

the initial electrophilic attack.[14] The mechanism involving the formation of **5** is compatible with the observation that the protodesilylation process of **3** is highly retarded.

Apart from the exact nature of this isomerization, a combination of BSA and silica gel provides us a useful route for the isomerization of (*Z*)-vinylsilanes.

Experimental Section

^{1}H NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in CDCl$_3$ solution with (CH$_3$)$_4$Si as an internal standard. Mass spectra were taken on a JEOL JMS-DX 300 spectrometer. Gas chromatographic analyses were carried out on a Shimazu Model GC-7AG gas chromatograph with a column of 20% silicone GE SF-96 on Chromosorb W (3 m). Merck silica gel 60 (70–230 and 230–400 mesh) was used for isomerization of (*Z*)-vinylsilanes. Thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254.

Preparation of Sulfinic Acids and Esters. Benzenesulfinic acid was obtained by acidification of an aqueous solution of the commercially available sodium salts with HCl.[2,4a] *p*-Methoxybenzenesulfinic acid and *p*-nitrobenzenesulfinic acid[15] were prepared by reduction of the sulfonyl chlorides with Na$_2$SO$_3$. Ethyl benzenesulfinate was obtained by the reaction of benzyl phenyl sulfoxide with *N*-bromosuccinimide.[16] Tributylstannyl benzenesulfinate[17] was prepared from sodium benzenesulfinate by reaction with chlorotributylstannane.[18] Trimethylsilyl benzenesulfinate was prepared by reaction of benzenesulfinic acid with chlorotrimethylsilane in the presence of triethylamine.[13]

Preparation of Vinylsilanes. Vinylsilanes, (*Z*)-1-(trimethylsilyl)dec-1-ene ((*Z*)-**3a**),[19] (*Z*)-3-phenyl-1-(trimethylsilyl)prop-1-ene ((*Z*)-**3b**),[20] and (*Z*)-4-phenyl-1-(trimethylsilyl)but-1-ene ((*Z*)-**3c**) were prepared by hydroalumination–protonolysis[21] of the corresponding 1-(trimethylsilyl)acetylenes and purified by column chromatography over silver nitrate (5%) impregnated silica gel using pentane/benzene (1:1). **(*Z*)-3c**: ^{1}H NMR δ 7.20 (5 H), 6.35 (dt, J = 14, 7 Hz, 1 H), 5.52 (dt, J = 14, 1 Hz), 2.84–2.25 (4 H), 0.12 (s, 9 H).

Reaction of (*Z*)-3a with Benzenesulfinic Acid. To a solution of benzenesulfinic acid (0.2 mmol) in 5 mL of chloroform was added (*Z*)-**3a** (0.2 mmol) in nitrogen. The mixture was stirred under the conditions described in Figures 1 and 2. As an internal standard, undecane was added, and the time course for the reaction was determined by gas chromatography (column oven temperature, 150 °C). Retention times of 1-decene and (*E*)-[19] and (*Z*)-**3a** were 4.9, 21.7, and 23.3 min, respectively.

General Procedure for Sulfinic Acid Catalyzed Isomerization of (*Z*)-3 in the Presence of Silica Gel. A mixture of arenesulfinic acid (0.2 mmol) and silica gel (1.0 g) in an appropriate solvent (5 mL) was refluxed for 1 h in nitrogen. (*Z*)-**3** (0.2 mmol) was added and the mixture was stirred under the conditions described above. The yield of products was determined by gas chromatography. Compound, retention time, and column oven temperature were as follows: (*E*)-[20] and (*Z*)-**3b**, 29.4 and 34.4 min, 140 °C; (*E*)- and (*Z*)-**3c**, 32.4 and 35.1 min, 150 °C. **(*E*)-3c**: ^{1}H NMR δ 7.20 (5 H), 6.08 (dt, J = 18.5, 6 Hz, 1 H), 5.65 (dt, J = 18.5, 1 Hz), 2.82–2.30 (4 H), 0.07 (s, 9 H).

Isomerization of (*Z*)-3a with Deuteriobenzenesulfinic Acid. Deuteriobenzenesulfinic acid was prepared by acidification of a solution of the sodium salt in D$_2$O with 20% DCl. For the preparation of deuterio-silica gel, the following operation was repeated two times: silica gel (230–400 mesh, 3.0 g) was treated with D$_2$O (10 mL) at room temperature for 1 h and the solvent was evaporated in vacuo. Finally deuterio-silica gel was dried at 130 °C for 3 h under 35 Torr. Isomerization of (*Z*)-**3a** with deuteriobenzenesulfinic acid and deuterio-silica gel in chloroform was carried out at 60 °C for 5 h according to the general procedure described above. (*E*)-**3a** with 95% isomeric purity was isolated in 79% yield by preparative TLC (hexane). The ^{1}H NMR and mass spectra showed no deuterium incorporation at the vinylic protons.

Isomerization of (*Z*)-3a on the Surface of Activated Silica Gel. A mixture of benzenesulfinic acid (30 mg, 0.21 mmol) and silica gel (230–400 mesh, 1.1 g) in chloroform (4.4 mL) was refluxed for 1 h under nitrogen. Filtration of the reaction mixture under nitrogen afforded a clear chloroform solution and an insoluble precipitate, which was washed with chloroform three times. To the clear chloroform solution was added (*Z*)-**3a** (45 mg, 0.21 mmol) and then the solution was refluxed for 5 h. Analytical gas chromatography showed no evidence for isomerization as well as protodesilylation. To a solution of (*Z*)-**3a** (45 mg, 0.21 mmol) in chloroform (4 mL) was added the insoluble precipitate described above and then the reaction mixture was refluxed for 5 h. Analytical gas chromatography showed the formation of (*E*)-**3a** (96% isomeric purity, 96% yield) and 1-decene (4% yield).

Isomerization of (*Z*)-3a with Ethyl Benzenesulfinate. A solution of (*Z*)-**3a** (58 mg, 0.27 mmol) and ethyl benzenesulfinate (9 mg, 0.05 mmol) in chloroform (3 mL) was refluxed for 5 h under nitrogen. Analytical gas chromatography showed the formation of (*E*)-**3a** (88% isomeric purity, 99% recovery of **3a**) and 1-decene (1% yield).

Isomerization of (*Z*)-3a with Tributylstannyl Benzenesulfinate. A solution of (*Z*)-**3a** (29 mg, 0.14 mmol) and ethyl benzenesulfinate (60 mg, 0.14 mmol) in chloroform (3 mL) was refluxed for 5 h under nitrogen. Analytical gas chromatography showed the formation of (*E*)-**3a** with 91% isomeric purity in quantitative recovery of the material.

Isomerization of (*Z*)-3a with Trimethylsilyl Benzenesulfinate. A solution of (*Z*)-**3a** (42 mg, 0.20 mmol) and trimethylsilyl benzenesulfinate (42 mg, 0.20 mmol) in chloroform (4 mL) was refluxed for 0.5 h under nitrogen. Analytical gas chromatography showed the formation of (*E*)-**3a** (95% isomeric purity, 80% yield) and 1-decene (20% yield).

Registry No. (*Z*)-**3a**, 71779-78-7; (*E*)-**3a**, 71779-75-4; (*Z*)-**3b**, 73727-44-3; (*E*)-**3b**, 58541-15-4; (*Z*)-**3c**, 88261-99-8; (*E*)-**3c**, 88261-98-7; BSA, 618-41-7; *p*-MeOC$_6$H$_4$SO$_2$H, 1709-60-0; *p*-NO$_2$C$_6$H$_4$SO$_2$H, 1199-67-3; PhSO$_2$D, 119948-45-7; ethyl benzenesulfinate, 1859-03-6; benzyl phenyl sulfoxide, 833-82-9; tributylstannyl benzenesulfinate, 101459-86-3; trimethylsilyl benzenesulfinate, 73116-75-3; sodium benzenesulfinate, 873-55-2; chlorotributylstannane, 1461-22-9.

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