A Convenient Route to (*E*)-1-Alkenylsilanes via Isomerization of (*Z*)-1-Alkenylsilanes

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Alkenylsilanes of defined stereochemistry are proving to be remarkably versatile starting materials for use in a variety of syntheses, and a number of routes for their preparation have become available[1]. For example, (*Z*)-1-alkenylsilanes **(2)** may be obtained in high yields and with high isomeric purities through hydroalumination-protonolysis of the readily accessible 1-alkynylsilanes[2] **(1)**. The corresponding (*E*)-1-alkenylsilanes **(3)** have been prepared via hydrosilylation of 1-alkynes[3,4]. Unfortunately, however, applying the latter method to 1-alkynes possessing primary alkyl groups leads to appreciable amounts of the regioisomers resulting from addition of silicon to C-2.

We now wish to report that (*E*)-1-alkenylsilanes **(3a–e)** can be advantageously prepared via isomerization of the readily accessible (*Z*)-isomers **(2a–e)**. This new method not only provides the (*E*)-alkenylsilanes in higher isomeric purities than was previously possible using the hydrosilylation procedure but also is operationally more convenient.

Monohydroalumination of 1-alkynylsilanes **(1)** with diisobutylaluminum hydride in ether proceeds in a stereo- and regiospecific manner to produce (*Z*)-1-alumino-1-alkenylsilanes[2,5]. Quenching the reaction mixtures with dilute aqueous acid furnishes the (*Z*)-1-alkenylsilanes **2a–e**. The etheral solutions of the (*Z*)-1-alkenylsilanes are then treated with one equivalent of pyridine[6] followed by 15 mol% of *N*-bromosuccinimide, added in three equal portions at 15 min intervals over a 45 min period while irradiating with a U.V. sunlamp (275 W). Finally, work up and distillation affords the (*E*)-1-alkenylsilanes **3a–e** containing less than 4% of the (*Z*)-isomers[7].

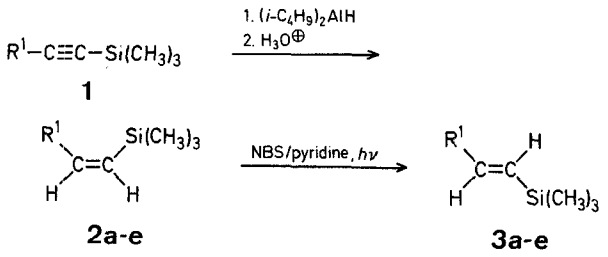

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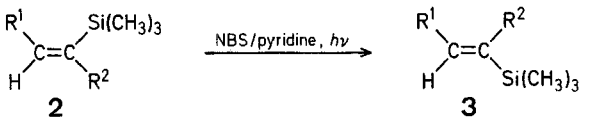
Table. (*E*)-1-Alkenylsilanes (**3**) obtained from (*Z*)-1-Alkenylsilanes (**2**)

	R^1	R^2	*N*-Bromosuccinimide[a] [mol%]	Reaction Time [min]	Yield[b] [%]	Isomeric Purity[c] [%]	b.p./torr [°C]	b.p./torr [°C] reported or Molecular Formula	n_D [°C]
a	n-C_4H_9	H	15	45	77[d]	96	68–69°/30	72–76°/30[4]	1.4257 (23°)
b	i-C_3H_7	H	15	45	76	98	74–75°/140	$C_8H_{18}Si$[f] (142.1178)	1.4170 (22°)
c	c-C_6H_{11}	H	15	45	88[d]	98	66–67°/4	71–74°/4[4]	1.4608 (21°)
d	t-C_4H_9	H	15	45	82[d]	99	77–80°/142	75–78°/98[4]	1.4213 (22°)
e	Cl–$(CH_2)_3$–	H	15	45	88	97	59–60°/6	$C_8H_{18}ClSi$[g] (176.1)	1.4500 (24°)
f	n-C_4H_9	CH_3	20	60	84[d]	97	58–59°/8	66–68°/7[4]	1.4371 (25°)
g	n-C_4H_9	n-C_4H_9	20	60	90[d,e]	91	50–54°/0.5	51–54°/0.1[4]	1.4472 (24°)

[a] Added in 5 mol-% portions at 15 min intervals.
[b] Isolated product.
[c] Determined on a SE-30 glass capillary column (90 m).
[d] The I.R. and ^{1}H-N.M.R. spectra were identical with those of authentic samples (Ref.[4]).
[e] Determined by G.L.C. analysis.
[f] M.S.: $m/e = 142.1174$ (M^+).
[g] Calc. C 54.05 H 10.20 Cl 19.94
found 54.14 9.70 19.80

This new procedure, which may be carried out *in situ* on the initially prepared (*Z*)-silane precursors **2a–e**, is very effective and proceeds readily regardless of the steric requirements of the alkyl group at C-2[8,9].

The observed strong tendency of the trimethylsilyl moiety in 2-alkyl-substituted vinylsilanes (**3**) to occupy the sterically more favorable *trans* position also prevails in isomerizations of 1,2-disubstituted vinylsilanes containing primary alkyl groups. Thus, treatment of an etheral solution of (*Z*)-2-trimethylsilyl-2-heptene (**2f**, $R^1 = n$-C_4H_9; $R^2 = CH_3$)[4] with 1 equiv of pyridine followed by addition of four 5 mol% portions of *N*-bromosuccinimide at 15 min intervals over a 60 min period while irradiating affords the corresponding (*E*)-silane **3f** in 96% isomeric purity. However, as anticipated, with increasing size of the alkyl substituent R^2, the isomerization **2**→**3** becomes less effective. For example, isomerization of **2g** ($R^1 = n$-C_4H_9; $R^2 = t$-C_4H_9)[4] produces an 80/20 mixture of the vinylsilanes **2g** and **3g**. A similar isomer distribution is observed when the (*E*)-isomer **3g** is treated with 20 mol% of *N*-bromosuccinimide while irradiating with a sun lamp.



2 **3**

It is important to note that the *E*/*Z* ratios of vinylsilanes reported in the Table may not reflect the actual equilibrium distributions of the alkenylsilanes. Treatment of the reaction mixtures with additional *N*-bromosuccinimide might have afforded the desired (*E*)-isomers in higher isomeric purities.

(*E*)-(2-Cyclohexylethenyl)-trimethylsilane (3c); Typical Procedure: In a dry, 50-ml three-necked round-bottomed flask equipped with a nitrogen-inlet tube, reflux condenser, thermometer, magnetic stirrer and kept under a static pressure of nitrogen is placed a solution of diisobutylaluminum hydride (22.0 mmol) in hexane (22.0 ml). The hexane is removed under reduced pressure at room temperature and ether (10 ml) is introduced while maintaining the temperature at 20–30 °C (water bath). Then, by means of a syringe, (2-cyclohexylethynyl)-trimethylsilane (3.60 g, 20.0 mmol) is added at such a rate as to maintain the temperature at 20–30 °C (water bath). After 15 min, the flask is placed in a preheated 40 °C bath for 1 h to complete the hydroalumination of the alkynylsilane. The resultant clear solution is transferred by means of a double-ended needle to a vigorously stirred, chilled solution of 10% aqueous hydrochloric acid (50 ml). The flask is rinsed with ether (20 ml), the mixture is stirred until the resulting phases become nearly clear. The layers are separated, and the aqueous phase is extracted with ether (40 ml). The combined organic extracts are washed successively with 20% hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and saturated sodium chloride solution, and then dried with magnesium sulfate. To the resultant etheral solution (90 ml) containing the (*Z*)-(2-cyclohexylethenyl)-trimethylsilane (**2c**) is added pyridine (1.6 g, 20 mmol). Then, while irradiating with a U.V. sunlamp (275 W), the mixture is treated at 25–30 °C (water bath, cooled as needed) with 5 mol-% portions of *N*-bromosuccinimide (0.180 g) at 15 min intervals over a 45 min period. The reaction mixture is decanted from a gummy residue and washed with 10% hydrochloric acid (50 ml), 20% aqueous cadmium chloride (to remove traces of pyridine), water, 1 molar sodium hydroxide solution, and saturated sodium chloride solution, and then dried with magnesium sulfate. The filtrate is concentrated and distilled under reduced pressure; yield: 3.21 g (88%); b.p. 66–67 °C/4 torr (Ref.[4], b.p. 71–74 °C/4 torr); n_D^{21}: 1.4608.

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[6] Although the isomerization may be carried out in the absence of pyridine, the (*E*)-alkenylsilanes are usually obtained in lower isomeric purities.
[7] Attempted isomerization of a 79/21 mixture of the (*Z*)- and (*E*)-alkenylsilanes **2** ($R^1 = n\text{-}C_3H_7$, $R^2 = H$) with iodine/benzoyl peroxide for 9 h at elevated temperature produced a 59/41 ratio of the (*Z*)- and (*E*)-isomers[3].
[8] The isomerization does not proceed satisfactorily when the (*E*)-alkenylsilanes **2** contain additional unsaturation or possess oxygen containing substituents.
[9] The facile isomerization of (*Z*)-alkenylsilanes is reminiscent of the NBS-catalyzed isomerization of *cis*-olefins[10] and the bromine-catalyzed isomerization of (*E*)-1-halo-1-alkenylsilanes[5].
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