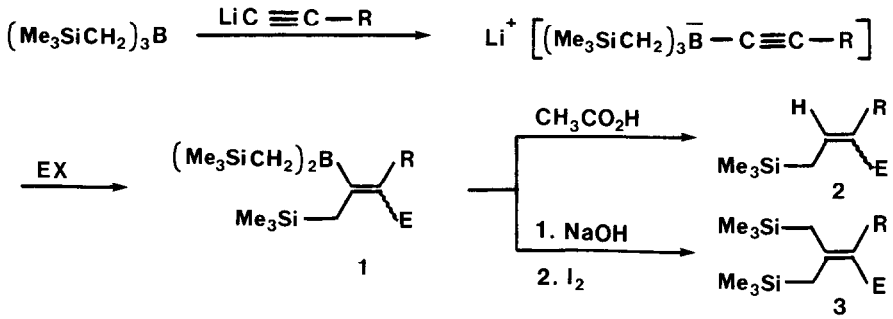
Tetrahedron Letters,Vol.28,No.10,pp 1007-1010,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A SIMPLE SYNTHESIS OF ALLYLSILANES VIA TRIS[(TRIMETHYLSILYL)METHYL]BORANE

Kung K. Wang* and Sujitra Dhumrongvaraporn
Department of Chemistry, West Virginia University
Morgantown, West Virginia 26506

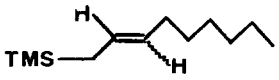
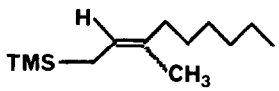
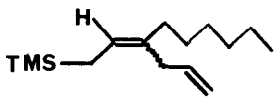
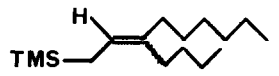
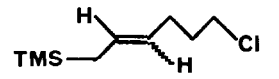
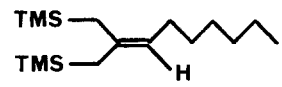
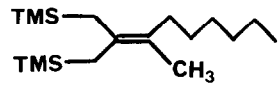
Abstract: Allylsilanes were prepared by protonation or alkylation of lithium 1-alkynyltris[(trimethylsilyl)methyl]borates followed by protonolysis or treatment with aqueous sodium hydroxide and iodine.

We have shown in the preceding note one example of using tris[(trimethylsilyl)-methyl]borane for the preparation of an allylsilane.[1] We now report an extension of this work to the synthesis of a variety of allylsilanes using the same organoborate reaction but with the migration of the (trimethylsilyl)methyl group induced by other electrophiles.[2] The migration of the second (trimethylsilyl)methyl group was also promoted by treating the resulting alkenylborane with aqueous sodium hydroxide followed by iodine as described previously.[3] A summary of the results is given in Table I.[4]



In contrast to the β,γ-disubstituted allylsilanes of the preceding paper, allylsilanes 2 prepared by this procedure are either γ-monosubstituted or γ,γ-disubstituted. Compound 2e thus represents yet another type of bifunctional conjunctive reagent as compared to 2c of the preceding paper.

Table I. Synthesis of Allylsilanes

1-alkyne	EX		product[a]	isolated yield, %	isomer ratio[b]
1-octyne	$MeSO_3H$	2a		58	E:Z=4:1[c]
1-octyne	MeI	2b		65	E:Z=3:1[c]
1-octyne	$H_2C=CHCH_2Br$	2c		59	2:1
1-octyne	n-BuOTs	2d		55	3:1[d]
1-octyne	n-BuOTf			51	3:1[d]
5-chloro-1-pentyne	$MeSO_3H$	2e		55	2:1
1-octyne	$MeSO_3H$	3a		52	-
1-octyne	MeI	3b		55	-

[a] The isolated products have been fully characterized by IR, ^1H and ^{13}C NMR (270 M Hz, $CHCl_3$ at δ7.26 for ^1H and $CDCl_3$ at δ77.02 for ^{13}C as internal reference), and mass spectroscopy.

[b] The isomer ratio was determined by integration of either the ^1H NMR spectrum or the GC chromatogram.

[c] The assignment of the geometry was based upon the comparison of the ^{13}C NMR spectrum with the reported data.[5]

[d] The isomer ratio was estimated from the ^{13}C NMR spectrum.

The pathway to 3 by the double migration of the (trimethylsilyl)methyl groups provides a simple and versatile method for the preparation of a variety of such compounds bearing two reactive sites as described previously.[1] It is also interesting to note that the origin of the two (trimethylsilyl)methyl substituents in 3 is very different from those prepared in the preceding paper, and thus these two procedures could complement each other for making structural variations.

Although n-butyl tosylate did induce the migration, prolonged heating of the reaction mixture was required. However, the reaction rate was dramatically enhanced by using n-butyl trifluoromethanesulfonate as the inducing electrophile. The reaction was essentially complete in less than one hour at room temperature.

The lack of stereoselectivity in the migration step is observed again. However, this may not be a drawback for certain subsequent reactions. Although the stereochemical outcome of condensations with aldehydes was found to be sensitive to the double bond geometry of the γ-monosubstituted allylsilanes,[6] it is essentially completely independent of the double bond geometry of either the γ-monosubstituted or the γ,γ-disubstituted allylsilanes in the intramolecular Sakurai reaction.[7] We are now actively exploring the use of this method for synthesizing highly functionalized allylsilanes and then converting them into complex natural products.

The following procedure for the preparation of 2a is representative. To a 100-mL round-bottomed flask purged with nitrogen were successively charged with syringes 0.74 mL of 1-octyne (0.551 g, 5 mmol), 10 mL of THF, and 2.15 mL of n-butyllithium (2.33 M in hexane, 5 mmol). After 15 min of stirring at 0°C, 1.8 mL of tris[(trimethylsilyl)methyl]borane[8] (1.36 g, 5 mmol) was introduced and the resulting solution was stirred for an additional hour before 0.32 mL of methanesulfonic acid (5 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for one hour.[9] Hydrolysis was then carried out with 15 mL of a 0.5 M solution of acetic acid in hexane at refluxing temperature for 15 h.[10] After oxidative workup with alkaline hydrogen peroxide at room temperature, the organic layer was separated, dried over $MgSO_4$, and concentrated. Distillation on a short-path distilling head afforded 0.571 g (58%) of 2a[5] as a colorless liquid: bp 55°C (1.5 torr); IR (neat) 1650 (w), 1460 (m), 1245 (s), 1150 (s), 965 (s), 850 (s), 745 (w), 722 (w), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.44-5.16 (2H, m), 1.97 (2H, br q), 1.46 (CH_2Si of the Z isomer, d, J=8.4 Hz), 1.40 (CH_2Si of the E isomer, dd, J=7.5 and 0.9 Hz), 1.28 (8H, br), 0.89 (3H, t), 0.005 (Me_3Si of the Z isomer, s), -0.01 (Me_3Si of the E isomer, s); ^{13}C NMR ($CDCl_3$) δ (E isomer, major set) 129.10, 125.91, 32.82, 31.81, 30.03, 28.83, 22.71, 22.61, 14.11, -1.97; (Z isomer, minor set) 127.83, 125.21, 31.88, 29.83, 29.17, 27.13, 18.43, -1.75; MS, m/e 198 (M^+), 183, 155, 127, 124, 99, 73.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The JEOL GX-270 NMR spectrometer used in this research was purchased by funds derived in part from an NSF grant (RII 8011453).

REFERENCES AND NOTES

1. Wang, K. K.; Yang, K. E. Tetrahedron Lett. preceding paper.
2. Pelter, A.; Harrison, C. R.; Kirkpatrick, D. J. Chem. Soc., Chem. Commun. 1973, 544-545.
3. (a) Zweifel, G.; Arzoumanian, H.; Whitney, C. C. J. Am. Chem. Soc. 1967, 89, 3652-3653.

(b) Pelter, A.; Harrison, C. R.; Subrahmanyam, C.; Kirkpatrick, D. J. Chem. Soc., Perkin Trans. 1 1976, 2435-2438.

4. Spectral data for 2c, 2e, and 3b.

2c: IR (neat) 1635 (m), 1460 (m), 1245 (s), 1150 (s), 1045 (w), 990 (s), 910 (s), 850 (s), 755 (m), 695 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.86-5.67 (1H, m), 5.22 (1H, t), 5.02 (1H, d, J=17 Hz), 4.97 (1H, d, J=11 Hz), 2.74 (2H, d, J=6.2 Hz), 1.97 (2H, t, J=7 Hz), 1.43 (2H, d, J=8.4 Hz), 1.27 (8H, br), 0.88 (3H, t), -0.01 (9H, s); ^{13}C MNR ($CDCl_3$) δ (major set) 136.72, 134.64, 121.24, 114.86, 36.98, 34.37, 31.84, 29.05, 28.32, 22.72, 18.40, 14.11, -1.66; (minor set) 137.99, 135.61, 121.34, 115.00, 41.65, 31.88, 29.75, 29.56, 28.07, 22.68, 18.43; MS, m/e 238 (M^+), 223, 164, 153, 94, 73.

2e: IR (neat) 1650 (w), 1440 (m), 1245 (s), 1150 (m), 965 (m), 850 (s), 725 (w), 695 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.53-5.40 (1H, m), 5.28-5.14 (1H, m), 3.54 (H_2CCl of the minor isomer, t, J=6.6 Hz), 3.53 (H_2CCl of the major isomer, t, J=6.6 Hz), 2.14 (2H, q), 1.81 (2H, m), 1.49 (CH_2Si of the minor isomer, dm, J=8.6 Hz), 1.42 (CH_2Si of the major isomer, dd, J=7.9 and 0.7 Hz), 0.01 (Me_3Si of the minor isomer, s), -0.01 (Me_3Si of the major isomer, s); ^{13}C NMR ($CDCl_3$) δ (major set) 127.94, 126.59, 44.42, 32.75, 29.85, 22.74, -1.97; (minor set) 127.14, 125.37, 44.67, 32.66, 24.29, 18.55, -1.77; MS, m/e 190 (M^+), 93, 73.

3b: IR (neat) 1450 (w), 1245 (s), 1150 (w), 830 (s), 760 (w), 685 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.92 (2H, t), 1.55 (3H, s), 1.46 (2H, s), 1.44 (2H, s), 1.28 (8H, br), 0.89 (3H, t), 0.01 (18 H, s); ^{13}C NMR ($CDCl_3$) δ 126.88, 122.12, 34.92, 32.03, 29.47, 28.50, 25.33, 24.87, 22.77, 18.73, 14.14, -0.30, -0.34; MS, m/e 298 (M^+), 227, 139, 73.

5. Negishi, E. -i.; Luo, F. -T.; Rand, C. L. Tetrahedron Lett. 1982, 20, 27-30.

6. Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. Tetrahedron Lett. 1983, 21, 2865-2868.

7. (a) Majetich, G.; Defauw, J.; Hull, K.; Shawe, T. Tetrahedron Lett. 1985, 26, 4711-4714.

(b) Tokoroyama, T.; Tsukamoto, M.; Iio, H. Tetrahedron Lett. 1984, 25, 5067-5070.

8. Seyferth, D. J. Am. Chem. Soc. 1959, 81, 1844-1847.

9. Alkylation with methyl iodide, allyl bromide, or n-butyl tosylate was carried out at reflux for 7 h, 24 h, and 144 h, respectively. Alkylation with n-butyl triflate was performed at room temperature for one hour. The in situ preparation of n-butyl triflate was carried out in a separate flask containing lithium n-butoxide (5 mmol) in hexane generated from 1-butanol and n-butyllithium at 0°C. To this flask was introduced by syringe 0.84 mL of trifluoromethanesulfonic anhydride (5 mmol). The resulting solution was warmed to room temperature and then transferred via cannula to the flask containing the organoborate complex.

10. In the cases of 3a and 3b, the reaction mixture was first treated with 1.7 mL of 3N NaOH and then stirred for 30 min at 0°C before 5 mL of 1.0 M iodine in diethyl ether was introduced. The resulting solution was stirred for an additional 15 min before oxidative workup.

(Received in USA 20 November 1986)