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Et_3B-Induced Hydrogermylation of Alkenes and Silyl Enol Ethers

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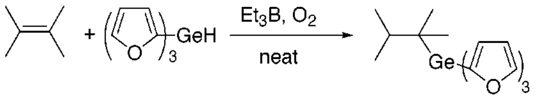
ABSTRACT

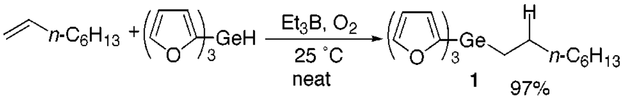


Tri-2-furanylgermane in the presence of a catalytic amount of Et_3B adds to internal alkenes as well as terminal alkenes effectively to give the corresponding adducts in good to excellent yields. The addition of tri-2-furanylgermane to silyl enol ethers followed by elimination of germyl and siloxy moieties provides a new route for the conversion of ketones into alkenes.

Hydrostannylation[1] and hydrosilylation,[2] as well as hydrogermylation,[3] of alkynes have been extensively studied and widely used in organic synthesis. We have previously shown that in the presence of Et_3B, R_3SnH, R_3GeH, and R_3SiH add to carbon−carbon triple bonds via a radical process.[4] Reports of hydrostannylation and hydrosilylation of alkenes via a radical mechanism are limited in organic synthesis. Hydrostannylation of alkenes via a radical intermediate[5] often gives low yields because the addition of stannyl radicals is reversible and the equilibrium favors the starting materials.[6] Radical-chain hydrosilylation of alkenes is also difficult because the hydrogen-atom abstraction step is relatively slow and competing telomerization of alkenes can be a problem.[7] Here we describe that tri-2-furanylgermane[8] adds to not only terminal alkenes but also internal alkenes in the presence of a catalytic amount of Et_3B.

A mixture of tri-2-furanylgermane (0.27 g, 1.0 mmol) and 1-octene (0.22 g, 2.0 mmol) was placed in a 20 mL reaction flask and flushed with argon.[9] To this mixture was added a hexane solution of triethylborane (1.0 M, 0.1 mL, 0.1 mmol) at 25 °C. After stirring for 1 h at 25 °C, the reaction mixture was subjected directly to silica gel column chromatography to give 1-(tri-2-furanyl)germyloctane[10] **(1)** in 97% yield (Scheme 1).

Scheme 1



The results are summarized in Table 1. Several comments are worth noting. (1) Tri-2-furanylgermane adds to not only

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(1) Davis, A. G. *Organotin Chemistry*; VCH Verlagsgesellschaft mbH: Weinheim, 1997; Chapter 3. 4, p 37.

(2) (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*: Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, Chapter 3. 12, p 763. (b) Ojima, I. In *The Chemistry of Organosilicon Compounds*; Patai. S., Rappoport. Z., Eds.; Wiley: Chichester, 1989; Part 2, Chapter 25. (c) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI: Greenwich, 1991; Vol. 1, p 355. (d) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organosilicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Part 2, Chapter 29.

(3) Selected references: (a) Piers, E.; Lemieux, R. *J. Chem. Soc., Perkin Trans 1* **1995**, 3. (b) Wada, F.; Abe, S.; Yonemaru, N.; Kikukawa, K.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1701. (c) Lukevics, E.; Barabanov, D. I.; Ignatovich, L. M. *Appl. Organomet. Chem.* **1991**, *5*, 379. (d) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1972**, *40*, 73. (e) Bernardoni, S.; Lucarini, M.; Pedulli, G. F.; Valgimigli, L.; Gevorgyan, V.; Chatgilialoglu, C. *J. Org. Chem.* **1997**, *62*, 8009.

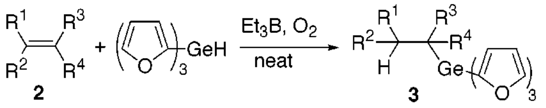
(4) (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron* **1989**, *45*, 923. (c) Nozaki, K.; Ichinose, Y.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2268. (d) Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356.

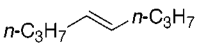
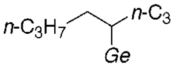
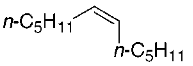
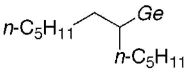
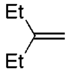
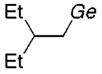
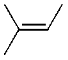
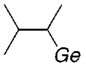
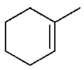
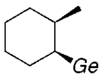
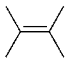
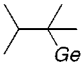
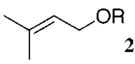
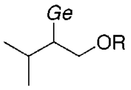
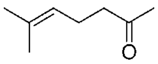
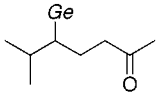
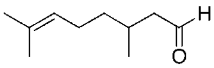
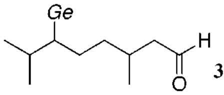
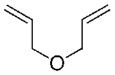
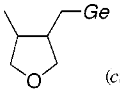
(5) Hydrostannylation of alkenes via radical process, see: (a) Miura, K.; Saito, H.; Uchinokura, S.; Hosomi, A. *Chem. Lett.* **1999**, 659. (b) Hanessian, S.; Leger, R. *J. Am. Chem. Soc.* **1992**, *114*, 3115.

(6) Sommer, R.; Kuivila, H. G. *J. Org. Chem.* **1968**, *33*, 802.

10.1021/ol005977n CCC: $19.00

Table 1. Addition of Tri-2-furanylgermane to Alkenes[a]

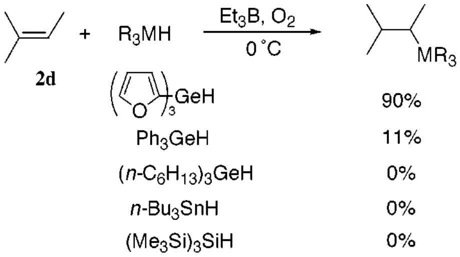


Entry	Alkene		Product		Yield (%)
1		**2a**		**3a**	82
2		**2b**		**3b**	90
3		**2c**		**3c**	100
4		**2d**		**3d**	90
5		**2e**		**3e**	85
6		**2f**		**3f**	84
7		**2g**		R=H **3g** R=CH_2Ph **3g′**	70 85
8		**2h**		**3h**	88
9		**2i**		**3i**	74
10		**2j**		**3j** (*cis*/*trans* = 75/25)	95

[a] Tri-2-furanylgermane (1.0 mmol), alkene (2.0 mmol), and Et_3B (0.1 mmol) were employed unless otherwise noted.

disubstituted olefins but also to tri- and tetrasubstituted olefins very easily under quite mild conditions to give the corresponding adducts in good to excellent yields. (2) Although a small amount of hexane from the solution of Et_3B was present in the reaction mixture, no additional solvent was necessary.[11] (3) A unique feature of tri-2-furanylgermane was demonstrated by the reaction with 2-methyl-2-butene (**2d**). Whereas the Et_3B-induced reaction of tri-2-furanylgermane with **2d** provided the adduct **3d** in 90% yield, the reaction of Ph_3GeH, $(n\text{-}C_6H_{13})_3GeH$, $n\text{-}Bu_3SnH$, or $(Me_3Si)_3SiH$ with 2-methyl-2-butene gave the corresponding adduct in miserable yield, or failed to give the desired products (Scheme 2).[12] (4) In the case of 1-methylcyclohexene (**2e**), *cis*-1-(tri-2-furanyl)germyl-2-methylcyclohexane (**3e**)[13] was obtained as a single diastereomer.[14] (5) Many functional groups are tolerated under the reaction conditions. For instance, hydrogermylation proceeded in the presence of carbonyl groups such as ketones and aldehydes (entries 8 and 9). The reduction of the carbonyl groups to the corresponding alcohols was not observed. (6) Even under the concentrated conditions, diallyl ether **2j** afforded tetrahydrofuran derivative **3j** by the sequential addition−cyclization process (entry 10). (7) The reversibility of the addition reaction was ascertained by the following experiment. Treatment of an excess amount of (*Z*)-6-dodecene (2.0 mmol) with tri-2-furanylgermane (1.0 mmol) gave the corresponding adduct in 90% yield. The recovered 6-dodecene was determined as a stereoisomeric mixture of *E* and *Z* isomer (*E*/*Z* = 84/16) by ^1H NMR (Scheme 3).

Scheme 2. Hydrometalation to Trisubstituted Alkene



The reason for the successful addition of tri-2-furanylgermane to alkenes is not clear at this stage. It is conceivable that the addition of tri-2-furanylgermyl radical to alkenes is less reversible than the analogous reactions of other trialkyl- or triarylgermyl radicals. It is also possible that the hydrogen atom transfer from tri-2-furanylgermane to the initial radical adduct is more rapid than for other hydrogermanes.[15]

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(7) For hydrosilylation of alkenes via radical process, see: Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994 and references therein.

(8) Tri-2-furanylgermane was easily prepared according to the literature. Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Synlett* **1999**, 1415.

(9) Ethyl radicals were formed from the reaction of Et_3B with trace amounts of O_2 remaining in the reaction flask. Additional oxygen was not necessary.

(10) Compound data for **1**: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.88 (t, J = 6.9 Hz, 3H), 1.18−1.40 (m, 10H), 1.50−1.65 (m, 4H), 6.46 (dd, J = 3.3 Hz, 1.5 Hz, 3H), 6.75 (d, J = 3.3 Hz, 3H), 7.73 (d, J = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.97, 14.42, 22.53, 24.31, 28.95, 29.06, 31.74, 32.57, 109.75, 120.98, 147.33, 153.69; IR (neat, cm^{-1}) 2920, 1550, 1458, 1361, 1206, 1150, 1100, 1003, 896, 884, 814, 741. Anal. Calcd for $C_{20}H_{26}GeO_3$: C, 62.07; H, 6.77. Found: C, 61.83; H, 6.77.

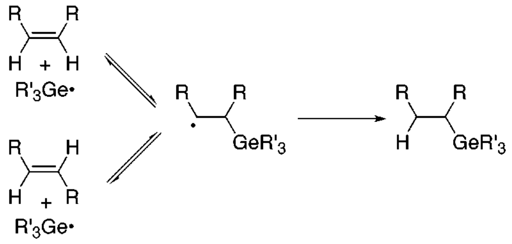
(11) Various solvents were examined for the addition of tri-2-furanylgermane to 4-octene. In hexane (5 mL), tetrafuranylgermane was obtained in 23% yield as a byproduct in addition to the adduct **3a** (60% yield). Tetrafuranylgermane might be formed by the attack of germyl radical to the carbon having a germyl group. The yields of **3a** and tetrafuranylgermane in other solvents were as follows: benzene, 52% and 20%; THF, 46% and 21%; EtOH, 55% and 20%; MeOH, 58% and 16%; H_2O, 80% and 8%. The best results were obtained without solvent.

(12) The Et_3B-mediated radical reaction of terminal olefin such as 1-octene with Ph_3GeH, $(Me_3Si)_3SiH$, or $n\text{-}Bu_3SnH$ afforded the corresponding adduct in 82%, 94%, or <20% yield, respectively.

(13) Compound data for **3e**: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.00 (d, J = 6.9 Hz, 3H), 1.30−1.46 (m, 3H), 1.50−1.60 (m, 2H), 1.62−1.88 (m, 3H), 2.10−2.26 (m, 2H), 6.45 (dd, J = 3.0 Hz, 1.5 Hz, 3H), 6.75 (d, J = 3.0 Hz, 3H), 7.73 (d, J = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 17.35, 21.79, 24.32, 27.30, 31.01, 33.78, 34.79, 109.74, 121.20, 147.19, 154.03; IR (neat, cm^{-1}) 2920, 1549, 1453, 1361, 1205, 1149, 1099, 1063, 1003, 895, 884, 814, 740, 595. Anal. Calcd for $C_{19}H_{22}GeO_3$: C, 61.52; H, 5.98. Found: C, 61.77; H, 6.09.

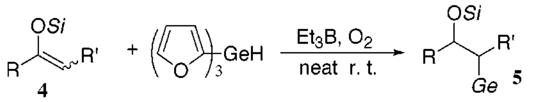
(14) The stereochemical outcome, which is tentative, might be explained by the steric hindrance of tri-2-furanylgermyl group. Tri-2-furanylgermane would approach the intermediary carbon radical from the opposite side of germyl moiety.

Scheme 3

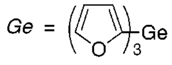


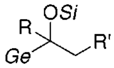
The addition of tri-2-furanylgermane to silyl enol ethers also proceeds efficiently to afford β-siloxygermanes with high regioselectivity. The regioisomer **6** could not be detected in the reaction mixture. The results are shown in Table 2.

Table 2. Et$_3$B-Induced Addition of Tri-2-furanylgermane to Silyl Enol Ethers[a]

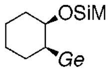


Entry		R	R'	*Si*	Product	Yield(%)	d. r.
1	**4a**	n-C$_6$H$_{13}$	n-C$_5$H$_{11}$	SiMe$_3$	**5a**	69	83 : 17[b]
2	**4b**	–(CH$_2$)$_4$–		SiMe$_3$	**5b**	95	*cis* only
3	**4c**	n-C$_{10}$H$_{21}$	H	SiMe$_3$	**5c**	98	–
4	**4d**	H	n-C$_{11}$H$_{23}$	SiMe$_3$	**5d**	95	–
5	**4e**	n-C$_6$H$_{13}$	n-C$_5$H$_{11}$	Si-t-BuMe$_2$	**5e**	26	(S.M. 69%)





6



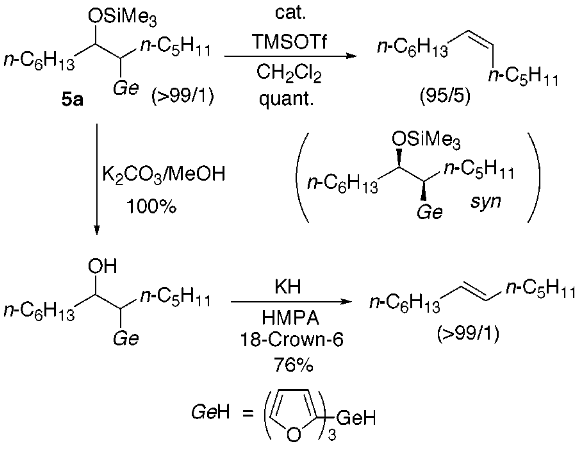
5b

[a] Tri-2-furanylgermane (1.0 mmol), silyl enol ether (2.0 mmol), and Et$_3$B (0.1 mmol) were employed unless otherwise noted. [b] *E*/*Z* ratio of **4a** was 35/65.

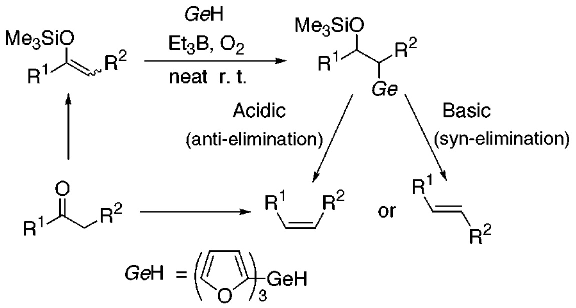
Trimethylsilyl enol ether **4b**, generated from cyclohexanone, gave *cis*-1-(trimethylsiloxy)-2-(tri-2-furanyl)germylcyclohexane (**5b**) as a single stereoisomer.[14] In the case of the *tert*-butyldimethylsilyl ether **4e**, the addition reaction was sluggish. The product was obtained in only 26% yield along with recovered starting material **4e** (69%) after stirring the reaction mixture for 5 h at 25 °C.

Then, the conversion of β-siloxygermanes to alkenes was examined. Stereospecific 1,2-elimination of β-hydroxysilanes under acidic or basic conditions is well-known for the synthesis of alkenes.[16] However, there have been few reports on the related β-hydroxy- or β-siloxygermanes.[17] Treatment of **5c** with a catalytic amount of trimethylsilyl triflate provided 1-dodecene in 92% yield. In a similar fashion, the major stereoisomer of **5a**[18] gave (*Z*)-6-tridecene selectively in quantitative yield upon treatment with TMSOTf. On the other hand, sequential treatment of the major stereoisomer of **5a** with K$_2$CO$_3$/methanol and then KH/18-Crown-6/HMPA provided (*E*)-6-tridecene exclusively (Scheme 4). On the basis of similar arguments to β-hydroxysilanes, these results indicate that the major stereoisomer is the syn isomer. The transformation of ketones to alkenes has received much attention in organic synthesis and many methods have been published.[19] Because silyl enol ethers are readily available from ketones, this new method will provide an alternative route for the formation of alkenes starting from ketones (Scheme 5).

Scheme 4



Scheme 5



In summary, radical-mediated hydrogermylation of internal alkenes can be achieved by using tri-2-furanylgermane. This method can provide a new method for stereoselective conversion of silyl enol ethers into alkenes. The procedure for this reaction is extremely simple and avoids the use of excess reaction solvent.

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(15) For a mechanistic discussion of the addition of germyl radicals to alkenes, see ref 3e.

(16) (a) Ager, D. J. *Org. React.* **1990**, *38*, 1. (b) Kelly, S. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, Chapter 3.1, p 729.

(17) Kawashima, T.; Iwama, N.; Tokitoh, N.; Okazaki, R. *J. Org. Chem.* **1994**, *59*, 491−493.

(18) The major stereoisomer of **5a** can be separated by silica gel column chromatography.

(19) Shapiro, R. H. *Org. React.* **1976**, *23*, 405.

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