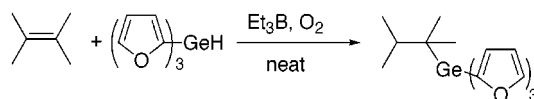


Et₃B-Induced Hydrogermylation of
Alkenes and Silyl Enol EthersShinobu Tanaka, Tomoaki Nakamura, Hideki Yorimitsu, Hiroshi Shinokubo, and
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ABSTRACT



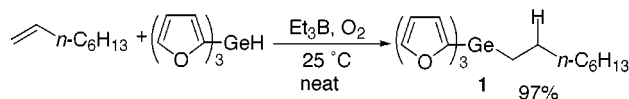
Tri-2-furanylgermane in the presence of a catalytic amount of Et₃B adds to internal alkenes as well as terminal alkenes effectively to give the corresponding adducts in good to excellent yields. The addition of tri-2-furanylgermane to silyl enol ethers followed by elimination of germlyl and siloxy moieties provides a new route for the conversion of ketones into alkenes.

Hydrostannylation¹ 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 Et₃B, R₃SnH, R₃GeH, and R₃SiH 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 intermediate⁵ 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-furanylgermane⁸ adds to not only terminal alkenes but also internal alkenes in the presence of a catalytic amount of Et₃B.

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)germyloctane¹⁰ (**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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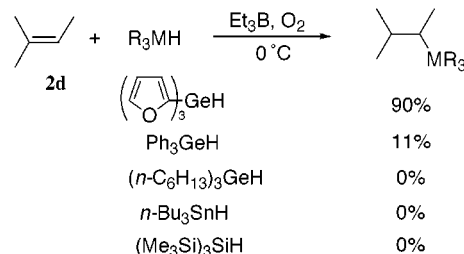
Table 1. Addition of Tri-2-furanylgermane to Alkenes^a

| Entry | Alkene | Product | Yield (%) |
|-------|--------|---------|--|
| 1 | | | 82 |
| 2 | | | 90 |
| 3 | | | 100 |
| 4 | | | 90 |
| 5 | | | 85 |
| 6 | | | 84 |
| 7 | | | R=H 3g: 70 R=CH ₂ Ph 3g': 85 |
| 8 | | | 88 |
| 9 | | | 74 |
| 10 | | | 95 (cis/trans = 75/25) |

^a Tri-2-furanylgermane (1.0 mmol), alkene (2.0 mmol), and Et₃B (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 Et₃B 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 Et₃B-induced reaction

of tri-2-furanylgermane with **2d** provided the adduct **3d** in 90% yield, the reaction of Ph₃GeH, (*n*-C₆H₁₃)₃GeH, *n*-Bu₃SnH, or (Me₃Si)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

Scheme 2. Hydrometalation to Trisubstituted Alkene

1-methylcyclohexene (**2e**), *cis*-1-(tri-2-furanylgermyl)-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).

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

(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%; H₂O, 80% and 8%. The best results were obtained without solvent.

(12) The Et₃B-mediated radical reaction of terminal olefin such as 1-octene with Ph₃GeH, (Me₃Si)₃SiH, or *n*-Bu₃SnH afforded the corresponding adduct in 82%, 94%, or <20% yield, respectively.

(13) Compound data for **3e**: ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₂₂GeO₃: 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.

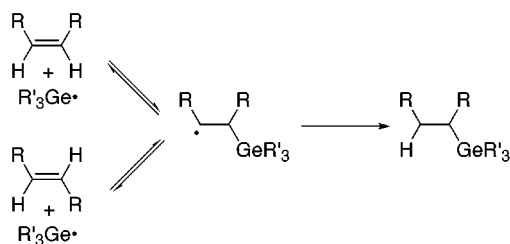
(7) For hydrosilylation of alkenes via radical process, see: Kopping, B.; Chatgililoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, 57, 3994 and references therein.

(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 Et₃B with trace amounts of O₂ remaining in the reaction flask. Additional oxygen was not necessary.

(10) Compound data for **1**: ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₂₀H₂₆GeO₃: C, 62.07; H, 6.77. Found: C, 61.83; H, 6.77.

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. Et₃B-Induced Addition of Tri-2-furanylgermane to Silyl Enol Ethers^a

| | | | | | | | |
|-------|-----------|---|---|--|-----------|-------|----------------------|
| | | + | | $\xrightarrow[\text{neat r. t.}]{\text{Et}_3\text{B}, \text{O}_2}$ | | | |
| Entry | R | R' | Si | Product | Yield(%) | d. r. | |
| 1 | 4a | <i>n</i> -C ₆ H ₁₃ | <i>n</i> -C ₅ H ₁₁ | SiMe ₃ | 5a | 69 | 83 : 17 ^b |
| 2 | 4b | -(CH ₂) ₄ - | | SiMe ₃ | 5b | 95 | <i>cis</i> only |
| 3 | 4c | <i>n</i> -C ₁₀ H ₂₁ | H | SiMe ₃ | 5c | 98 | — |
| 4 | 4d | H | <i>n</i> -C ₁₁ H ₂₃ | SiMe ₃ | 5d | 95 | — |
| 5 | 4e | <i>n</i> -C ₆ H ₁₃ | <i>n</i> -C ₅ H ₁₁ | Si- <i>t</i> -BuMe ₂ | 5e | 26 | (S.M. 69%) |

$Ge = \left(\text{2-furyl} \right)_3 Ge$
6
5b

^a Tri-2-furanylgermane (1.0 mmol), silyl enol ether (2.0 mmol), and Et₃B (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-furanylgermyl)cyclohexane (**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

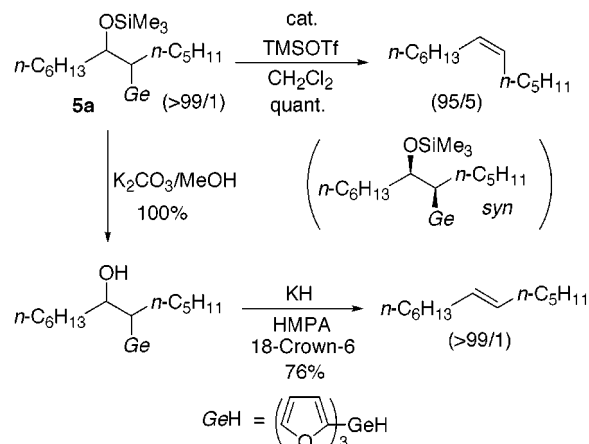
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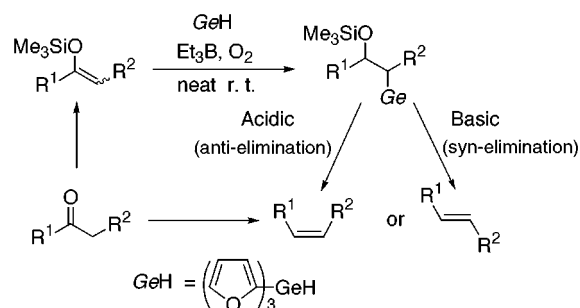
major stereoisomer of **5a**¹⁸ gave (*Z*)-6-tridecene selectively in quantitative yield upon treatment with TMSOTf. On the other hand, sequential treatment of the major stereoisomer of **5a** with K₂CO₃/methanol and then KH/18-Crown-6/HMPA provided (*E*)-6-tridecene exclusively (Scheme 4). On

Scheme 4



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 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.

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

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