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Nucleophilic addition of tri-2-furylgermane to aldehydes and α,β-unsaturated carbonyl compounds in the presence of a catalytic amount of base

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Abstract—Nucleophilic addition of tri-2-furylgermane to various aldehydes and α,β-unsaturated carbonyl compounds in the presence of a catalytic amount of base such as ^{t}BuOK and Cs_2CO_3 afforded α-hydroxy germanes and β-germyl carbonyl compounds, respectively, in good to excellent yields. The reaction of aldehydes proceeded with high chemoselectivity under mild conditions, so α-hydroxy germanes bearing various functional groups were obtained effectively. α-Hydroxy germanes could be converted into acylgermanes by Swern oxidation.

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1. Introduction

Triorganogermyl-alkali metal compounds are one of the most useful reagents for an introduction of germyl group into organic compounds.[1] Two typical procedures are known for the preparation of these reagents (Scheme 1). One is reduction of hexaorganodigermanes or triorganogermyl halides with a slight excess of alkali metal in HMPA.[2] The other is direct deprotonation of triorganogermanes with a stoichiometric amount of butyllithium or *tert*-butyllithium in the presence of TMEDA in THF.[3] However, reaction conditions of these methods are so severe that their applications are limited to the preparation of simple tetraorganogermanes having no functional groups.

We previously demonstrated that tri-2-furylgermane (**1**) has a unique reactivity in triethylborane-induced hydrogermylation of internal alkenes[4] and in palladium-catalyzed hydrogermylation of acetylenes.[5] Here we describe that a catalytic amount of base promotes nucleophilic addition of tri-2-furylgemane to aldehydes and α,β-unsaturated carbonyl compounds under mild conditions (Scheme 2).[6]

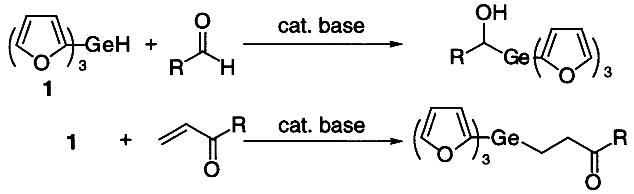
$$R_3GeGeR_3 \xrightarrow[\text{HMPA}]{\text{2M}} 2R_3GeM$$

$$R_3GeX \xrightarrow[\text{HMPA}]{\text{2M}} R_3GeM + MX$$

$$(\text{M} = \text{Li, Na, K} \quad \text{X} = \text{Cl, Br})$$

$$R_3GeH \xrightarrow[\text{THF}]{^t\text{BuLi, TMEDA}} R_3GeLi$$

Scheme 1.



Scheme 2.

2. Result and discussion

We first investigated the nucleophilic addition of tri-2-furylgermane to aldehydes in the presence of a catalytic amount of potassium *tert*-butoxide. A solution of tri-2-furylgermane and hexanal (1.2 equiv.) in THF was treated with ^{t}BuOK (10 mol%) at 0°C under air. After being stirred for 10 min at 0°C, the reaction was quenched with water, and the products were extracted with ethyl acetate. The crude oil was purified by silica gel column chromatography (hexane/AcOEt=10/1) to afford α-hydroxy germane **3a** in 75% yield (Scheme 3). This result demonstrates that hydrogen of tri-2-furylgermane was abstracted very easily by ^{t}BuOK. Moreover, the fact that the reaction proceeded in the presence of a catalytic amount of ^{t}BuOK, suggests that α-germyl alkoxide **3a′** also could abstract hydrogen from tri-2-furylgermane to generate **3a** and tri-2-furylgermyl anion.[7] It is very interesting that $^t BuO^-$ or $R'CH(GeR_3)O^-$ can abstract hydrogen from tri-2-furylgermane, since trialkylgermane

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Keywords: germanium and compounds; addition reactions; aldehydes.

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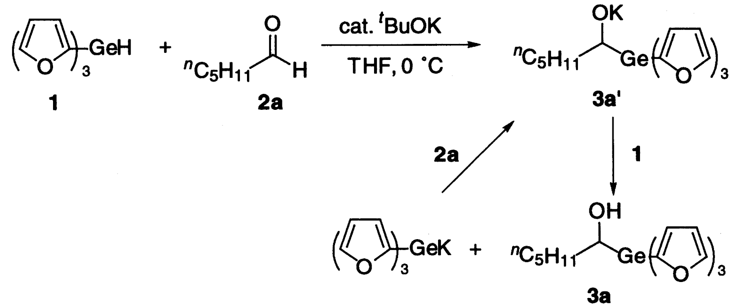


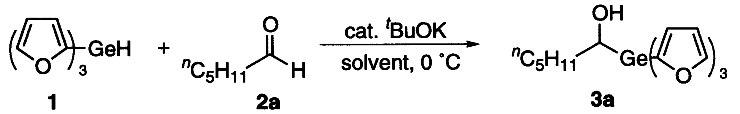
Scheme 3.

(so called trialkylgermanium hydride) usually behaves as $R_3Ge^{\delta+}H^{\delta-}$ (vide infra).[8]

We then studied this reaction in various solvents. The results are shown in Table 1. The use of aprotic polar solvents such as DMF and DMI (1,3-dimethyl-2-imidazolidinone) increased the reaction rate. In the case of DMI, the reaction completed within 5 min (entry 3). Although longer reaction time was required, nonpolar (entries 4 and 5) or protic solvents (entries 6 and 7) also could be employed. None of the self-aldol product was observed in all cases examined.

Next, various bases were examined in DMI (Table 2). Fujita and Hiyama reported that treatment of aldehydes with hydrosilanes in the presence of a catalytic amount of tetrabutylammonium fluoride (TBAF) in aprotic polar solvents afforded silyl ethers **4** (Scheme 4).[9] In contrast, α-hydroxy germane **3a** was formed as a single product in good yield in the reaction of tri-2-furylgermane with hexanal in the presence of TBAF in DMI (entry 2). With cesium carbonate[10] instead of TBAF, **3a** was obtained almost quantitatively at room temperature within 10 min (entry 4). Whereas triethylamine was not effective, more basic

Table 1. Addition of tri-2-furylgermane to hexanal in various solvents



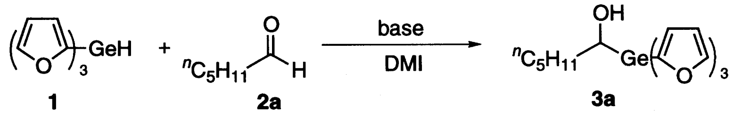
Entry	Solvent	Time	Yield (%)	Recovery of **1**
1	THF	10 min	75[a]	0
2	DMF	10 min	81[a]	0
3	DMI	5 min	75[a]	0
4	CH_2Cl_2	15 min	78[b]	17[b]
5	Benzene	15 min	85[b]	9[b]
6	EtOH	15 min	66[b]	28[b]
7	EtOH	2.5 h	77[a]	0
8	None	5 min	66[b]	20[b]

Tri-2-furylgermane (0.50 mmol), hexanal (0.60 mmol), ᵗBuOK (0.05 mmol), and solvent (1 mL) were employed.

[a] Isolated yield.

[b] NMR yield.

Table 2. Addition of tri-2-furylgermane to hexanal in the presence of various bases



Entry	Base	Temperature	Time	Yield (%)[a]
1	ᵗBuOK	0°C	5 min	75
2	TBAF[b]	0°C	5 min	85
3	Cs_2CO_3	0°C	40 min	96
4	Cs_2CO_3	rt	10 min	94
5	K_2CO_3	rt	12 h	83
6	Et_3N	rt	12 h	20
7	DBU	rt	10 min	96

Tri-2-furylgermane (0.50 mmol), hexanal (0.60 mmol), base (0.05 mmol), and DMI (1 mL) were employed.

[a] Isolated yield.

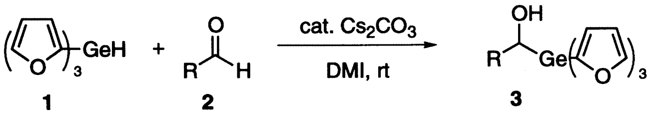
[b] 1.0 M THF solution was used.

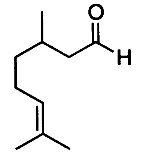
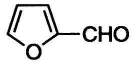
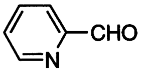
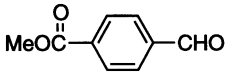
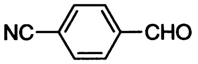
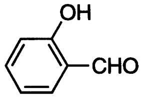
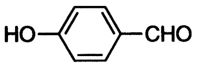
Scheme 4.

amine such as DBU was very efficient for the formation of the adducts (entries 6 and 7).

Cesium carbonate-induced nucleophilic addition of tri-2-furylgermane to various aldehydes in DMI were then examined (Table 3). Several comments are worth noting. (1) α-Hydroxy germanes were obtained in good to excellent

Table 3. Addition of tri-2-furylgermane to various aldehydes



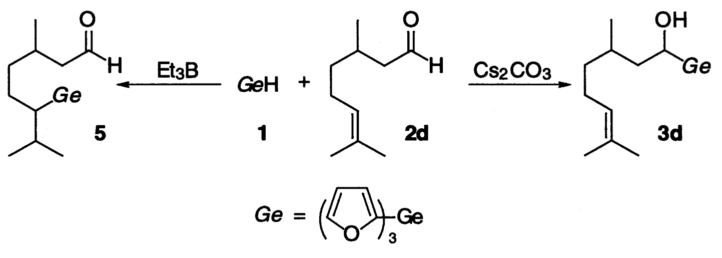
Entry	Aldehyde	Product	Time	Yield (%)[a]
1	$^{n}C_5H_{11}CHO$ **2a**	**3a**	10 min	94
2	$^{i}PrCHO$ **2b**	**3b**	10 min	99
3	$^{t}BuCHO$ **2c**	**3c**	10 min	73
4	 **2d**	**3d**	15 min	93
5[b]	$^{n}C_5H_{11}-\equiv-CHO$ **2e**	**3e**	2 h	92
6	PhCHO **2f**	**3f**	5 min	92
7	 **2g**	**3g**	15 min	84
8	 **2h**	**3h**	15 min	91
9	 **2i**	**3i**	10 min	74
10	 **2j**	**3j**	5 min	81
11	 **2k**	**3k**	30 min	74
12	 **2l**	**3l**	5 h	0
13	$HCHO/H_2O$ **2m**[c]	**3m**	5 min	91

Tri-2-furylgermane (0.50 mmol), aldehyde (0.60 mmol), Cs_2CO_3 (0.05 mmol), and DMI (1 mL) were employed.

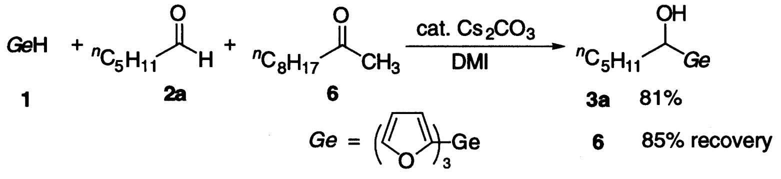
[a] Isolated yield.

[b] Cs_2CO_3 (0.05 mmol×2) was used.

[c] Solution (37 wt%) in water was used.

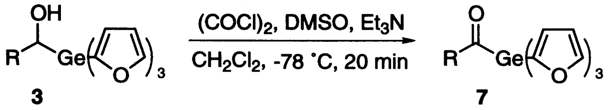


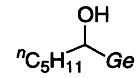
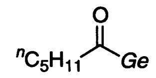
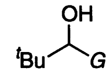
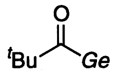
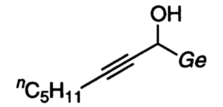
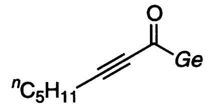
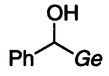
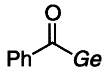
Scheme 5.



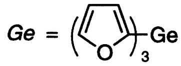
Scheme 6.

Table 4. Preparation of acyltri(2-furyl)germanes



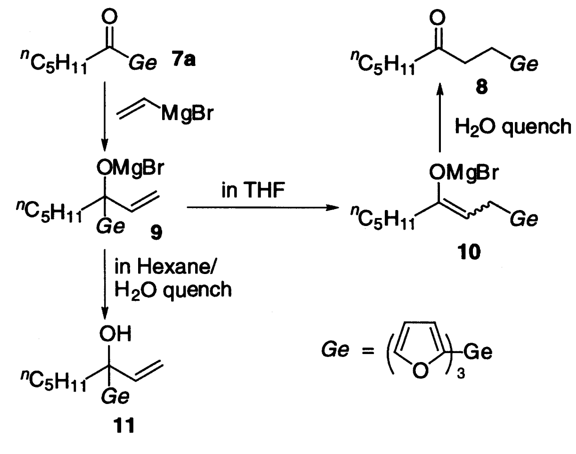
Entry	Substrate		Product		Yield (%)[a]
1		3a		7a	94
2		3c		7c	68
3		3e		7e	81
4		3f		7f	76

3 (0.50 mmol), $(COCl)_2$ (0.60 mmol), DMSO (1.2 mmol), Et_3N (2.5 mmol), and CH_2Cl_2 (2 mL) were employed.

[a] Isolated yield. *Ge* = 

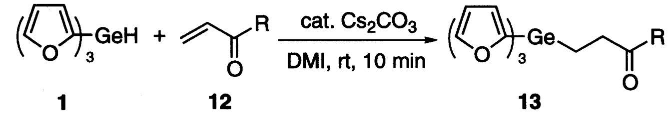
yields, even in the case of sterically hindered aldehydes such as isobutyraldehyde and pivalaldehyde (entries 2 and 3). (2) Cesium carbonate-promoted addition of tri-2-furylgermane to aldehydes bearing carbon–carbon multiple bonds such as citronellal (**2d**) or 2-octynal (**2e**) gave α-hydroxy germane **3d** or **3e** exclusively. This finding shows sharp contrast to the result that triethylborane-induced radical addition of tri-2-furylgermane to citronellal (**2d**) provided **5** exclusively without affecting the carbonyl moiety (entries 4, 5 and Scheme 5).[4] (3) Not only aliphatic aldehydes but also aromatic and heteroaromatic aldehydes reacted effectively (entries 6–8). (4) The reaction proceeded with high chemoselectivity. For instance, as shown in Scheme 6, treatment of a mixture of hexanal and 2-decanone (**6**) (1:1) in DMI with tri-2-furylgermane in the presence of Cs_2CO_3 provided the adduct **3a** along with **6** which was recovered unchanged. Ester and cyano moieties also survived under the reaction conditions (entries 9 and 10). Furthermore, addition of tri-2-furylgermane to salicylaldehyde (**2k**), which has an acidic proton, also gave α-hydroxy germane **3k** in good yield. Although, the reaction with *p*-hydroxybenzaldehyde (**2l**) resulted in complete recovery after 5 h (entries 11 and 12). Thus, the position of hydroxy group played a critical role for the successful reaction. (5) Intriguingly, this reaction proceeded in an aqueous solution. Formalin afforded hydroxymethylgermane **3m** in excellent yield upon treatment with tri-2-furylgermane in the presence of Cs_2CO_3 (entry 13).

Swern oxidation[11] of α-hydroxy germanes **3** provided acyltri(2-furyl)germanes **7** effectively (Table 4).[12] Whereas **7a** was generated in excellent yield upon oxidation of **3a** (entry 1), the oxidation of α-hydroxygermanes **3c**, **3e**, and **3f** gave the corresponding acylgermanes **7c**, **7e**, and **7f** in slightly lower yields compared to **7a** (entries 2–4). Treatment of **3a** with the Dess–Martin oxidant[13] in place of Swern oxidant afforded **7a** in only 30% yield along with unidentified complex mixture.

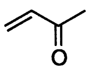
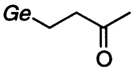
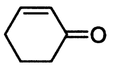
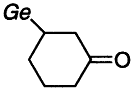
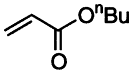
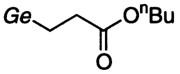
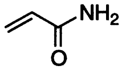
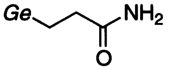


Scheme 7.

Table 5. 1,4-Addition of tri-2-furylgermane to α,β-unsaturated carbonyl compounds

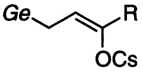


1 **12** **13**

Entry	Substrate		Product		Yield (%)[a]
1		**12a**		**13a**	84
2		**12b**		**13b**	83
3		**12c**		**13c**	95
4		**12d**		**13d**	87

Tri-2-furylgermane (0.50 mmol), **12** (0.60 mmol), Cs_2CO_3 (0.05 mmol), and DMI (1 mL) were employed.

[a] Isolated yield.



14

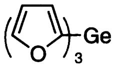
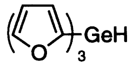
Ge = 

Table 6. Addition of R_3MH to hexanal

2a **3**

Entry	R_3MH	Time	Yield (%)[a]	R_3MH recovery
1		10 min	94	0
2	Ph_3SiH	15 min	0	ND[b]
3	Ph_3SnH	25 min	0	ND[b]
4	Ph_3GeH	2 h	45	46
5	Hex_3GeH	2 h	0	93

R_3MH (0.50 mmol), hexanal (0.60 mmol), Cs_2CO_3 (0.05 mmol), and DMI (1 mL) were employed.

[a] Isolated yield.

[b] Not determined.

Further application of acylgermane was studied briefly. Treatment of acylgermane **7a** with vinylmagnesium bromide in THF afforded β-germyl ketone **8** in 58% yield (Scheme 7). The formation of **8** could be explained as follows. At first, an addition of vinylmagnesium bromide to **7a** would afford **9**. Subsequent rearrangement of the germyl group could give magnesium enolate **10** which provided β-germyl ketone **8** upon aqueous workup.[14] Simple adduct **11** was obtained in 85% yield by the use of hexane as a solvent instead of THF where rearrangement of the germyl group did not occur.

Table 7. $R_3GeH+OH^- \rightarrow R_3Ge^- + H_2O$

	R_3GeH[a] (a.u.)	R_3Ge^{-a} (a.u.)	ΔG[b] (kcal mol^{-1})
R=Me	−2169.747761	−2168.984276	−76.29
R=Ph	−2734.083957	−2733.366287	−105.04
R=2-furyl	−2727.786912	−2727.088912	−117.38

[a] The energies were calculated at RHF/STO-3G. $E(OH^-)=-74.074196$ a.u.; $E(H_2O)=-74.959260$ a.u.

[b] $\Delta G=[E(R_3Ge^-)+E(H_2O)]-[E(R_3GeH)+E(OH^-)]$.

Next, an addition of tri-2-furylgermane to α,β-unsaturated carbonyl compounds was examined (Table 5). The reaction completed within 10 min, and butyl acrylate (**12c**) and acrylamide (**12d**) as well as α,β-unsaturated ketone afforded the corresponding 1,4-adducts in excellent yields. Enolate **14** would abstract hydrogen from tri-2-furylgermane to give the product **13** and regenerate germyl anion. No 1,2-adducts was observed in the reaction mixtures.

Table 8. The coordinates of atoms in tri(2-furyl)germyl anion −2727.088912 a.u. at the RHF/STO-3G level of theory

Atom	*x*	*y*	*z*
Ge	−0.000032	−0.000003	1.136535
C	−0.349724	1.635044	0.136891
C	−1.241125	−1.120317	0.136766
C	1.590863	−0.514657	0.136974
C	−1.108442	−2.248717	−0.598950
C	−2.424058	−2.702276	−0.973095
C	−3.278986	−1.823608	−0.439836
O	−2.599899	−0.845696	0.251463
C	−1.393722	2.084636	−0.598030
C	−1.128430	3.450574	−0.972698
C	0.060542	3.751243	−0.440472
O	0.567796	2.674254	0.251022
C	2.502231	0.164617	−0.597987
C	3.552364	−0.748206	−0.972844
C	3.218574	−1.928032	−0.440006
O	2.032159	−1.828816	0.251330
H	−0.183754	−2.729784	−0.862926
H	−2.671119	−3.568892	−1.564456
H	−4.357084	−1.752447	−0.460016
H	−2.273074	1.524637	−0.861277
H	−1.755569	4.097948	−1.563777
H	0.661602	4.649048	−0.461365
H	2.456905	1.206124	−0.861359
H	4.426449	−0.528882	−1.564150
H	3.695698	−2.897410	−0.460604

Table 9. The coordinates of atoms in tri(2-furyl)germane −2727.786912 a.u. at the RHF/STO-3G level of theory

Atom	*x*	*y*	*z*
Ge	0.000092	−0.000092	−0.724492
C	−0.286340	1.751634	−0.071007
C	1.660318	−0.627768	−0.070790
C	−1.373725	−1.123930	−0.070894
C	1.975505	−1.493961	0.910615
C	3.413092	−1.586096	0.961691
C	3.865357	−0.765338	0.004333
O	2.826615	−0.156468	−0.654475
C	0.308369	2.459084	0.908086
C	−0.331739	3.749553	0.959931
C	−1.271421	3.729110	0.005306
O	−1.280123	2.524543	−0.652470
C	−2.281430	−0.963486	0.910508
C	−3.080240	−2.162235	0.961732
C	−2.595651	−2.964522	0.004526
O	−1.548883	−2.369672	−0.654382
H	0.000208	−0.000124	−2.164888
H	1.285408	−2.026980	1.545007
H	3.999207	−2.191767	1.632633
H	4.864969	−0.511495	−0.324269
H	1.117179	2.129277	1.540423
H	−0.099108	4.560761	1.629527
H	−1.992744	4.466893	−0.321808
H	−2.397845	−0.099214	1.544759
H	−3.897882	−2.366756	1.632677
H	−2.875765	−3.957140	−0.323925

These reactions, described earlier, were specific to tri-2-furylgermane. Silanes, stannanes, or other germanes such as triphenylgermane or trihexylgermane gave the corresponding adducts in lower yields, or failed to give the desired products (Table 6). For example, Cs_2CO_3-induced reaction of tri-2-furylgermane with hexanal provided α-hydroxy germane **3a** in 94% yield in 10 min. On the other hand, neither α-hydroxy silane nor α-hydroxy stannane was obtained starting from triphenylsilane or triphenylstannane (entries 2 and 3). In the case of triphenylgermane (entry 4), the corresponding adduct was formed in 45% yield after 2 h, and the starting material was recovered (46%). Reaction of trihexylgermane with hexanal resulted in almost complete recovery of trihexylgermane (entry 5).

In order to discuss the uniqueness of tri-2-furylgermane, we conducted ab initio calculations of tri-2-furylgermane, triphenylgermane, trimethylgermane, and their corresponding germyl anions. We set up a hypothetical reaction in vacuum as shown in Table 7, and the changes in the free energies for these three reactions were calculated. The results are summarized in Table 7. Judging from Table 7, the order of the acidity of the proton that binds to germanium proved to be $(2\text{-furyl})_3GeH > Ph_3GeH > Me_3GeH$. The proton in $(2\text{-furyl})_3GeH$ was calculated to be most easily abstracted. Additionally, the highest acidity of $(2\text{-furyl})_3GeH$ was confirmed by focussing the charge for the proton. The Mulliken atomic charges for the protons in $H{-}GeR_3$ were calculated to be −0.119957, −0.141793, and −0.153274 for $(2\text{-furyl})_3GeH$, Ph_3GeH, and Me_3GeH, respectively. Thus, the proton of $(2\text{-furyl})_3GeH$ is the most

Table 10. The coordinates of atoms in trimethylgermyl anion −2168.984276 a.u. at the RHF/STO-3G level of theory

Atom	*x*	*y*	*z*
Ge	0.000062	−0.000029	−0.504963
C	−0.620214	1.564720	0.528720
C	−1.045162	−1.319343	0.528764
C	1.665204	−0.245295	0.528868
H	−1.652421	1.818529	0.302913
H	−0.043056	2.457156	0.302206
H	−0.571925	1.444221	1.608223
H	−0.964199	−1.217845	1.608265
H	−2.106702	−1.264663	0.302925
H	−0.749927	−2.340330	0.302304
H	1.536668	−0.226622	1.608363
H	2.149298	−1.191498	0.302559
H	2.401293	0.521509	0.302935

Table 11. The coordinates of atoms in trimethylgermane −2169.747761 a.u. at the RHF/STO-3G level of theory

Atom	*x*	*y*	*z*
Ge	0.000035	−0.000049	−0.280012
C	−0.443693	1.747294	0.351563
C	−1.291447	−1.257761	0.351816
C	1.735031	−0.489366	0.351896
H	0.000095	−0.000190	−1.719875
H	−1.423778	2.056228	0.012091
H	0.264671	2.488001	0.003979
H	−0.449741	1.791234	1.432765
H	−1.323312	−1.288018	1.433035
H	−2.287719	−1.011981	0.007900
H	−1.071654	−2.260394	0.008799
H	1.776959	−0.502297	1.433118
H	2.020789	−1.474780	0.007593
H	2.493226	0.202761	0.009341

Table 12. The coordinates of atoms in triphenylgermyl anion −2733.366287 a.u. at the RHF/STO-3G level of theory

Atom	*x*	*y*	*z*
Ge	−0.000030	−0.000026	−1.238091
C	1.145283	−1.273717	−0.287626
C	0.530429	1.628697	−0.287692
C	−1.675745	−0.355008	−0.287654
C	−2.293756	0.481198	0.649475
C	−3.527034	0.195325	1.216641
C	−4.207332	−0.958872	0.871434
C	−3.631617	−1.815388	−0.053781
C	−2.404535	−1.509764	−0.616078
C	0.730249	−2.226576	0.650028
C	1.594473	−3.151637	1.217260
C	2.934065	−3.164093	0.871593
C	3.387837	−2.237704	−0.054138
C	2.509601	−1.327880	−0.616492
C	1.563399	1.745727	0.649681
C	1.932502	2.956702	1.216847
C	1.273338	4.123025	0.871390
C	0.243933	4.052780	−0.054071
C	−0.104968	2.837291	−0.616363
H	−1.799036	1.393001	0.957699
H	−3.958648	0.877946	1.938648
H	−5.168088	−1.187449	1.312398
H	−4.147497	−2.723713	−0.340296
H	−1.994565	−2.200698	−1.343191
H	−0.306656	−2.253709	0.958621
H	1.219223	−3.866377	1.939679
H	3.612406	−3.881805	1.312606
H	4.432314	−2.230623	−0.341013
H	2.902869	−0.627725	−1.344010
H	2.105483	0.861329	0.958099
H	2.739305	2.989119	1.939046
H	1.555793	5.069345	1.312353
H	−0.284557	4.953764	−0.340784
H	−0.908139	2.827776	−1.343676

Table 13. The coordinates of atoms in triphenylgermane −2734.083957 a.u. at the RHF/STO-3G level of theory

Atom	*x*	*y*	*z*
Ge	0.000007	−0.000018	−0.858109
C	−1.428887	−1.096408	−0.236542
C	1.663965	−0.689258	−0.236546
C	−0.235076	1.785626	−0.236524
C	0.368985	2.244610	0.932722
C	0.182274	3.541518	1.387083
C	−0.621791	4.416759	0.675266
C	−1.233753	3.984196	−0.490781
C	−1.039428	2.685919	−0.935501
C	−2.127882	−0.803074	0.933100
C	−3.157688	−1.613168	1.387548
C	−3.514180	−2.746761	0.675419
C	−2.834113	−3.060151	−0.491016
C	−1.806923	−2.242781	−0.935819
C	1.759481	−1.441572	0.932891
C	2.975995	−1.928333	1.387250
C	4.135953	−1.669926	0.675236
C	4.067267	−0.923985	−0.491015
C	2.845766	−0.443139	−0.935732
H	0.000024	0.000007	−2.297115
H	1.005940	1.582420	1.507044
H	0.666316	3.869050	2.298468
H	−0.770001	5.430278	1.025892
H	−1.863338	4.660046	−1.055604
H	−1.528867	2.375540	−1.851118
H	−1.872463	0.079354	1.507674
H	−3.682938	−1.357985	2.299245
H	−4.317809	−3.381837	1.026107
H	−3.105050	−3.943026	−1.056082
H	−1.293829	−2.511210	−1.851746
H	0.867575	−1.661853	1.507378
H	3.017663	−2.511053	2.298786
H	4.967320	−0.716931	−1.056001
H	2.821642	0.135668	−1.851506

protic. These results indicate that a furyl group has an electron-withdrawing character. Assuming that generation of a germyl anion would be rate-determining, the characteristic addition of (2-furyl)$_3$GeH is due to the facile formation of tri-2-furylgermyl anion (Tables 8–13).

3. Conclusion

We have demonstrated that a catalytic amount of base such as Cs$_2$CO$_3$ induced the nucleophilic addition of tri-2-furylgermane to various aldehydes and α,β-unsaturated carbonyl compounds under mild conditions. The success of the reaction is ascribed to the characteristic nature of tri-2-furylgermane.

4. Experimental

^{1}H (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in CDCl$_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tri-2-furylgermane was prepared according to the literature.[15] All aldehydes were commercially available, and were used as received.

4.1. Addition of tri-2-furylgermane to hexanal in the presence of a catalytic amount of a base in various solvents (Tables 1 and 2)

Reaction with hexanal in the presence of ^{t}BuOK in THF is representative. ^{t}BuOK (5.6 mg, 0.050 mmol) was added to a solution of tri-2-furylgermane (**1**) (0.14 g, 0.50 mmol) and hexanal (**2a**) (0.060 g, 0.60 mmol) in THF (1 mL) at 0°C under air. After being stirred for 10 min at 0°C, the reaction mixture was poured into water and extracted with ethyl acetate three times. Combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residual oil was subjected to silica gel column chromatography (hexane/AcOEt=10/1) to give 1-tri(2-furyl)germyl-1-hexanol (**3a**) in 75% yield.

4.1.1. 1-Tri(2-furyl)germyl-1-hexanol (3a). IR (neat) 3423, 2930, 2858, 1551, 1454, 1362, 1205, 1150, 1099, 1005, 897, 745, 596 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.86 (t, *J*=6.9 Hz, 3H), 1.20–1.44 (m, 5H), 1.48–1.64 (m, 1H), 1.79–1.92 (m, 3H), 4.39 (ddd, *J*=6.0, 6.0, 8.7 Hz, 1H), 6.49 (dd, *J*=3.3, 1.8 Hz, 3H), 6.85 (d, *J*=3.3 Hz, 3H), 7.76 (d, *J*=1.8 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 13.84, 22.41, 25.89, 31.40, 34.69, 67.57, 109.91, 122.02, 147.66, 152.01. Found: C, 57.73; H, 5.81%. Calcd for $C_{18}H_{22}GeO_4$: C, 57.66; H, 5.91%.

4.2. Addition of tri-2-furylgermane to various aldehydes in the presence of Cs$_2$CO$_3$ in DMI (Table 3)

Addition to isobutyraldehyde is representative. Cs$_2$CO$_3$ (0.016 g, 0.050 mmol) was added to a solution of tri-2-furylgermane (**1**) (0.14 g, 0.50 mmol) and isobutyraldehyde (**2b**) (0.043 g, 0.60 mmol) in DMI (1 mL) at room temperature under air. The mixture was stirred for 10 min. The reaction was quenched with water, and the products were extracted with ethyl acetate three times. The organic layers were washed with brine, dried and concentrated. The crude product was purified by column chromatography to afford 2-methyl-1-tri(2-furyl)germyl-1-propanol (**3b**) in 99% yield. Aldehydes **2a**, **2c**, **2d**, and **2f–m** (0.60 mmol) and **1** (0.14 g, 0.50 mmol) were treated in the same way to give **3a**, **3c**, **3d**, and **3f–m**, respectively.

4.2.1. 2-Methyl-1-tri(2-furyl)germyl-1-propanol (3b). IR (neat) 3564, 3441, 3125, 2961, 1549, 1454, 1362, 1205, 1150, 1099, 1005, 897, 883, 745, 596 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.94 (d, *J*=6.6 Hz, 3H), 0.99 (d, *J*=6.6 Hz, 3H), 2.00 (OH, d, *J*=6.6 Hz, 1H), 2.12 (dqq, *J*=6.6, 6.6, 6.6 Hz, 1H), 4.20 (dd, *J*=6.6, 6.6 Hz, 1H), 6.48 (dd, *J*=3.3, 1.8 Hz, 3H), 6.84 (d, *J*=3.3 Hz, 3H), 7.76 (d, *J*=1.8 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 18.79, 19.60, 32.98, 74.26, 109.96, 121.95, 147.58, 152.50. Found: C, 55.36; H, 5.25%. Calcd for $C_{16}H_{18}GeO_4$: C, 55.40; H, 5.23%.

4.2.2. 2,2-Dimethyl-1-tri(2-furyl)germyl-1-propanol (3c). IR (neat) 3566, 3447, 2957, 1549, 1456, 1362, 1205, 1150, 1099, 1003, 897, 818, 743, 596 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.92 (s, 9H), 2.20 (OH, d, *J*=7.5 Hz, 1H), 4.14 (d, *J*=7.5 Hz, 1H), 6.48 (dd, *J*=3.6, 1.8 Hz, 3H), 6.85 (d, *J*=3.6 Hz, 3H) 7.76 (d, *J*=1.8 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 26.69, 36.13, 78.82, 110.03, 121.91, 147.45, 153.00.

Found: C, 56.63; H, 5.60%. Calcd for $C_{17}H_{20}GeO_4$: C, 56.57; H, 5.59%.

4.2.3. 3,7-Dimethyl-1-tri(2-furyl)germyl-6-octen-1-ol (3d, diastereomer mixture). IR (neat) 3564, 3445, 2916, 1549, 1454, 1377, 1205, 1150, 1099, 1005, 897, 745, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (d, J=6.6 Hz, 3H), 1.00–1.57 (m, 3H), 1.58 (s, 3H), 1.67 (s, 3H), 1.70–2.03 (m, 5H), 4.50–4.58 (m, 1H), 5.07 (t, J=6.9 Hz, 1H), 6.49 (dd, J=3.0, 1.8 Hz, 3H), 6.85 (d, J=3.0 Hz, 3H), 7.76 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 17.50, 18.30, 20.12, 25.10, 25.44, 25.60, 28.71, 29.24, 30.82, 35.75, 37.67, 41.59, 41.94, 64.91, 65.54, 109.92, 122.07, 124.82, 131.21, 147.71, 151.90. Found: C, 61.55; H, 6.58%. Calcd for $C_{22}H_{28}GeO_4$: C, 61.58; H, 6.58%.

4.2.4. Phenyltri(2-furyl)germylmethanol (3f). IR (neat) 3425, 3125, 1599, 1549, 1452, 1362, 1205, 1150, 1101, 1005, 897, 700, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (bs, 1H), 5.50 (s, 1H), 6.45 (dd, J=3.3, 1.8 Hz, 3H), 6.71 (d, J=3.3 Hz, 3H), 7.10–7.30 (m, 5H), 7.74 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 70.44, 109.93, 122.40, 125.15, 126.69, 128.18, 141.56, 147.74, 150.97. Found: C, 59.73; H, 4.05%. Calcd for $C_{19}H_{16}GeO_4$: C, 59.91; H, 4.23%.

4.2.5. 2-Furyltri(2-furyl)germylmethanol (3g). IR (neat) 3406, 3125, 1549, 1501, 1454, 1362, 1207, 1101, 1005, 897, 746, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.32 (OH, d, J=6.3 Hz, 1H), 5.38 (d, J=6.3 Hz, 1H), 6.21 (d, J=3.3 Hz, 1H), 6.31 (dd, J=3.3, 1.8 Hz, 1H), 6.47 (dd, J=3.3, 1.8 Hz, 3H), 6.81 (d, J=3.3 Hz, 3H), 7.35 (d, J=1.8 Hz, 1H), 7.75 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 62.76, 107.39, 109.95, 110.62, 122.27, 142.35, 147.82, 150.86, 154.48. Found: C, 54.86; H, 3.79%. Calcd for $C_{17}H_{14}GeO_5$: C, 55.05; H, 3.80%.

4.2.6. 2-Pyridyltri(2-furyl)germylmethanol (3h). IR (nujol) 3111, 1593, 1205, 1150, 1097, 1003, 899, 748, 598 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.78 (bs, 1H), 5.60 (s, 1H), 6.45 (dd, J=3.3, 1.8 Hz, 3H), 6.77 (d, J=3.3 Hz, 3H), 6.84 (d, J=8.1 Hz, 1H), 7.09 (dd, J=7.5, 5.1 Hz, 1H), 7.51 (dd, J=8.1, 7.5 Hz, 1H), 7.72 (d, J=1.8 Hz, 3H), 8.47 (d, J=5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 69.64, 109.91, 119.81, 121.42, 122.37, 136.18, 147.72, 147.98, 151.00, 159.22. Found: C, 56.65; H, 4.09%. Calcd for $C_{18}H_{15}GeNO_4$: C, 56.61; H, 3.96%.

4.2.7. 4-Methoxycarbonylphenyltri(2-furyl)germylmethanol (3i). IR (neat) 3445, 1717, 1609, 1283, 1105, 1005, 897, 748, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52 (OH, d, J=3.6 Hz, 1H), 3.89 (s, 3H), 5.58 (d, J=3.6 Hz, 1H), 6.46 (dd, J=3.3, 1.8 Hz, 3H), 6.73 (d, J=3.3 Hz, 3H), 7.14 (d, J=8.4 Hz, 2H), 7.75 (d, J=1.8 Hz, 3H), 7.89 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 51.91, 70.35, 110.04, 122.68, 124.69, 128.22, 129.51, 147.04, 147.93, 150.37, 167.23. Found: C, 57.22; H, 4.08%. Calcd for $C_{21}H_{18}GeO_6$: C, 57.46; H, 4.13%.

4.2.8. 4-Cyanophenyltri(2-furyl)germylmethanol (3j). IR (nujol) 3479, 2224, 1602, 1205, 1101, 1003, 897, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (OH, d, J=3.9 Hz, 1H), 5.56 (d, J=3.9 Hz, 1H), 6.47 (dd, J=3.3, 1.5 Hz, 3H), 6.74 (d, J=3.3 Hz, 3H), 7.14 (d, J=8.4 Hz, 2H), 7.47 (d, J=8.4 Hz, 2H), 7.74 (d, J=1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 70.12, 109.84, 110.13, 119.19, 122.85, 125.25, 131.92, 147.33, 148.07, 149.95. Found: C, 59.07; H, 3.92%. Calcd for $C_{20}H_{15}NO_4$: C, 59.18; H, 3.72%.

4.2.9. 2-Hydroxyphenyltri(2-furyl)germylmethanol (3k). IR (neat) 3325, 1585, 1489, 1456, 1362, 1242, 1151, 1101, 1005, 897, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.99 (OH, d, J=3.0 Hz, 1H), 5.70 (d, J=3.0 Hz, 1H), 6.47 (dd, J=3.3, 1.8 Hz, 3H), 6.74 (d, J=3.3 Hz, 3H), 6.70–6.82 (m, 3H), 7.05–7.12 (m, 1H), 7.39 (OH, s, 1H), 7.75 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 71.45, 110.09, 116.94, 119.73, 122.49, 124.43, 126.27, 128.47, 147.88, 150.69, 155.36. Found: C, 57.20; H, 3.97%. Calcd for $C_{19}H_{16}GeO_5$: C, 57.49; H,4.06%.

4.2.10. Tri(2-furyl)germylmethanol (3m). IR (neat) 3391, 1551, 1454, 1362, 1205, 1150, 1101, 1005, 897, 746, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.58 (bs, 1H), 4.33 (s, 2H), 6.49 (dd, J=3.3, 1.8 Hz, 3H), 6.86 (d, J=3.3 Hz, 3H), 7.76 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 54.37, 110.00, 121.92, 147.79, 151.49. Found: C, 51.32; H, 3.97%. Calcd for $C_{13}H_{12}GeO_4$: C, 51.22; H, 3.97%.

4.3. Addition of tri-2-furylgermane to 2-octynal (2e)

Cs_2CO_3 (0.016 g, 0.050 mmol) was added to a solution of **1** (0.14 g, 0.50 mmol) and 2-octynal (**2e**) (0.075 g, 0.60 mmol) in DMI (1 mL) at room temperature. After 30 min, another Cs_2CO_3 (0.016 g, 0.050 mmol) and DMI (1 mL) were added to the reaction mixture. The whole mixture was stirred for additional 1.5 h. Workup and purification afforded **3e** in 92% yield.

4.3.1. 1-Tri(2-furyl)germyl-2-octyn-1-ol (3e). IR (neat) 3425, 2932, 1549, 1454, 1362, 1207, 1151, 1103, 1005, 897, 746, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J=7.2 Hz, 3H), 1.22–1.34 (m, 4H), 1.38–1.50 (m, 2H), 1.92 (OH, d, J=6.0 Hz, 1H), 2.21 (dt, J=2.1, 7.2 Hz, 2H), 4.97 (dt, J=6.0, 2.1 Hz, 1H), 6.50 (dd, J=3.3, 1.5 Hz, 3H), 6.95 (d, J=3.3 Hz, 3H), 7.77 (d, J=1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 13.79, 18.88, 22.08, 28.16, 30.72, 56.20, 78.47, 90.58, 109.92, 122.40, 147.86, 150.77. Found: C, 59.93; H, 5.54%. Calcd for $C_{20}H_{22}GeO_4$: C, 60.21; H, 5.56%.

4.4. Chemoselective addition of tri-2-furylgermane to a mixture of aldehyde and ketone (Scheme 6)

Cs_2CO_3 (0.016 g, 0.050 mmol) was added to a solution of tri-2-furylgermane (**1**) (0.14 g, 0.50 mmol), hexanal (**2a**) (0.060 g, 0.60 mmol), and 2-decanone (**6**) (0.094 g, 0.60 mmol) in DMI (1 mL), and the reaction mixture was stirred at room temperature for 20 min. The reaction mixture was poured into water and extracted with ethyl acetate (3×20 mL). The organic layers were purified by silica gel chromatography to obtain **3a** in 81% yield. Ketone **6** (0.080 g, 85%) was recovered.

4.5. Preparation of acyltri(2-furyl)germanes (Table 4)

DMSO (0.094 g, 1.2 mmol) was added to a solution of oxalyl chloride (0.076 g, 0.60 mmol) in dichloromethane (1 mL) at −78°C under an argon atmosphere. A dichloromethane solution (1 mL) of **3a** (0.19 g, 0.50 mmol) was added to a reaction mixture, and triethylamine (0.25 g, 2.5 mmol) was then added. After being stirred for 20 min at −78°C, the reaction mixture was poured into water and extracted with hexane three times. Combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography to give **7a** in 94% yield.

4.5.1. Tri(2-furyl)hexanoylgermane (7a). IR (neat) 2932, 1674, 1549, 1454, 1362, 1207, 1151, 1103, 1005, 897, 746, 596 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, J=6.9 Hz, 3H), 1.16–1.32 (m, 4H), 1.58 (tt, J=7.2, 7.2 Hz, 2H), 2.85 (t, J=7.2 Hz, 2H), 6.50 (dd, J=3.3, 1.5 Hz, 3H), 6.91 (d, J=3.3 Hz, 3H), 7.77 (d, J=1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 13.67, 21.76, 22.21, 31.06, 51.08, 111.12, 122.46, 148.02, 150.27, 231.26. Found: C, 58.23; H, 5.61%. Calcd for $C_{18}H_{20}GeO_4$: C, 57.97; H, 5.41%.

4.5.2. 2,2-Dimethylpropanoyl-tri(2-furyl)germane (7b). IR (neat) 2968, 1668, 1549, 1454, 1364, 1207, 1151, 1101, 1005, 934, 897, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9H), 6.50 (dd, J=3.3, 1.8 Hz, 3H), 6.90 (d, J=3.3 Hz, 3H), 7.77 (d, J=3.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 23.94, 50.07, 110.14, 122.29, 147.79, 151.49, 233.54. Found: C, 57.16; H, 5.17%. Calcd for $C_{17}H_{18}GeO_4$: C, 56.89; H, 5.05%.

4.5.3. Tri(2-furyl)-2-octynoylgermane (7e). IR (neat) 2932, 2185, 1622, 1549, 1454, 1362, 1207, 1105, 1005, 899, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=7.2 Hz, 3H), 1.22–1.36 (m, 4H), 1.50 (tt, J=7.2, 7.2 Hz, 2H), 2.40 (t, J=7.2 Hz, 2H), 6.52 (dd, J=3.3, 1.8 Hz, 3H), 6.98 (d, J=3.3 Hz, 3H), 7.78 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 13.80, 19.56, 22.04, 27.16, 30.76, 83.86, 108.96, 110.04, 122.79, 148.07, 149.17, 210.27. Found: C, 60.38; H, 5.10%. Calcd for $C_{20}H_{20}GeO_4$: C, 60.51; H, 5.08%.

4.5.4. Benzoyl-tri(2-furyl)germane (7f). IR (neat) 1634, 1580, 1448, 1362, 1207, 1103, 1005, 899, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.51 (dd, J=3.3, 1.8 Hz, 3H), 6.95 (d, J=3.3 Hz, 3H), 7.43–7.60 (m, 3H), 7.78 (d, J=1.8 Hz, 3H), 7.94–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 110.15, 122.66, 128.86, 128.94, 133.91, 140.27, 147.98, 150.60, 220.02. Found: C, 60.05; H, 3.86%. Calcd for $C_{19}H_{14}GeO_4$: C, 60.23; H, 3.72%.

4.6. Reaction of acylgermane with vinyl Grignard reagent (Scheme 7)

A THF solution of vinylmagnesium bromide (0.94 M, 0.80 mL, 0.75 mmol) was added to a solution of acylgermane **7a** (0.19 g, 0.50 mmol) in THF (3 mL) at room temperature under an argon atmosphere. After being stirred for 15 min, the reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. Combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was chromatographed on a silica gel column to give 1-tri(2-furyl)germyl-3-octanone (**8**) in 58% yield. On the other hand, the same reaction was performed in hexane (3 mL) for 15 min to give 3-tri(2-furyl)germyl-1-octen-3-ol (**11**) in 85% yield.

4.6.1. 1-Tri(2-furyl)germyl-3-octanone (8). IR (neat) 2928, 1712, 1550, 1454, 1362, 1205, 1150, 1099, 1005, 897, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=7.2 Hz, 3H), 1.16–1.37 (m, 4H), 1.53 (tt, J=7.2, 7.2 Hz, 2H), 1.76 (t, J=7.2 Hz, 2H), 2.34 (t, J=7.2 Hz, 2H), 2.70 (t, J=7.2 Hz, 2H), 6.47 (dd, J=3.3, 1.5 Hz, 3H), 6.78 (d, J=3.3 Hz, 3H), 7.73 (d, J=1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 7.83, 13.74, 22.28, 23.42, 31.26, 37.21, 42.19, 109.84, 121.30, 147.46, 152.91, 210.87. Found: C, 59.64; H, 6.02%. Calcd for $C_{20}H_{24}GeO_4$: C, 59.91; H, 6.03%.

4.6.2. 3-Tri(2-furyl)germyl-1-octen-3-ol (11). IR (neat) 3460, 2932, 1630, 1549, 1454, 1362, 1205, 1150, 1099, 1005, 897, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J=6.6 Hz, 3H), 1.16–1.48 (m, 6H), 1.80–2.00 (m, 2H), 2.08 (bs, 1H), 5.10 (d, J=18.9 Hz, 1H), 5.11 (d, J=12.3 Hz, 1H), 6.08 (dd, J=18.9, 12.3 Hz, 1H), 6.49 (dd, J=3.3, 1.8 Hz, 3H), 6.87 (d, J=3.3 Hz, 3H), 7.77 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 13.86, 22.19, 22.47, 32.00, 38.08, 77.30, 109.84, 111.69, 122.33, 140.86, 147.65, 151.78. Found: C, 59.99; H, 6.08%. Calcd for $C_{20}H_{24}GeO_4$: C, 59.91; H, 6.03%.

4.7. 1,4-Addition of tri-2-furylgermane (Table 5)

A DMI solution (1 mL) of tri-2-furylgermane (**1**) (0.14 g, 0.50 mmol) and 3-buten-2-one (**12a**) (0.042 g, 0.60 mmol) was treated with Cs_2CO_3 (0.016 g, 0.050 mmol) at room temperature under air. After 10 min, the reaction mixture was poured into water and extracted with ethyl acetate. The crude product was purified by silica gel column chromatography to give **13a** in 84% yield.

4.7.1. 4-Tri(2-furyl)germyl-2-butanone (13a). IR (nujol) 2856, 1705, 1456, 1377, 1223, 1148, 1097, 1003, 897, 775, 596 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (t, J=8.1 Hz, 2H), 2.10 (s, 3H), 2.72 (t, J=8.1 Hz, 2H), 6.47 (dd, J=3.3, 1.5 Hz, 3H), 6.78 (d, J=3.3 Hz, 3H), 7.73 (d, J=1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 7.83, 29.11, 38.14, 109.81, 121.27, 147.43, 152.78, 208.32. Found: C, 55.68; H, 4.62%. Calcd for $C_{16}H_{16}GeO_4$: C, 55.72; H, 4.68%.

4.7.2. 3-Tri(2-furyl)germylcyclohexanone (13b). IR (nujol) 1705, 1315, 1227, 1150, 1101, 1003, 897, 746, 596 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72–1.85 (m, 2H), 2.05–2.26 (m, 3H), 2.27–2.51 (m, 3H), 2.57–2.64 (m, 1H), 6.48 (dd, J=3.3, 1.8 Hz, 3H), 6.80 (d, J=3.3 Hz, 3H), 7.76 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 26.77, 28.48, 28.71, 41.72, 43.11, 109.88, 122.05, 147.79, 151.72, 211.32. Found: C, 58.01; H, 4.75%. Calcd for $C_{18}H_{18}GeO_4$: C, 58.29; H, 4.89%.

4.7.3. Butyl 3-tri(2-furyl)germylpropanoate (13c). IR (neat) 2961, 1732, 1551, 1456, 1360, 1205, 1005, 897, 746, 596 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J=7.2 Hz, 3H), 1.35 (tq, J=6.9, 7.2 Hz, 2H), 1.57 (tt, J=6.9, 6.9 Hz, 2H), 1.81 (t, J=5.7 Hz, 2H), 2.59 (t, J=5.7 Hz, 2H), 4.03 (t, J=6.9 Hz, 2H), 6.46 (dd, J=3.0, 1.5 Hz, 3H), 6.78 (d, J=3.0 Hz, 3H), 7.73 (d, J=1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 9.33, 13.55, 18.96, 29.15, 30.50, 64.42, 109.84, 121.36, 147.54, 152.58, 174.08. Found: C, 56.67; H, 5.57%. Calcd for $C_{19}H_{22}GeO_5$: C, 56.63; H, 5.50%.

4.7.4. 3-Tri(2-furyl)germylpropanamide (13d). IR (nujol) 3460, 1666, 1205, 1148, 1101, 1005, 897, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83 (t, J=8.4 Hz, 2H), 2.51 (t, J=8.4 Hz, 2H), 5.30 (bs, 2H), 6.47 (dd, J=3.3, 1.8 Hz, 3H), 6.79 (d, J=3.3 Hz, 3H), 7.73 (d, J=1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 9.75, 30.36, 109.91, 121.45, 147.57, 152.57, 175.62. Found: C, 51.88; H, 4.28%. Calcd for $C_{15}H_{15}GeNO_4$: C, 52.09; H, 4.37%.

4.8. Calculation procedure

Ab initio calculations were conducted with the Gaussian 98 program.[16] All the structures were optimized with the RHF/STO-3G level of theory. Zero-point energy and thermal energy corrections were made for all of the calculated energies, and the sums of electronic and thermal free energies were obtained. The zero-point energies were not scaled, and the enthalpic corrections were made at 298.150 K. Mulliken's atomic charges of the optimized structures were obtained from the output files.

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