First oxazagermete: synthesis, structure and thermal cycloreversion into a germanone

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A novel four-membered ring compound, 1,2,4-oxazagermete, is obtained by the reaction of diarylgermylene tbt(tip)Ge: with mesitonitrile oxide; its thermolysis generates germanone tbt(tip)Ge=O as evidenced by trapping reactions with dimethylbutadiene and ethanol.

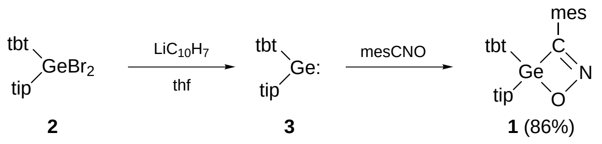
Small-ring compounds containing a group 14 element have been of current interest because of their intriguing structural properties and potential utility as precursors of reactive intermediates taking advantage of their ring strain. Since many such small-ring compounds are highly reactive under ambient conditions, some stabilization is often necessary for their isolation, for example, the use of a very bulky substituent.[1]

Here we report the synthesis of kinetically stabilized 1,2,4-oxazagermete **1**, a novel four-membered ring compound containing germanium, by an efficient steric protecting group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (tbt).[2] There have been several reports on 1,2-oxazetes. They were observed as reactive intermediates in the thermal and photochemical reactions of α,β-unsaturated nitro compounds or in the reaction of vinyl radicals and NO,[3] and some oxazetes having bulky substituents have been isolated although their molecular structures were not established.[4] In contrast, there has been no report so far on the heavier group 14 element analogue of an 1,2-oxazete.

Oxazagermete **1** was synthesized as stable colourless crystals in 87% by the reaction of diarylgermylene tbt(tip)Ge: **3** (tip = 2,4,6-triisopropylphenyl), generated from dibromogermane **2** and lithium naphthalenide in thf,[5] with mesitonitrile oxide (Scheme 1). This represents the first synthesis of an oxazagermete as well as the first isolation of a [1 + 3]-cycloaddition reaction product of a germylene with 1,3-dipolar reagents.[6]

Oxazagermete **1** showed characteristic spectral data.† The C=N bond stretching was observed at 1612 cm^{-1} in the IR spectrum, which is similar to those reported for 1,2-oxazetes.[4] In the ^{13}C NMR spectrum, a singlet peak was observed at δ 174.8 assignable to the carbon in the four-membered ring, which is more shielded than that of an oxazete owing to the more electropositive Ge atom on the carbon.[4c]

The molecular structure of **1** has been determined by X-ray crystallographic analysis and an ORTEP drawing is shown in Fig. 1.‡ The bond angle C(34)–Ge–O considerably shrinks from that of normal sp^3 configuration to 68.7(2)°, suggesting the large ring strain of the four-membered ring, which is also reflected on the long Ge–O bond length [1.872(4) Å] compared with that of a typical Ge–O single bond (1.75–1.85 Å).[7] The four-membered ring of **1** is perfectly planar with the sum of the bond angles being 360°.



Scheme 1

Thermolysis of **1** was carried out in the expectation that it would dissociate into a germanium–oxygen double-bond species (germanone) tbt(tip)Ge=O **4** and mesitonitrile, since an 1,2-oxazete is known to undergo thermal cycloreversion into the corresponding ketone and nitrile.[3,4] The chemistry of germanones has not been fully disclosed yet, although they have been a fascinating subject of considerable attention in recent years.[1b,8]

When a [$^2H_6$]benzene solution of **1** and 2,3-dimethylbuta-1,3-diene in a sealed NMR tube was heated at 120 °C for 12 h, the starting materials were consumed completely (^1H NMR) to afford **5**–**7** and mesitonitrile (Scheme 2).§ Formation of compounds **5**–**7** and an almost quantitative yield of mesitonitrile clearly indicates the generation of intermediary germanone **4**, since we previously reported the formation of **7** from germanone **4** generated from by the reaction of germylene **3** with tribenzylamine *N*-oxide.[8]

Compounds **6** and **7** are most likely produced from germanone **4** *via* intramolecular cyclization,[9] while the formation of compound **5** is reasonably explained in terms of an ene

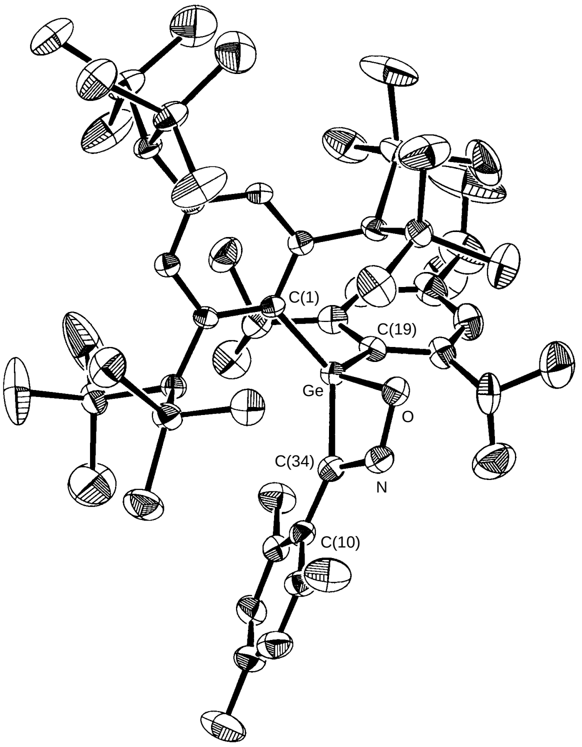
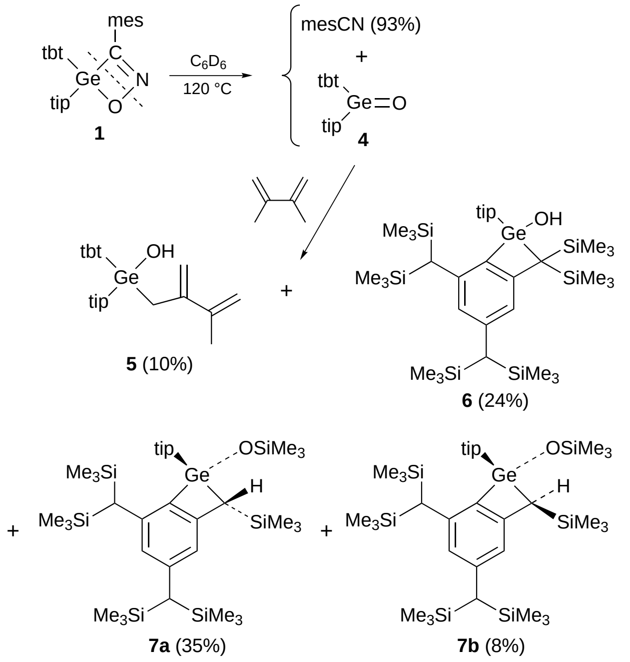


Fig. 1 ORTEP drawing of oxazagermete **1** with thermal ellipsoid plots (30% probability). Selected bond lengths (Å) and angles (°): Ge–O 1.872(4), Ge–C(1) 1.968(6), Ge–C(19) 1.974(6), Ge–C(34) 2.001(6), C(34)–N 1.291(9), N–O 1.418(8), C(10)–C(34) 1.459(10); C(1)–Ge–O 105.9(2), C(1)–Ge–C(19) 114.9(2), C(1)–Ge–C(34) 123.0(3), C(19)–Ge–O 112.9(3), C(19)–Ge–C(34) 119.1(3), O–Ge–C(34) 68.7(2), Ge–O–N 92.7(3), O–N–C(34) 107.6(5), Ge–C(34)–N 91.1(5), Ge–C(34)–C(10) 146.2(5), N–C(34)–C(10) 122.7(6).



Scheme 2

reaction of germanone **4** with the butadiene. In the cases of chalcogen double-bond species, tbt(tip)Ge=X (X = S, Se, Te), the corresponding [4 + 2] cycloadducts were obtained in the reactions with dienes.[2] The reason for this difference is not clear at present.

The total yield of the silyl-migrated compounds **7a** and **7b** is higher than that of the hydrogen-migrated compound **6**, which is probably due to the higher affinity of silicon for oxygen. The product ratio of **7a** to **7b** is considered to be kinetically determined since no isomerization from **7a** to **7b** is observed even at 180 °C.

The generation of germanone **4** was also confirmed by the thermal reaction of **1** in benzene (at 120 °C, in a sealed tube) in the presence of ethanol, in which ethoxy(hydroxy)germane tbt(tip)Ge(OH)(OEt) **8**, an ethanol adduct of **4**, was obtained in 82%. This finding indicates that the intermolecular reaction with ethanol was faster than the intramolecular silyl or hydrogen migration mentioned above. It was also confirmed by thermolysis (120 °C) of a [$^2H_6$]benzene solution of oxazagermete **1** in the presence of 0.3 equiv of ethanol while being monitored by ^1H NMR. In the initial stage, the ethanol adduct **8** was observed exclusively, and, after consumption of ethanol, the rearrangement reaction to **6**, **7a** and **7b** occurred.

In summary, we have succeeded in the isolation and crystallographic analysis of the first 1,2,4-oxazagermete **1**, which undergoes thermal cycloreversion into mesitonitrile and germanone tbt(tip)Ge=O.

Footnotes and References

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† *Spectral data* for **1**: white crystals; mp 196–197 °C (decomp.) (CH_2Cl_2–EtOH); ^1H NMR ($CDCl_3$, 500 MHz, 350 K) δ −0.12 (s, 18 H), 0.07 (s, 18 H), 0.09 (s, 18 H), 1.03 (br s, 6 H), 1.24 (d, *J* 6.9 Hz, 6 H), 1.25 (br s, 6 H), 1.39 (s, 1 H), 1.58 (br s, 2 H), 2.25 (s, 3 H), 2.39 (s, 6 H), 2.87 (spt, *J* 6.9 Hz, 1 H), 3.37 (br s, 2 H), 6.39 (br s, 2 H), 6.81 (s, 2 H), 7.06 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz, 340 K) δ 1.00 (q), 1.08 (q), 1.97 (q), 2.21 (q), 2.23 (q), 20.86 (q), 23.68 (q), 23.73 (q), 24.03 (q), 24.93 (q), 26.94 (q), 29.36 (d), 31.04 (d), 33.99 (d), 34.32 (d), 123.41 (d), 128.71 (d), 129.86 (d), 133.43 (s), 134.28 (s), 137.49 (s), 137.90 (s), 145.58 (s), 149.96 (s), 151.69 (s), 155.17 (s). High-resolution FABMS: observed *m/z* 990.5158 ([M + H]$^+$). Calc. for $C_{52}H_{94}{}^{74}GeNOSi_6$ 990.5163.

‡ *Crystallographic data* for **1**: $C_{52}H_{93}GeNOSi_6$, *M* = 989.42, triclinic, space group $P\bar{1}$, *a* = 13.002(3), *b* = 19.433(4), *c* = 12.503(5) Å, α = 101.48(2), β = 91.22(2), γ = 77.17(1)°, *U* = 3018(1) Å^3, *Z* = 2, D_c = 1.083 g cm^{-3}, *T* = 296 K, *F*(000) = 1072, colourless prism with dimensions 0.60 × 0.50 × 0.40, μ(Mo-Kα) = 6.48 cm^{-1}, $R(R_w)$ = 0.056(0.062). Weighting scheme; $w = 1/\sigma^2(F_o)$. The intensity data ($2\theta < 55°$) for **1** were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), and 14 509 reflections (13 892 unique) were measured. The structure of **1** was solved by direct methods (structure solution methods; MITHRIL[10] and DIRDIF[11]), and refined by full-matrix least squares using the TEXSAN crystallographic software package.[12] All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed in calculated positions. The final cycles of the least-squares refinement were based on 5387 observed reflections $[I > 3\sigma|I|]$ and 550 variable parameters. The maximum and minimum peaks on the final difference Fourier map correspond to 0.40 and −0.37 e Å^{-3}, respectively. CCDC 182/526.

§ New compounds **5** and **6** here obtained gave satisfactory spectral and analytical data. For **5**: white crystals; mp 189–191 °C (deccomp.) (CH_2Cl_2–EtOH); ^1H NMR ($CDCl_3$, 500 MHz, 300 K) δ −0.17 (s, 9 H), 0.00 (s, 9 H), 0.03 (s, 9 H), 0.05 (s, 9 H), 0.06 (s, 9 H), 0.13 (s, 9 H), 0.82 (d, *J* 6.9 Hz, 3 H), 1.02 (d, *J* 6.9 Hz, 3 H), 1.13 (s, 1 H), 1.173 (d, *J* 6.9 Hz, 3 H), 1.174 (d, *J* 6.9 Hz, 3 H), 1.27 (br s, 6 H), 1.84 (s, 3 H), 2.09 (s, 1 H), 2.13 (s, 1 H), 2.37 (d, *J* 12.3 Hz, 1 H), 2.66 (br s, 1 H), 2.79 (spt, *J* 6.9 Hz, 1 H), 2.85 (d, *J* 12.3 Hz, 1 H), 3.95 (br s, 1 H), 4.28 (s, 1 H), 4.86 (s, 1 H), 5.00 (s, 1 H), 5.17 (s, 1 H), 6.29 (s, 1 H), 6.40 (s, 1 H), 6.89 (s, 1 H), 6.93 (s, 1 H). High-resolution FABMS: observed *m/z* 927.5016 ([M + H]$^+$). Calc. for $C_{48}H_{92}{}^{74}GeOSi_6$ 927.5054. For **6**: white crystals; mp 177–179 °C (CH_2Cl_2–EtOH); ^1H NMR ($CDCl_3$, 500 MHz, 300 K) δ −0.09 (s, 9 H), 0.04 (s, 18 H), 0.06 (s, 9 H), 0.16 (s, 9 H), 0.17 (s, 9 H), 1.24 (d, *J* 6.9 Hz, 6 H), 1.29 (br s, 6 H), 1.33 (d, *J* 6.9 Hz, 6 H), 1.66 (s, 1 H), 1.72 (br s, 1 H), 2.87 (spt, *J* 6.9 Hz, 1 H), 3.29 (br s, 2 H), 6.44 (s, 1 H), 6.46 (s, 1 H). High-resolution FABMS: observed *m/z* 845.4339 ([M+H]$^+$); calc. for $C_{42}H_{83}{}^{74}GeOSi_6$ 845.4271.

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