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INTRAMOLECULAR ALKYLATION OF VINYLGERMANES AND IODODEGERMYLATION OF 1-CYCLOALKENYLGERMANES

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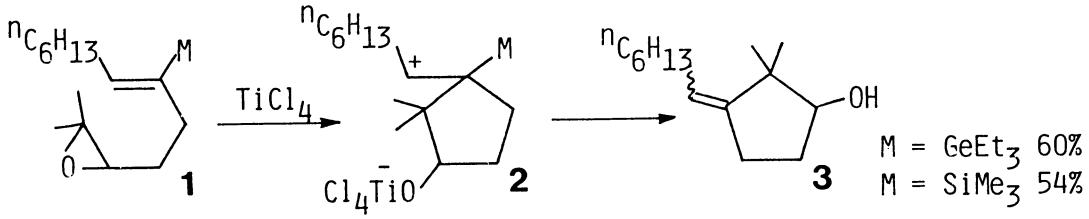
Whereas 2-methyl-2,3-epoxy-6-triethylgermyl-6-tridecene gave the expected alkylidenecyclopentanol upon treatment with $TiCl_4$, 5-triethylgermyl-5-dodecenal dimethyl acetal provided the unexpected cyclohexene derivative. Transformation of 1-triethylgermylcycloalkenes into 1-iodocycloalkenes is also described.

The application of vinylsilanes to the organic synthesis has been limited because of the lower reactivity compared with allylsilanes. During the course of our study on the relative reactivity of vinylgermanes and vinylsilanes,[1] (1) intramolecular reactions of vinylgermanes and vinylsilanes toward carbon-electrophiles and (2) iododegermylation of 1-triethylgermylcycloalkenes were examined.

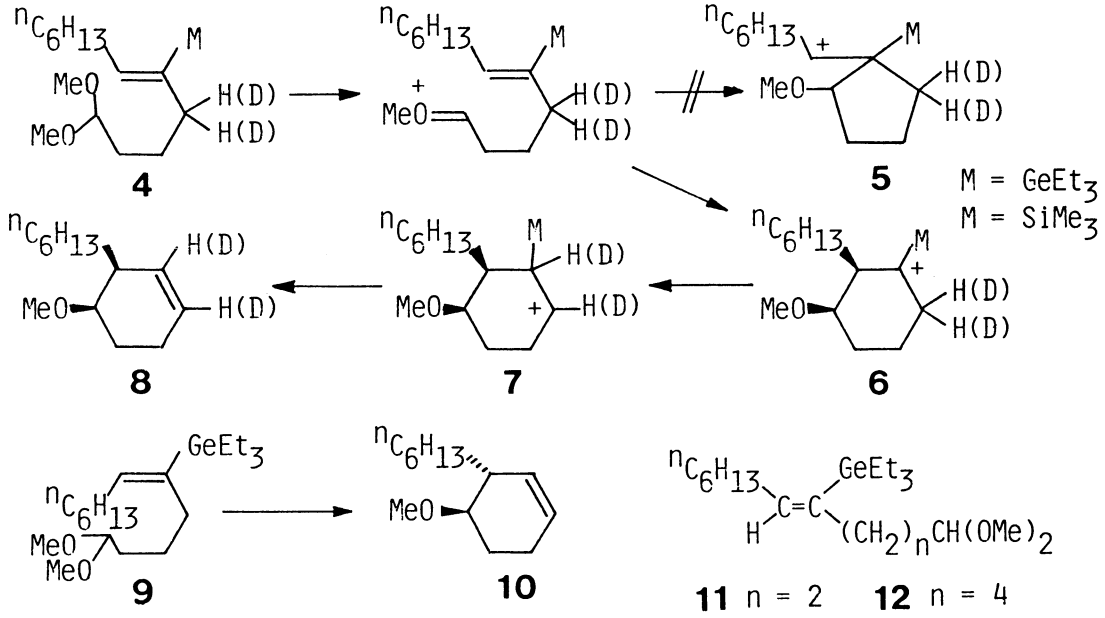
Treatment of epoxide **1** (M = $GeEt_3$) with $TiCl_4$ gave cyclopentanol **3**[2] exclusively. The corresponding vinylsilane also provided the same cyclopentanol derivative. These reactions proceed via β-germyl- or β-silylcarbenium ion **2** and the formation of five-membered ring product **3** is consistent with the reported intramolecular acylation of 5-trimethylsilyl-5-heptenoyl chloride with $AlCl_3$ producing 1-ethylidenecyclopentanone.[3,4]



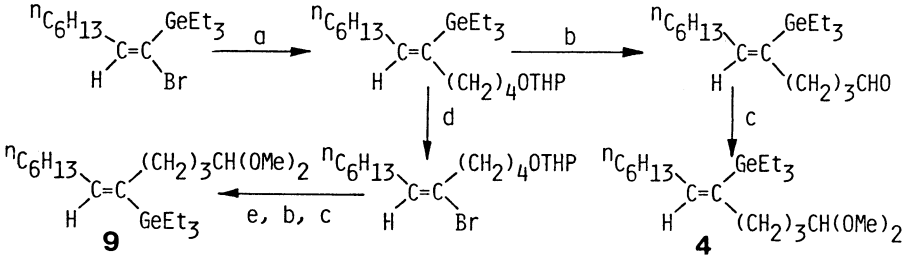
In contrast, (Z)-5-triethylgermyl-5-dodecenal dimethyl acetal (**4**) provided cis-3-hexyl-4-methoxy-1-cyclohexene (**8**) on treatment with $TiCl_4$. A dichloromethane solution of $TiCl_4$ (1.0 mol dm^{-3}, 0.52 ml, 0.52 mmol) was added dropwise to a solution of vinylgermane **4** (0.20 g, 0.52 mmol) in dichloromethane (15 ml) at -78 °C under an argon atmosphere. The resulting orange solution was stirred for 2 min at the same temperature and poured into 1.0 mol dm^{-3} HCl. Workup and

purification by preparative thin layer chromatography on silica-gel gave the cyclohexene **8**[5] (58 mg) in 57% yield. The (E)-isomer **9** provided trans-3-hexyl-4-methoxy-1-cyclohexene **10**[6] as a single product. Thus, the reactions proceeded with high stereospecificity. In order to determine the stereochemistry of the products, the compound **8** and **10** were hydrogenated to give cis- and trans-1-hexyl-2-methoxycyclohexane, respectively, which were identical with authentic samples.[7,8] The corresponding vinylsilane **4** (M = $SiMe_3$) gave the same cyclohexene **8**, but the yield was low (33% yield). Acetals **11** and **12** provided complex mixture containing no cyclized products.

The apparently disrotatory cyclization seems to proceed as follows. The α-germyl cation **6** is possibly preferred kinetically to **5**. The rearrangement to more stable β-germyl cation **7** followed by degermylation provides **8**. The disappearance of olefin protons in the product **8-d_2** derived from 4,4-dideuterio acetal **4-d_2** is consistent with this sequence.

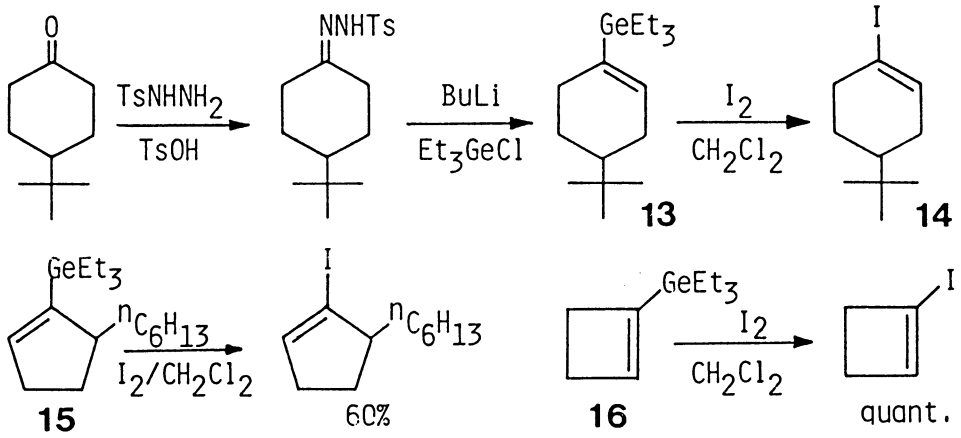


The starting vinylgermanes **4** and **9** were prepared as follows.



a: $2\,^tBuLi/I(CH_2)_4OTHP$, 66% b: 1) $C_5H_6N^+p\text{-}TsO^-$ 2) Pyridinium chlorochromate, 84% c: $HC(OMe)_3$, MeOH, $CeCl_3 \cdot 7H_2O$,[9] quant. d: Br_2/CH_2Cl_2[1] quant. e: $2\,^tBuLi/Et_3GeCl$, 36%

Acyclic vinylsilanes have been easily converted into alkenyl halides and the stereochemistry of the reactions has been widely studied.[10] On the other hand, cyclic vinylsilanes are reluctant to react with iodine.[11] In contrast, cycloalkenylgermanes are converted into the corresponding iodide effectively. For instance, treatment of 1-triethylgermyl-4-t-butylcyclohexene **13**[12] with iodine in dichloromethane at 25 °C for 2 h gave the alkenyl iodide **14** in 89% yield.[13] The cyclopentene **15** and cyclobutene **16**[14] were also transformed into the corresponding iodides without any difficulties. The starting alkenes **13** and **15** were prepared through reaction of ketone tosylhydrazones with butyllithium and triethylgermyl chloride in tetramethylethylenediamine.[15] The C(sp)-Ge bond also can be cleaved with iodine more easily than the corresponding C(sp)-Si bond. Thus, 1-triethylgermyl-1-octyne gave the 1-iodo-1-octyne in 75% yield on treatment with iodine in dichloromethane at 25 °C for 1 h. Meanwhile, 1-trimethylsilyl-1-octyne was recovered practically unchanged under the same reaction conditions.



References

1) H. Oda, Y. Morizawa, K. Oshima, and H. Nozaki, Tetrahedron Lett., 25, 3221 (1984).

2) Bp 97 °C/1 Torr (bath temp); IR (neat) 3360, 2885, 1460, 1045 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.85-0.99 (m, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.18-1.55 (bs, 8H), 1.60-1.89 (m, 3H), 1.89-2.05 (m, 2H), 2.05-2.20 (m, 2H), 3.53 (dd, J = 3.2 and 8.6 Hz, 1H), 5.30-5.40 (m, 1H); ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 14.1, 21.6, 22.7, 22.9, 26.0, 26.3, 29.1, 29.5, 31.2, 31.9, 39.5, 76.0, 119.0, 143.3. Found: C, 79.66; H, 12.56%. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%.

3) K. Mikami, N. Kishi, and T. Nakai, Tetrahedron Lett., 24, 795 (1983); E. Nakamura, K. Fukuzaki, and I. Kuwajima, J. Chem. Soc., Chem. Commun., 1983, 499; S. D. Burke, C. W. Murtiashaw, M. S. Dike, S. M. S. Stickland, and J. O. Saunders, J. Org. Chem., 46, 2400 (1981).

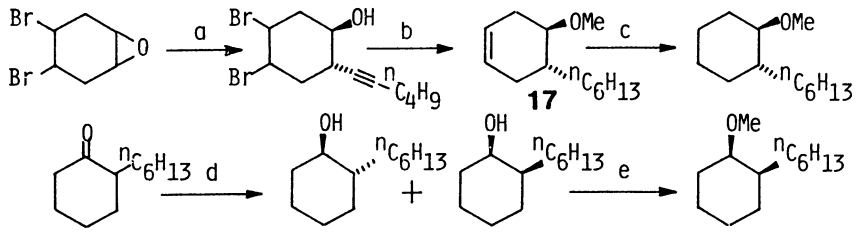
4) The epoxide derived from $n\text{-}C_6H_{13}CH{=}C(GeEt_3)CH_2CH_2CH_2CH{=}CMe_2$ gave the chlorohydrin $n\text{-}C_6H_{13}CH{=}C(GeEt_3)CH_2CH_2CH_2CH(OH)C(Cl)Me_2$ on treatment with $TiCl_4$. Any trace of cyclohexanol derivative could not be observed.

5) Bp 70 °C/1 Torr (bath temp); IR (neat) 2890, 2820, 1455, 1095 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.83-0.98 (m, 3H), 1.18-1.48 (bs, 10H), 1.48-2.35 (m, 5H), 3.38 (s, 3H), 3.43-3.55 (m, 1H), 5.53-5.75 (m, 2H); ^{13}C-NMR ($CDCl_3$,

22.5 MHz) δ 14.1, 22.7, 22.9, 24.1, 27.2, 29.7, 30.5, 31.9, 38.9, 56.2, 77.4, 126.2, 129.5; MS (m/z, rel intensity) 196 (M^+, 1), 164 (75), 138 (62), 110 (55), 96 (63), 81 (59), 79 (57), 68 (68), 67 (76), 54 (100). Found: C, 79.49; H, 12.40%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

6) IR (neat) 2890, 2825, 1450, 1100 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.83-0.95 (m, 3H) 1.03-1.44 (bs, 10H), 1.44-2.26 (m, 5H), 3.09-3.20 (m, 1H), 3.38 (s, 3H), 5.51-5.73 (m, 2H); ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 14.1, 22.7, 23.2, 24.7, 26.8, 29.7, 31.9, 33.4, 41.2, 56.1, 80.1, 126.1, 129.3.

7) The both isomers were prepared as follows.



a: $Et_2AlC{\equiv}C\text{-}^nC_4H_9$ b: 1) H_2/PtO_2 2) Zn/AcOH 3) BuLi/MeI

c: H_2/PtO_2 d: $LiAlH_4$ e: 1) separation 2) BuLi/MeI

Trans-1-hexyl-2-methoxycyclohexane : ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.81-0.99 (m, 3H), 0.99-1.49 (m, 14H), 1.54-1.93 (m, 4H), 2.01-2.16 (m, 1H), 2.70-2.85 (m, 1H), 3.34 (s, 3H); ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 14.1, 22.8, 24.7, 25.5, 26.8, 29.9, 30.3, 30.4, 32.0, 32.3, 43.0, 56.2, 83.6. cis-isomer: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.83-0.99 (m, 3H), 1.13-1.76 (m, 18H), 1.83-2.00 (m, 1H), 3.28-3.39 (m, 1H), 3.30 (s, 3H); ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 14.1, 21.3, 22.8, 25.0, 27.4, 27.5, 28.1, 29.8, 31.1, 32.0, 40.8, 56.2, 79.0.

8) The position of double bond in the compound **8** and **10** was confirmed as follows. Decoupling the proton attached to the carbon bearing methoxy group did not affect two olefinic protons. Thus, 4-hexyl-3-methoxy-1-cyclohexene was excluded among three possible structures. Other isomeric structure **17** (see Ref. 7) was also ruled out by the comparison of its ^{13}C-NMR spectrum with that of the cyclized product **10**. The thermodynamically more stable olefin, 2-hexyl-3-methoxy-1-cyclohexene, could not be detected in the reaction mixtures.

9) J.-L. Luche and A. L. Gemal, J. Chem. Soc., Chem. Commun., 1978, 976.

10) E. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981) Chap.7.

11) E. Negishi, private communication. We found that treatment of 3-hexyl-2-trimethylsilylcyclopentene with iodine in dichloromethane at 25 °C for 2 h resulted in the recovery of the starting material quantitatively.

12) IR (neat) 2910, 2840, 1450, 1360, 1020, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90MHz) δ 0.65-1.14 (m, 15H), 0.86 (s, 9H), 1.14-2.20 (m, 7H), 5.65-5.81 (m, 1H). Found: C, 64.69; H, 11.04%. Calcd for $C_{16}H_{32}Ge$: C, 64.70; H, 10.86%.

13) The compound **13** gave the corresponding cycloalkenyl bromide in 90% yield upon treatment with NBS in CH_2Cl_2 (25 °C, 3 h), but **16** was recovered unchanged under the same reaction conditions.

14) Prepared from 1-triethylgermyl-4-bromo-1-butyne according to the reported procedure for silylacetylenes. E. Negishi, L. D. Boardman, J. M. Tour, H. Sawada, and C. L. Rand, J. Am. Chem. Soc., 105, 6344 (1983).

15) L. A. Paquette, W. E. Fristad, D. S. Dime, and T. R. Bailey, J. Org. Chem., 45, 3017 (1980).

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