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STEREOSELECTIVE SYNTHESIS OF VINYLGERMANES AND THEIR FACILE TRANSFORMATION INTO VINYL HALIDES

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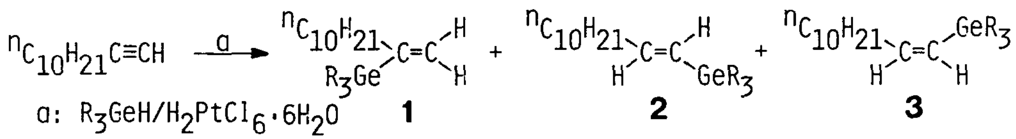
Abstract: Whereas iododegermylation of (Z)-1-triethylgermyl-1-dodecene gives (Z)-1-iodo-1-dodecene, bromodegermylation proves to give (E)-1-bromo-1-dodecene. Two general procedures for the preparation of vinylgermanes are also described.

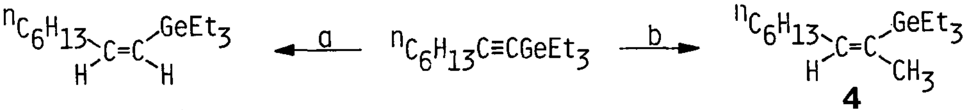
Vinylsilanes and vinylstannanes are recognized to be versatile synthetic intermediates and their use for the stereoselective synthesis of di- and tri-substituted alkenes is widely studied.[1] In contrast, the chemistry of vinylgermanes is not well developed due to the lack of their preparative method. Here we wish to report two general methods for stereo- and regioselective synthesis of vinylgermanes and stereospecific transformation of germylalkenes into haloalkenes.

Platinum ($H_2PtCl_6 \cdot 6H_2O$) catalyzed hydrogermylation[2] of terminal acetylenes gave (E)-1-germyl-1-alkenes as major products. For instance, treatment of 1-dodecyne with equimolar amount of $^nPr_3GeH$ in the presence of $H_2PtCl_6 \cdot 6H_2O$ catalyst[3] (0.15 mol%) at 25°C for 1 h provided a mixture of 2-germyl-1-dodecene (**1**) and the 1-germyl regioisomer (**2**) (R = ^nPr, **1**/**2** = 13/87) in 93% combined yield. The use of Ph_3GeH instead of $^nPr_3GeH$ gave 99% yield of a mixture of **1** and **2** (R = Ph, **1**/**2** = 25/75) after heating at 100°C for 0.5 h. The regio- and stereochemistry of the reaction heavily depended on the nature of the catalysts employed. Other platinum catalyst such as $Na_2PtCl_6 \cdot 4H_2O$ or $H_2PtCl_4 \cdot xH_2O$ also provided a similar mixture of **1** and **2** as $H_2PtCl_6 \cdot 6H_2O$ (R = ^nPr, **1**/**2** = 20/80 or 15/85). In contrast, hydrogermylation catalyzed by K_2PtCl_4 (4.8 mol%) or $PtCl_2(PPh_3)_2$ (0.5 mol%) gave a mixture of **2** and **3** (R = ^nPr) in **2**/**3** = 68/32 (78%) or 10/90 ratio (47% yield). The regioisomer **1** was not detected among the hydrogermylation products under



this condition. Moreover, heating a mixture of $^{n}Pr_3GeH$ and 1-dodecyne with no added catalysts at 80°C for 3 h gave a mixture of **2** and **3** (**2**/**3** = 13/87) in 74% yield.

Hydralumination or hydroboration of germylacetylenes[4] is a second procedure for the vinylgermane synthesis. An addition of $^{i}Bu_2AlH$ to a solution of 1-triethylgermyl-1-octyne in hexane followed by hydrolysis gave a mixture of (Z)-1-germyl-1-octene and (E)-isomer (Z/E = 80/20, after 2 h at 25°C). The presence of ether as a cosolvent (hexane/ether = 2/1) improved the stereoselectivity to afford the (Z)-isomer exclusively (96% yield).[5] Hydroboration and methylation[6] provided (Z)-2-triethylgermyl-2-nonene (**4**).[7]



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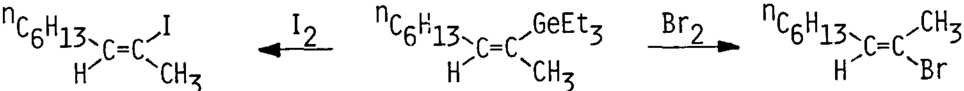
a: 1) $^{i}Bu_2AlH$ 2) H_3O^+ b: 1) R_2BH 2) MeLi 3) CuI 4) MeI

Now we have developed three methods[8] for the preparation of vinylgermanes and started to study on their reaction with iodine or bromine as an electrophile. Treatment of (Z)-2-triethylgermyl-2-nonene (**4**) with equimolar amount of iodine in CH_2Cl_2 at 25°C for 1 h gave (Z)-2-iodo-2-nonene quantitatively (>95%(Z)). Iododegermylation proceeded stereospecifically with complete retention of configuration for various alkenes having different substitution patterns shown below, yield and purity being as follows: 88%, >97%(Z) for **5**; 80%, >97%(E) for **6**; 98%, >95%(E) for **7**.



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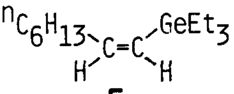

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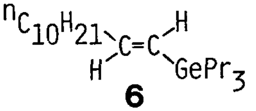

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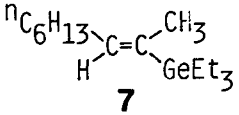

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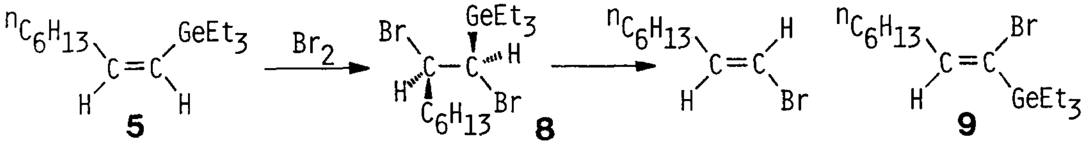
In contrast, bromodegermylation proved to proceed with inversion of configuration. For instance, an addition of bromine to **4** in CH_2Cl_2 at -78°C gave (E)-2-bromo-2-nonene quantitatively (>95%(E)). The nature of the substrates slightly affects the stereochemical results. Whereas (Z)-germylalkenes such as **4** or **5** gave (E)-vinyl bromide cleanly (91% yield, >95%(E) for **5**), (E)-germylalkene **6** or **7** gave (Z)-bromide stereoselectively which was contaminated by (E)-isomer (yield and purity: 80%, >72%(Z) for **6**; 95%, >90%(Z) for **7**).[8] In the case of bromination of (Z)-1-triethylgermyl-1-

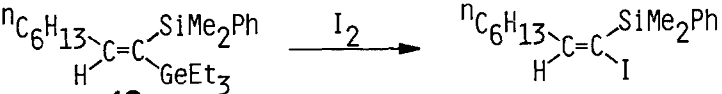
octene (5), the intermediary dibromide **8** could be isolated. Further treatment of the dibromide with silica gel in hexane at 25°C for 1 h gave (E)-1-bromo-1-octene. Other three substrates did not provide the intermediary dibromides isolated. The inversion of stereochemistry is attributed to anti-addition of bromine followed by anti-elimination of bromogermane. Dehydrobromination of **8** was achieved with KO^{t}Bu/^{t}BuOH to give a single (Z) isomer of germylated alkenyl halide **9**.[9]



5 **8** **9**

Bromodegermylation was also achieved with N-bromosuccinimide. The reaction proceeded mainly with retention of the configuration, but the stereospecificity depended on the nature of the substrates. Germylalkene **5** provided (Z)-1-bromo-1-alkene quantitatively (>96%(Z)) upon treatment with 2 equivalents of NBS in CH_2Cl_2 at 25°C for 4 h. On the other hand, alkene **4** or **7** afforded a mixture of the corresponding (E)- and (Z)-isomeric vinyl bromide (98% yield, Z/E = 68/32 for **4**; 100% yield, E/Z = 81/19 for **7**).

As mentioned above, the substitution of the germyl group on sp^2 carbon with halogen proceeded much more easily than the corresponding silyl group with improved stereochemical outcome.[10] Treatment of the compound **10** with I_2 afforded a single isomer of the vinylsilane below in 91% yield.



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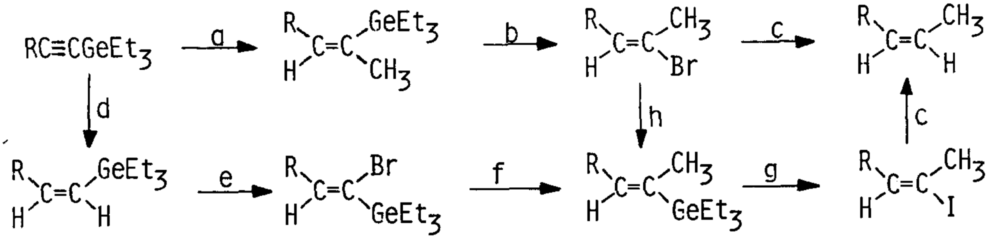
Scheme 1 correlates the stereochemistry of the compounds and summarizes the effectiveness of the halodegermylation technique.[11]

Scheme 1



R = $^nC_6H_{13}$ a: R'_2BH, MeLi, CuI, MeI b: Br_2 c: $^tBuLi/H_2O$ d: $^iBu_2AlH$
e: Br_2, KO^{t}Bu/^{t}BuOH f: $Me_2Cu(CN)Li_2$ g: I_2 h: $^tBuLi/Et_3GeCl$

References and Notes

1. E. W. Colvin, "Silicon in Organic Synthesis", Butterworth and Co Ltd, 1981, pp 44-82; W. P. Weber, "Silicon Reagents for Organic Synthesis", Springer-Verlag, New York, 1983, pp 79-113; E. Negishi, "Organometallics in Organic Synthesis", vol. 1, John Wiley & Sons, New York, 1980, pp394-454.
2. Hydrogermylation of phenylacetylene has been extensively studied. R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **40**, 73 (1972). More recently the reaction of propargylic alcohol derivatives with Et_3GeH has been reported. K. I. Cherkezishvili, K. Sh. Gelashvili, R. I. Kublashvili, *Soobshch. Akad. Nauk. Gruz. SSR*, **109**, 297 (1983). Hydrogermylation of simple alkynes has not been well established to our knowledge.
3. A solution of $H_2PtCl_6 \cdot 6H_2O$ (58 mg) in ^iPrOH (15 ml) was prepared and 0.21 ml (0.15 mol%) was used per 1.0 mmol of substrate.
4. Hydralumination of phenyltrimethylgermylacetylene has been briefly reported. J. J. Eisch and M. W. Foxton, *J. Org. Chem.*, **36**, 3520 (1971).
5. Similar results have been reported for hydralumination of silylacetylenes. K. Uchida, K. Utimoto, and H. Nozaki, *ibid.*, **41**, 2215 (1976); J. J. Eisch and G. A. Damasevitz, *ibid.*, **41**, 2214 (1976); G. Zweifel and W. Lewis, *ibid.*, **43**, 2739 (1978).
6. Utimoto's method for the 1-trimethylsilyl-1-alkynes could be successfully applied to germyl compounds. K. Uchida, K. Utimoto, and H. Nozaki, *Tetrahedron*, **33**, 2987 (1977).
7. Bp 80°C (bath temp, 1 Torr); IR (neat) 2880, 2830, 1450, 1010, 700 cm^{-1}; NMR (CCl_4) δ0.6-1.1 (m, 18H), 1.1-1.5 (bs, 8H), 1.73 (m, 3H), 1.8-2.1 (m, 2H), 5.7-6.0 (m, 1H). Found: C, 63.48; H, 11.55%. Calcd for $C_{15}H_{32}Ge$: C, 63.21; H, 11.32%.
8. For the third method, see the preceding paper.
9. Bp 69°C (bath temp, 0.1 Torr); IR (neat) 2880, 2830, 1450, 1010, 700 cm^{-1}; NMR (CCl_4) δ0.7-1.1 (m, 18H), 1.1-1.5 (bs, 8H), 2.1-2.4 (m, 2H), 5.97 (t, *J* = 6.0 Hz, 1H). Found: C, 48.31; H, 8.64%. Calcd for $C_{14}H_{29}BrGe$: C, 48.06; H, 8.35%.
10. The yields of vinyl halides were much higher than those for the corresponding transformation of vinylsilanes. T. H. Chan, P. W. K. Lau, and W. Mychajlowskij, *Tetrahedron Lett.*, **1977**, 3317.

11. Financial support by the Ministry of Education , Science, and Culture, Japanese Government (Grant-in-Aid for Special Project Research 58110005) is acknowledged.

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