Michael-Type Reactions between Electron-Deficient 1,3-Dienes and Dimethylgermylene/Water [☆]

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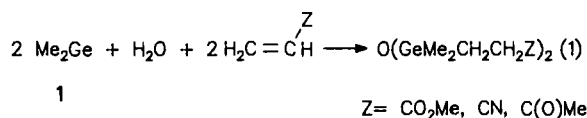Otto-Hahn-Straße 6, W-4600 Dortmund 50, F.R.G.

A new type of reaction between dimethylgermylene (Me$_2$Ge) (1), generated in situ from a 7-germanobornadiene, and electron-deficient 1,3-dienes RR'C=CH−CH=CH−Z [Z = C(O)Me, CO$_2$R" 2a−f] or cyclic dienones 8, 9 in the presence of water is described. The Michael-type behaviour of the system Me$_2$Ge/H$_2$O is clearly shown by the nucleophilic addition to the unsaturated systems resulting in the formation of β- and δ-adducts, the new allylgermanes 3a−g, 4a−c, 10a, b, 11. The cis configuration of the resulting double bond of the δ adducts 4a−c is remarkable. With open-chain dienes cycloaddition of 1 without participation of water, yielding germacyclopentenes 5a, b or germacyclopentanes 7a, b, competes with the Michael-type reaction. A slight variation of the substitution pattern of the dienes has a strong influence on the reaction course.

The chemistry of organogermylenes R$_2$Ge, explored mainly by means of dimethylgermylene Me$_2$Ge (1) as a prototype, has taken an impressive development in the last decade[1]. The behaviour of carbenes and silylenes as reactive intermediates differs significantly from its heavier analogue, germylene[2], although Me$_2$Ge (1) undergoes principally carbene analogous reactions, that means insertion[1a,3] and cycloaddition reactions[1,4].

1,2-Cycloadditions of free Me$_2$Ge to alkenes yielding stable germiranes are unknown so far. The reaction[5] between a sterically crowded thiacycloheptyne and a 7-germanorbornadiene has turned out to be not a germylene reaction[1a]. 1,2-Cycloaddition plays an important role in the carbene[6] and silylene chemistry[7].

Quantum mechanical calculations of the strain enthalpy of a germirane, the 1,2-addition product of a germylene to an alkene, shows a comparative instability relative to the homologues cyclopropanes and siliranes[8]. It is assumed that germiranes are intermediates in the reaction with styrenes, the only mono-alkenes that react with Me$_2$Ge, leading lastly to germacyclopentanes[9]. Electron-deficient alkenes do not yield stable products with Me$_2$Ge, but react regiospecifically, when water is present, to digermoxanes, with the germanium being attached to the electrophilic carbon atom of the alkenes[10] [see eq. (1)].

$$2\ Me_2Ge\ +\ H_2O\ +\ 2\ H_2C=\overset{\underset{\displaystyle |}{Z}}{C}H\ \longrightarrow\ O(GeMe_2CH_2CH_2Z)_2\quad (1)$$

1

Z= CO$_2$Me, CN, C(O)Me

Recently, we have reported that this Michael-type reaction is not a hydrogermylation of the unsaturated system by 1,1,3,3-tetramethyldigermoxane. A precomplexation of Me$_2$Ge by water had to be stated, instead[3b]. But, details of the reaction between alkenes and Me$_2$Ge · OH$_2$ are still lacking.

In this paper we report on the reaction between Me$_2$Ge and electron-deficient dienes in the presence of water. The extension of the reaction principle mentioned above to dienes provides an access to unusually substituted allylgermanes 3a−g, 4a−c, 10a, b, 11, and allows new mechanistic insights. The nucleophilic behaviour of Me$_2$Ge · OH$_2$, which acts as a Michael donor, is clearly shown by the regioselective reaction to the allylgermanes. Stereoselectivity and formation of unexpected products 7a, b gives further insight into reaction mechanisms.

Results and Discussion

Me$_2$Ge, generated in situ from a 7-germanorbornadiene[1a,10], reacts with electron-deficient 1,3-dienes in the presence of water to yield digermoxanes in high yields (^{1}H NMR).

In order to simplify a structure determination, the digermoxanes are split by aqueous halogen acids to form halogenoallyldimethylgermanes, see eq. (2). A mixture of isomeric heptadienones 2a, b (5E/5Z = 3:1) reacts, like a simple enone[10], only with the β-carbon atom of the conjugated system, see eq. (2).

Methyl and ethyl (2E,4E)-2,4-hexadienoates (2c and 2d) supply the first examples of an attack at the electrophilic δ-carbon atom, resulting in the stereoselective formation of 4a, b as the minor products, see eq. (2). The main products 3c, d are still formed by addition to the β-carbon atom. Increase of the temperature raises the content of the δ addition product (70°C 3c/4a = 1:0.38; 110°C 3c/4a = 1:0.77). With methyl (2E)-2,4-pentadienoate (2e) the determination (^{1}H NMR, decoupling experiments) of the new double bond in 4c, the δ-addition product, is possible: it shows a cis configuration. A decrease of the steric hindrance in the δ-position of 2e favours the formation of 4c, which is the main product in this case.

δ-Addition, i.e. 1,6-addition of organometallic reagents, has been reported very seldom so far. However, it has also been observed in the case of organocopper reagents and conjugated dienoates[11]. Whatever the nature of the intermediate leading to the allylgermanes 4a−c is, a germylene/water complex[3a] or an adduct between the diene and 1, the nucleophilic character of this addition is obvious.

The system Me$_2$Ge/H$_2$O reacts with the dienes 2a−f to allylgermanes in the solvent benzene, although an insertion of Me$_2$Ge into water has not been observed in a benzene/water mixture[3b]. Further on, 1,1,3,3-tetramethyldigermoxane H−GeMe$_2$−O−GeMe$_2$−H does not react with, e.g., 2c in chlorobenzene, in which the germoxane is generated[3b], within 4 h at 70°C. Thus, a hydrogermylation mechanism in eq. (2) is excluded.

(2)
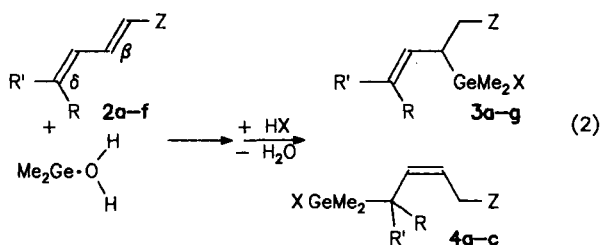
	R	R'	Z
2a,b[a]	H(CH$_3$)	CH$_3$(H)	C(O)Me
2c	H	CH$_3$	CO$_2$CH$_3$
2d	H	CH$_3$	CO$_2$C$_2$H$_5$
2e	H	H	CO$_2$CH$_3$
2f	CH$_3$	CH$_3$	CO$_2$CH$_3$

	R	R'	Z	X
3a,b[a]	H(CH$_3$)	CH$_3$(H)	C(O)Me	F
3c,4a	H	CH$_3$	CO$_2$CH$_3$	F
3d,4b	H	CH$_3$	CO$_2$C$_2$H$_5$	F
3e,4c	H	H	CO$_2$CH$_3$	F
3f	CH$_3$	CH$_3$	CO$_2$CH$_3$	F
3g	CH$_3$	CH$_3$	CO$_2$CH$_3$	Br

[a] Isomeric mixture (5E : 5Z = 3 : 1)

The expected 1,4-cycloaddition products[1a,4] 5a and 5b are detected in low yields as by-products. A disrotatory ring closure can be stated in the case of 5a, revealing once again the involvement of free singlet Me$_2$Ge[1a], see eq. (3). 5a and 5b do not react with water. They are, therefore, no intermediates on the way to the δ addition products, corresponding to 4a, c.


(3)

5a : R' = CH$_3$
5b   R' = H
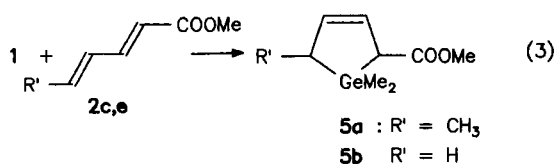
Consequently, an increase of steric hindrance in the δ-position by another methyl group in 2f prevents 1,4-cycloaddition as well as a δ-addition by Me$_2$Ge · OH$_2$. Exclusive and quantitative formation of the allylgermanes 3f and 3g is observed, see eq. (2).

Analogously, the steric situation in methyl (2E)-2-methyl-2,4-pentadienoate (6a) should prevent 1,4-cycloaddition of Me$_2$Ge and favour addition of Me$_2$Ge · OH$_2$ to the δ-carbon atom. Surprisingly, no traces of the expected product can be detected. The main products are the trans- and cis-3,4-dialkenyl-1,1-dimethyl-1-germacyclopentanes 7a and 7b, which are isolated in 85% yield. The trans isomer 7a is separated from 7b by repeated crystallization from methanol. An X-ray structure determination[12] confirms the proposed structure. 7a shows a symmetric twist form with Ge on the twofold axis. The bond angle around Ge in the ring is 92.1°, the others around Ge are 113.5, 113.1 and 110.6°. Ge−C bond distances are 1.950(5) (ring) and 1.929(4) (exocyclic) Å. Besides some 1,3-dienes bearing no functional groups[1a,1c,4], this is the first electron-deficient diene that forms a germacyclopentane.


(4)
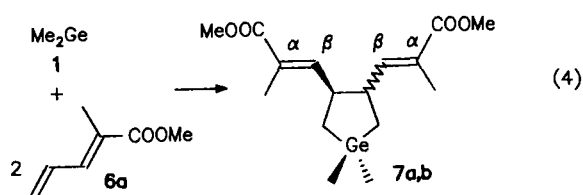
In a competitive experiment Me$_2$Ge is treated with a mixture of 2e and 6a in the presence of water. 7a, b are not formed, but the digermoxanes that correspond to 3e, 4c. Obviously, the cycloaddition of 6a with Me$_2$Ge is much slower than the reaction of Me$_2$Ge · OH$_2$ with 2e. Therefore, a slow insertion of Me$_2$Ge into water and a subsequent hydrogermylation of 2e is ruled out.

Methyl (2E,4E)-2-methyl-2,4-hexadienoate (6b) gives neither a cycloaddition product with Me$_2$Ge nor an addition product with Me$_2$Ge · OH$_2$, in the absence of a suitable scavenger 1 polymerizes to (Me$_2$Ge)$_n$, see eq. (5).

(5)
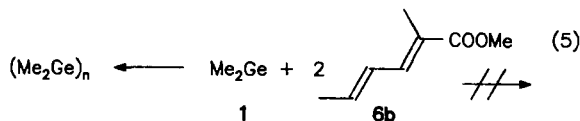
The strong influence of a methyl group in the 2-position of the dienonates 6a and 6b with respect to 2e and 2c may be due to a drastic lowering of the content of the s-cis conformer, see Scheme 1. It can be assumed that a germylene/water complex is added to the δ-carbon atom while a coordination of the carboxylate group in the transition state takes place. This interpretation gains support from the stereoselective introduction of the new double bond in 4a−c.

In cyclic conjugated dienones 8 and 9 the steric hindrance at the β-carbon atom, see eq. (6) and (7), favours the δ-addition. In this case, an intermediate coordination of the carbonyl group is not possible. In contrast to 10a, b the

Scheme 1. Conformers of **2e** and **6a**
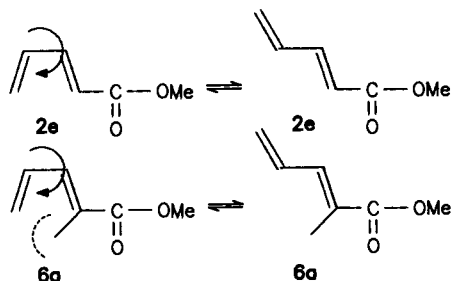
substitution pattern in **11** prevents the formation of a mixture of diastereomers.

$$Me_2Ge \cdot OH_2 + HX \xrightarrow{- H_2O} \quad (6)$$

10a: X = F
10b: X = Br

$$Me_2Ge \cdot OH_2 + HBr \xrightarrow{- H_2O} \quad (7)$$
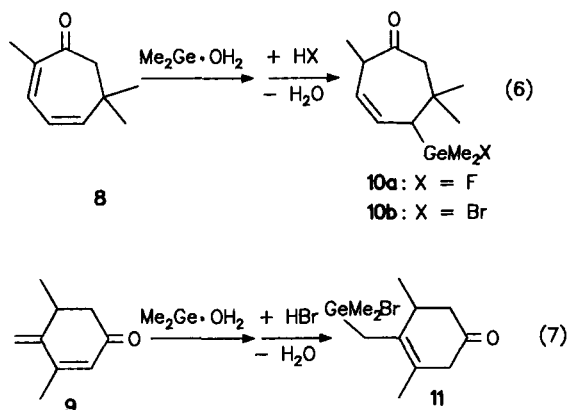
Once again the behaviour of the system Me$_2$Ge · OH$_2$ as a Michael donor is observed; the entering proton is always located adjacent to the electron-withdrawing group, which makes an intermediate protonation of the carbonyl group plausible. This reaction opens the way to a broad variety of functionalized allylgermanes.

Experimental

Melting points: Büchi SMP 20. — NMR: Bruker AM 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz). — MS: Finnigan MAT 8230, 70 eV. — GC/MS: DANI 8521-A, Finnigan Mat ITD 800, 70 eV. — Elemental analyses: Carlo Erba 1106.

Dienes **2a−f**, **6a**, **b**, **8**, **9** are prepared according to literature procedures: (3E,5E/Z)-3,5-Heptadien-2-one[13] (**2a**, **b**), methyl and ethyl (2E,4E)-2,4-hexadienoates[14] (**2c**, **d**), methyl (2E)-2,4-pentadienoate[14,15] (**2e**), methyl (2E)-5-methyl-2,4-hexadienoate[16] (**2f**), methyl (2E)-2-methyl-2,4-pentadienoate[17] (**6a**), methyl (2E,4E)-2-methyl-2,4-hexadienoate[18] (**6b**), eucarvone[19] (**8**), 3,5-dimethyl-4-methylene-2-cyclohexen-1-one[20] (**9**).

Allylgermanes **3a−g**, **4a−c**, **10a**, **b**, **11**. — *General Procedure:* To a solution of 1.0 g (1.9 mmol) of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germa-2,3-benzonorbornadiene[1a,10] in 10 ml of anhydrous benzene under argon the diene (5−9 mmol) and 0.30 ml (17 mmol) of water are added. The two-phase mixture is slowly stirred at 70°C for 4 h. After cooling to room temp. the organic layer is separated, dried with MgSO$_4$, and the volatile components are removed in vacuo at 50−70°C/0.01 Torr. After stirring the residue

is treated with 20 ml of pentane for 1 h and the precipitated 1,2,3,4-tetraphenylnaphthalene is filtered off. To the filtrate is added 10 ml of an aqueous HF or HBr solution, and the mixture is stirred at room temp. for 1 h. The organic layer is separated and the pentane removed in vacuo. Kugelrohr distillation of the residue affords the allylgermanes in 40−80% yield.

(5E/Z)-4-(Fluorodimethylgermyl)-5-hepten-2-one (**3a**, **b**): (GC: 5E/5Z = 3:1, compare ref.[13]). From 0.95 g (8.6 mmol) of **2a**, **b** 0.37 g (84%) of **3a**, **b** is obtained as a colourless oil, b.p. 120°C/15 Torr. — ^{1}H NMR (CDCl$_3$): δ = 0.5 (m, 6H, GeCH$_3$), 1.6 (m, 4H, =CHCH$_3$, =CHCH), 2.16, 2.19 (2 s, 3H, COCH$_3$), 2.7 (m, 2H, CH$_2$), 5.3 (m, 2H, =CH). — ^{13}C NMR (CDCl$_3$): δ = −0.25, 0.54 [2 d, $^2J(^{13}C,^{19}F)$ = 12.9 Hz, GeCH$_3$], 12.95, 17.91 (CH$_3$), 27.10 [d, $^2J(^{13}C,^{19}F)$ = 13.0 Hz, GeCH], 29.42, 29.57 (CH$_3$), 31.51 [d, $^2J(^{13}C,^{19}F)$ = 13.1 Hz, GeCH], 44.70, 45.15 (CH$_2$), 123.83, 123.92, 128.72, 129.50 (CH), 210.00, 210.24 (C=O). — GC/MS, *m/z* (%): 215 (100) [M$^+$ − F], 123 (22) [Me$_2$GeF$^+$], 67 (12) [C$_5$H$_7^+$].

$$C_9H_{17}FGeO \; (232.8) \quad \text{Calcd. C } 46.43 \; \text{H } 7.36$$
$$\text{Found C } 46.2 \; \text{H } 7.4$$

Methyl (4E)-3-(Fluorodimethylgermyl)-4-hexenoate (**3c**)/*Methyl (3Z)-5-(Fluorodimethylgermyl)-3-hexenoate* (**4a**): From 1.0 g (8.1 mmol) of **2c** 0.30 g (65%) of **3c/4a** (1:0.38) is obtained as a colourless oil, b.p. 120°C/15 Torr. — ^{1}H NMR (CDCl$_3$): δ = 0.48, 0.49, 0.52, 0.54 [4 d, $^3J(^1H,^{19}F)$ = 7.1 Hz, 6H, GeCH$_3$], 1.21 (d, ^3J = 7.2 Hz, 0.8H, CHCH$_3$), 1.64 (d, ^3J = 5.0 Hz, 2.2H, =CHCH$_3$), 2.4, 3.1 (2 m, 3H, CH, CH$_2$), 3.64, 3.66 (2 s, 3H, CO$_2$CH$_3$), 5.4 (m, 2H, CH). — ^{13}C NMR (CDCl$_3$) **3c**: δ = −0.35, −0.06 [2 d, $^2J(^{13}C,^{19}F)$ = 9.5 Hz, GeCH$_3$], 17.94 (CH$_3$), 32.55 [d, $^2J(^{13}C,^{19}F)$ = 12.3 Hz, CH], 34.48 (CH$_2$), 51.99 (CH$_3$), 124.55, 128.78 (CH), 174.64 (C=O); **4a**: δ = −1.66, −1.12 [2 d, $^2J(^{13}C,^{19}F)$ = 11.2 Hz, GeCH$_3$], 14.45 (CH$_3$), 26.40 [d, $^2J(^{13}C,^{19}F)$ = 10.6 Hz, CH], 32.95 (CH$_2$), 51.74 (CH$_3$), 119.67, 133.65 (CH), 171.93 (C=O). — GC/MS **3c**, *m/z* (%): 250 (7) [M$^+$], 231 (20) [M$^+$ − F] 123 (27) [Me$_2$GeF$^+$], 68 (100) [C$_5$H$_8^+$]. **4a**, *m/z* (%): 250 (4), 231 (5), 123 (28), 68 (100).

$$C_9H_{17}FGeO_2 \; (248.8) \quad \text{Calcd. C } 43.44 \; \text{H } 6.89$$
$$\text{Found C } 43.2 \; \text{H } 7.0$$

Methyl (2α,5α)-1,1,5-Trimethyl-1-germa-3-cyclopentene-2-carboxylate (**5a**): During preparation of **3c/4a** removal of excess diene **2c** gives a fraction of 0.09 g, b.p. 60°C/0.01 Torr, which contains 30 mol-% of **5a**. — ^{1}H NMR (CDCl$_3$): δ = 0.47, 0.59 (2 s, 6H, GeCH$_3$), 1.13 (d, ^3J = 7.5 Hz, 3H, CHCH$_3$), 2.00 (m, 1H, CHCH$_3$), 2.94 (d, ^3J = 2.5 Hz, 1H, CH), 3.60 (s, 3H, CH$_3$); signals of the olefinic protons are superimposed by the diene signals. — ^{13}C NMR (CDCl$_3$): δ = −7.75, −2.07 (GeCH$_3$), 16.31 (CH$_3$), 26.86 (CH), 40.28 (CH), 51.10 (CH$_3$), 126.40, 141.30 (CH), 175.14 (C=O). — GC/MS, *m/z* (%): 230 (13) [M$^+$], 199 (29) [M$^+$ − OMe], 198 (38) [M$^+$ − HOMe], 135 (19) [GeOMe$_3^+$], 105 (43) [GeOMe$^+$], 95 (100) [C$_6$H$_7$O$^+$], 89 (17) [GeMe$^+$], 67 (69) [C$_6$H$_7^+$].

Ethyl (4E)-3-(Fluorodimethylgermyl)-4-hexenoate (**3d**)/*Ethyl (3Z)-5-(Fluorodimethylgermyl)-3-hexenoate* (**4b**): From 1.1 g (7.8 mmol) of **2d** 0.35 g (70%) of **3d/4b** (1:0.5) is obtained as a colourless oil, b.p. 130°C/15 Torr. — ^{1}H NMR (CDCl$_3$): δ = 0.47, 0.49 [2 d, $^3J(^1H,^{19}F)$ = 6.9 Hz, GeCH$_3$], 0.54, 0.52 [2 d, $^3J(^1H,^{19}F)$ = 7.2 Hz, GeCH$_3$], 1.21 (d, ^3J = 7.2 Hz, CHCH$_3$), 1.22, 1.23 (2 t, ^3J = 7.2 Hz, CH$_2$CH$_3$), 1.62 (dd, ^3J = 5.9, ^4J = 1.0 Hz, =CHCH$_3$), 2.4 (m, CHCH$_2$), 2.62 (dd, ^3J = 5.9, ^4J = 1.6, =CHCH$_2$), 3.0 (m, CH), 4.1 (m, CH$_2$CH$_3$), 5.2−5.6 (m, CH). — ^{13}C NMR (CDCl$_3$) **3d**: δ = 0.29, 0.08 [2 d, $^2J(^{13}C,^{19}F)$ = 12.9 Hz, GeCH$_3$], 14.14 (CH$_3$), 17.94 (CH$_3$), 32.58 [d, $^2J(^{13}C,^{19}F)$ = 12.7 Hz, CH], 34.73 (CH$_2$), 60.61 (CH$_2$), 124.41, 128.89 (CH), 174.34 (C=O); **4b**: δ = −1.68, −1.08 [2 d, $^2J(^{13}C,^{19}F)$ = 11.4 Hz, GeCH$_3$], 14.14 (CH$_3$), 14.47 (CH$_3$), 26.43 [d, $^2J(^{13}C,^{19}F)$ = 10.1 Hz], 33.24 (CH$_2$), 61.08 (CH$_2$), 119.86, 133.49

(CH), 171.51 (C=O). — GC/MS **3d**, m/z (%): 264 (4) [M$^+$], 245 (199) [M$^+$ — F], 123 (12) [Me$_2$GeF$^+$], 68 (37) [C$_5$H$_8^+$], 53 (9) [C$_4$H$_5^+$]; **4b**: 264 (5), 245 (100), 123 (6), 68 (17), 53 (7).

C$_{10}$H$_{19}$FGeO$_2$ (262.9)   Calcd. C 45.69 H 7.29
                                   Found C 44.8 H 7.5

Methyl 3-(Fluorodimethylgermyl)-4-pentenoate (**3e**)/*Methyl (3Z)-5-(Fluorodimethylgermyl)-3-pentenoate* (**4c**): From 0.90 g (8.0 mmol) of **2e** 0.28 g (63%) of **3c**/**4c** (1:2.3) is obtained as a colourless oil, b.p. 110°C/15 Torr. — ^{1}H NMR (CDCl$_3$) **3e**: δ = 0.58, 0.65 [2 d, $^3J(^1$H,^{19}F) = 7.4 Hz, 6H, GeCH$_3$], 2.6 (m, 3H, CH,CH$_2$), 3.70 (s, 3H, CH$_3$), 4.91 (ddd, ^3J = 17.2, ^2J = 1.2, ^4J = 1.2 Hz, 1H, =CH—H), 5.00 (ddd, ^3J = 10.5, ^4J = 1.2, ^2J = 1.2 Hz, 1H, =CH—H), 5.83 (m, 1H, CH=CH$_2$); **4c**: δ = 0.55 [d, $^3J(^1$H,^{19}F) = 7.5 Hz, 6H, GeCH$_3$], 1.99 [ddd, $^3J(^1$H,^{19}F) = 5.6, ^3J = 8.4, ^4J = 0.6 Hz, 2H, GeCH$_2$], 3.06 (d, ^3J = 6.5 Hz, 2H, CH$_2$), 3.67 (s, 3H, CH$_3$), 5.56 (dtt, ^3J = 10.7, ^3J = 6.7, ^4J = 0.8 Hz, =CHCH$_2$CO$_2$), 5.68 (dtt, ^3J = 10.7, ^3J = 8.4, ^4J = 1.2 Hz, GeCH$_2$CH=); assignments are confirmed by selective decoupling. — ^{13}C NMR (CDCl$_3$) **3e**: δ = 0.08, 0.40 [2 d, $^2J(^{13}$C,^{19}F) = 11.5 Hz, GeCH$_3$], 33.64 (CH$_2$), 33.81 [d, $^2J(^{13}$C,^{19}F) = 11.0 Hz, GeCH], 52.10 (CH$_3$), 114.63 (CH$_2$), 137.56 (CH), 172.95 (C=O); **4c**: δ = 0.50 [d, $^2J(^{13}$C,^{19}F) = 11.5 Hz, GeCH$_3$], 20.47 [d, $^2J(^{13}$C,^{19}F) = 11.4 Hz, GeCH$_2$], 32.55 (CH$_2$), 51.78 (CH$_3$), 120.26 (GeCH$_2$CH=), 126.98 (=CHCH$_2$CO$_2$), 171.99 (C=O). — GC/MS **3e**, m/z (%): 217 (59) [M$^+$ — F], 123 (27) [Me$_2$GeF$^+$], 82 (39) [C$_2$H$_6$O$^+$], 54 (C$_4$H$_6^+$]; **4c** 236 (1) [M$^+$], 217 (100), 123 (6), 82 (14), 54 (38).

C$_8$H$_{15}$FGeO$_2$ (234.8)   Calcd. C 40.92 H 6.44
                                Found C 39.8 H 6.7

Methyl 1,1-Dimethyl-1-germa-3-cyclopentene-2-carboxylate (**5b**): During preparation of **3e**/**4c** removal of excess of the diene gives a fraction of 0.15 g (25%) of **5b** as a colourless oil, b.p. 100°C/15 Torr. — ^{1}H NMR (CDCl$_3$): δ = 0.25, 0.47 (2 s, 6H, GeCH$_3$), 1.54 (dd, ^2J = 13.0, ^3J = 3.0 Hz, 1H, CH—H), 1.64 (dd, ^2J = 13.0, ^3J = 3.1 Hz, 1H, CH—H), 2.94 (d, ^3J = 2.8 Hz, CH), 3.59 (s, 3H, CH$_3$), 5.8 (m, 1H, CH), 6.1 (m, 1H, CH). — ^{13}C NMR: δ = 4.34, −1.58 (GeCH$_3$), 19.43 (CH$_3$), 39.93 (CH), 51.12 (CH$_3$), 128.50, 134.07 (CH), 175.26 (C=O). — MS, m/z (%): 216 (26) [M$^+$], 184 (10) [M$^+$ — HOMe], 169 (8) [M$^+$ — HOMe-Me], 135 (45) [Me$_3$GeO$^+$], 105 (50) [MeGeO$^+$], 89 (46) [MeGe$^+$], 81 (81) [C$_5$H$_5$O$^+$], 53 (100) [C$_4$H$_5^+$].

C$_8$H$_{14}$GeO$_2$ (214.8)   Calcd. C 44.73 H 6.57
                               Found C 44.5 H 6.7

Methyl 3-(Fluorodimethylgermyl)-5-methyl-4-hexenoate (**3f**): From 1.2 g (8.5 mmol) of **2f** 0.29 g (58%) of **3f** is obtained as a colourless oil, b.p. 75°C/0.08 Torr. — ^{1}H NMR (CDCl$_3$): δ = 0.48, 0.51 [2 d, $^3J(^1$H,^{19}F) = 7.1 Hz, 6H, GeCH$_3$], 1.60 (d, ^4J = 1.3 Hz, 3H, CH$_3$), 1.67 (d, ^4J = 1.4 Hz, 3H, CH$_3$), 2.5 (m, 3H, CH, CH$_2$), 3.64 (s, 3H, CH$_3$), 4.92 (m, 1H, =CH). — ^{13}C NMR (CDCl$_3$): δ = −0.23, −0.16 [2 d, $^2J(^{13}$C,^{19}F) = 12.7 Hz, GeCH$_3$], 18.00, 25.71 (CH$_3$), 29.45 [d, $^2J(^{13}$C,^{19}F) = 12.8 Hz, GeCH], 35.32 (CH$_2$), 51.83 (CH$_3$), 121.98 (CH), 132.47 (C$_q$), 174.45 (C=O). — MS, m/z (%): 264 (10) [M$^+$], 245 (4) [M$^+$ — F], 123 (18) [Me$_2$GeF$^+$], 109 (15) [C$_7$H$_9$O$^+$], 99 (23) [C$_5$H$_7$O$_2^+$], 82 (100) [C$_6$H$_{10}^+$], 67 (50) [C$_5$H$_7^+$].

C$_{10}$H$_{19}$FGeO$_2$ (262.9)   Calcd. C 45.70 H 7.29
                                   Found C 44.9 H 7.7

Methyl 3-(Bromodimethylgermyl)-5-methyl-4-hexenoate (**3g**): From 1.2 g (8.5 mmol) of **2f** 0.38 g (62%) of **3g** is obtained as a yellow oil, b.p. 100°C/0.08 Torr. — ^{1}H NMR (CDCl$_3$): −0.73, −0.77 (2 s, 6H, GeCH$_3$), 1.63, 1.68 (2 d, ^4J = 1.2 Hz, 6H, CH$_3$), 2.48 (dd, ^2J = 16.1, ^3J = 9.2 Hz, 1H, CH—H), 2.64 (dd, ^2J = 16.1, ^3J = 4.3 Hz, 1H, CH—H), 2.80 (ddd, ^3J = 11.8, ^3J = 9.2, ^3J =

4.3 Hz, 1H, GeCH), 3.62 (s, 3H, CH$_3$), 4.90 (m, 1H, CH). — ^{13}C NMR (CDCl$_3$): 2.56, 3.45 (GeCH$_3$), 18.40, 25.83 (CH$_3$), 30.80 (CH), 35.75 (CH$_2$), 51.69 (CH$_3$), 121.57 (CH), 133.66 (C$_q$), 173.55 (C=O). — MS, m/z (%): 324 (3) [M$^+$], 245 (100) [M$^+$ — Br], 109 (75) [C$_6$H$_{10}^+$], 67 (49) [C$_5$H$_7^+$].

C$_{10}$H$_{19}$BrGeO$_2$ (323.8)   Calcd. C 37.10 H 5.87
                                    Found C 37.1 H 6.0

Dimethyl (3α,4α)- and (3α,4β)-α,α′,1,1-Tetramethyl-1-germa-3,4-cyclopentanediacrylate (**7a, b**): To a solution of 1.0 g (1.9 mmol) of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germa-2,3-benzonorbornadiene in 20 ml of anhydrous benzene under argon is added 1.1 g (8.1 mmol) of **6a**. After stirring at 70°C for 4 h the mixture is cooled to room temp., and the volatile components are removed in vacuo (20°C/15 Torr). 1,2,3,4-Tetraphenylnapthalene is precipitated by addition of 20 ml of pentane and filterd off. Kugelrohr distillation of the filtrate yields 0.52 g (77%) of **7a**/**7b** (1:1) as a colourless oil, b.p. 150°C/0.01 Torr, that crystallizes upon standing. Repeated crystallization from methanol gives 0.11 g (16%) of the pure *trans* isomer **7a**, m.p. 111°C. Addition of water to the reaction mixture does not change the reaction course. — ^{1}H NMR (CDCl$_3$) **7a**: δ = 0.34 (s, 6H, GeCH$_3$), 0.57 (dd, ^2J = 13.3, ^3J = 11.2 Hz, 2H, CH$_2$), 1.17 (dd, ^2J = 13.4, ^3J = 5.6 Hz, 2H, CH$_2$), 1.76 (d, ^4J = 1.4 Hz, 6H, CH$_3$), 2.3 (m, 2H, CH), 3.67 (s, 6H, CH$_3$), 6.53 (d, ^4J = 1.4 Hz, 2H, =CH); **7b**: δ = 0.33, 0.41 (2 s, 6H, GeCH$_3$), 0.82 (dd, ^2J = 13.5, ^3J = 6.3 Hz, 2H, CH$_2$), 0.99 (dd, ^2J = 13.4, ^3J = 6.3 Hz, 2H, CH$_2$), 1.79 (d, ^4J = 1.4 Hz, 6H, CH$_3$), 2.9 (m, 2H, CH), 3.69 (s, 6H, CH$_3$), 6.57 (d, ^4J = 1.4 Hz, 2H, =CH). — ^{13}C NMR (CDCl$_3$) **7a**: δ = −1.70 (GeCH$_3$), 12.62 (CH$_3$), 21.33 (CH$_2$), 46.26 (CH), 51.54 (CH$_3$), 126.02 (C$_q$), 146.61 (CH), 168.46 (C=O); **7b**: δ = −1.82, −0.63 (GeCH$_3$), 12.52 (CH$_3$), 19.59 (CH$_2$), 43.68 (CH), 51.54 (CH$_3$), 126.85 (C$_q$), 144.06 (CH), 168.37 (C=O). — MS: **7a**, m/z (%): 325 (3) [M$^+$ — OMe], 230 (100) [M$^+$ — C$_7$H$_{10}$O$_2$], 215 (18) [M$^+$ — C$_8$H$_{13}$O$_2$], 135 (68) [Me$_3$GeO$^+$], 105 (32) [MeGeO$^+$], 95 (73) [C$_6$H$_7$O$^+$], 67 (58) [C$_5$H$_7^+$]. — GC/MS: **7a** and **7b** show a similar fragmentation pattern.

C$_{16}$H$_{26}$GeO$_4$ (355.0)   Calcd. C 54.13 H 7.38
                                  Found C 54.3 H 7.8

5-(Fluorodimethylgermyl)-2,6,6-trimethyl-3-cyclohepten-1-one (**10a**): From 1.0 g (6.7 mmol) of eucarvone (**8**) 0.20 g (40%) of **10a** is obtained as a colourless oil, b.p. 130°C/0.5 Torr. NMR spectra show the existence of two diastereomeres (GC 7:1). — ^{1}H NMR (CDCl$_3$): δ = 0.57, 0.63 [2 d, $^3J(^1$H,^{19}F) = 7.2 Hz, GeCH$_3$], 0.99 (s, CH$_3$), 1.15 (d, ^3J = 7.1 Hz, CH$_3$), 1.20 (s, CH$_3$), 2.04 [dd, $^3J(^1$H,^{19}F) = 9.4, ^3J = 8.0 Hz, GeCH], 2.13 (d, ^2J = 11.3 Hz, CH$_2$), 2.99 (d, ^2J = 11.3 Hz, CH$_2$), 3.3 (m, CH), 5.42 (dd, ^3J = 11.3, ^3J = 4.3 Hz, =CH), 5.72 (ddd, ^3J = 11.3, ^3J = 8.3, ^4J = 2.7 Hz, =CH); 0.51, 0.55 [2 d, $^3J(^1$H,^{19}F) = 7.2 Hz, GeCH$_3$], 1.00 (s, CH$_3$), 1.16 (s, CH$_3$), 2.20 (m, GeCH), 2.25 (d, ^2J = 12.0 Hz, CH$_2$), 2.69 (d, ^2J = 11.8 Hz, CH$_2$), 3.18 (m, CH), 5.48 (ddd, ^3J = 10.8, ^3J = 3.4, ^4J = 1.6 Hz, =CH). — ^{13}C NMR (CDCl$_3$): δ = 2.70, 3.78 [2 d, $^2J(^{13}$C,^{19}F) = 11.2 Hz, GeCH$_3$], 14.89, 29.27, 31.24 (CH$_3$), 39.18 (C$_q$), 46.81 [d, $^2J(^{13}$C,^{19}F) = 11.1 Hz, GeCH], 46.95 (CH), 56.85 (CH$_2$), 128.73 (CH), 141.17 (CH), 207.88 (C=O); 16.74, 28.19, 30.31 (CH$_3$), 46.27 [d, $^2J(^{13}$C,^{19}F) = 11.0 Hz, GeCH], 56.53 (CH$_2$), 128.03 (CH), 133.01 (CH), 210.00 (C=O). — GC/MS major product, m/z (%): 274 (3) [M$^+$], 255 (50) [M$^+$ — F], 239 (12) [M$^+$ — Me — F], 135 (10) [C$_9$H$_{11}$O$^+$], 123 (44) [Me$_2$GeF$^+$], 119 (67) [Me$_3$Ge$^+$], 109 (100) [C$_8$H$_{13}^+$], 93 (93) [GeF$^+$], 81 (28) [C$_6$H$_9^+$], 67 (69) [C$_5$H$_7^+$]; minor product: 274 (4), 255 (43), 135 (18), 123 (34), 119 (47), 109 (100), 93 (28), 81 (22), 67 (52).

C$_{12}$H$_{21}$FGeO (272.9)   Calcd. C 52.81 H 7.76
                               Found C 53.5 H 8.0

5-(Bromodimethylgermyl)-2,6,6-trimethyl-3-cyclohepten-1-one **(10b)**: From 1.0 g (6.7 mmol) of eucarvone **(8)** 0.30 g (48%) of **10b** is obtained as a yellow oil, b.p. 140°C/0.5 Torr. NMR spectra show the existence of two diastereomeres (GC 4:1). — ^{1}H NMR (CDCl$_3$): δ = 0.88 (s, GeCH$_3$), 1.02 (s, CH$_3$), 1.08 (d, ^3J = 7.9 Hz, CH$_3$), 1.11 (s, CH$_3$), 2.09 (d, ^2J = 11.2 Hz, CH$_2$), 2.25 (d, ^3J = 8.5 Hz, CH), 3.03 (d, ^2J = 11.2 Hz, CH$_2$), 3.2 (m, CH), 5.54 (dd, ^3J = 11.0, ^3J = 6.4 Hz, =CH), 5.75 (ddd, ^3J = 11.0, ^3J = 8.3, ^4J = 1.9 Hz, =CH); 0.85 (s, GeCH$_3$), 0.99 (CH$_3$), 1.15 (s, CH$_3$), 2.11 (d, ^2J = 11.5 Hz, CH$_2$), 2.38 (d, ^3J = 7.2 Hz, CH$_3$), 2.68 (d, ^2J = 11.5 Hz, CH$_2$). Selective decoupling experiments reveal coupling between olefinic protons (δ = 5.54 and 5.75) and signals according to CHCH$_3$ and GeCH. — ^{13}C NMR (CDCl$_3$): δ = 6.98, 7.43 (GeCH$_3$), 14.78, 29.72, 30.40 (CH$_3$), 39.93 (C$_q$), 47.15, 47.33 (CH), 55.84 (CH$_2$), 128.91, 131.20 (CH), 208.50 (C=O); 5.83 (GeCH$_3$), 16.81, 27.75, 30.42 (CH$_3$), 40.41 (C$_q$), 45.53, 46.84 (CH), 56.92 (CH$_2$), 129.50, 133.10 (CH), 210.10 (C=O). — GC/MS major product, m/z (%): 334 (4) [M$^+$], 319 (37) [M$^+$ − Me], 255 (83) [M$^+$ − Br], 237 (14) [M$^+$ − C$_6$H$_9$O], 135 (100) [Me$_3$GeO$^+$], 109 (82) [C$_8$H$_{13}^+$], 94 (19) [MeBr$^+$], 81 (22) [C$_6$H$_9^+$], 67 (27) [C$_5$H$_7^+$]; minor product: 334 (1), 319 (11), 255 (18), 135 (33), 109 (100), 94 (7), 81 (34), 67 (43).

C$_{12}$H$_{21}$BrGeO (333.8) Calcd. C 43.18 H 6.34
Found C 43.2 H 6.6

4-[(Bromodimethylgermyl)methyl]-3,5-dimethyl-3-cyclohexen-1-one **(11)**: From 0.71 g (5.2 mmol) of **9** 0.22 g (40%) of **11** is obtained as a yellow oil, b.p. 120°C/0.01 Torr. — ^{1}H NMR (CDCl$_3$): δ = 0.81, 0.84 (2 s, 6H, GeCH$_3$), 0.96 (d, ^3J = 6.1 Hz, 3H, CHCH$_3$), 1.60 (s, 3H, CH$_3$), 2.0−2.7 (br. m, 7H, CH$_2$, CH). — ^{13}C NMR (CDCl$_3$): δ = 4.86, 5.23 (GeCH$_3$), 19.39 (CH$_3$), 19.50 (CH$_3$), 26.91 (CH$_2$), 36.78 (CH), 45.04, 46.55 (CH$_2$), 122.87, 131.76 (C$_q$), 210.10 (C=O). — MS, m/z (%): 320 (41) [M$^+$], 305 (79) [M$^+$ − Me], 278 (21) [M$^+$ − C$_2$H$_2$O], 225 (16) [M$^+$ − CH$_4$Br], 183 (100) [Me$_2$GeBr$^+$], 137 (15) [M$^+$ − Me$_2$GeBr], 109 (55) [C$_8$H$_{13}^+$], 95 (95) [C$_7$H$_{11}^+$], 67 (73) [C$_5$H$_7^+$], 55 (45) [C$_4$H$_7^+$].

C$_{11}$H$_{20}$BrGeO (320.8) Calcd. C 41.18 H 6.28
Found C 40.1 H 6.0

* Dedicated to Prof. *Klaus Hafner* on the occasion of his 65th birthday.

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