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MEDIUM-SIZED ORGANOMETALLIC DERIVATIVES

IX * TRANSANNULAR NUCLEOPHILIC SUBSTITUTION IN ORGANOSILICON AND ORGANOGERMANIUM ELEVEN-MEMBERED RINGS **

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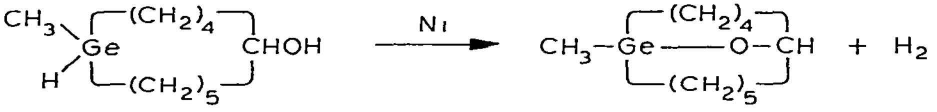
Summary

Olah's reagent (HF-pyridine) reacts easily at room temperature with 6,6-dimethyl-6-sila-(and 6,6-dimethyl-6-germa-)-cycloundecanols. In each case, the principal product formed is not the expected cyclic organosilicon (or organogermanium) fluoride but the compound resulting from a transannular substitution reaction at the heteroatom with cleavage of one intracyclic heteroatom-carbon bond The structures of the derivatives obtained were determined by ^{19}F NMR and, after methylation, by mass spectrometry, ^{1}H and ^{13}C NMR, and chemically

Introduction

The study of functional medium-sized organosilicon and organogermanium compounds, and especially eleven-membered derivatives, pointed out the existence of transannular interactions between the heteroatom and a function located on the opposite side of the ring [1,2,3]

Similarly, for this ring size, transannular dehydrocondensation [4] (eq. 1)



(1)

and hydrogermylation [5] (eq 2) reactions were carried out

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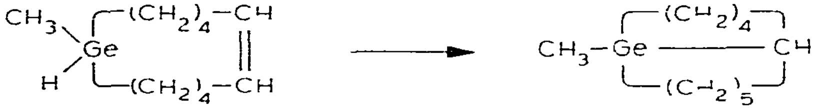
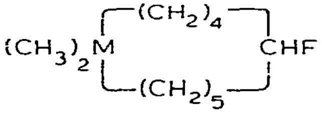
* For Part VIII see ref 1

** Dedicated to Professor Henri Normant on the occasion of his 72nd birthday on 25th June 1979



(2)

With the aim of detecting a possible transannular interaction between a fluorine atom and a silicon or germanium atom using ^{19}F NMR spectroscopy we tried to synthetize 6,6-dimethyl-6-sila-(and 6,6-dimethyl-6-germa)-1-fluorocycloundecanes



(M = Si Ge)

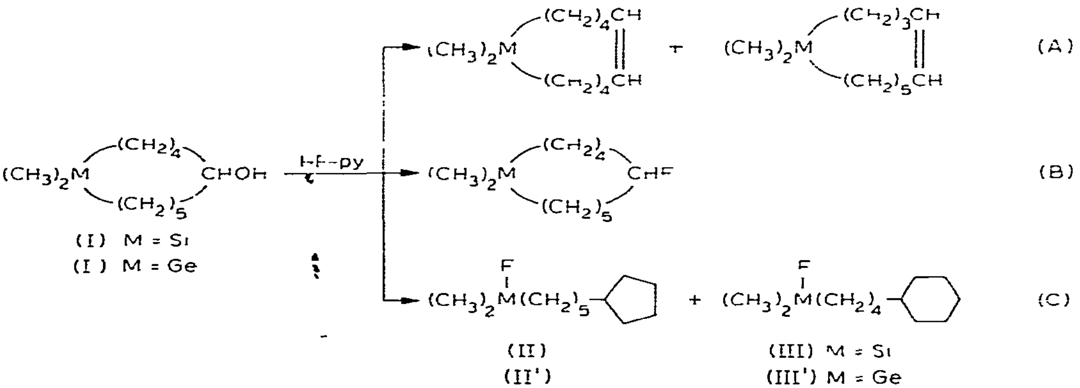
from the corresponding sila- and germacycloalcanols

Results and discussion

The synthesis of fluorocycloalkanes from the cyclanols is usually difficult and only Olah's reagent (HF-pyridine) [6,7] seems to achieve this substitution with a good yield. This reagent was therefore used for the preparation of fluorosila- (and germa-) cycloalcanes from sila- and germa cycloundecanols [8,9]

Several compounds may result from elimination (A) or substitution (B) reactions (Scheme 1)

SCHEME 1



However, in the two cases (M = Si, Ge) the reaction leads to a liquid giving a single peak on GLC (SE30 20%, 20 ft column) which is not the expected organometallic fluoroalkane:

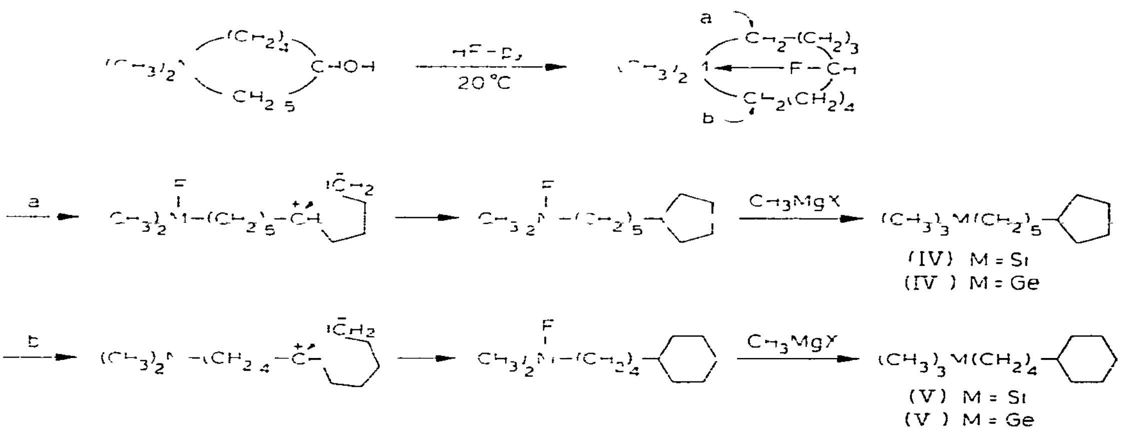
— the absence of a ν_{OH} absorption band in the IR spectrum excludes the presence of the starting cyclanol.

— the presence of a weak absorption band in the range 1640 cm^{-1} could correspond to a small quantity of ethylenic compounds coming from reaction (A) and (or) the linear derivatives resulting from the cleavage of these rings with HF.

— weak downfield (4 to 6 ppm/TMS) resonance peaks are observed in the ^{1}H NMR spectrum, confirming the presence of a small quantity of ethylenic compounds Upfield (0 2 ppm/TMS) are two peaks of equal intensity corresponding to six methyl protons $(CH_3)_2\overset{|}{M}$—F In the ^{19}F NMR spectrum only the signal corresponding to $-\underset{|}{\overset{|}{M}}-F$ appears (δ, ppm/$CFCl_3$· 160 for the silicon compound and 190 for the germanium derivative) and not that of $>$CH—F

Thus the product formed in this reaction is not the expected cyclic fluoride arising from reaction (B) but may contain isomers II and III (M = Si) or II′ and III′ (M = Ge) resulting from the transannular reaction of type C shown in Scheme 2

SCHEME 2



The first step involves the nucleophilic substitution of a hydroxyl group with a fluorine atom and leads to the corresponding fluoride, but fluorine may be near enough to the heteroatom to allow the possibility of a transcyclic intramolecular S_N2 substitution. In this reaction, owing to the dissymetry of the molecule, two chain isomers (II and III for M = Si; II′ and III′ for M = Ge) may result from the cleavage of either of the intracyclic metal-carbon bonds. The mechanism is quite similar to that proposed by Cope (10) for transannular reactions in organic chemistry

Because of the difficulty in isolating fluoride isomers in GLP, we attempted their chemical identification after methylation

The resulting product, (M) for Si and (M′) for Ge, gives two principal peaks in gas chromatography (Fig. 1) A (triple: A_1, A_2, A_3) and B (single) for M = Si, A′ (triple· A'_1, A'_2, A'_3) and B′ (single) for M = Ge.

Peak A_3 (or A'_3) corresponds to a small quantity of unreacted fluoro derivatives Peak A_2 (or A'_2) has the same retention time as that of the linear alkane $(CH_3)_3M(n\text{-}C_{10}H_{21})$ prepared according to eq 3 but, at least in the case of the

$$(CH_3)_3MCl + n\text{-}C_{10}H_{21}MgBr \rightarrow (CH_3)_3M(n\text{-}C_{10}H_{21}) + MgBrCl \qquad (3)$$

germanium derivative where the product corresponding to peak A′ was isolated by GLP, the ^{13}C spectrum unequivocally shows the absence of the saturated linear compound in it. Peaks A and A′ probably consist of a mixture of linear ethylenic isomers $(CH_3)_3M\ C_{10}H_{19}$ (IR: ν(C=C) 1640 cm^{-1}, ^{1}H NMR complex signal from 4 to 6 ppm/TMS, mass spectrum: peak M-CH_3 m/e 243 for the

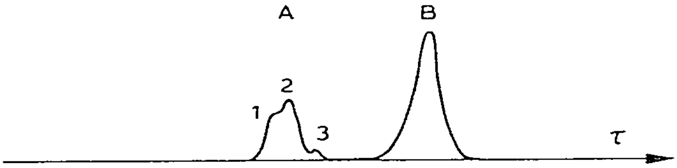
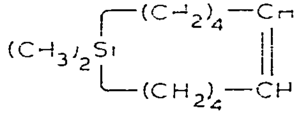
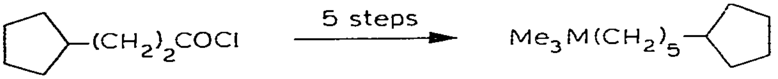


Fig. 1 Chromatogram (SE 30 20%, 20 ft, 160°C, He) of the mixture (M) resulting from the action of HF-pyridine with 6,6-dimethyl-6-silacycloundecanol followed by methylation

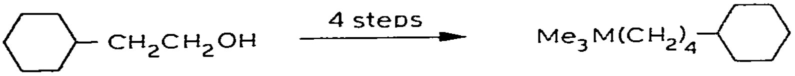
germanium derivative (^{74}Ge)) The co-injection of A and  and A′ with the corresponding germacycloundecene points out the absence of these cyclenes in A and A′ respectively

In order to identify the second peak of the mixtures (M) and (M′) chemically, the isomers (IV) and (V) for M = Si and (IV′) and (V′) for M = Ge were synthesized (cf Experimental part) from commercial 3-cyclopentyl propanoyl chloride:



(IV) M = Si
(IV′) M = Ge

and 2-cyclohexyl ethanol respectively



(V) M = Si
(V) M = Ge

In spite of their different structures, isomers IV and V have exactly the same retention time in GLC (SE30 20%, 20 ft and OV17 20%, 10 ft.) and in liquid chromatography (Micropack SI 10, 1 ft., pentane). This retention time is also exactly the same as that of the second peak B of the mixture M.

Likewise, the organogermanium isomers IV′ and V′ have the same retention time as the second peak B′ of the corresponding organogermanium mixture (M′). Chromatography, therefore, does not enable the respective percentage of these isomers to be found in the mixture.

Mass spectra (GLC-coupled spectrometer) of the beginning, the center and the end of peak B are identical, this means that peak B corresponds to only one isomer or to derivatives having the same retention time. The mass spectrum of peak B (M = Si) contains, besides the molecular ion M^+ for m/e 212, a series of fragments which are again found integrally in the spectrum of the reference product IV. The mass spectra of IV and V are similar, the difference lying only in the absence, in V, of the fragments m/e 169 and 69 which seem therefore characteristic of isomer IV.

In the case of the germanium derivative, where it was possible to isolate by GLP a sufficient quantity of the corresponding second peak B', ^{13}C NMR allowed the nature of this product to be established with some certainty ^{13}C NMR spectra of compounds B' and IV' are identical On the other hand, some important signals of the spectrum of isomer V' (which is very different from that of IV) do not appear in the spectrum of the compound B', thus compound B' only consists of isomer IV' within the limits of NMR spectroscopy

Conclusion

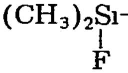
The action of Olah's reagent (HF-pyridine) with 6,6-dimethyl-6-sila-(and 6,6-dimethyl-6-germa-)-cycloundecanols at room temperature does not lead to the expected cyclic organometallic fluorides Several products are formed in this reaction, the most abundant of them proceeds from a transannular nucleophilic substitution at the heteroatom with cleavage of one intracyclic heteroatom-carbon bond

The preferential cleavage of only one of the two intracyclic metal—carbon bonds probably results from a particular conformation of these strained rings

Experimental

NMR spectra were recorded on VARIAN T 60 and CAMECA 250 (^1H and ^{13}C) spectrometers, mass spectra on coupled PYE UNICAM-AEI MS 20 and RIBER R 10-10 spectrometers, and IR spectra on a Perkin—Elmer 457 spectrophotometer

Action of HF-pyridine on 6,6-dimethyl 6-sila cycloundecanol

In a polythene flask a mixture of dimethylsilacycloundecanol (I) (2 08 g, 9 mmol) and Olah's reagent (15 6 g) is stirred at room temperature for 3 h The reaction is slightly exothermic After extraction of the mixture with pentane and subsequent washing, the organic solution is dried with sodium sulfate and distilled, giving a mixture (F) of organosilicon fluorides (1 28 g, 65% yield) B.p 118—119°C/14 mmHg, GLC single peak (SE30 20% 20 ft and OV17 20% 10 ft columns) ^{19}F NMR (δ, ppm/CFCl$_3$, CCl$_4$) 160 multiplet corresponding to  $(CH_3)_2\underset{\underset{F}{|}}{Si}—CH_2—$ $^3J(HF)$ 7 Hz, this value is in good agreement with that of trimethylfluorosilane (CCl$_4$, δ 159 ppm/CFCl$_3$) ^1H NMR (δ, ppm/TMS, CCl$_4$) 0.2 doublet corresponding to 6 protons of $(CH_3)_2SiF$, J 7 Hz, 0 3 to 1 8 multiplet (19 protons), 4 to 6, weak complex signal.

Action of CH$_3$MgI on organosilicon fluorides (F)

The action of a large excess of methylmagnesium iodide on the mixture of fluorides (F) (1 13 g) leads to the mixture (M) of methylated organosilicon derivatives (0.59 g) b p. 126°C/33 mmHg. GLC (SE30 20% 20 ft column, 150°C, He) 2 peaks. A (triple) and B (single). ^1H NMR (δ, ppm/TMS, CCl$_4$) 0 02, singlet $(CH_3)_3Si$; 0 3 to 2,2, multiplet; 4 to 6, weak complex signal Mass spectra (GLC-coupled spectrometer) peak A *m/e*. 140, 83, 70, 57, 56, 55, 44, 43, 42, 40, 28 peak B m/e 212 (M^+), 197 ($M - CH_3$) 169 ($M - C_3H_7$) 83 (C_6H_{11}), 73 $(CH_3)_3Si$, 69 (C_5H_9), 59 $(CH_3)_2SiH$, 55 (C_4H_7)

1-Trimethylsilyl-5-cyclopentylpentane (IV)

(a) 3-Cyclopentyl 1-propanol (IVa) The reduction in diethyl ether of 3-cyclopentyl propanoylchloride (54 5 g, 339 mmol) with lithium aluminium hydride (17 g, 446 mmol) gives after hydrolysis, alcohol IVa (40 6 g 92% yield) b p 103.5°C/17 mmHg

(b) 1-Bromo-3-cyclopentylpropane (IVb) A mixture containing alcohol (IVa) (40 0 g, 312 mmol), 48% HBr (100 g) and sulfuric acid (82 g) was refluxed for 8 h After extraction with pentane, drying over sodium sulfate and removal of the solvent bromide (IVb) is obtained (51 8 g, 87% yield) b p 95°C/15 mmHg

(c) 5-Cyclopentyl-1-pentanol (IVc) The action of an excess of ethylene oxide, on the Grignard reagent prepared with bromide IVb (51 8 g, 271 mmol) and 8 g of magnesium turnings, leads to alcohol IVc (25 2 g, 60% yield), b p 135°C/20 mmHg, n_D^{20} 1 4619 Anal Found C, 76 68, H 12 70 $C_{10}H_{20}O$ calcd . C, 76.86, H, 12.90%

(d) 1-Bromo-5-cyclopentylpentane (IVd) Similar experimental conditions as for IVb. From alcohol IVc (25 0 g, 159 mmol) 48% hydrobromic acid (75 g) and sulfuric acid (61 g), bromide IVd is obtained (28 2 g, 80% yield), b p 128 5°C/15 mmHg, n_D^{20} 1 4814. Anal Found C, 54 96, H, 8 58, Br, 35 95 $C_{10}H_{19}Br$ calcd . C, 54.79, H, 8.74, Br, 36 46%

(e) 1-Trimethylsilyl-5-cyclopentyl pentane (IV) To the ethereal Grignard reagent solution prepared with bromide (IVd) (13 4 g, 61 mmol) and magnesium (2 g), trimethylchlorosilane (6 5 g, 59 mmol) is added After refluxing for 3 days, the mixture is hydrolyzed, extracted and distilled, giving silane IV (5.0 g, 47% yield), b.p. 115—116°C/12 mmHg, n_D^{20} 1 4498, d_4^{20} 0 8275 Anal Found. C, 73 79; H, 13 06. $C_{13}H_{28}Si$ calcd C, 73 49, H, 13 28%

1-Trimethylsilyl-4-cyclohexyl butane (V)

(a) 1-Bromo 2-cyclohexyl ethane (Va) Refluxing 2-cyclohexylethanol (88.7 g, 693 mmol), 48% hydrobromic acid (200 g) and sulfuric acid (164 g), bromide Va is obtained (128.2 g, 97% yield), b.p 90°C/13 mmHg, n_D^{20} 1 4908 Anal. Found: C, 50.34; H, 7.70, Br, 41 63. $C_8H_{15}Br$ calcd C, 50 28, H, 7.91, Br, 41.81%

(b) 4-Cyclohexyl 1-butanol (Vb) The action of an excess of ethylene oxide on the Grignard reagent prepared with the bromide Va (55 8 g, 292 mmol) leads after hydrolysis to alcohol Vb (21 9 g, 48% yield), b p 135°C/20 mmHg, n_D^{20} 1.4678. Anal. Found: C, 77 02; H, 12.74 $C_{10}H_{20}O$ calcd.. C, 76 86, H, 12 90%

(c) 1-Bromo 4-cyclohexyl butane (Vc) Heating for 8 h alcohol Vb (29 2 g, 250 mmol), 48% hydrobromic acid (80 g) and sulfuric acid (65 g), bromide Vc is isolated (40.5 g, 74% yield), b p. 131°C/17 mmHg, n_D^{20} 1.4867. Anal Found C, 54.48; H, 8.71; Br, 36.71. $C_{10}H_{19}Br$ calcd : C, 54 79, H, 8 74, Br, 36 46%

(d) 1-Trimethylsilyl 4-cyclohexylbutane (V). Trimethylchlorosilane (6 44 g, 59 mmol) is added to the Grignard reagent prepared with bromide Vc (10 9 g, 50 mmol). Distillation gives silane V (2.62 g, 25% yield), b.p. 122°C/14 mmHg,

n_D^{20} 1 4521, d_H^{20} 0 8261 Anal Found C, 73 57 H, 13 15 $C_{13}H_{28}Si$ calcd C, 73 49, H, 13 29%

Trimethyl-n-decylsilane (VI)

This derivative was obtained by the action of trimethylchlorosilane on n-decylmagnesium bromide B p 117°C/15 mmHg (Lit [11] 191°C/200 mmHg)

Action of HF-pyridine on 6,6-dimethyl-6-germa cycloundecanol

Dimethylgermacycloundecanol (I') (1 85 g, 7 mmol) is stirred for 1 h at room temperature with 16 5 g of Olah's reagent A mixture (F') of organogermanium fluorides is obtained (0 68 g, 36% yield), b p 140—141°C/14 mmHg, n_D^{20} 1 4431 GLC single peak (SE30 20%, 20 ft and OV17 20% 10 ft column) ^1H NMR (δ, ppm/TMS, CCl_4) 0 5, doublet *J* 7 Hz corresponding to 6 protons $(CH_3)_2\underset{|}{Ge}-F$, 0 8 to 2 0 multiplet ^{19}F NMR (δ ppm/$CFCl_3$ CCl_4) 190 divided septuplet $(CH_3)_2\underset{\substack{|\\ F}}{Ge}-CH_2$ $^3J(HF)$ 7 Hz (for trimethylfluorogermane, CCl_4, δ 189 ppm/$CFCl_3$). Irradiation of F in ^1H NMR gives an upfield singlet

Action of CH_3MgI on organogermanium fluorides (F')

Organogermanium fluorides resulting from the action of dimethylgermacycloundecanol (2 00 g) on HF-pyridine (12 66 g) are treated with an excess of an ethereal solution of methylmagnesium iodide After the usual treatment, the two major components of the residue (M') were separated by preparative gas chromatography (SE30 15%, 25 ft , 170°C)
First peak A' (triple) 0 120 g ^{13}C NMR (proton-decoupled $CDCl_3$) (δ(C), ppm/TMS) —2 31, 16 85, 25.10, 28 98, 29 21, 29.26, 29 35, 29 42, 29,49, 29,68, 32 64, 33 29, 33 86, 114 20 ^1H NMR (δ ppm/TMS, CCl_4) 4 to 6 complex signal. IR ν(C=C) 1640 cm^{-1} Mass spectrum *m/e* (rel intensity), Ge fragments for ^{74}Ge. 258 (M^+, 0 7), 243 ($M - CH_3$, 30), 119 (Me_3Ge, 100), 105 (Me_2GeH, 42), 89 (MeGe, 11), 69 $(CH_2)_4CH$, 7), 67 (9), 57 (10), 55 (21)
Second peak B' (single) 0 200 g ^{13}C NMR (proton-decoupled $CDCl_3$) (δ(c) ppm/TMS) —2 32, 16 87, 25 22, 28 56, 32 77, 33 62, 36 26, 40 26 Mass spectrum *m/e* (rel intensity), Ge fragments for ^{74}Ge 259 (M^+ +1,6), 243 ($M - CH_3$, 38), 227 (14), 213 (1 1), 199 (4), 185 (1 2), 171 (4), 145 (9), 131 (6), 119 (Me_3Ge, 100), 105 (Me_2GeH, 80), 89 (MeGe, 28), 81 (8), 69 (6), 67 (10)

1-Trimethylgermyl-5-cyclopentylpentane (IV')

The action of trimethylchlorogermane (6 35 g, 41 mmol) on the Grignard reagent prepared from the bromide IVd (10 95 g, 50 mmol) leads to the germane IV' (6 51 g, 50% yield), b p 136°C/17 mmHg, n_D^{20} 1.4608, d_4^{20} 0.9815. Anal Found C, 61 44; H, 11.02 $C_{13}H_{28}Ge$ calcd C, 60 76, H, 10.98%. ^{13}C NMR (proton-decoupled $CDCl_3$) (δ(C), ppm/TMS) —2 33, 16 94, 25 29, 28.69, 32 86, 33 76, 36.41, 40 37

1-Trimethylgermyl-4-cyclohexylbutane (V')

In a similar way, the action of trimethylchlorogermane (5 0 g, 33 mmol) on

Grignard reagent prepared from the bromide Vc (10 95 g 50 mmol) gives the germane V′ (3 73 g, 30% yield). b p 136—137°C/17 mmHg n_D^{20} 1 4647 d^{20} 0 9889 Anal Found C, 60 78 H, 11 00 $C_{13}H_{28}Ge$ calcd C, 60 76, H 10 98%. ^{13}C NMR (proton-decoupled $CDCl_3$) (δ(C) ppm/TMS) −2 33 16 94 25 58, 26 56, 26 87, 30 63, 33 62 37 43, 37 84

Trimethyl-n-decylgermane (VI′)

Trimethyl-n-decylgermane was prepared by the action of trimethylchlorogermane (5 00 g, 33 mmol) on n-decylmagnesium bromide Pure product 1.75 g, 21% yield B p 118°C/12 mmHg, n_D^{20} 1 4433 Anal Found C, 60 49 H, 11.55. $C_{13}H_{30}Ge$ calcd.. C, 60 29, H, 11 68% ^{13}C NMR (proton-decoupled $CDCl_3$) (δ(C) ppm/TMS) −2 33, 14 16, 16 98, 22 85, 25 26, 29 58, 29 87 29.89, 32 14, 33 51

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