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Journal of Organometallic Chemistry 580 (1999) 128–136

Journal of Organometallic Chemistry

New optically active organogermane compounds containing the adamantyl radical for heterogeneous bimetallic catalysis. Part II☆

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Received 27 July 1998

Abstract

Chiral organogermane(IV) derivatives $H_3GeAdCH_2CO_2(-)$-menthyl, $H_3GeAdCH_2CH_2O(-)$-bornyl and $H_3GeAdCH_2CH_2O_2CCH_2O(-)$-menthyl (Ad = adamantyl) have been prepared in six steps from the 1-bromoadamantane. The new optically pure organogermane reagents which have been fully characterised have been used in the preparation of heterogeneous bimetallic catalysts. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Germanium; Optically active organogermane compounds; Heterogeneous bimetallic catalysts

1. Introduction

It is now possible to graft organotin fragments, namely $Sn(n\text{-}C_4H_9)_x$ onto the surface of Rh and Pt particles supported on silica [2]. These organometallic fragments may be obtained by partial hydrogenolysis of $Sn(n\text{-}C_4H_9)_4$ on a reduced metallic surface. These new catalytic materials in which a metallic surface is partially covered by an organotin fragment, exhibit for some specific reactions much higher activity and selectivity than conventionally prepared metallic catalysts. For example, a rhodium surface modified by organotin fragments becomes fully selective for the reduction of the carbonyl function of α,β-unsaturated aldehydes [3]. In principle, by changing the steric and the electronic properties of the grafted organometallic fragments, it should be possible to control the chemio, regio and stereoselectivity of any catalytic reaction catalysed by metallic surfaces. Preliminary studies on the hydrogenolysis of chiral silyl ethers to Pd or (−)-menthylSnMe$_3$ to Rh surfaces afforded enantioselective heterogeneous catalysts, even though the enantiomeric excess (e.e) are still low [4]. In the latter case, the lability of the Sn–C bond under catalytic conditions was proposed to explain the low optical excess. The Ge–C is more stable and less labile under these conditions: for example, hydrogenolysis of $AdGeH_3$ onto SiO_2/Rh afforded [SiO_2/Rh{Ge(Ad)$(H)_{0.8}$}] where 80% of the grafted fragment had an Ad–Ge bond thermally stable until 200°C [5]. This high thermal stability and the regioselectivity of the hydrogenolysis of Ge–C versus Ge–H led us to chose an optically active organogermane derivative R*GeH_3 to modify metallic surfaces in order to obtain an enantioselective heterogeneous bimetallic catalyst.

The germane derivatives $RGeH_3$ are generally synthesised by reduction of halide derivatives $RGeX_3$ (X = Cl, Br) by Group 16 metal hydrides [6,7] in anhydrous organic solvent or by $NaBH_4$ in water [8].

The two main synthetic routes to $RGeX_3$ are the hydrogermylation reaction of unsaturated compounds with $HGeCl_3$ [6,9–13] or the oxidative addition of germylene $GeX_2 \cdot$ dioxane [14] into a carbon–halide

☆ For Part I see [1].

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PII: S0022-328X(98)01137-1

bond of various derivatives of alkyl halides. Among these derivatives we can mention AdCl [15], CBr_4 [16], α or β-haloketones, α-haloethers, or acyl halides [17,18]. The second route being more general was chosen. With linear alkyl groups, the presence of a functional group in the α, β or even γ and δ-position with respect to the metal decreases the M–C stability [M = Si, Sn, Ge], leading to intramolecular rearrangements or even decomposition [19]. Hence, the oxidative addition of $GeX_2 \cdot$dioxane has been attempted with rigid cyclic alkyl halides for which the γ-effect is weaker, in particular, in the 1–3, disubstituted adamantyl [21].

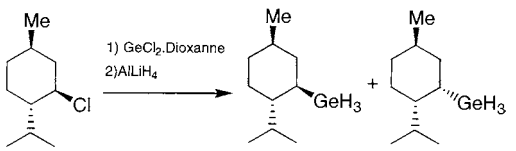
This publication reports the synthesis of these precursors $H_3GeAdCH_2CO_2(-)$-menthyl, $H_3GeAdCH_2CH_2O(-)$-bornyl and $H_3GeAdCH_2CH_2O_2CCH_2O(-)$-menthyl.

2. Results

Our preliminary experiments showed that the yield of the insertion of germylene into carbon–halide of cyclic or polycyclic alkyls varies in the same order as germylene with aliphatic alkyls [17], i.e. $C_{tertiary} > C_{secondary} > C_{primary}$.

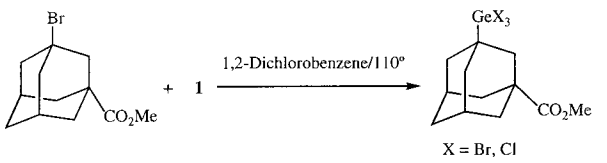
Thus, no reaction was observed with a primary halide, e.g. 9,10-dibromo(+)-camphor.

With (−)-menthyl chloride, the reaction of insertion occurred in a 60% yield. But a partial racemisation [17,20] was observed as shown by the presence in the ^{1}H-NMR spectrum of two doublets centred at 3.4 and 3.6 ppm [$^3J_{H-H} = 5$ Hz] in a ratio of 1:3 for the resonance of δ(Ge–H), (Eq. (1)):



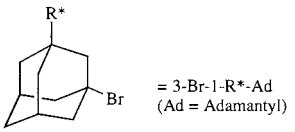
(1)

But, with a tertiary bridgehead carbon as in adamantyl halides with a functional group in 3 for instance, methyl [3-bromo, 1-adamantylacetate] the insertion reaction was nearly quantitative. The derivative **2** was isolated in a 90% yield after distillation, (Eq. (2)).



(2)

A similar synthesis has been developed to obtain a new family of chiral organogermanes derived from 1-halide adamantane substituted in the 3-position by a chiral functional group, 3-Br-1-R*–Ad, Ad = adamantyl, structure **I**:



2.1. Synthesis of chiral enantiomerically pure bromide precursors 7, 8, and 9

The bromide precursors **7**, **8**, and **9** [3-Br-1-R*–Ad; R* = $CH_2CH_2O_2CCH_2O(-)$menthyl; $CH_2CO_2(-)$menthyl; $CH_2CO_2(-)$bornyl] were prepared from 1-bromo adamantane (1-Br–Ad) in three steps, Scheme 1.

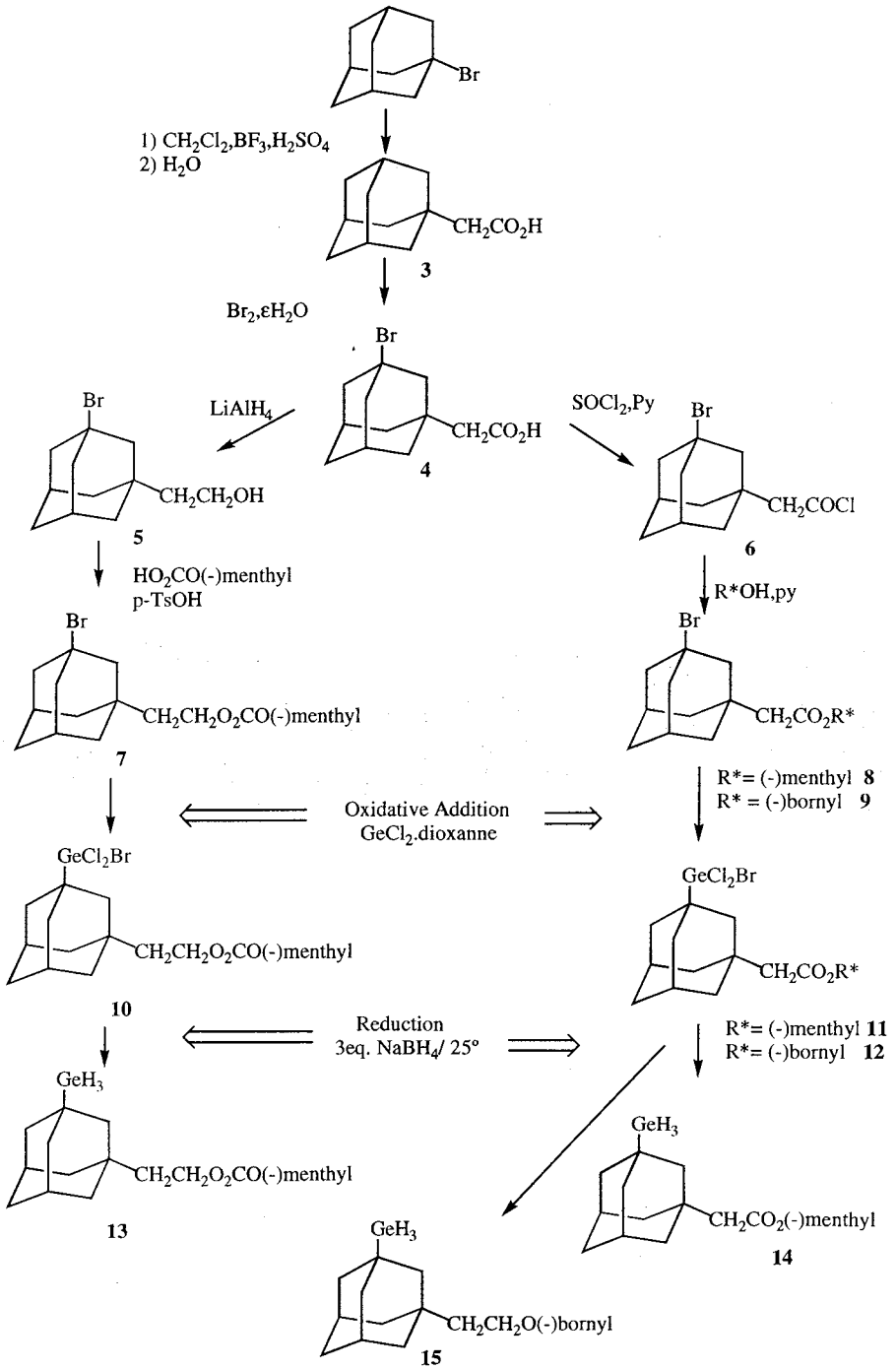
The reaction of 1-bromo adamantane and 1,1-dichoroethene in the presence of BF_3–OEt_2 in sulphuric acid medium generated in situ a cation which was converted by hydrolysis into 1-adamantylcarboxylic acid, **3** in a 71% yield. This reaction has already been observed by Bott [22].

The selective bromination of **3** at the carbon in the 3 position, was performed by reaction of **3** with 2.7 equivalents of water, in freshly distilled bromine [23]. It is worth noting that, an excess of water gave 3-hydroxy adamantyl acetic acid by a further substitution of the 3-bromide atom. Moreover, the reaction time should to be less than 2 h to avoid polybromation of the adamantyl group. Under these conditions the reaction was regioselective affording 3-bromoadamantyl acetic acid, **4** in a 94% yield.

The synthesis of enantiomerically pure esters was realised by the reaction of either (−)-menthoxyacetic acid with alcohol **5**, formed by reduction of **4**, or (−) menthol, or (−) borneol with the acid chloride **6**, obtained from **4**.

The reaction of **4** with three equivalents of $LiAlH_4$ in diethyl ether afforded the alcohol **5** in an 89% yield after purification by chromatography. Ethyl 3-bromo 1-[2′-menthoxyacetate] adamantane **7** was prepared by reaction of **5** with (−)-menthoxyacetic acid in benzene, in the presence of a catalytic amount of *p*-toluenesulphonic acid, using a Dean and Stark apparatus, giving a 68% yield, after purification by chromatography.

The reaction of 3-bromoadamantyl acetic acid **4** with (−)menthol, in benzene catalysed by *p*-toluenesulphonic acid or transesterification of methyl [3-bromo, 1-adamantylacetate] in the presence of 4-dimethylaminopyridine in benzene afforded the expected products **8** and **9** but in low yields. To solve this problem, firstly, the acid chloride **6** was synthesised by reaction of **4** with thionyl chloride in the presence of pyridine then reacted with either (−)-menthol or (−)-borneol, in the presence of triethylamine to give after chromatography **8** and **9** in an 80 and 85% yield, respectively.



Scheme 1. Synthetic route of chiral organogermanes **13**–**15**.

These new compounds **7**, **8** and **9** were fully characterised by IR, ^{1}H- and ^{13}C-NMR spectroscopy, and MS spectrometry and determination of the α_D. In the ^{13}C-NMR, the resonance of C_3 linked to the bromine atom was similar for the three compounds **7**, **8** and **9** (65.3, 64.5 and 65.5, respectively). It may be remarked that in the ^{13}C-NMR of **8** the resonances of the C_7 and $C_{7'}$ carbon were different, implying that C_7 and $C_{7'}$ were not equivalent, Table 1.

*2.2. Synthesis of enantiomerically pure trihalidealkylgermanes, **10**, **11**, and **12***

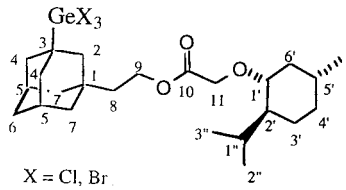
The oxidative addition of $GeCl_2 \cdot$ dioxane, **1**, into the carbon–bromide bond of the esters **7**, **8**, and **9**, [3-Br-1-R*–Ad], at 110°C in 1,2-dichlorobenzene, in 12 h, afforded the alkyl trihalidegermanes **10**, **11**, and **12**. The presence in the ^{13}C-NMR spectrum of four signals for the δ C_3 resonance, showed that scrambling of halide

atoms [15] occurred during the reaction, affording a mixture of species 3-[1-R*–Ad]$GeBr_{3-x}Cl_x$ ($x = 0–3$). So, no further purification was attempted. The crude products were analysed by IR and ^{13}C-NMR spectroscopy.

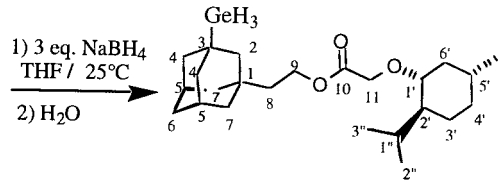
2.3. Synthesis of enantiomerically pure alkylgermanes *13*, *14*, and *15*

The alkylgermane derivatives $RGeH_3$ were generally produced by an exchange reaction between $RGeX_3$ and a Group 16 metal hydride [6,7,12]. The presence of an ester group in **10**, **11**, and **12** led us to use $NaBH_4$ and improve experimental conditions to prevent the reduction of the ester group and the loss of the chiral fragment.

The reaction of (−)-menthyl ester **10** with $NaBH_4$, in THF, was very sensitive to experimental conditions (temperature, excess of hydride). If the reaction temperature was above 25°C and/or if more than three equivalents of $NaBH_4$ were used, there was reduction of the ester into the alcohol [3-[1-$HOCH_2CH_2$–Ad}]GeH_3. However, the reaction of **10** in THF at room temperature (r.t.) with three equivalents of $NaBH_4$ afforded **13**, in a 20% isolated yield after bulb-to-bulb distillation (Eq. (3)).



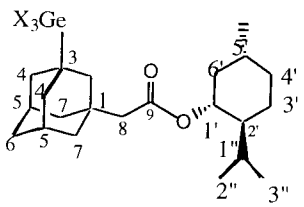
10



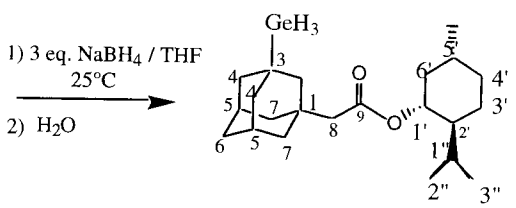
13

(3)

The(−)-menthyl ester **14** was formed under the same conditions in a 59% yield (b.p. 150°C/0.02 mm) from **11** (Eq. (4)).



11



14

(4)

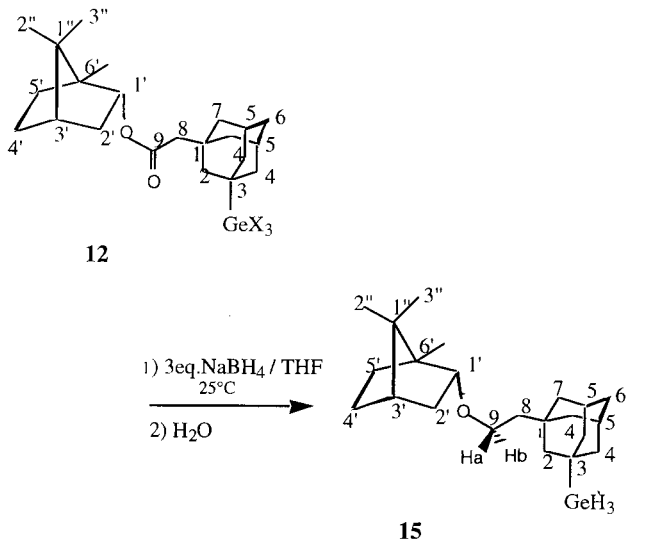
The structure of **13** and **14** was supported by elemental analysis, $[\alpha]_D = -44.31°$ ($c = 1.108$ mol l^{-1}, benzene) and $[\alpha]_D = -46.9°$ ($c = 1.125$ mol l^{-1}, benzene) for **13** and **14**, respectively, and IC-SM (NH_3). The IR spectrum showed two strong vibrations at ν(Ge–H) 2050 and ν(C=O) 1730, 1728 cm^{-1} for **13** and **14**, respectively. In the ^{1}H-NMR spectrum, there was a singlet at 3.9 ppm for **13** and 4 ppm for **14** corresponding to the resonance of δ_{Ge-H}. In the ^{13}C-NMR spectrum, resonances at 170.5 and 171.0 ppm assigned to the C=O group of the ester were still present; all δ_C of **13** and **14** were shifted upfield, except δ_{C6} and δ_{C7}, comparatively with δ_C of bromide precursors **7** and **8**. In particular, δ_{C3} was shifted from 65.3 in **7** to 26.6 ppm in **13**; and from 64 in **8** to 27.4 in **14**, Table 1. This shift might be related to the difference in electronegativity between bromine and germanium atoms (χBr = 2.8; χGe = 1.9).

Table 1
Chemical shifts in ^{13}C-NMR of compounds **7**–**15**

δ ppm ^{13}C	**7**	**13**	**8**	**14**	**9**	**15**
C1	36.94	32.1	37.24	33.8	38.15	31
C2	53.84	46.74	53.69	49.77	54.69	45.81
C3	**65.34**	**26.66**	**64.56**	**27.44**	**65.45**	**25.57**
C4	48.46	41.23	48.51	41.8	49.37	40.1
C5	32.27	29.25	32.49	30.13	33.35	28.2
C6	34.77	36.34	34.70	37.01	35.54	35.34
C7	40.3	41.71	40.85	42.29	41.18	41
C7′	40.3	41.71	40.377	42.41	41.18	41
C8	39.97	40.15	47.8	47.3	48.77	43.05
C9	60.57	60.9	**169.8**	**171.04**	**171.41**	**64.36**
C10	170.75	170.53				
C11	66.03	66.11				
C1′	80.07	79.8	73.81	74.38	**80.62**	**83.64**
C2′	48.02	48.74	47.25	48.06	38.34	35.10
C3′	23.2	23.73	23.48	24.25	46.04	44.17
C4′	34.13	34.7	34.51	35.23	28.44	25.87
C5′	31.41	31.6	31.46	32.23	29.27	27.33
C6′	41.2	42.56	41.42	42.78	49.66	48.11
C1″	25.36	25.8	26.48	27.22	48.66	46.44
C2″	20.96	21.3	16.35	17.12	19.63	17.7
C3″	16.26	16.72	20.9	21.65	14.63	12.94
Me–C5′	22.23	22.5	22.13	22.89	20.57	18.6

The reaction of **12** with three equivalents of $NaBH_4$ in THF at r.t. was monitored by IR spectroscopy. As observed during the synthesis of **13** and **14**, a band at 2050 cm^{-1} assigned to ν(Ge–H) appeared and increased in intensity. But, in contrast to the reactions described above, the band due to the ν(C=O) vibration at 1730 cm^{-1} decreased simultaneously in intensity, until complete disappearance after 5 h of reaction. A clear oil was isolated by bulb-to bulb-distillation (150°C/0.02 mm). IR and ^{1}H-NMR spectra supported the formation of a Ge–H bond in the derivative **15**, ν(Ge–H) at 2050 cm^{-1} and δ_{Ge-H} at 3.9 ppm, vide supra.

In the ^{13}C-NMR spectrum of **15**, the resonance at 171.4 ppm assigned to the carbonyl group of the ester was absent. A new signal at 64.36 ppm appeared and was attributed to the CH_2 carbon, by DEPT135 experiment. In the ^{1}H-NMR spectrum, the new massif centred at 3.2 ppm could also be assigned to CH_2 protons. The different analytical results, IR, MS, elemental analysis, were in agreement with the fact that the (−)-bornyl fragment was still present, but not the ester group. This ester function has been reduced into an ether group to afford **15** in a yield of 31% (Eq. (5)).



12 **15** (5)

3. Discussion and conclusion

We reported the synthesis of new optically pure alkylgermanes **13**–**15** in six steps (Scheme 1) from the 1-bromoadamantane, in an 8–31% yield.

Firstly, the enantiomerically pure brominated adamantyl groups were synthesised: [3-Br-1-R*Ad]. Then the oxidative addition of germylene into C–Br afforded the expected trihalides compounds, (Eq. (6)). No reaction of germylene **1** with carbonyl group was observed [24].

$$\text{3-Br-1-R*Ad} + GeCl_2 \cdot \text{dioxane} \rightarrow \text{3-[1-\{R*Ad\}]}GeBr_xCl_{3-x} \quad (6)$$

The exchange reaction between 3-[1-{R*Ad}]$GeBr_xCl_{3-x}$ [3-Br-1-R*Ad] and $NaBH_4$ was more complex. However, the reaction of **10** and **11** in THF at r.t. with three equivalents of $NaBH_4$ afforded the new optically pure alkylgermanes **13** and **14** in a 21 and 59% yield, respectively.

In the same conditions as above, **12** was reduced into the alkylgermane **15** in which the ester function has been reduced into an ether function, but the chiral fragment was still present.

Few examples of this kind of reaction are reported in the literature [25]. However, in the case of sterically hindered steroids and lactones [26,27], the reduction of an ester function with $NaBH_4$ and BF_3–OEt_2, afforded alcohol or ether derivatives. The authors demonstrated that the nature of the final product was determined by the steric hindrance of the R group in the ester –C(O)OR function. The steric hindrance of R controlled the approach and the coordination of the Lewis acid BF_3 to the oxygen atom of ester function. If the coordination of BF_3 occurred on the O of carbonyl group –C(O)–OR, there was formation of ether; if the co-ordination of BF_3 occurred on the O alkoxyde group –C(O)–**O**R there was formation of alcohol and, in our case, loss of the chiral fragment R*. The coordination site was determined by the steric hindrance of the R group in the ester –C(O)OR function [26,27].

These literature data indicate that two factors are essential in this reduction, the presence of a Lewis acid and the steric hindrance of the group bound to the ester function. Following the same hypothesis, we attempted to explain the difference in the reactivity of **11** and **12** with $NaBH_4$.

When **11** and **12** were involved in the reaction with $NaBH_4$ one molecule of borane BH_3 was generated in situ when the Ge–halide bond was converted into a Ge–H bond [17] (Eq. (7)).

$$R_3GeCl + NaBH_4 \rightarrow R_3GeH + BH_3 + NaCl \quad (7)$$

BH_3 is a Lewis acid. To understand the importance of its role in the reduction of **12**, the reaction of precursors **8** and **9** with three equivalents of $NaBH_4$, in the same experimental conditions as **11** and **12** was realised. No reaction was observed, i.e. $NaBH_4$ alone did not reduce the ester function. But, when the reaction of **8** and **9** with three equivalents of $NaBH_4$ was performed in presence $BF_3 \cdot OEt_2$, **8** did not react, but **9**, was reduced in ether **16** in a 90% yield. Therefore, as expected, the presence of a Lewis acid was necessary to observe the reduction.

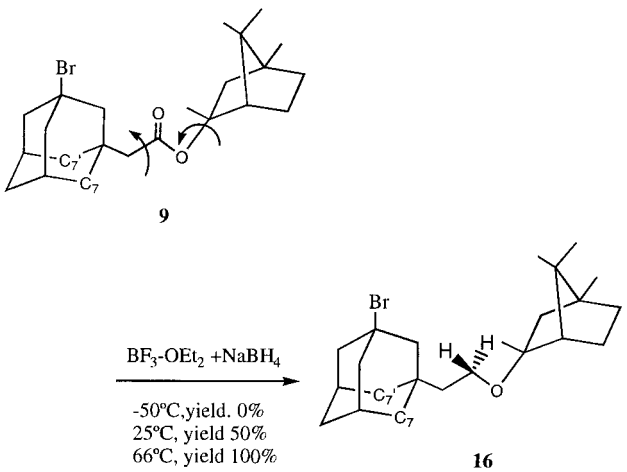
Following the literature, the second major factor was the steric hindrance of the ester group. We already reported that in the ^{13}C-NMR spectrum of **9** the C_7 and

$C_{7'}$ showed the same chemical shift at 41.18 ppm, but in the ^{13}C-NMR spectrum of **8** the C_7 and $C_{7'}$ showed two different resonances at 40.85 and 40.4 ppm, at 25°C. The difference between these chemical shifts decreased from 16 Hz at 25°C to 12 Hz at 66°C. For **9**, C_7 and $C_{7'}$ gave only one resonance above 30°C (coalescence temperature) but, at −60°C, there was a splitting between C_7 and $C_{7'}$ signals of 3 Hz, $\Delta(\delta C_7 - \delta C_{7'})$.

These results suggest that there was, in **9**, above 30°C, a free rotation of the ester group. The (−)bornyl group could rotate around the C_8–C_9 or C_1–O bond while in **8**, the (−)menthyl group could not rotate, even at 66°C. The free energy of activation for this rotation was $\Delta G^{\neq} = 16.85$ kcal mol^{-1} for **9**, superior to 51 kcal mol^{-1} for **8** [28].

The correlation between the free rotation of the ester group and its possible reduction by $NaBH_4$ was supported by the following results: there was no reaction between **9** and $NaBH_4$ and BF_3–O_2Et at −50°C. At this temperature, δC_7 $\delta C_{7'}$ were different. At 25°C, 50% of chiral ether **16** was formed, at that temperature, the ^{13}C-NMR spectra of **9** showed a single broad peak for C_7 and $C_{7'}$. At +66°C, there was a single sharp singlet for C_7 and $C_{7'}$ in the ^{13}C-NMR spectra, and at this temperature the conversion of **9** into **16** was quantitative. Hence, the reduction of the ester into ether was observed when there was free rotation of the ester group.

So, as in the literature, the conversion in **9** of the ester function into an ether function may probably be ascribed to the presence of a Lewis acid and to the steric hindrance of the ester group (Eq. (8)).



(8)

The enantiomerically pure $H_3GeAdCH_2CO_2[(-)$-menthyl], **14**, reacted selectively with the metallic surface of the catalyst Rh/SiO_2 to produce the surface species $\{[H_yGeAdCH_2CO_2(-)\text{-menthyl}]_y[Ge^o]_{0.3}\}Rh_s/SiO_2$; y increasing from 0 to 0.7 when the quantity of **14** by surface atom of rhodium varies from 0.3 to 1. Catalysts with $y = 0.3$ and 0.5 show low activity and give weak enantiomeric excess (ee < 10) for the asymmetric hydrogenation of ketone and alkene derivatives. These results can be explained either by the electronic effect of germanium or steric hindrance of the alkyl group [29].

4. Experimental

All reactions and preparations were performed under a dried atmosphere, oxygen-free argon using Schlenk techniques. Solvents and reagents were appropriately dried and purified.

The melting points were determined with an Electrothermal digital melting point apparatus. ^{1}H-NMR spectra were recorded on a Bruker AM200 and AM300 (200 and 300 MHz) spectrometers. ^{13}C-NMR spectra (75 MHz, ^{1}H decoupled) were also recorded on the Bruker AM300 spectrometer, respectively at 25°C in $CDCl_3$ and C_6D_6; the position of the signals is reported in ppm (δ) down field from TMS. Optical rotations were determined with Perkin–Elmer 241 polarimeter. Microanalyses were performed by the analysis centre of CNRS at Solaize. FTIR spectra were recorded on a Nicolet 205 FTIR spectrometer. Mass spectra were obtained with a Nermag R10-10S (70 eV, 300 μÅ) ion trap mass detector interfaced with a Delsi DI700 gas chromatography having a 25 m × 0.25 mm OV73 fused silica capillary column. A Nermag R10-10S mass spectrometer was used in chemical ionisation mode with ammonia as a reagent. Analytical gas chromatographic analyses were carried out using an Intersmat IGC 120FL gas chromatography equipped with a flame ionisation detector, a Merck D200 recording integrator, a conventional heated splitess injector, and a DB-5 fused silica capillary column.

Anhydrous toluene and 1,2-dichlorobenzene, anhydrous dioxane were obtained from Aldrich Chemical Co. and were used without purification.

The complexes $GeCl_2 \cdot$dioxane, **1**, [14], 1-adamantaneacetic acid, **3**, [22] and 3-bromo-1-adamantaneacetic acid, **4** [23] have been synthesised as described in the literature.

*4.1. 2-(3-Bromo-1-adamantane)ethanol, **5***

A solution of 3 g (10.45 mmol) of **4** in 40 ml of diethyl ether was added dropwise to a solution of 0.407 g (10.6 mmol) of lithium aluminium hydride in 15 ml of diethyl ether. The mixture was kept under stirring and reflux for 17 h. Then the excess of hydride was hydrolysed by the dropwise addition of 3 ml of 4% NaOH. When precipitation was complete, the mixture was filtered, and the solid residue washed with ether. The ether layer and ethereal extracts of the aqueous layer were combined, washed with water, and dried over $MgSO_4$ and the solvent was evaporated at r.t.

under atmospheric pressure. Flash chromatographic separation eluting with hexane–ether (80/20) gave 2.4 g of **5** (88.9%), white solid, m.p. 58–60°C. IR (KBr, cm^{-1}) 3300 (OH), 2935, 2910, 2856 (CH).—^{1}H [($CDCl_3$, 300 MHz, δ(ppm)] 1.45 [t, $J_{H9,8} = 7.2$ Hz, 2H, H_{-8}], 1.4–1.7 (m, 6H + O–H, exchanged with D_2O), 2–2.5 (m, 8H, CH), 3.7 (t, $J_{H9,8} = 7.2$ Hz, 2H, H_{-9}).—^{13}C-NMR [($CDCl_3$, 300 MHz, δ(ppm)] 30.99 (C-5), 32.34 (C-1);. 37.2 (C-6), 40.26 (C-7), 47.3 (C-8), 48.37 (C-4), 53.41 (C-2), 65.1 (C-3), 178.8 (C=O).

4.2. 3-Bromo-1-adamantaneacetic chloride, **6**

In total 6 ml (80 mmol) of thionyl chloride was added dropwise to a solution containing 5.6 g (20 mmol) of **4** in 60 ml of benzene and 3 ml (46 mmol) of pyridine. The mixture was stirred at reflux for 12 h. After removal of the insoluble substances by filtration, the reaction mixture was evaporated to give a colourless oil in a 96% yield.—IR (neat film, cm^{-1}): 2935, 2910, 2856 (CH), 1775 (C=O).—^{1}H-NMR [($CDCl_3$, 300 MHz, δ(ppm)]: 1.5–1.8 (m, 6H), 2.1–2.4 (m, 8H), 2.8 (s, 2H, CH_2COCl).—^{13}C-NMR [($CDCl_3$, 300 MHz, δ(ppm)] 32.59 (C-5), 35.17 (C-1), 37.3 (C-6), 40.05 (C-7), 47.3 (C-8), 48.58 (C-4), 53.35 (C-2), 65.72 (C-3), 177.82 (C=O).

4.3. 3-Bromo-1{ethyl-(2′-menthoxyacetate)}adamantane, **7**

To a solution of 2.33 g (9 mmol) of **5** and 2.9 g (13.5 mmol) of (−)menthoxy-acetic acid in 200 ml of benzene, *p*-toluenesulphonic acid (0.4 g) was added and the mixture was kept under reflux for 2 days employing a Dean–Stark trap. The mixture was cooled to r.t. and was washed with a saturated solution of $NaHCO_3$ (4 × 30 ml) and water (3 × 40 ml). The organic layer was dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography eluting with hexane–ether (80/20) to afford 2.7 g (68%) of compound **7** as a colourless oil.—$[\alpha]_D^{25} = -46.9°$ (c 1.5, C_6H_6).—IR (neat film, cm^{-1}): 2935, 2910, 2856 (C–H), 1728 (C=O).—^{1}H-NMR [($CDCl_3$, 300 MHz, δ(ppm)]: 0.8 [d, $J = 6.9$ Hz, 3H, Me at C-5′], 0.90 (d, $J = 7.1$ Hz, 3H, H-2″), 0.92 (d, $J = 6.4$ Hz, 3H, H-3″), 2–2.3 (m, 10H), 1.2–1.7 (m, 15H), 3.15 (td, $^3J_{H1',6'} = 10.55$ Hz, $J_{H1',2'} = 4.13$ Hz, 1H, H-1′), 4.08 (AB, $J_{11a,11b} = 9.2$ Hz, 2H, H-11a–11b), 4.2 (t, $J = 7.2$ Hz, 2H, H-9).—MS (70 eV); *m*/*z* (%): 456 (2) [M^+], 161 (39), 155 (100) [Menthol$^+$]; 135 (8) $Ad^+ - C_{24}H_{39}O_3Br$: Calc. C 64.41, H 8.65; Br, 17.37; Found: C 63.34, H 8.64; Br 16.34.

4.4. (3-Bromo 1-adamantyl) (−)-menthyl acetate, **8**

To a solution containing 5 g (17.18 mmol) of **6** in 80 ml of anhydrous benzene was added 3.21 g (20.61 mmol) of (−)-menthol in 15 ml of benzene and 2.1 ml of anhydrous pyridine at r.t. The mixture was stirred at 80°C for 12 h. After filtration the solvents were distilled under low pressure to afford a residue, which was purified by flash chromatography on a silica gel column. Elution with (80/20) hexane–ether afforded 6 g of **8** (85%) as a colourless oil.—$[\alpha]_D^{25} = -41°$ (c 1, C_6D_6).—IR (neat film, cm^{-1}): 2935, 2910, 2856 (CH), 1728 (C=O). ^{1}H-NMR [(C_6D_6, 300 MHz, δ(ppm)] 0.78 (d, $J = 6.5$ Hz, 3H, Me at C-5′), 0.85 (d, $J = 7.1$ Hz, 3H, H-2″), 0.91 (d, $^3J = 6.9$ Hz, 3H, H-3″), 1–1.5 (m, 15H), 1.93 (s, 2H, H-8), 2–2.2 (m, 8H), 4.8 (td, $J_{H1',6'} = 10.9$ Hz, $J_{H1',2'} = 4.29$ Hz, 1H, H-1′).—MS (IC, NH_3); *m*/*z* (%): 429 (100) ($M^+ + 18$).—$C_{22}H_{35}O_2Br$: Calc. C 64.23, H 8.51, Br 19.4; Found C, 64.52; H, 8.52; Br, 18.83.

4.5. (3-Bromo 1-adamantyl) (−)-bornyl acetate **9**

The same experimental procedure as **8** was followed, with 5 g (17.18 mmol) of acid chloride and 3.2 g (26.61 mmol) of [(1*S*)-endo]-(−)-borneol. The product **9** was isolated in the form of a colourless oil 5.6 g (80%).—$[\alpha]_D^{25} = -14.6°$ (c 1.17, C_6D_6).—IR (neat film, cm^{-1}) 2935, 2910, 2856 (CH), 1732 (C=0). ^{1}H-NMR [($CDCl_3$, 300 MHz, δ(ppm)]: 0.93 (s, 6H, H2″ + 3″), 1.06 (s, 3H, Me at $C_{6'}$), 1.4–2.5 (m, 23H), 5.25 (m, 1H, H-1′).—MS (70 eV); *m*/*z* (%): 410 (9) [M^+], 329 (12) [M^+–Br], 137 (100) [bornyl$^+$], 136 (83) [Ad^+].—MS (CI, NH_3); 428 (100). [M + 18].—$C_{22}H_{33}O_2Br$: Calc. C 64.23, H 8.06, Br 19.55; Found C 61.8, H 7.91, Br 19.40.

4.6. General procedure for the preparation of alkyltrihalogermanes **2**, **10**, **11** and **12**

A flask fitted with a magnetic stirrer was charged with the haloadamantane 3-Br-1-[R*CH_2CO_2]Ad and $GeCl_2 \cdot$ dioxane (1.5 equivalents) in 30 ml of dry 1,2-dichlorobenzene. The mixture was stirred at 110°C for 17 h. After cooling at r.t., the solvent was removed under reduced pressure and the residue was diluted with benzene and filtered. The solvent was then removed to give $RGeX_3$ **2**, **10**, **11** and **12**.

4.6.1. Procedure (a)

A total of 1.8 g of **1** and 2.1 g of methyl(3-bromoadamantane)acetate afforded, after distillation (130–160°C at 0.6 Torr), 2.83 g of **2**.

Rdt = 90%.—IR (neat, cm^{-1}): 2935, 2910, 2856 *v*(C–H); 1725 *v*(C=O). ^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)]: 1.25 (m, 6H), 1.6–1.8 (m, 10H), 3.25 (s, 3H, CH_3). $C_{13}H_{19}O_2GeCl_nBr_{3-n}$: Calc. C 36.29, H 4.45, Ge 16.85, Cl 16.46, Br 18.55. Found: C 36.54, H 4.57, Ge 16.88, Cl 16.68, Br 18.83.

4.6.2. Procedure (b)

Complex **10** was synthesised from (4.14 g) of **7** and (5.5 g) of **1**.—IR (neat, cm^{-1}): 2935, 2910, 2856 ν(C–H); 1726 ν(C=O). ^{1}H-NMR [C_6D_6, 300 MHz, δ(ppm)]: 0.65 (d, $^3J = 6.9$ Hz, 3H, Me at $C_{5'}$); 0.83 (d, $^3J = 7.1$ Hz, 3H, $H_{2''}$); 0.9 (d, $^3J = 6.9$ Hz, 3H, $H_{3''}$); 1–1.6 (m, 15H); 1.7–2.1 (m, 10H); 4.7 (td, $^3J_{H1',6'} = 10.9$ Hz, $^3J_{H1',2'} = 4.29$ Hz, 1H, $H_{1'}$).

4.6.3. Procedure (c)

A total of 5 g of **8** and 3.474 g of **1** afforded 3.7 g (9 mmol) of **11**.—IR (neat, cm^{-1}): 2935, 2910, 2856 ν(C–H); 1728 ν(C=O). ^{1}H-NMR [C_6D_6, 300 MHz, δ(ppm)]: 0.8 (d, $^3J = 6.5$ Hz, 3H, Me at $C_{5'}$); 0.75 (d, $^3J = 7.1$ Hz, 3H, $H_{2''}$); 0.78 (d, $^3J = 6.4$ Hz, 3H, $H_{3''}$); 1.2–1.7 (m, 15H); 2–2.3 (m, 10H); 2.95 (td, $^3J_{H1',6'} = 10.55$ Hz, $^3J_{H1',2'} = 4.13$ Hz, 1H, $H_{1'}$); 3.82 (AB, $^2J_{H11a,11b} = 9.2$ Hz, $H_{11a,11b}$); 3.95 (t, $^3J = 7.2$ Hz, 2H, H_9).

4.6.4. Procedure (d)

A total of 4.08 g (10 mmol) of **9** and 3.474 g of **1** afforded 5.45 g of **12**.—IR (film, cm^{-1}): 2859–2951 ν(C–H); 1732 ν(C=O).

*4.7. General procedure for the preparation of organogermanes **13**, **14** and **15***

A solution of trihalogermane 3-[1-{R*CH_2CO_2 Ad}]$GeBr_nCl_{3-n}$ (9 mmol) in dry THF (10 ml) was added dropwise to a suspension of $NaBH_4$ (27 mmol) in dry THF (40 ml). The mixture was stirred at r.t. for 5 h and then poured into 10 ml of water. After dilution with diethyl ether (20 ml), the organic layer was separated, washed with water dried over anhydrous $MgSO_4$, and solvents were removed under reduced pressure. The residue was purified by bulb-to-bulb distillation to give the expected products **13**–**15** as a colourless oil in a 20–60% yield.

*4.7.1. 3-{1-[2'-(−)Menthoxyacetate ethyl] adamantyl}germane, **13***

The yield of chiral ester **13** was 810 mg (20%), b.p. 200°C/0.02 Torr.—$[\alpha]_D^{25} = -44.31°$ ($c = 1.108$, C_6H_6).—IR (neat film, cm^{-1}): 2935, 2910, 2856 (C–H), 2050 (Ge–H), 1728 (C=O).—^{1}H-NMR [(C_6D_6, 300 MHz, δ(ppm)] 0.65 (d, $J = 6.9$ Hz, 3H, Me at $C_{5'}$), 0.75 (d, $J = 7.1$ Hz, 3H, H-2″), 0.78 (d, $J = 6.4$ Hz, 3H, H-3″), 1.2–1.7 (m, 15H), 2–2.3 (m, 10H), 2.95 (td, $J_{H1',6'} = 10.55$ Hz, $J_{H1',2'} = 4.13$ Hz, 1H, H-1′), 3.42 (s, 3H, Ge–H), 3.82 (AB, $J_{A,B} = 9.2$ Hz, 2H, H11a–11b); 3.95 (t, $J = 7.2$ Hz, 2H, H-9).—MS (CI, NH_3): 470 (15) [$M + NH_3 + 1$], 161 (76); 137 (100) [menthyl$^+$], 135 (10) [Ad].—$C_{24}H_{42}O_3Ge$: Calc. C 63.68, H 9.36. Found: C, 64.60 H 9.80.

*4.7.2. 3-{1-[(−)-Menthyl acetate] adamantyl} germane, **14***

The yield of chiral ester **14** was 2.167 g (59%), b.p. 150°C/0.02 Torr.—$[\alpha]_D^{25} = -46.9°$ (c 1.125, C_6D_6).—IR (neat film, cm^{-1}): 2935, 2910, 2856 (C–H), 2050 (Ge–H), 1728 (C=O). ^{1}H-NMR [(C_6D_6, 300 MHz, δ(ppm)]: 0.93 (d, $J = 6.4$ Hz, 3H, Me at $C_{5'}$), 0.98 (d, $J = 7$ Hz, 3H, $H_{2''}$), 1.01 (d, $^3J = 6.9$ Hz, 3H, H-3″), 1.2–2 (m, 23H), 2.12 (s, 2H, H-8), 4.99 (td, $J_{H1',6'} = 10.7$ Hz, $J_{H1',2'} = 4.4$ Hz, 1H, H-1′), 3.75 (s, 3H, Ge–H).—MS (CI, NH_3): 426 (13) [$M + NH_3 + 1$], 409 (16) [$M + 1$], 348 (94), 193 (100), 135 (4) [Ad$^+$].—$C_{22}H_{38}O_2Ge$: Calc. C 64.52, H 9.60; Found C 65.38, H 9.60.

*4.7.3. 3-{1-[2'(−)-Bornylethyloxyde] adamantyl} germane, **15***

The yield of chiral ether **15** was 1.2 g (30.7%), b.p. 150°C/0.02 Torr.—IR (neat film, cm^{-1}): 2935, 2910, 2856 (C–H), 2050 (Ge–H), 1230 (C–O–C).—^{1}H-NMR [(C_6D_6, 300 MHz, δ(ppm)]: 0.56 (s, 6H, H2″ + 3″), 0.72 (s, 3H, Me à $C_{6'}$), 1–1.7 (m, 23H), 3 (m, 1H, H-9′), 3.2–3.4 (m, 2H, H1′ + 9), 3.5 (s, 3H, Ge–H).—MS (70 eV); m/z (%): 391 (7) [M^+], 137 (100) [bornyl$^+$], 135 (8) [Ad$^+$].—$C_{22}H_{38}OGe$: Calc. C 67.31 H 9.76; Found C 67.80, H 10.24.

*4.8. 3-Bromo[2'(−)-bornylethyloxyde]adamantane, **16***

A solution of 1 g (2.44 mmol) of 3-bromo 1-adamantyl) (−)-bornyl acetate, **9** in dry THF (10 ml) was added to 0.28 g of $NaBH_4$ (7.32 mmol) and 0.76 ml of a solution of $BF_3 \cdot OEt_2$. The mixture was stirred at 66°C for 5 h and then poured into 10 ml of water. After dilution with diethyl ether (20 ml), the organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and solvents were removed under reduced pressure. The residue was purified by column chromatography eluting with hexane–ethyl acetate (95:5) to afford 0.88 g of **16** as a yellow liquid, yield 90%.

IR (neat film, cm^{-1}): 2960–2820 (C–H), 1230 (C–O–C) 680 (C–Br).—^{1}H-NMR [(C_6D_6, 300 MHz, δ(ppm)]: 0.62 [s, 6H, H-2″ + H-3″), 1–1.2 (m, 23H), 3–3.1 (dt, $^3J_{H9,9'} = 9.15$ Hz, $^3J_{H9,8} = 6.52$ Hz, 1H, H-9), 3.11–3.15 (td, $^3J_{H9,9'} = 9.15$ Hz, $^3J_{H9',8} = 6.52$ Hz, 1H, H-9′), 3.19–3.27 (m, 1H, H-1′).—MS (70 eV); m/z (%): 397 (42) [^{81}Br, $M + 1$]$^+$, 395 (36) [^{79}Br, $M + 1$]$^+$, 137 (16) [bornyl$^+$], 136 (34) [Ad$^+$], 95 (100) [MeBr$^+$].

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