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Chiral organochlorosilanes derived from terpenes: diastereoselective hydrosilylation of methylene bicyclo[2.2.1]heptanes with $HSiMe_nCl_{n-2}$ ($n = 0$–2)

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Abstract

The H_2PtCl_6 catalysed hydrosilylation of the terpenes (+)-α-fenchene (**XI**), (−)-2-methylene bornane (**XII**), (+)-camphene (**XIII**) and (−)-3-methylene fenchane (**XIV**) using $HSiMe_2Cl$ or $HSiMeCl_2$ proceeds with high regioselectively and in some cases, with high diastereoselectivity. KF-assisted oxidation of the hydrosilylation products gives predominately *endo*-terpene alcohols. The alcohols have inverted *endo*/*exo* ratios to those formed by oxidative hydroboration. Reaction of **XIV** with $HSiMe_2Cl$ or $HSiMeCl_2$ is accompanied by a clean rearrangement of the isocamphane skeleton into (+)-2-methylene bornane (**XII**) prior to hydrosilylation.

Keywords: Hydrosilylation; Hydroboration; Terpenes; Silanes; Silicon

1. Introduction

Hydrosilylation of alkenes is a well-established and versatile method for the preparation of organosilanes [1] and can occur with high enantioselectivity when chiral transition metal catalysts are applied [2]. For example, the hydrosilylation of norbornene (**I**) with $HSiCl_3$ takes place under mild conditions in the presence of an optically active 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO–MOP) complex of palladium to produce *exo*-2-(trichlorosilyl)norbornane (**II**) with 99% ee in quantitative yield [3]. The KF-assisted oxidation of **II** with H_2O_2 provided the corresponding *exo*-norboran-2-ol (**III**) in high yields [3]. However, enantioselective hydrosilylations often require the tedious preparation of a chiral catalyst, which in the case of the aforementioned MeO–MOP palladium(II) complex is a five-step synthesis starting from rather expensive 1,1′-binaphthol [3] (Chart 1).

On the other hand, excellent diastereoselectivity was reported for the hydrosilylations of inexpensive (−)-β-pinene (**IV**) using $HSiMeCl_2$ or $HSiMe_2Cl$, in the presence of H_2PtCl_6. This route provides easy access to optically active *trans*-myrtanyl chlorosilanes, *trans*-$MyrMe_2SiCl$ (**Va**) and *trans*-$MyrMeSiCl_2$ (**Vb**) [4]. The KF-assisted oxidation [5] of *trans*-$MyrMeSiCl_2$ (**Vb**) with H_2O_2 provides (−)-*trans*-mytranol (**VI**) in reasonable yields [6]. By contrast, no hydrosilylation was observed for (−)-β-pinene (**IV**) and $HSiCl_3$ under similar reaction conditions [6]. However, in the presence of radical initiators and prolonged heating **IV** and $HSiCl_3$ eventually react under ring-opening of the [3.1.1]-skeleton to give 7-(trichlorosilyl)-Δ(1,2)-*p*-menthene (**VII**) [7]. For the high temperature/high pressure reaction of (−)-β-pinene (**IV**) and $HSiCl_3$ somewhat contradicting results were reported. Under $Ni(acac)_2/PPh_3$ catalysis, the formation of *trans*-myrtanyl trichlorosilane (**Vc**) was claimed [8]. However, subsequent work disclosed a more complex product mixture consisting of **VII**,

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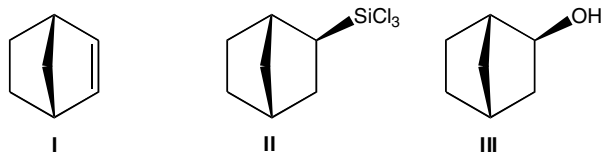


Chart 1.

camphenilanyl trichlorosilane (**VIII**) and *cis*-myrtanyl trichlorosilane (**IX**) [9]. Apart from these examples, there are only a few other works that report on the hydrosilylations of terpenes with chlorosilanes, whereby little attention has been given to the stereochemistry of the products [10–13].

Diastereoselective hydroboration of terpenes is an extremely powerful method for the preparation of chiral organoboranes, which can be further utilized in asymmetric organic synthesis [14]. The reaction of (−)-β-pinene (**IV**) with BH_3 and subsequent oxidation with H_2O_2 affords (−)-*cis*-myrtanol (**X**) in high yield (Chart 2) [15]. Interestingly, both the aforementioned oxidative hydrosilylation and the oxidative hydroboration of (−)-β-pinene (**IV**) provide anti-Markovnikov products (**VI** and **X**), and the stereochemical outcome seems to be complementary [6].

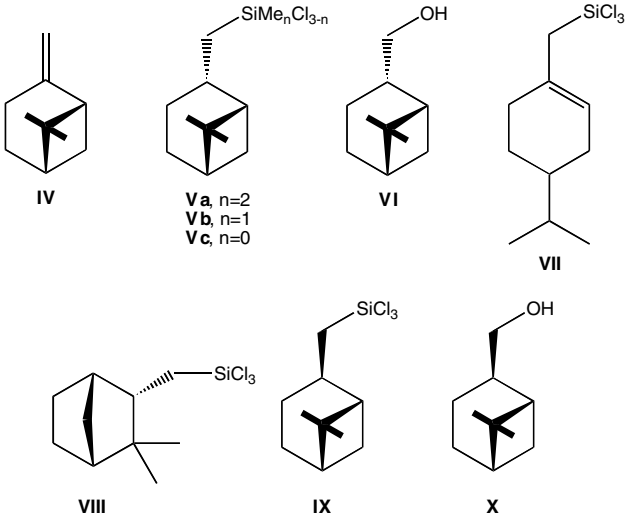


Chart 2.

We now report on the diastereoselective hydrosilylation of four related terpenes, namely (+)-α-fenchene (**XI**), (−)-2-methylene bornane (**XII**), (+)-camphene (**XIII**) and (−)-3-methylene fenchane (**XIV**) (Chart 3), with the H-chlorosilanes $HSiCl_3$, $HSiMeCl_2$ and $HSiMe_2Cl$, and the subsequent KF-assisted oxidation of the hydrosilylation products. The stereochemistry of the resultant terpene alcohols is compared with that of the products from the oxidative hydroboration of **XI** [16], **XII** [17], **XIII** [18], and **XIV** [19] with BH_3.

2. Results and discussion

2.1. Hydrosilylations with (+)-α-fenchene (*XI*)

The H_2PtCl_6 catalyzed hydrosilylation of **XI** with $HSiMe_2Cl$ or $HSiMeCl_2$, occurred regioselectively with formation of the anti-Markovnikov product mixtures, [(2*R*)-*endo*]- and [(2*S*)-*exo*]-(7,7-dimethyl-2-norbornane)-methyl dimethylchlorosilane (**1a**) and [(2*R*)-*endo*]- and [(2*S*)-*exo*]-(7,7-dimethyl-2-norbornane)methyl methyldichlorosilane (**1b**), respectively, in high yields (Scheme 1). The *endo*/*exo* ratios of **1a** and **1b** (88:12 and 90:10, respectively) are almost the same for both chlorosilanes, $HSiMe_2Cl$ and $HSiMeCl_2$, and indicate effective shielding of the *syn*-face of the double bond by the methyl group in the 8-position of the bicyclo[2.2.1]heptane. No hydrosilylation took place between **XI** and $HSiCl_3$ under the same reaction conditions. The KF-assisted oxidation of **1b** with H_2O_2 provided a mixture of [(2*R*)-*endo*]- and [(2*S*)-*exo*]-7,7-dimethyl-2-norbornane methanol (**2**) in a ratio of 90:10 in reasonable yields (Scheme 1). The oxidative hydroboration of **XI** with BH_3 was studied by Brown et al. who reported the same alcohol mixture of **2**, albeit with an almost inverted *endo*/*exo* ratio of 15:85 [16]. Selected ^{29}Si, ^{13}C and ^{1}H NMR data of the *endo* and *exo* isomers of **1a**, **1b** and **2** are collected in Table 1.

2.2. Hydrosilylations with (−)-2-methylene bornane (*XII*)

The hydrosilylation of **XII** with $HSiMe_2Cl$ or $HSiMeCl_2$ under the same reaction conditions regioselectively produced anti-Markovnikov product mixtures of

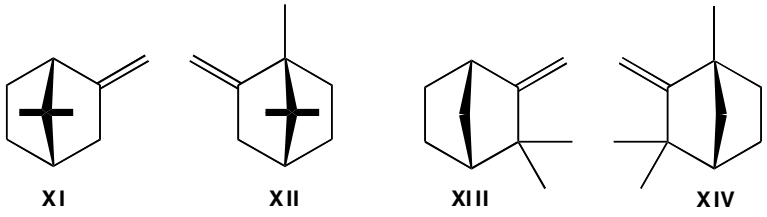
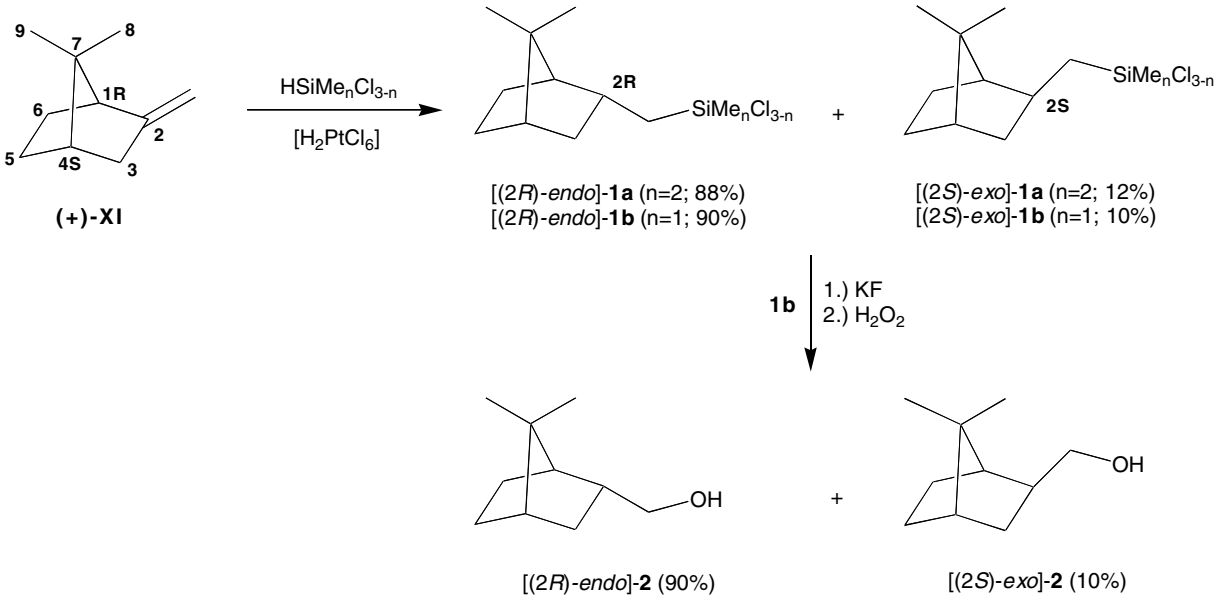


Chart 3.



Scheme 1.

[(2*S*)-*endo*]- and [(2*R*)-*exo*]-(2-bornane)methyl dimethylchlorosilane (**3a**) and [(2*S*)-*endo*]- and [(2*R*)-*exo*]-(2-bornane)methyl methyldichlorosilane (**3b**), respectively, in high yields (Scheme 2). The *endo*/*exo* ratio of **3b** (95:5) is consistent with those observed for **1a** and **1b**, however, for **3a** the *endo*/*exo* ratio (70:30) is somewhat lower. No hydrosilylation was observed for **XII** and $HSiCl_3$ under the same reaction condition. The KF assisted oxidation of **3b** with H_2O_2 provided a mixture of [(2*S*)-*endo*]- and [(2*R*)-*exo*]-2-bornane methanol (**4**) in a ratio of 95:5 in reasonable yields (Scheme 2). The oxidative hydroboration of **XII** with BH_3 has been investigated twice previously and afforded the same alcohol mixture, however, again with an inverted *endo*/*exo* ratio (20:80) [17]. Selected ^{29}Si, ^{13}C and ^{1}H NMR data of the *endo* and *exo* isomers of **3a**, **3b** and **4** are collected in Table 1.

2.3. Hydrosilylations with (+)-camphene (*XIII*)

The H_2PtCl_6 catalyzed hydrosilylation of **XIII** with $HSiMe_2Cl$, $HSiMeCl_2$ and $HSiCl_3$, has been investigated previously by Voronkov et al. [11b] Apparently mixtures of camphenilanyl chlorosilanes and isocamphenilanyl chlorosilanes were obtained, however neither *endo*/*exo* ratios nor NMR data were disclosed [11b]. Moreover, Yur'ev et al. [11a] reported the high pressure/high temperature $Ni(acac)_2/PPh_3$ catalyzed hydrosilylation of **XIII** with $HSiCl_3$ which afforded stereoselectively camphenilanyl trichlorosilane (**VIII**, Chart 2). In our hands, the H_2PtCl_6 catalyzed hydrosilylation of **XIII** with $HSiMe_2Cl$, $HSiMeCl_2$ and $HSiCl_3$ provided product mixtures of [(3*R*)-*endo*]- and [(3*S*)-*exo*]-(2,2-dimethylnorbornane)methyl dimethylchlorosilane (**5a**), [(3*R*)-*endo*]- and [(3*S*)-*exo*]-(2,2-dimethylnorbornane)methyl methyldichlorosilane (**5b**) and [(3*R*)-*endo*]- and [(3*S*)-*exo*]-(2,2-dimethylnorbornane)methyl trichlorosilane (**5c**), respectively, in high yields (Scheme 3). Although the hydrosilylation occurred regioselective, (almost) no diastereoselectivity was observed (*endo*/*exo* ratios: 50:50 (**5a**), 50:50 (**5b**), 55:45 (**5c**)), presumably due to the lack of a methyl group attached to the carbon atom in He 7-position. The KF-assisted oxidation of **5b** with H_2O_2 provided an equimolar mixture of [(3*R*)-*endo*]- and [(3*S*)-*exo*]-2,2-dimethylnorbornane methanol (**6**) in reasonable yield (Scheme 3) [20]. By contrast, the oxidative hydroboration of **XIII** with BH_3 occurs with high diastereoselectively and provides mixtures of the alcohols **6** with a more favourable *endo*/*exo* ratio of 80:20 [18]. Selected ^{29}Si, ^{13}C and ^{1}H NMR data of the *endo* and *exo* isomers of **5a**, **5b**, **5c** and **6** are collected in Table 1.

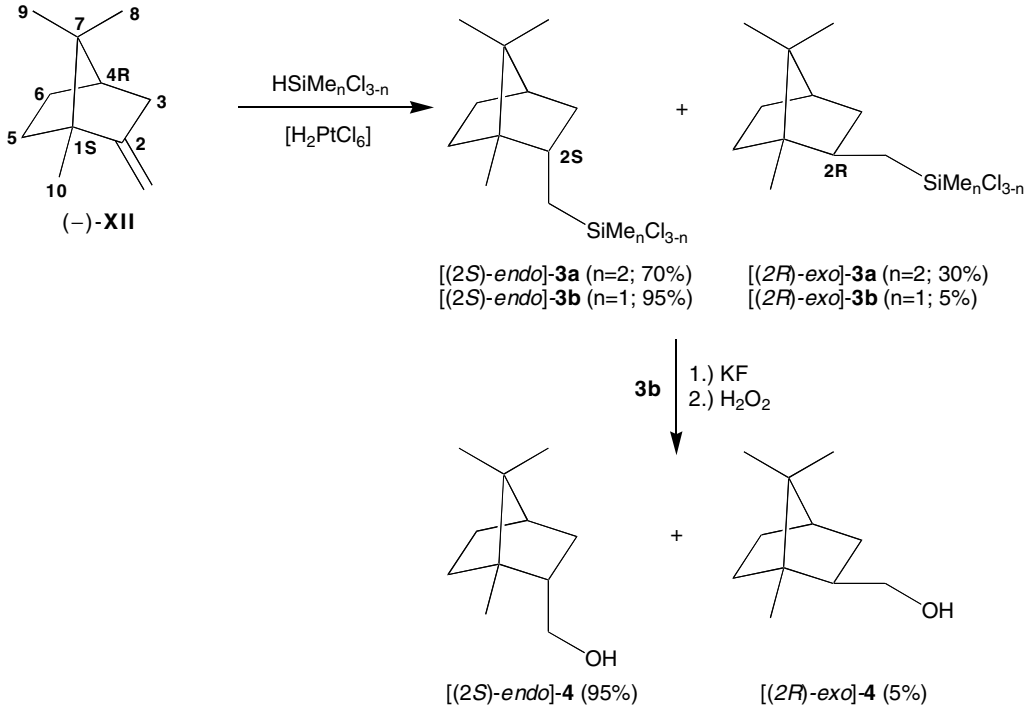
2.4. Hydrosilylations with (−)-3-methylene fenchane (*XIV*)

The H_2PtCl_6 catalyzed hydrosilylation of **XIV** with $HSiMe_2Cl$ or $HSiMeCl_2$ proceeded with an unexpectedly clean rearrangement of the isocamphane skeleton and provided mixtures of [(2*R*)-*endo*]- and [(2 *S*)-*exo*]-(2-bornane)methyl dimethylchlorosilane (**3a**) and [(2*R*)-*endo*]- and [(2*S*)-*exo*]-(2-bornane)methyl methyldichlorosilane (**3b**), respectively, in high yields (Scheme 4). The *endo*/*exo* ratios of 62:38 and 92:8 obey a similar trend as observed for the hydrosilylation of **XII**, however, the diastereoselectivity is in both cases is slightly lower. No hydrosilylation was observed for **XIV** and $HSiCl_3$ under the same reaction conditions. The KF-assisted oxidation of **3b** with H_2O_2 provided a mixture of [(2 *R*)-*endo*]- and [(2*S*)-*exo*]-2 bornane methanol (**4**) in

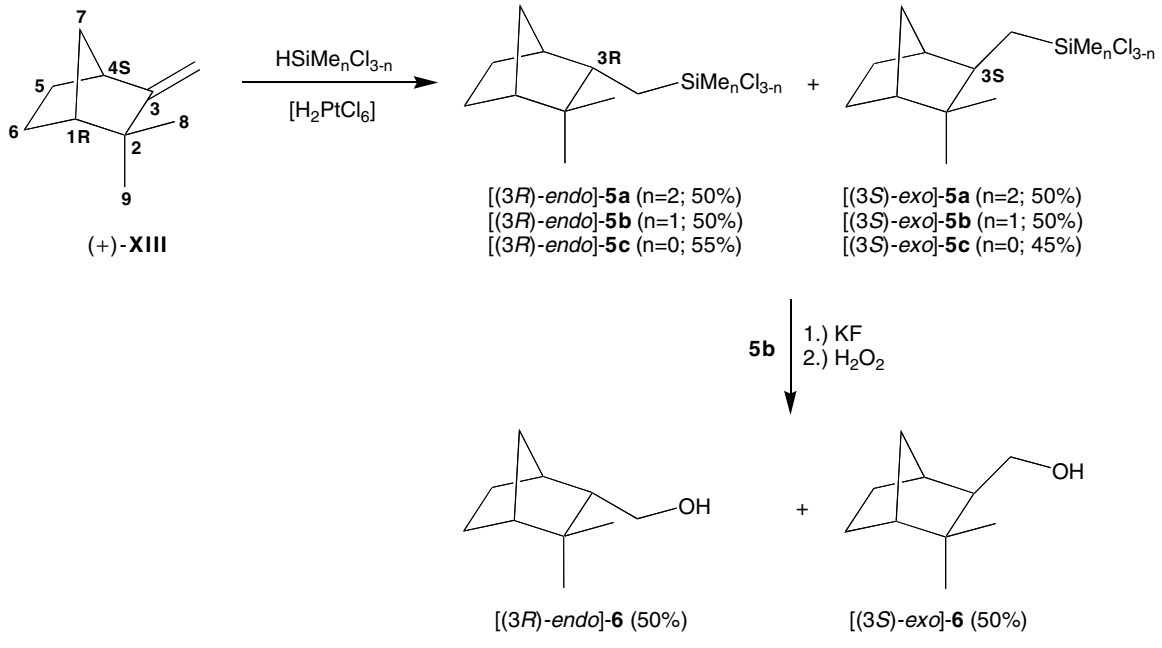
Table 1
Selected ^{29}Si, ^{13}C and ^{1}H (in brackets) NMR data of *endo* and *exo* isomers of **1–6**

	Si	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	CH_2X[a]	SiMe
endo-**1a**	31.91	44.76 (1.39)	32.91 (2.37)	39.77 (2.09) (0.65)	49.42 (1.39)	29.84 (1.10) (1.75)	21.33 (1.45) (1.59)	47.59	21.00 (0.98)	22.03 (1.40)		23.21 (1.34)	2.61 (0.40)
exo-**1a**	30.94												
endo-**1b**	32.92	44.69 (1.48)	32.40 (2.45)	39.55 (2.13) (0.70)	49.42 (1.48)	29.83 (1.10) (1.77)	21.45 (1.57) (1.64)	47.63	21.01 (1.05)	22.01 (1.00)		25.94 (1.23)	6.26 (0.77)
exo-**1b**	31.75												
endo-**2**		45.20 (1.60)	40.50 (2.35)	33.80 (1.95) (0.64)	43.80 (1.45)	29.60 (1.78) (0.95)	21.40 (1.60) (1.45)	47.50	20.80 (1.04)	21.50 (0.99)		64.80 (3.60)	
exo-**2**		45.90 (1.52)	48.20 (1.72)	34.50 (1.48)	43.90 (1.56)	28.20 (1.74) (1.18)	31.30 (1.80) (1.14)	46.10	22.70 (1.00)	22.80 (0.94)		67.40 (3.70) (3.54)	
endo-**3a**	33.12	49.00	38.29 (0.71) (2.06)	38.44 (1.90)	45.6 (1.58)	28.66 (1.06) (1.69)	28.11 (1.27) (1.60)	48.11	18.59 (0.89)	20.17 (0.89)	13.85 (0.74)	20.8 (0.75)	2.44 2.60 (0.4)
exo-**3a**	32.47	49.80	44.41 (1.17) (1.56)	38.44 (1.90)	49.3 (1.67)	26.84 (0.94) (1.35)	26.29 (1.07) (1.35)	49.89	18.58 (0.89)	20.66 (0.89)	14.17 (0.74)	22.9 (0.84)	2.60 2.60 (0.4)
endo-**3b**	34.50	49.12	37.88 (1.95)	38.08 (0.80) (2.09)	45.55 (1.62)	28.65 (1.04) (1.69)	28.21 (1.28) (1.52)	48.15	18.59 (0.85)	20.13 (0.85)	13.83 (0.73)	23.81 (1.15) (1.04)	6.13 (0.78)
exo-**3b**	31.81												
endo-**4**		47.01	50.60 (1.92)	34.28 (2.00) (0.85)	45.09 (1.60)	27.38 (1.70) (1.10)	39.79 (1.42) (1.37)	47.12	20.60 (0.86)	20.60 (0.87)	12.90 (0.87)	66.90 (3.45) (3.76)	
exo-**4**		47.10	46.00 (1.92)	34.50 (2.00) (0.85)	45.10 (1.60)	28.40 (1.70) (1.08)	29.00 (1.40) (1.37)	49.20	18.60 (0.84)	19.00 (0.88)	15.06 (0.88)	65.90 (3.60) (3.70)	
endo-**5a**	34.45	48.67 (1.70)	37.68	45.87 (1.68)	42.85 (2.10)	20.05 (1.17)	24.86 (1.53)	37.21 (1.13) (1.60)	32.03 (0.83)	22.21 (0.77)		15.91 (1.03) (1.17)	2.69 2.50 (0.89)
exo-**5a**	34.45	45.23 (1.97)	41.38	49.14 (1.32)	49.33 (1.69)	24.30 (1.29) (1.68)	29.98 (1.10) (1.54)	35.65 (1.08) (1.69)	27.58 (0.90)	25.70 (0.75)		20.66 (1.29)	2.69 2.50 (0.89)
endo-**5b**	33.29	48.57 (1.76)	37.86	45.33 (1.70)	42.66 (2.21)	23.64 (1.19)	24.80 (1.56)	37.20 (1.19) (1.63)	31.96 (0.93)	22.22 (0.76)		19.08 (1.08) (1.18)	6.19 (0.77)
exo-**5b**	33.40	45.07 (2.00)	41.53	48.70 (1.34)	49.13 (1.71)	24.23 (1.31) (1.68)	29.86 (1.14) (1.55)	35.67 (1.10) (1.70)	27.56 (0.97)	25.69 (0.88)		20.13 (1.28)	6.24 (0.78)
endo-**5c**	13.61	48.55 (1.78)	38.02	45.17 (1.78)	42.45 (2.31)	24.73 (1.28) (1.54)	26.48 (1.22) (1.47)	37.18 (1.20) (1.67)	31.88 (0.99)	22.16 (0.80)		22.13 (1.34) (1.44)	
exo-**5c**	13.71	44.85 (2.16)	41.66	48.49 (1.44)	49.16 (1.73)	24.18 (1.34) (1.67)	29.74 (1.22) (1.55)	35.65 (1.13) (1.67)	27.51 (0.89)	25.64 (0.96)		20.16 (1.32)	
endo-**6**		49.20 (1.74)	36.86	52.60 (1.56)	39.88 (2.26)	20.37 (1.30–1.38)	24.65 (1.26) (1.58)	37.20 (1.19) (1.62)	20.57 (0.84)	32.69 (0.99)		60.93 (3.50-3.60)	
exo-**6**		49.36 (1.64)	39.68	56.30 (1.19)	40.97 (2.08)	29.63 (1.27) (1.57)	24.10 (1.29) (1.66)	35.89 (1.09) (1.64)	23.76 (0.89)	28.14 (1.01)		62.98 (3.58) (3.38)	

[a] X = Si or O.

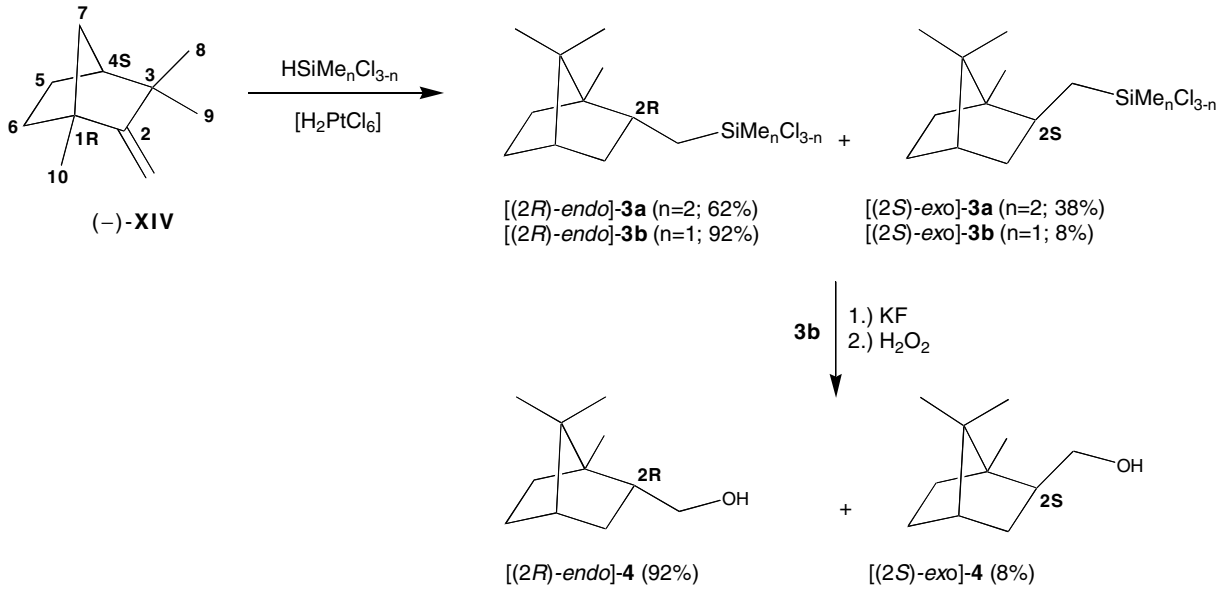


Scheme 2.

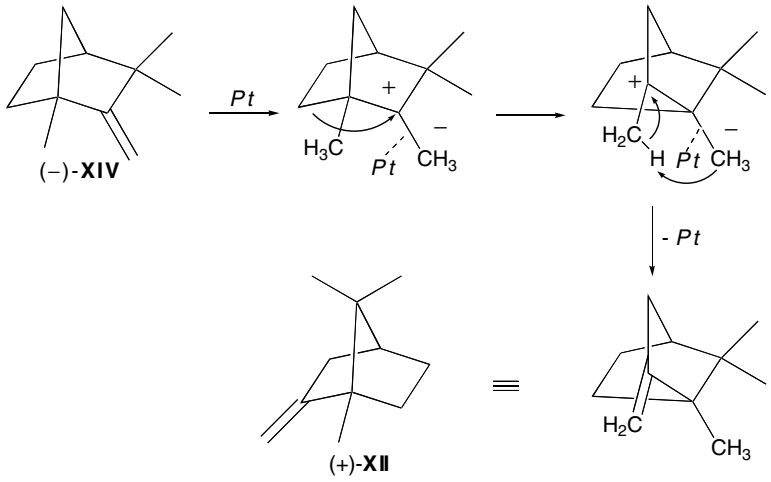


Scheme 3.

a ratio of 92:8 in reasonable yields (Scheme 4). A possible mechanism to account for the rearrangement of the isocamphane skeleton under hydrosilylation conditions is proposed in Scheme 5. Thus, complexation and polarization of the double bond by the Pt catalyst occurs, which is followed by a 1,3-alkyl shift (Wagner–Meerwein rearrangement) and a subsequent elimination involving the methyl group (10-position) that is attached to the bridgehead carbon atom (1-position) to give (+)-2-methylene bornane (**XII**) [21]. The involvement of the



Scheme 4.



Scheme 5.

methyl group in the 10-position provides a straightforward explanation as to why the related **XIII** lacking this group does not rearrange under the same conditions. The absolute stereochemistry of the rearrangement product (+)-2-methylene bornane (**XII**) is proven by the measurement of the optical rotations of the corresponding 2-borane methanols **4**, which are +6.6 and −5.9 for the products obtained according to Schemes 2 and 4, respectively ($c = 0.5\%$ in $CHCl_3$). It is worth mentioning that the hydroboration of 3-methylene fenchane (**XIV**) with BH_3 leads to the formation of an isomeric mixture of 1,3,4-trimethylbicyclo[2.2.1]heptan-2-ylmethanol with an undisclosed *endo*/*exo* ratio; thus no rearrangement of the terpene skeleton takes place under these reaction conditions [19].

3. Conclusion

For (+)-α-fenchane (**XI**) and (−)-2-methylene bornane (**XII**) the oxidative hydrosilylation and oxidative hydroboration with $HSiMeCl_2$ and BH_3, respectively, are complementary. In both cases, the oxidative hydrometalation is highly regioselective and gives exclusively anti-Markovnikov products. However, while the oxidative hydroboration affords predominately *exo*-terpene alcohols, the oxidative hydrosilylation gives mainly the *endo*-terpene alcohols. A similar observation was made before for (−)-β-pinene (**IV**) [6]. No hydrosilylation occurs with the same terpenes (**XI**, **XII** and **IV**) and $HSiCl_3$. The hydrosilylation of (+)-camphene (**XIII**) with $HSiCl_3$, $HSiMeCl_2$ and $HSiMe_2Cl$, also occurs

regioselectively, however with (almost) no diastereoselectivity. The reaction of (−)-3-methylene fenchane (**XIV**) with $HSiMeCl_2$ and $HSiMe_2Cl$, respectively, occurs with a clean rearrangement of the isocamphane skeleton into (+)-2-methylene bornane (**XII**) prior to hydrosilylation, while no hydrosilylation takes place with $HSiCl_3$.

4. Experimental

Hydrosilylations were performed under Ar using standard Schlenk and vacuum-line techniques. (+)-Camphene (**XIII**) was purchased (Aldrich; purity 85%) and used as supplied. The major impurity being tricycline (15%) is inactive under hydrosilylation conditions and was removed during the distillative work-up. (+)-α-Fenchene (**XI**) was prepared by a tosylate elimination/Wagner–Meerwein rearrangement of *endo*-(+)-fenchyl alcohol (Aldrich; purity 96%) [22]. (−)-2-Methylene bornane (**XII**) [17a,23] and (−)-3-methylene fenchane (**XIV**) [24] were accessible via Wittig reactions from (−)-fenchone (Aldrich; purity 98%) and (+)-camphor (Aldrich; purity 98%), respectively. The purity of **XI**–**XIV** was established by GC (95%, 97% and 96%, respectively). NMR spectra were collected using a Jeol Eclipse Plus 400 spectrometer (at 399.78 MHz (^{1}H), 100.54 (^{13}C), and 79.42 (^{29}Si)) and were referenced against $SiMe_4$. Optical rotations were collected using a JASCO DIP-1000 Digital Polarimeter. GC traces were measured using an Agilent Technologies 6890N Network GC System. Microanalyses were carried out by CMAS, Belmont, Australia.

4.1. Hydrosilylation of *XI*–*XIV* with $HSiCl_3$, $HSiMeCl_2$ and $HSiMe_2Cl$

A mixture of the appropriate terpene (30.0 mmol: 4.09 g of **XI** or **XIII**; 4.51 g of **XII** or **XIV**) and chlorosilane (32.0 mmol: 3.03 g for $HSiMe_2Cl$; 3.68 g for $HSiMeCl_2$; 4.33 g for $HSiCl_3$) was cooled to 0 °C with an ice-bath. The reaction was initiated by the addition of H_2PtCl_6 20.5 mg; 0.05 mmol) and the mixture was allowed to stir for 1 h at 0 °C, for 10 h at room temperature and was eventually heated for 2 h at 35 °C. Then, the excess of chlorosilane was removed by condensation in vacuum and the crude product was distilled under reduced pressure, whereby no attempts were made to separate the *exo* and *endo* isomers.

4.1.1. From *XI*

[(2*R*)-*endo*]- and [(2*S*)-*exo*]-1*R*,4*S*-7,7-dimethylbicyclo[2.2.1]heptan-2-ylmethyl-dimethylchlorosilane (**1a**). (Yield 6.37 g, 27.6 mmol, 92%; bp. 90–125 °C; *endo*/*exo* = 88:12.) Anal. Calc. for $C_{12}H_{23}ClSi$ (230.85): C, 62.43; H, 10.04. Found: C, 62.28; H, 9.87%.

[(2*R*)-*endo*]- and [(2*S*)-*exo*]-1*R*,4*S*-7,7-dimethylbicyclo[2.2.1]heptan-2-ylmethyl-methyldichlorosilane (**1b**). (Yield 6.78 g, 27.0 mmol, 90%; bp. 90–120 °C; *endo*/*exo* = 90:10.) Anal. Calc. for $C_{11}H_{20}Cl_2Si$ (251.27): C, 52.58; H, 8.02. Found: C, 52.69; H, 7.91%.

4.1.2. From *XII*

[(2*S*)-*endo*]- and [(2*R*)-*exo*]-1*S*,4*R*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylmethyl-dimethylchlorosilane (**3a**). (Yield 6.54 g, 26.7 mmol, 89%; bp. 135–155 °C; *endo*/*exo* = 70:30.) Anal. Calc. for $C_{13}H_{25}ClSi$ (244.88): C, 63.76; H, 10.29. Found: C, 63.91; H, 10.48%.

[(2*S*)-*endo*]- and [(2*R*)-*exo*]-1*S*,4*R*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylmethyl-methyldichlorosilane (**3b**). (Yield 7.40 g, 27.9 mmol, 93%; bp. 135–155 °C; *endo*/*exo* = 95:5.) Anal. Calc. for $C_{12}H_{22}Cl_2Si$ (265.30): C, 54.33; H, 8.36. Found: C, 54.31; H, 8.29%.

4.1.3. From *XIII*

[(3*R*)-*endo*]- and [(3*S*)-*exo*]-1*R*,4*S*-2,2-dimethylbicyclo[2.2.1]heptan-3-ylmethyl-dimethylchlorosilane (**5a**). (Yield 6.51 g, 28.2 mmol, 94%; bp. 100–110 °C; *endo*/*exo* = 50:50.) Anal. Calc. for $C_{12}H_{23}ClSi$ (230.85): C, 62.43; H, 10.04. Found: C, 62.35; H, 10.00%.

[(3*R*)-*endo*]- and [(3*S*)-*exo*]-1*R*,4*S*-2,2-dimethylbicyclo[2.2.1]heptan-3-ylmethyl-methyldichlorosilane (**5b**). (Yield 6.63 g, 26.4 mmol, 88%; bp. 100–115 °C; *endo*/*exo* = 50:50.) Anal. Calc. for $C_{11}H_{20}Cl_2Si$ (251.27): C, 52.58; H, 8.02. Found: C, 52.43; H, 8.24%.

[(3*R*)-*endo*]- and [(3*S*)-*exo*]-1*R*,4*S*-2,2-dimethylbicyclo[2.2.1]heptan-3-ylmethyl-trichlorosilane (**5c**). (Yield 5.87 g, 21.6 mmol, 72%; bp. 145–170 °C; *endo*/*exo* = 55:45.) Anal. Calc. for $C_{10}H_{17}Cl_3Si$ (271.69): C, 44.21; H, 6.31. Found: C, 43.96; H, 6.22%.

4.1.4. From *XIV*

[(2*R*)-*endo*]- and [(2*S*)-*exo*]-1*R*,4*S*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylmethyl-dimethylchlorosilane (**3a**). (Yield 6.61 g, 27.0 mmol, 90%; bp. 135–155 °C; *endo*/*exo* = 62:38.) Anal. Calc. for $C_{13}H_{25}ClSi$ (244.88): C, 63.76; H, 10.29. Found: C, 63.70; H, 10.21%.

[(2*R*)-*endo*]- and [(2*S*)-*exo*]-1*R*,4*S*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylmethyl-methyldichlorosilane (**3b**). (Yield 7.24 g, 27.3 mmol, 91%; bp. 135–155 °C; *endo*/*exo* = 92:8.) Anal. Calc. for $C_{12}H_{22}Cl_2Si$ (265.30): C, 54.33; H, 8.36. Found: C, 54.15; H, 8.47%.

4.2. KF-assisted oxidation of *1b*–*4b* with H_2O_2

The appropriate methyldichlorosilane (10.0 mmol: 2.51 g of **1b** or **5b**; 2.65 g of **3b**) was slowly added under vigorous stirring to a suspension of KF (2.91 g, 50.0 mmol) in MeOH (10 mL) and THF (10 mL). After 30 min, the mixture was cooled at 0 °C and H_2O_2 (10 mL) was added slowly. The mixture was allowed to warm to room temperature and was then heated under reflux for

2d. The product was extracted with hexane (2 × 20 mL), the combined organic extracts were dried over Na_2SO_4 and the solvents removed in vacuum. The product was purified by Kugelrohr distillation between 50 and 80 °C/0.02 mm. The residue contained siloxanes.

4.2.1. From *1b*/*XI*

[(2*R*)-*endo*]- and [(2*S*)-*exo*]-1*R*,4*S*-7,7-dimethylbicyclo[2.2.1]heptan-2-yl-methanol (**2**). (Yield 571 mg, 3.71 mmol, 37%; *endo*/*exo* = 90:10.) Anal. Calc. for $C_{10}H_{18}O$ (154.25): C, 77.87; H, 11.76. Found: C, 77.72; H, 11.72%.

4.2.2. From *3b*/*XII*

[(2*S*)-*endo*]- and [(2*R*)-*exo*]-1*S*,4*R*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl-methanol (**4**). (Yield 690 g, 4.12 mmol, 41%; *endo*/*exo* = 95:5.) Anal. Calc. for $C_{11}H_{20}O$ (168.28): C, 78.51; H, 11.98. Found: C, 78.30; H, 11.99%.

4.2.3. From *5b*/*XIII*

[(3*R*)-*endo*]- and [(3*S*)-*exo*]-1*R*,4*S*-2,2-dimethylbicyclo[2.2.1]heptan-3-yl-methanol (**6**). (Yield 591 mg, 3.83 mmol, 38%; *endo*/*exo* = 50:50.) Anal. Calc. for $C_{10}H_{18}O$ (154.25): C, 77.87; H, 11.76. Found: C, 77.77; H, 11.75%.

4.2.4. From *3b*/*XIV*

[(2*R*)-*endo*]- and [(2*S*)-*exo*]-1*R*,4*S*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl-methanol (**4**). (Yield 574 mg, 3.41 mmol, 34%; *endo*/*exo* = 92:8.) Anal. Calc. for $C_{11}H_{20}O$ (168.28): C, 78.51; H, 11.98. Found: C, 78.59; H, 12.08%.

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