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Organosamariums: preparation using diiodosamarium and reactivity in tetrahydropyran

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Abstract

Diiodosamarium prepared in tetrahydropyran reduces allylic, benzylic and alkyl halides at 0 or −15°C to give organosamariums which are stable under these conditions. The reactivity of these organometallics has been explored, showing that they are very selective reagents. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Diiodosamarium; Tetrahydropyran; Organosamariums; Allylic halides; Benzylic halides; Alkyl halides

1. Introduction

Organosamariums may be generated in THF from organic iodides and bromides and SmI_2 according to Eq. 1. However, they are quite unstable and need to be trapped as soon as possible by electrophiles [1,2].

$$RX + 2\,SmI_2 \xrightarrow{THF} RSmI_2 + XSmI_2 \quad (1)$$

Alkyl samariums abstract hydrogen from THF to give alkanes unless they are kept at −78°C [3]. Wurtz coupling reactions are exclusively observed in reactions of allylic or benzylic halides with SmI_2 in THF [4].

On the other hand, stable organosamariums can be prepared in THF by using $SmCp_2$ [2] [5] or $Sm(OTf)_2$/LiOTf [6] as the reducing agent. We have previously described the beneficial effect of THP in the reaction of SmI_2 (prepared in THP) on acid chlorides RCOCl for the formation of isolable acylsamarium species $RC(O)SmI_2$ [7]. The competitive coupling to give samarium-enediolates could be avoided, allowing the use of acylsamariums as nucleophilic reagents (e.g. formation of α-ketols by addition to aldehydes). Ito has also reported that the use of THP as solvent for SmI_2 allows the generation of (α-aminoalkyl)samarium(III) [8]. We wish to report here that stable organosamariums are easily prepared according to Eq. 1 with SmI_2 in tetrahydropyran (THP) instead of THF.

2. Results and discussion

We found that isolable allylsamarium species are formed in THP at −15°C by the action of SmI_2 on (*E*)-1-iodo-2-dodecene (Table 1 Scheme 1). The presence of organometallic species was established by quenching with D_2O and product analysis. Deuteration has been clearly demonstrated with iodide **1** giving a mixture of olefins **2** and **3**, with a high content of deuteration (85%) for **3**. Quenching after 15 min by an electrophile such as butanone gave regioselectively, and in good yield, the alcohol resulting from attack by the terminal position of the allylsamarium.

Obviously, the regioselectivity of electrophilic attack on the allylic samarium species strongly depends upon the electrophiles: D_2O reacts predominantly on the more substituted carbon, whereas butanone almost exclusively attacks the less hindered carbon. Furthermore,

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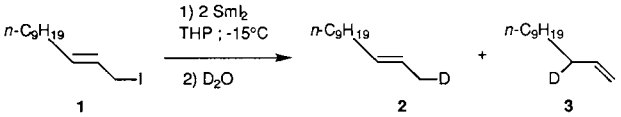
Table 1
Deuteration of allylic samarium species



t (min) [a]	2/3 ratio [b]	deuteration % of 2	deuteration % of 3
15	0.49	17	85
30	1.08	<10	65
60	5.25	<10	27

[a] Dropwise addition of **1** in 10 min, then standing time t (min) before deuterolysis.

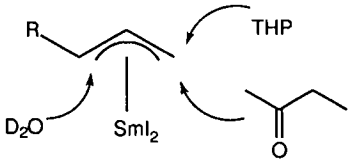
[b] The conversion of **1** into alkenes is quantitative, the ratio **2/3** is determined by GC and percentages of deuteration by GC/MS.

the degradation of the organometallic species (presumably through a reaction with THP) preferentially occurs by reaction on the terminal position of the allylic species. Assuming that a η^3-allyl samarium species is formed [5] these results are illustrated in Scheme 2. A thorough interpretation of the reactivity of this organometallic requires further investigation.

The organosamarium prepared from allyl iodide is much more stable than the one described above. It is prepared at 0°C and can be used for at least 24 h provided it is stored at 0°C. The allyl transfer has been realized on various functions such as aldehydes, ketones, imines, esters α-,β- or γ-keto esters. The low basicity of the allylsamarium reagent is highlighted by its successful addition to allyl acetoacetate, a ketone prone to enolization [9,10]. The allylation is very stereoselective both on camphor and fenchone (Table 2).

The Grignard technique (method A) is clearly superior to the Barbier technique (method B) and avoids by-products due to ketone pinacolization or acid chloride decarbonylation (see Table 3).

Organosamariums have been successfully prepared in a similar way from other allylic halides (and propargyl bromide). Cinnamyl halides and 3-bromocyclohexene, however give Wurtz coupling products on reaction with



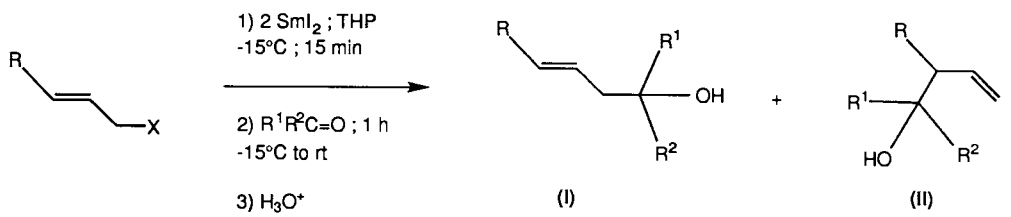
Scheme 2. Regioselectivity of reactions of allylic samarium species.

SmI_2. Quenching by an electrophile such as 2-octanone gave regioselectively, and in good yield, the alcohols resulting from attack by the terminal position of the allylsamarium compounds; propargylsamarium dihalide gives mainly allenic alcohol (Table 4)

The above procedure also applies to the preparation of benzylic samarium diiodide as evidenced by some reactions with benzylic bromides (deuterolysis or addition on 2-octanone). In the case of 4-*t*-Bu benzyl bromide, deuterolysis leads to quantitative conversion into hydrocarbons; the ratio (82:18) is measured by GC, (Scheme 3).

The generation of stable alkyl samarium complexes from SmI_2 is a difficult task which can be carried out by the use of THP as solvent, as evidenced by the following experimental results (deuterolysis or addition to 2-butanone) (Scheme 4). In contrast to allylic and benzylic halides, reduction of alkyl halides to organometallic species must be performed in the presence of HMPA as a co-solvent. The conversions of the 1-iodo and 2-iodododecanes are almost quantitative ($>95\%$); after deuterolysis the dodecanes are formed with a high rate of deuterium incorporation (85%). The alkyl samarium diiodide reacts slowly with ketones, in order to enhance the rates of the reactions (and prevent any organometallic degradation) TMSCl is added as previously reported [3].

Reduction of *cis* and *trans* 1-iodo-4-*tert*-butylcyclohexane into organometallic species followed by trapping of the resulting products with butanone leads in both experiments to the same diastereomeric mixture of alcohols (the *trans* isomer broadly predominates) (Scheme 5).

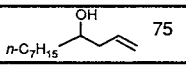
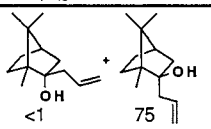
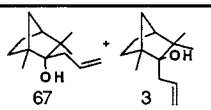
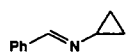
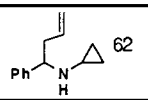
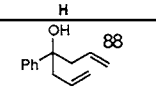
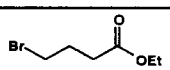
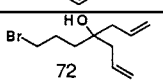
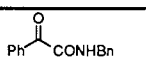
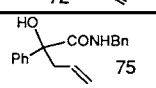
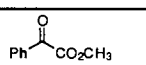
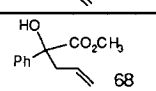
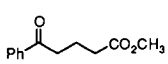
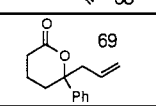
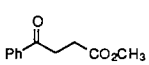
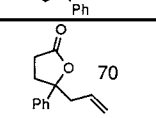
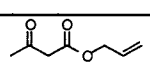
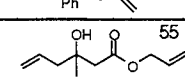


X = I ; R = *n*-C_9H_{19} ; $R^1 = CH_3$; $R^2 = C_2H_5$; (I) : 90 % (isolated yield), (II) : <1%

E/Z = 98/2

Scheme 1. Preparation and reactions of allylic samarium species.

Table 2
Reaction of allylsamarium diiodide in THP on various functional groups

Substrate	Reaction time [a] (h)	allyliodide/Substrate	Products, isolated yields %
n-$C_7H_{15}CHO$	0.25	1:0.5	
	4[b]	1:0.5	
	4[b]	1:0.5	
	4[b]	1:0.5	
$PhCO_2C_2H_5$	2	1:0.45	
	1.5	1:0.4	
	2	1:0.75	
	2	1:0.9	
	15	1:0.5	
	15	1:0.5	
	3	1:0.75	

[a] Reactions on 2 mmol of substrate: 2 eq. SmI_2 and 1 eq. allyl iodide in THP (1 h, 0°C), then addition of substrate (0°C to rt), acidic hydrolysis, isolated yield by respect to substrate.
[b] Reaction at 0°C.

These results are consistent with the transient formation of an alkyl radical, which undergoes further reduction into an organometallics species (Scheme 6).

3. Conclusions

Organosamariums are easily prepared in tetrahydropyran by SmI_2 reduction of allylic, benzylic or alkyl halides. The organometallics which are obtained in this solvent are much more stable than in THF. However, these compounds can react with many functionalities. The selectivity of these reagents can be highlighted by their successful addition to the keto group of keto esters or keto amides.

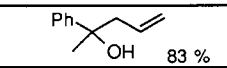
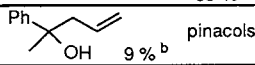
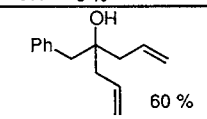
4. Experimental

4.1. General

^1H and ^{13}C-NMR spectra were recorded at 250 and 63 MHz, respectively on a Bruker AM 250 instrument (unless otherwise stated). Chemical shifts are reported in ppm (δ) downfield from TMS. Coupling constants are reported in Hertz. Infrared (IR) spectra were recorded neat on a FT-IR IFS 66 Bruker and are reported in cm^{-1}.

Mass spectra (MS) data were determined on a GC/MS Ribermag R10-10 instrument. Chemical ionisation (CI) was carried out using NH_3 as the reactant gas and electronic impact was performed at 70 eV. High resolu-

Table 3
Reactions of allylsamarium diiodide (prepared at 0°C in THP from 2 equivalents of SmI_2) on acetophenone and phenylacetyl chloride

Substrate	Method[a]	allyliodide/Substrate	Products and isolated yields
Acetophenone	A	1:0.9	 83 %
Acetophenone	B	1:0.9	 pinacols: 57 %
$PhCH_2COCl$	A[c]	1:0.45	 60 %
$PhCH_2COCl$	B[c]	1:0.45	complex mixture of products (decarbonylation)

[a] Method A: organosamarium prepared at 0°C in 1 h followed by addition of electrophile; reaction time 1 h. Method B: allyl iodide and electrophile are mixed and added to SmI_2 in THP at 0°C; reaction time 2 h.
[b] GC yield.
[c] Reaction time 15 h; full transformation after 2 h (method A) in the presence of 1% $NiCl_2$ dppe.

tion mass spectra were determined on a GC/MS Finningan-MAT-95-S. Flash chromatography was performed on silica gel (Merck 230–240 mesh; 0.0040–0.0630 mm).

All commercially available organic compounds were distilled before use, (*E*)-1-iodo-2-dodecene, *cis* and *trans* 1-iodo-4-*tert*-butylcyclohexane and 2-iodododecane were prepared according to literature procedures [11–13]. Samarium powder (40 mesh) was purchased from Labelcomat Company. Tetrahydropyran was distilled under argon from sodium benzophenone ketyl, HMPA was distilled from CaH_2 and degassed immediately prior to use. All the reactions were carried out under argon in Schlenk tubes using standard vacuum line techniques.

4.2. Preparation of SmI_2 in tetrahydropyran

To a mixture of samarium powder (601 mg, 4.00 mmol) and 1,2-diiodoethane (1.127 g, 4.00 mmol) under argon at room temperature THP was added (4.00 ml) with vigorous stirring. After a short induction period a slightly exothermic reaction took place and the mixture turned dark blue. After 8 h at room temperature, a slurry of SmI_2 was obtained.

4.3. Preparation of allylsamarium diiodide

To a slurry of SmI_2 (4 mmol) in 4 ml of THP under argon at 0°C, allyl iodide (0.336 g, 2 mmol) in THP (2 ml) was added with stirring. The mixture was kept at 0°C for 1 h and turned light blue (turquoise). The allyl samarium diiodide was obtained as a slurry. The same procedure was used for other allylic and benzylic halides except the preparation was performed at −15°C and the halide was added dropwise to SmI_2.

4.4. Preparation of alkylsamarium diiodide

A total of 2.1 ml of HMPA (12 mmol) was added to a slurry of SmI_2 (4 mmol) in 15 ml of THP under argon at 20°C. The mixture turned violet, the alkyl iodide was then added (2 mmol in 2 ml of THP). The mixture was kept at 20°C for 2 min, it was then cooled to −20°C.

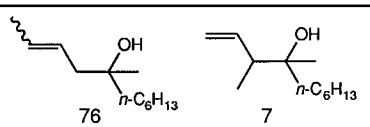
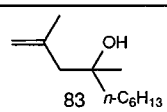
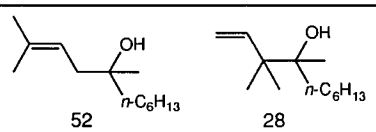
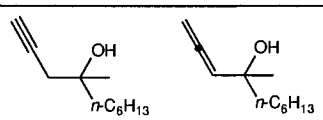
4.5. Procedure for reactions with allylsamarium diiodide

In a Schlenk tube under argon, allylsamarium diiodide (2 mmol) in 6 ml of THP (Section 4.3) and 1 mmol of substrate in 2 ml of THP were mixed and stirred at 0°C. The mixture turned yellow within a reaction time of 0.5 h. It was then quenched with HCl (0.1 M) to obtain a clear solution and extracted with ether. The combined extracts are washed with sodium thiosulfate and brine. The organic layer is dried over $MgSO_4$. After removal of solvent the crude material is purified by flash chromatography on silica gel. The same procedure is used for other allylic and benzylic samarium dihalides except that the reactions are performed from −15 to 20°C during 3 h.

4.6. Procedure for reactions with alkylsamarium diiodides

In a Schlenk tube under argon, alkylsamarium diio-

Table 4
Reactions of allylic samariums species prepared from allylic halides, with 2-octanone

Allylic halide[a]	Products and isolated yields %
Crotyl bromide	 76 7
Methallyl bromide	 83
Isoprenyl bromide	 52 28
3-bromocyclohexene	Wurtz coupling product.
Cinnamyl bromide (and chloride)	Mixture of Wurtz coupling products.
Propargyl bromide	 6 57

[a] Reactions on 2 mmol of organic halide, 2 eq. SmI_2 in THP (4 mL of solvent, 15 min, −15°C), then addition of 0.66 eq. ketone (−15°C to rt, 3 h), acidic hydrolysis, isolated yield by respect to ketone.

dide (2 mmol) in 15 ml of THP and 2 ml of HMPA (Section 4.4) were mixed with 1 mmol of substrate in 2 ml of THP and 0.4 ml (3.18 mmol) of chlorotrimethylsilane and stirred at −20°C. The temperature rose to 20°C within 4 h, the mixture turned yellow during this reaction time. Quenching and isolation of products was performed as described above (Section 4.5)

4.7. Identification of products

4.7.1. 3-Deutero-1-dodecen

MS m/z 169 (M^+), 141 ($M^+-C_2H_4$), 126 ($M^+-C_2H_4-CH_3$), 112, 98, 84, 70, 56 (100.00), 43. (1-dodecene: 168, 140, 125, 111, 97, 83, 69, 55, 41 (100.00).

4.7.2. (2E) 1-deutero-2-dodecen

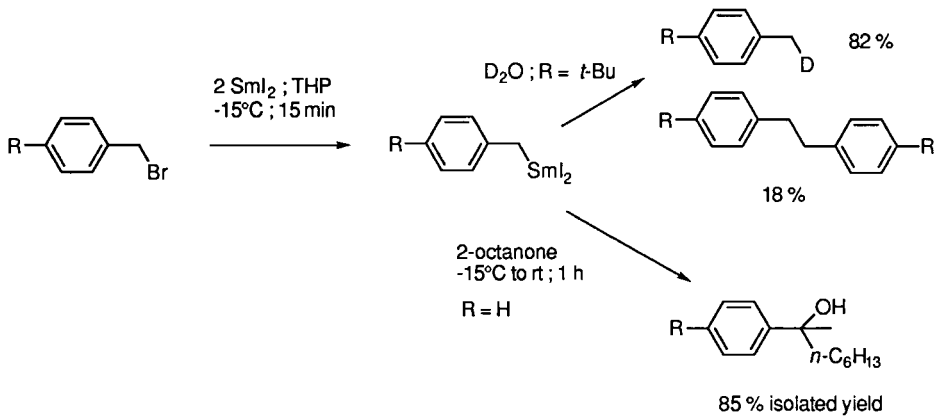
MS m/z 169 (M^+), 141 ($M^+-C_2H_4$), 126 ($M^+-C_2H_4.CH_3$), 112, 98, 84, 70, 56 (100.00), 43. ((2*E*) 2-dodecene: 168, 140, 125, 111, 97, 83, 69, 55 (100.00), 41).

4.7.3. Undecen-4-ol

Yield 75%, as colorless oil; IR ν_{max} (neat)/cm^{-1}: 3357, 2926, 2856, 1641, 1467, 1378, 995, 912; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 5.98–5.71 (1H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.23–5.03 (2H, m), 3.72–3.51 (1H, m), 2.39–2.11 (2H, m), 1.89–1.13 (12H, m), 0.87 (3H, t, $J = 6.3$ Hz); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 135.00, 118.03, 70.75, 42.00, 36.88, 31.88, 29.68, 29.34, 25.73, 22.71, 22.69, 14.14; MS m/z 129 ($M^+-C_3H_5$), 69 (100.00), 55; CI/NH_3 m/z 170 (MH^+), 188 (MNH_4^+). HRMS Calc. for $C_{11}H_{22}O$ $(M-C_3H_5)^+$ 152.1565 Found 152.1553.

4.7.4. (1R,2R) Endo-1-(prop-2'-enyl)-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol

Yield 75%, as orange oil; IR ν_{max} (neat)/cm^{-1}: 3568 (OH), 3074, 2949, 1636, 1457, 1389, 1272, 1120, 911; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 6.03–5.80 (1H, ddt, $J = 16.6$, 9.8, 7.8 Hz), 5.18–5.06 (2H, m), 2.27 (2H, dd, $J = 7.8$, 1.0 Hz), 2.12–1.87 (1H, dt, $J = 3.6$, 12.8 Hz), 1.85–1.56 (3H, m), 1.53–1.28 (3H, m), 1.07 (3H, m),

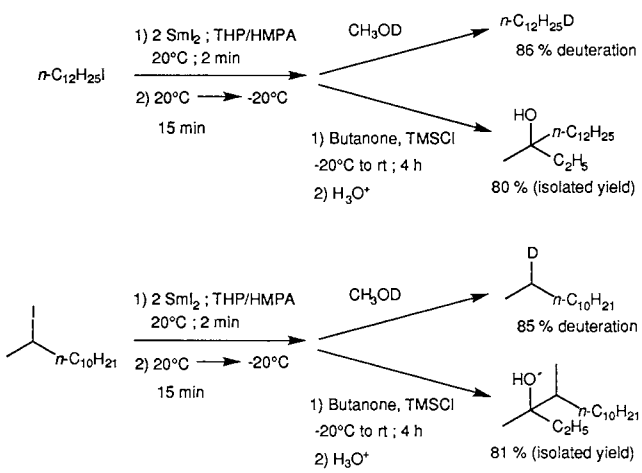


Scheme 3. Preparation and reactions of benzylic samarium species.

0.83 (6H, m); ^{13}C-NMR (50.8 MHz, $CDCl_3$) δ: 134.99, 118.91, 79.71, 52.18, 49.40, 45.98, 45.04, 44.56, 30.55, 27.05, 21.43, 20.99, 10.97; MS m/z 194 (M^+), 153 ($M^+-C_3H_5$), 109, 95 (100.00), 69, 41; CI/NH_3 m/z 195 (MH^+), 212 (MNH_4^+). HRMS Calc. for $C_{13}H_{22}O$ 194.1671 Found 194.1657.

4.7.5. (1R,2R)
1-(prop-2'-enyl)-1,3,3-Trimethyl-2-norbornanol

Yield 67%, as orange oil; IR ν_{max} (neat)/cm^{-1}: 3499 (OH), 3075, 2948, 1637, 1456, 1390, 1239, 1065, 977; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 6.09–5.90 (1H, m), 5.17–5.07 (2H, m), 2.39 (1H, dd, $J = 14.0$, 6.0 Hz), 2.19 (1H, dd, $J = 14.0$, 8.0 Hz), 1.03 (3H, s), 1.00 (3H, s), 0.89 (3H, s); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 135.86, 119.47, 79.42, 52.28, 50.04, 44.37, 41.01, 40.71, 30.62, 27.75, 25.04, 22.65, 18.11; MS m/z 194 (M^+), 153 ($M^+-C_3H_5$), 109, 95 (100.00), 69, 41; CI/NH_3 m/z 195 (MH^+), 212 (MNH_4^+). HRMS Calc. for $C_{13}H_{22}O$ 194.1671 Found 194.1663.



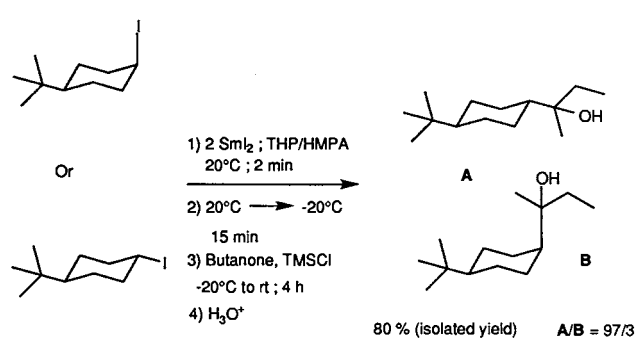
Scheme 4. Preparation and reactions of alkyl samarium species.

4.7.6. N-Cyclopropyl-1-allylbenzylamine

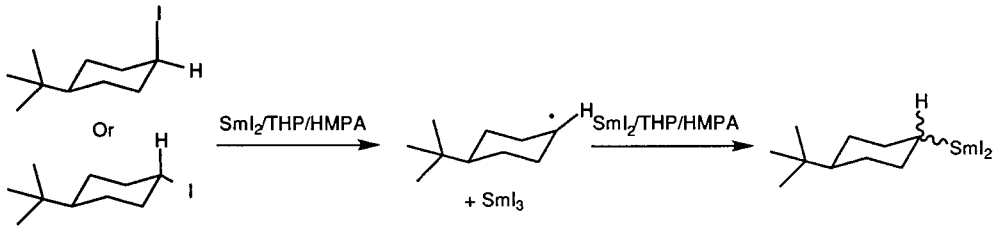
Yield 62%, as colorless oil; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.40–7.08 (5H, m), 5.75–5.53 (1H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.15–4.82 (2H, m), 3.71 (1H, t, $J = 7.5$ Hz), 2.53–2.28 (2H, m), 2.00 (1H, s), 1.91 (1H, q, $J = 5$ Hz), 0.39–0.13 (4H, m); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 144.17, 135.52, 128.30, 127.36, 126.97, 117.29, 63.02, 42.13, 29.13, 6.82, 6.10; MS m/z 187 (M^+), 146 ($M^+-C_3H_5$), 131 ($M^+-C_3H_6N$), 91 (100.00), 77 41;CI/NH_3 m/z 188 (MH^+), 205 (MNH_4^+). HRMS Calc. for $C_{13}H_{17}N$ 187.1361 Found 187.1344.

4.7.7. 4-Phenylheptadi-1,6-en-4-ol

Yield 88%, as orange oil; IR ν_{max} (neat)/cm^{-1}: 3466 (OH), 2932, 1641, 1446, 1259, 1030, 915, 701; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.36–7.11 (5H, m), 5.51 (2H, ddt, $J = 14.6$, 10.2, 7.5 Hz), 5.02 (4H, m), 2.67–2,38 (4H, système AB); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 145.78, 133.45, 128.11, 125.34, 119.14, 75.09, 46.83; SM m/z 170 (M^+-OH), 147 ($M^+-C_3H_5$), 105 (100.00), 77 ($M^+-C_7H_{11}O$); CI/NH_3 m/z 189 (MH^+), 206 (MNH_4^+). HRMS Calc. for $C_{13}H_{16}O$ $(M-C_3H_5)^+$ 147.0810; Found 147.0796.



Scheme 5. Preparation and reactions of cycloalkylsamarium diiodides.



Scheme 6. Mechanistic scheme for the formation of cycloalkylsamarium species.

4.7.8. 7-Bromo-4-(prop-2'-enyl)hept-1-en-4-ol

Yield 72%, as yellow oil; IR ν_{max} (neat)/cm^{-1}: 3435 (OH), 3076, 2930, 1640, 1445, 1253, 997, 917; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 5.91–5.62 (2H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.13–5.00 (4H, m), 3.35 (2H, t, $J = 6.6$ Hz), 2.16 (4H, dd, J = 8.2, 0.8 Hz), 1.98–1.38 (4H, m); ^{13}C-NMR (50.8 MHz, $CDCl_3$) δ: 133.28, 119.05, 73.05, 43.66, 37.58, 34.35, 26.93; MS m/z 191–193 ($M^+ - C_3H_5$), 149–151, 121–123 ($M^+ - C_7H_{11}O$), 111 ($M^+ - C_4H_6Br$), 69, 41 (100.00); IC/NH_3 m/z 233–235 (MH^+), 250–252 (MNH_4^+). HRMS Calc. for $C_{18}H_{19}BrO$ $(M-C_3H_6Br)^+$ 111.0810; Found 111.0796.

4.7.9. N-Benzyl-2-hydroxy-2-phenylpent-4-enamide

Yield 75%, as viscous colorless oil; IR ν_{max} (neat)/cm^{-1}: 3400 (OH), 2927, 1659 ($CONHCH_2Ph$), 1523, 1361 ($CONHCH_2Ph$), 1260, 1142, 1075, 921, 728; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.60–7.46 (2H, m), 7.38–6.90 (8H, m), 5.73–5.50 (1H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.20–5.06 (2H, m), 4.42–4.13 (2H, système AB), 3.16 (1H, s), 3.14–2.61 (2H, AB system); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 173.28, 141.84, 138.02, 132.66, 128.57, 128.26, 127.65, 127.48, 127.36, 125.33, 120.87, 77.69, 44.38, 43.26; MS m/z 281 (M^+), 240 ($M^+ - C_3H_5$), 147($M^+ - C_{10}H_{11}O$) 105, 91 ($M^+ - C_{11}H_{12}NO_2$), 77, 41; CI/NH_3 m/z 282 (MH^+), 299 (MNH_4^+). HRMS Calc. for $C_{18}H_{19}NO_2$ 281.1416; Found 281.1416.

4.7.10. Methyl-2-hydroxy-2-phenylpent-4-enoate

Yield 68%, as yellow oil; IR ν_{max} (neat)/cm^{-1}: 3509 (OH), 2856, 1741, 1643, 1494, 1350, 1232, 925, 865, 699; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.58–7.11 (5H, m), 5.75–5.58 (1H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.15–5.01 (2H, m), 3.67 (3H, s), 2.96–2.63 (2H, m); ^{13}C-NMR (50.8 MHz, $CDCl_3$) δ: 175.05, 141.21, 132.36, 128.29, 127.85, 125.52, 119.39, 78.15, 53.21, 44.1; SM m/z 188 ($M^+ - H_2O$), 165 ($M^+ - C_3H_5$), 105 (100.00), 77 ($M^+ - C_6H_9O_3$); CI/NH_3 m/z 209 (MH^+), 224 (MNH_4^+). HRMS Calc. for $C_9H_9O_3$ $(M-C_3H_5)^+$ 165.0551 Found 165.0541.

4.7.11. 1-(prop-2'-enyl)-1-Phenylpentanolide

Yield 69%, as yellow oil; IR ν_{max} (neat)/cm^{-1}: 2959, 1736 (lactone), 1640, 1447, 1240, 1040, 926, 850, 799; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.35–7.15 (5H, m), 5.75–5.50 (1H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.03–4.91 (2H, m), 2.67–2.54 (2H, m), 2.48–2.16 (3H, m), 2.12–1.97 (1H, m), 1.95–1.38 (2H, m); ^{13}C-NMR (50.8 MHz, $CDCl_3$) δ: 171.57, 142.92, 131.96, 128.61, 127.45, 125.03, 119.31, 86.93, 48.20, 31.48, 29.15, 16.16; MS m/z 175 ($M^+ - C_3H_5$), 147, 105 (100.00), 77 ($M^+ - C_8H_{11}O_2$), 55; IC/NH_3 m/z 217 (MH^+), 234 (MNH_4^+). Anal Calc. for $C_{14}H_{16}O_2$ (216.27): C: 77.75, H: 7.46; Found: C: 77.72, H: 7.29. HRMS Calc. for $C_{14}H_{16}O_2$ $(M-C_3H_5)^+$ 175.0759 Found 175.0748.

4.7.12. 1-(prop-2'-enyl)-1-Phenylbutanolide

Yield 70%, as yellow oil; IR ν_{max} (neat)/cm^{-1}: 2936, 1779 (lactone), 1641, 1448, 1272, 1193, 925, 764, 703; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.59–7.13 (5H, m), 5.82–5.45 (1H, m), 5.35–5.4.94, (2H, m), 2.94–2.28 (6H, m); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 176.44, 143.00, 131.58, 128.46, 127.64, 124.60, 119.89, 88.50, 46.64, 33.34, 28.70; MS m/z 161 ($M^+ - C_3H_5$), 133, 115, 105 (100.00), 91, 77 ($M^+ - C_7H_{10}O$), 51; CI/NH_3 m/z 203 (MH^+), 220 (MNH_4^+). HRMS Calc. for $C_{10}H_9O_2$ $(M-C_3H_5)^+$ 161.0603; Found 161.0600.

4.7.13. 4-Benzylheptadi-1,6-en-4-ol

Yield 60%, as yellow oil; IR ν_{max} (neat)/cm^{-1}: 3456 (OH), 2927, 1640, 1453, 1261, 915, 703; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.29–7.03 (5H, m), 5.95–4.96 (2H, ddt, $J = 16.6$, 10.7, 7.3 Hz), 5.15–4.96 (4H, m), 2.69 (2H, s), 2.13 (4H, d, $J = 7.3$ Hz), 1.58 (OH); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 137.17, 133.78, 130.78, 128.23, 126.54, 118.86, 73.52, 45.40, 43.48; MS m/z 161 ($M^+ - C_3H_5$), 111 ($M^+ - C_7H_7$), 91 (100.00, $M^+ - C_7H_{11}O$), 69, 41; IC/NH_3 m/z 203 (MH^+), 220 (MNH_4^+). HRMS Calc. for $C_{11}H_{13}O$ $(M-C_3H_5)^+$ 161.0966 Found 161.0955.

4.7.14. 5-Methyl-2-undecen-5-ol

Yield 83%; IR ν_{max} (neat)/cm^{-1} 3389 (OH), 2859, 2639, 2459, 2377, 2239, 969, 796; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: major isomer 5.43 (2H, m), 2.06 (2H, dd, $J = 5.8$, 2.4 Hz), 1.63 (3H, d, $J = 4.9$ Hz), 1.52–1.22 (10H, m), 1.06 (3H, s), 0.82 (3H, t, $J = 6.8$ Hz); minor isomer 5.43 (2H, m), 2.22 (2H, dd, $J = 5.8$, 2.4 Hz), 1.57 (3H, d, $J = 4.9$ Hz), 1.52–1.22 (10H, m), 1.09 (3H, s), 0.82 (3H, t, $J = 6.8$ Hz); ^{13}C-NMR (62.9 MHz,

$CDCl_3$) δ: major isomer: 129.79, 126.68, 72.63, 45.34, 42.29, 32.24, 30.27, 27.02, 24.28, 23.00, 28.52, 24.46; minor isomer 127.68, 125.83, 77.62, 73.42, 48.26, 39.30, 27.05, 24.44, 24.22, 24.00, 23.57, 23.42; MS m/z 169 (M^+-CH_3), 129 ($M^+-C_4H_7$), 99 ($M^+-C_6H_{23}$), 69, 55, 43 (100.00). IC/NH_3 m/z 285 (MH^+), 202 (MNH_4^+). Anal Calc. for $C_{12}H_{24}O$: C: 78.2; H: 23.22; found: C: 77.83; H: 23.06 (on mixture of isomers). major isomer: HRMS Calc. for $C_{12}H_{24}O$ $(M-C_4H_7)^+$ 129.1279; Found 129.1275; minor isomer: HRMS Calc. for $C_{12}H_{24}O$ $(M-C_4H_7)^+$ 129.1279; Found 129.1277.

4.7.15. 2,5-Dimethyl-2-undecen-5-ol

Yield 52%; IR ν_{max} (neat)/cm^{-1} 3433 (OH), 2931, 1636, 1466, 1375, 1297, 1262, 1125, 1011.; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 5.17 (1H, t, $J=7.8$ Hz), 2.12 (2H, dd, $J=7.8$, 1.4 Hz), 1.71 (3H, s), 1.60 (3H, s), 1.55–1.18 (10H, m), 1.11 (3H, s), 0.85 (3H, t, $J=6.8$ Hz).; ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 145.57, 134.89, 73.08, 41.79, 40.20, 31.88, 29.92, 26.60, 26.08, 23.90, 22.03, 17.94, 14.07.; MS m/z 198 (M^+), 183 (M^+-CH_3), 181 (M^+-OH), 129 ($M^+-C_5H_9$), 113, 70 (100.00), 55, 43. CI/NH3 m/z 199 (M^+), 216 (MNH_4^+). Anal Calc. for $C_{13}H_{26}O$: C: 78.72; H: 13.21; Found: C: 78.65; H: 13.15.

4.7.16. 3,3,4-Trimethyl-1-decen-4-ol

Yield 28%; IR ν_{max} (neat)/cm^{-1} 3433 (OH), 2931, 1636, 1466, 1375, 1297, 1262, 1125, 1011. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 6.05 (1H, dd, $J=16.6$, 9.8 Hz), 5.08 (1H, dd, $J=9.8$, 1.4 Hz), 5.03 (1H, dd, $J=16.6$, 1.4 Hz), 1.91 (3H, s), 1.87 (3H, s), 1.55–1.18 (10H, m), 1.11 (3H, s), 0.85 (3H, t, $J=6.8$ Hz); ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 119.52, 113.12, 75.60, 40.21, 36.49, 31.89, 29.93, 26.08, 23.76, 22.63, 22.04, 20.95, 14.07; MS m/z 198 (M^+), 183 (M^+-CH_3), 181 (M^+-OH), 129 ($M^+-C_5H_9$), 113, 70 (100.00), 55, 43; CI/NH_3 m/z 199 (M^+), 216 (MNH_4^+). Anal Calc. for $C_{13}H_{26}O$: C: 78.72; H: 13.21; Found: C: 78.65; H: 13.15.

4.7.17. 4-Methyl-2,2-decadien-4-ol

Yield 57%; IR ν_{max} (neat)/cm^{-1} 3374 (OH), 2932, 2958 (CH_2=C=CH_2), 2467, 2377, 2227, 922, 842; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 5.27 (2H, t, $J=6.3$ Hz), 4.87 (2H, d, $J=6.3$ Hz), 1.69–1.29 (10H, m), 1.26 (3H, s), 0.85 (3H, t, $J=6.3$ Hz); ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 205.64, 99.47, 78.42, 72.44, 42.95, 32.88, 29.72, 27.93, 24.25, 22.67, 24.24; MS m/z 153 (M^+-CH_3), 129 ($M^+-C_3H_3$), 83 ($M^+-C_6H_{13}$), 69, 43 (100.00); CI/NH_3 m/z 169 (MH^+), 186 (MNH_4^+). Anal Calc. for $C_{11}H_{20}O$: C: 78.52; H: 22.98; Found: C: 78.50; H: 22.99.

4.7.18. 4-Methyl-1-decyn-4-ol

Yield 6%; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.57 (1H, d, $J=2.7$ Hz), 2.42 (2H, d, $J=2.7$ Hz), 1.65–1.20 (10H, m), 1.29 (3H, s), 0.88 (3H, t, J = 6.3 Hz); ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ: 82.55, 72.43, 67.62, 42.25, 32.42, 29.79, 27.93, 22.73, 24.24; MS m/z 153 (M^+-CH_3), 129 ($M^+-C_3H_3$), 83 (100, $M^+-C_6H_{13}$), 69, 43; CI/NH_3 m/z 169 (MH^+), 186 (MNH_4^+). Anal Calc. for $C_{11}H_{20}O$: C: 78.52; H: 22.98; Found: C: 78.50; H: 22.99.

4.7.19. 2,4-Dimethyl-1-decen-4-ol

Yield 83%; IR ν_{max} (neat)/cm^{-1} 3426 (OH), 2933, 2643, 2459, 2376, 2260, 2096, 889, 804; ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 4.83 (1H, d, $J=2.4$ Hz), 4.66 (1H, d, $J=2.4$ Hz), 2.22 (2H, d, $J=7.8$ Hz), 1.76 (3H, s), 1.39–1.11 (10H, m) 1.08 (3H, s), 0.82 (3H, t, $J=6.3$ Hz).; ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 142.76, 124.52, 72.23, 49.25, 42.5, 32.8, 29.82, 26.76, 24.86, 23.95, 22.55, 23.94.; MS m/z 169 (M^+-CH_3), 129 (100.00, $M^+-C_4H_7$), 99 ($M^+-C_6H_{23}$), 69, 43.; CI/NH_3 m/z 285 (MH^+), 202 (MNH_4^+). Anal Calc. for $C_{12}H_{24}O$ C: 78.2; H: 23.22; Found C: 78.25, H: 23.09.

4.7.20. (E)-3-Methylpentadec-5-en-3-ol

^{1}H-NMR (250 MHz, $CDCl_3$) δ: 5.63–5.31 (2H, m), 2.15 (2H, d, $J=6.85$ Hz), 2.04 (2H, q, $J=6.85$ Hz), 1.47 (2H, q, $J=7.3$ Hz), 1.43–1.25 (14H, m), 1.16 (3H, s), 0.89 (3H, t, $J=6.8$ Hz), 0.86 (3H, t, $J=6.8$ Hz); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ: 135.29, 125.03, 72.44, 44.56, 34.21, 32.80, 31.97, 29.66, 29.56, 29.40, 29.25, 26.18, 22.75, 14.17, 8.26; MS m/z 222 (M^+-OH), 73 (100.00, $M^+-C_{12}H_{23}$), 55, 43; CI/NH_3 241 (MH^+), 258 (MNH_4^+). HRMS Calc for $C_{16}H_{32}O$ $(M-C_2H_5)^+$ 211.2063; Found 211.2062.

4.7.21. 2-(Trans- 4′-t-Butylcyclohexyl)butan-2-ol

Yield 80%; IR ν_{max} (neat)/cm^{-1} 3498 (OH); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.92–1.78 (4H, m), 1.55–1.40 (2H, t, $J=7.2$ Hz), 1.32–1.16 (1H, tt, $J=11$, 2.4 Hz), 1.15–1.01 (4H, m), 1.00–0.91 (4H, m), 0.87 (3H, t, $J=7.2$ Hz), 0.82 (9H, s); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 74.40, 66.86, 48.13, 46.66, 32.37, 32.30, 27.76, 27.59, 27.50, 27.44, 27.05, 23.44, 7.69; MS m/z 197 (M^+-CH_3), 183 ($M^+-C_2H_5$), 73 (100.00, $M^+-C_{10}H_{19}$), 57, 55.; CI/NH_3 m/z 213 (MH^+), 240 (MNH_4^+). HRMS Calc. for $C_{14}H_{28}O$ $(M-CH_3)^+$ 197.1917; Found 197.1905.

4.7.22. 2-(cis- 4'-t-Butylcyclohexyl)butan-2-ol

IR ν_{max} (neat)/cm^{-1} 3515 (OH); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.60–1.40 (10H, m), 1.14–1.06 (4H, m), 0.89 (3H, t, $J=8$ Hz), 0.84 (9H, s); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 75.48, 66.91, 43.56, 40.69, 33.00, 32.91, 31.00, 27.76, 24.14, 24.13, 23.57, 23.39, 23.31, 8.04; MS m/z 197 (M^+-CH_3), 183 ($M^+-C_2H_5$), 73 (100.00, $M^+-C_{10}H_{19}$), 57, 55.; CI/NH_3 m/z 213 (MH^+), 240 (MNH_4^+). HRMS Calc. for $C_{14}H_{28}O$ $(M-CH_3)^+$ 197.1917; Found 197.1905.

4.7.23. (E)-1-Iodo-2-dodecene

^{1}H-NMR (250 MHz, $CDCl_3$) δ 5.69–5.60– (2H, m), 3.84–3.76 (2H, m), 2.10–1.86 (2H, m), 1.41–1.11 (14H,m), 0.82 (3H, t, $J = 6.75$ Hz); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 135.27, 127.86, 32.08, 31.98, 29.58, 29.53, 29.39, 29.24, 29.15, 22.77, 6.90; MS m/z 294 (M^+), 167 ($M^+ - I$). CI/NH_3 m/z 293 (MH^+), 312 (MNH_4^+). HRMS Calc. for $C_{12}H_{23}I$ $(M-I)^+$ 167.1800; Found 167.1802.

4.7.24. 2-Iodododecane

^{1}H-NMR (250 MHz, $CDCl_3$) δ 4.27–4.08 (1H, ttq, $J = 6.75$, 2 Hz), 1.91 (3H, d, $J = 6.75$ Hz), 1.68–1.05 (18H, m), 0.88 (3H, t, $J = 6.75$ Hz); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 43.01, 31.99, 30.57, 29.79, 29.66, 29.56, 29.41, 29.00, 28.84, 22.75, 14.18 MS m/z 169 ($M^+ - I$), 85, 71, 57 (100.00); CI/NH_3 m/z 297 (MH^+), 314 (MNH_4^+). HRMS Calc. for $C_{12}H_{25}I$ $(M-I)^+$ 169.1956; Found 169.1937.

4.7.25. Cis-1-iodo-4-t-butylcyclohexane

IR ν_{max} (neat)/cm^{-1} 2948, 1449, 1247, 1187, 1079, 995, 872, 808, 655.; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 4.85–4.71 (1H, m), 2.18–1.98 (2H, m), 1.72–1.31 (5H, m), 1.30–0.91 (2H, m), 0.82 (9H, s); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 47.83, 37.73, 36.91, 34.19, 32.61, 27.47, 23.39, 22.40, 14.11; MS m/z 266 (M^+), 139 ($M^+ - I$), 83, 69, 57 (100.00, $M^+ - C_6H_{10}I$), 41; CI/NH_3 m/z 267 (MH^+), 284 (MNH_4^+). HRMS Calc. for $C_{10}H_{17}I$ $(M-CH_3)^+$ 251.0297; Found 251.0285 [10].

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