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Synthesis and Reactivity of Benzylic and Allylic Samarium Compounds

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Keywords : Dicyclopentadienyl samarium, Benzyl samarium complexes, Allyl samarium complexes, Ketones, Acid chlorides.

Abstract : *Benzyl and allyl samarium species are prepared by reaction of benzylic or allylic chlorides with* $SmCp_2$. *They present a wide scope of reactivity towards aldehydes, ketones and acid chlorides.*

Since our initial report on Barbier reaction mediated by samarium diiodide[1], numerous applications and developments of this reaction have been described and reviewed[2-7]. We also studied the reactivity of another divalent samarium compound $SmCp_2$ which is an efficient reagent for Barbier reactions in mild conditions and for coupling reactions of acid chlorides[8,9]. Several mechanisms have been proposed for the Barbier reaction mediated by diiodosamarium[10,11]. They involve radical and organometallic intermediates. By reaction of the divalent samarium compound with an halogenated derivative, a radical is formed. An organometallic samarium complex could be obtained by a second electron transfer. In the reduction of haloalkane derivatives by diiodosamarium in THF, no organosamarium species could be detected. Similarly, in intermolecular Barbier reactions involving these halogenated derivatives, there is not, up to now, definitive proof for the occurrence of organosamarium intermediates. In intramolecular Barbier reactions using functionalized halogeno derivatives in THF/HMPA mixtures, Molander and Curran recently had evidences of the formation of organosamarium $RSmI_2$[12-14].

$$RX + SmA_2 \longrightarrow XSmA_2 + R^{\bullet}$$

$$R^{\bullet} + SmA_2 \longrightarrow RSmA_2$$

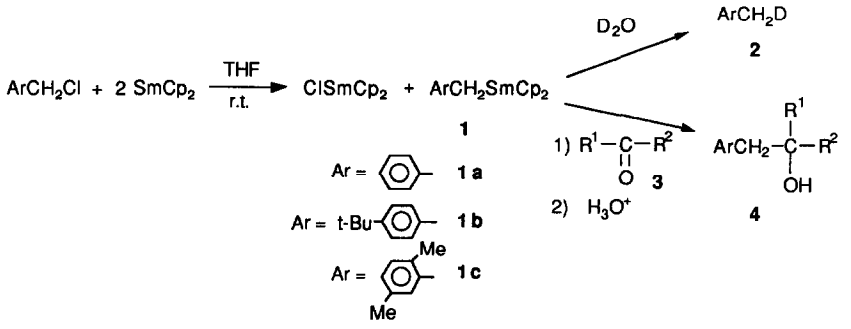
A = I, Cp

By reaction of halogenated derivatives with divalent ytterbium $YbCp^*_2$ ($Cp^*=C_5Me_5$), complex mixtures of products are obtained which arise from subsequent reactions on the metastable trivalent organometallic complexes $YbCp^*_2R$[15,16]. $SmCp^*_2$ leads to similar results with most of alkyl halides although organometallic compounds have been observed by NMR in some special cases[17,18]. Various alkyl complexes $RSmCp^*_2$ have been described by Evans and Marks but in general they are prepared from trivalent derivatives[19-21]. Using the cyclopentadienyl ligand only one compound has been described, $(CH_3)_3SiCH_2SmCp_2$ which is prepared by reaction of $SmCp_2Cl$ on alkyl lithium compound[22].

We have previously reported preliminary results indicating the formation of organosamarium compounds by reaction of benzylic or allylic chlorides with $SmCp_2$[23,24]. We now present the scope of their reactivity towards carbonyl compounds.

Results and discussion

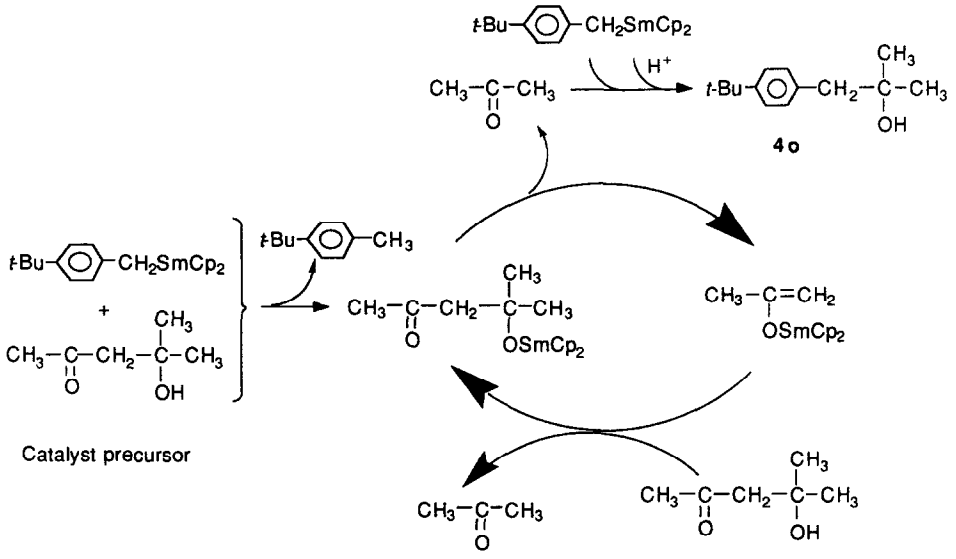
$SmCp_2$ was prepared in THF from diiodosamarium and NaCp as previously described[25]. When a solution of benzylic chloride in THF is added at room temperature to a suspension of two equivalents of $SmCp_2$ in THF, the purple precipitate of $SmCp_2$ disappears and the reaction mixture turns brown and homogeneous. This solution contains an organometallic samarium derivative as shown by its reactivity which is outlined in Scheme 1. After deuterolysis of complex **1**, incorporation of deuterium is observed in the benzylic derivatives **2**. By reaction with ketones or aldehydes followed by hydrolysis complexes **1** lead to alcohols **4**.



Scheme 1

Several organosamarium compounds have been prepared and are stable during 24h at room temperature in THF. The 80% yields obtained for **2b** and **2c** indicate that the corresponding organosamarium precursors are formed in good yields. Coupling products arising from Würtz type reactions have not been observed. A NMR spectrum of **1b** in deuterated benzene has been recorded. The two broad signals at 1.8 and 0.5 ppm are characteristic of THF coordinated to the complex. The benzyl group shows a chemical shift of 11.0 ppm. This is close to the value of 10.3 ppm obtained by Evans for the benzylic complex $PhCH_2SmCp^*_2(THF)$[26]. An X-ray structure of this latter indicates that the benzyl group is η^1-bonded to samarium, this is also probably the case for complexes **1**.

Table I gathers the results of the reactions of benzylic organometallic samarium **1** towards aldehydes and ketones **3**. Alcohols **4** are obtained in moderate to good yields and the scope of the reaction is broad. Reactions of organometallics **1** on aldehydes provide high yields in alcohols **4** as with reactions mediated by SmI_2[27]. With sterically hindered ketones (entries 6-9), the yields are lowered and similar to those obtained using SmI_2 in Barbier type conditions[28]. Reaction with an α,β-unsaturated ketone is regioselective and yields only the 1,2 addition product **4j** (entry 10). With enolisable ketones such as α or β-tetralone, the alcohol was produced in good yields (entries 12 and 13). In contrast, when SmI_2 was used in Barbier type conditions, formation of alcohols **4l** and **4m** was not observed, enolisation of the ketones by the divalent samarium reagent being then the main reaction. Alcohol was not obtained by reacting the organometallic **1** with 2-carboethoxycyclopentanone or ethyl trifluoroacetoacetate. Reactivity of **1** towards ketoalcohols was next examined. With one equivalent of 5-hydroxy-2-pentanone, the diol **4n** has been produced (entry 14). Reaction of **1b** on keto group of 5-hydroxy-2-pentanone is faster than on the OH group. By the use of 4-methyl-4-hydroxy-2-pentanone, the alcohol formed is not the expected one but the alcohol resulting from the addition of **1b** on acetone (entry 15). Formation of **4o** is explained by a retroaldolisation reaction which is catalyzed by an organometallic samarium species. A mechanism is proposed on Scheme 2.



Scheme 2

Table I : Reaction of benzyl samarium **1** towards aldehydes and ketones **3**.

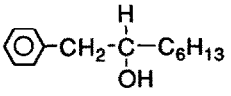
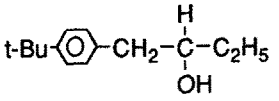
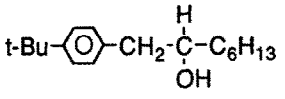
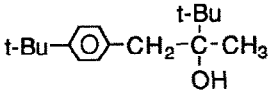
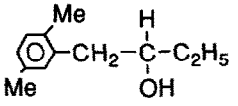
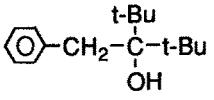
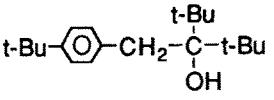
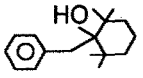
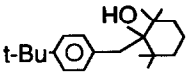
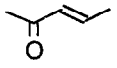
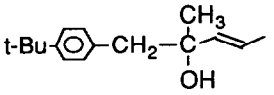
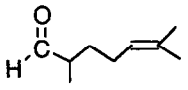
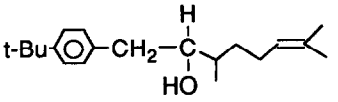
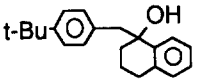
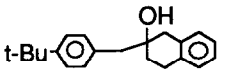
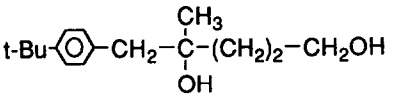
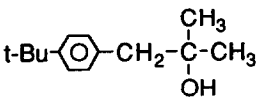
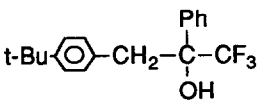
Entry	1	3	4	Isolated Yield (%)
1	**1a**	Heptanal		**4a** (80)
2	**1b**	Propanal		**4b** (80)
3	**1b**	Heptanal		**4c** (60)
4	**1b**	*t*-BuCOCH$_3$		**4d** (92)
5	**1c**	Propanal		**4e** (76)
6	**1a**	(*t*-Bu)$_2$CO		**4f** (61)
7	**1b**	(*t*-Bu)$_2$CO		**4g** (40)
8	**1a**			**4h** (34)

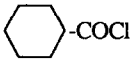
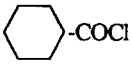
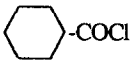
Table I continued

Entry	1	3	4	Isolated Yield (%)
9	**1b**			**4i** (42)
10	**1b**			**4j** (60)
11	**1b**			**4k** (42)
12	**1b**	α-Tetralone		**4l** (80)
13	**1b**	β-Tetralone		**4m** (58)
14	**1b**	5-hydroxy 2-pentanone		**4n** (48)
15	**1b**	4-hydroxy 4-methyl 2-pentanone		**4o** (56)
16	**1b**	CF_3COPh		**4p** (76)

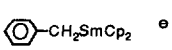
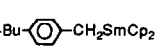
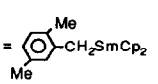
Reaction of the organometallic with the OH group of the aldol forms 4-*t*-butyl toluene and a samarium alcoholate which by retrogradation yields acetone and a samarium enolate. Acetone is transformed in tertiary alcohol **4o** by reaction with the benzylic compound **1b**. The enolate exchanges with the aldol to give acetone and the samarium aldolate. Coordination of the keto group of the aldol on samarium helps to the formation of the aldolate. This coordination also slowers addition reaction of the benzylic species to its keto group compared to the addition on acetone. We checked that the retroaldolisation was possible with catalytic amount of benzyl samarium **1b**. Alternatively when 10% of $SmCp_2$ are added to the aldol, retrogradation of the aldol was observed within a few minutes in THF at room temperature probably via the formation of samarium aldolate.

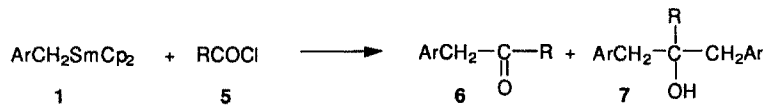
Organosamarium derivatives **1** show properties that have been already observed with other lanthanides derivatives such as 1,2 selectivity in alkylation of α,β-unsaturated aldehydes or ketones or reaction with enolisable ketones by the use of $CeCl_3$ or $La(OTf)_3$ added to alkyl magnesium or alkyl lithium[29-31,32]. These benzylic samarium derivatives **1** allow preparation of alcohols which are not easily obtained with other organometallics such as organomagnesium derivatives which give Wurtz coupling or with the recently described copper and zinc compounds[33-35]. The latter derivatives give 1,4 additions on α,β-unsaturated ketones and they are unreactive towards other ketones. The use of compounds **1** avoids also the lowering of the yield by side reactions such as pinacolisation of aldehydes or enolisation of ketones that occur in Barbier type conditions[8,28].

Table II : Reactivity of benzyl samarium complexes **1** towards acid chlorides **5** and ester

Entry	**1**	**5** [a]	t °C	**6** : **7** [b]	**6** (%)[c]
1	**1a**[d]	*t*-BuCOCl	- 30	1 : 0.13	**6a**(35)
2	**1b**[e]	*t*-BuCOCl	- 20	1 : 0.19	**6b**(46)
3	**1b**[e]		- 20	1 : 1.17	
4	**1b**[e]		- 70	1 : 0.5	**6c**(39)
5	**1c**[f]		- 30	1 : 0.05	**6d**(38)
6	**1b**[e]	CF_3COOEt	- 30	1 : 0.14	**6e**(47)

[a] RCOCl / $ArCH_2SmCp_2$ = 1 / 1, solvent THF. [b] Measured by ^1H NMR or GLC on the crude product.
[c] Isolated yield.

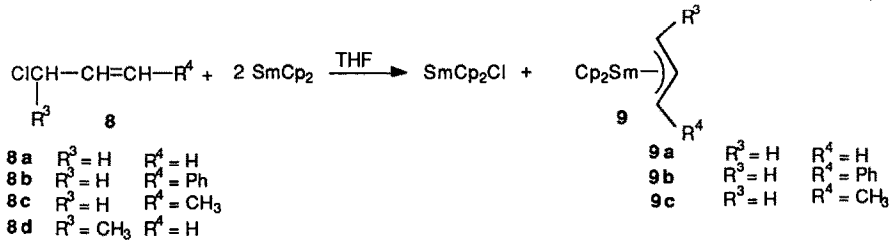
[d] **1a** =  [e] **1b** =  [f] **1c** = 



Scheme 3

Benzylic samarium complexes **1** react with acid chlorides to give a mixture of ketones **6** and alcohols **7** (Scheme 3). Results are collected in Table II. The reactions are very sensitive to temperature and to the steric hindrance of the reactants. The amount of ketone **6** is higher when an hindered acid chloride such as pivaloyl chloride is used compared to cyclohexanecarboxylic acid chloride (entries 2 and 3). Similarly organosamarium **1c** with a methyl group in ortho position leads more selectively to the ketone **6** than does **1b** (entries 3 and 5). By reacting ethyl trifluoroacetate with **1b** at -30°C the trifluoro ketone **6e** is formed selectively although in moderate yield (entry 6).

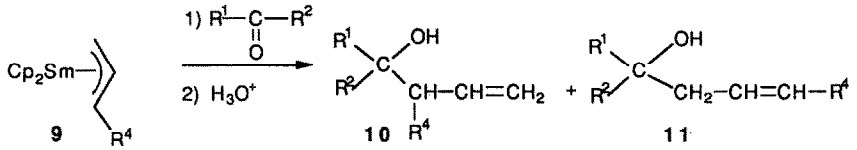
With the aim of broadening the field of organosamarium reagents we have studied the reactions of allylic chlorides with $SmCp_2$ and also obtained the formation of species with organometallic behaviour (Scheme 4). The allylic samarium derivatives **9** must be prepared at low temperatures, (-20°C to -40°C) according to the structure and they are stable during two hours if the temperature is raised to room temperature. Deuterolysis of complex **9b** shows incorporation of deuterium in the olefin formed, and addition of ketones or aldehydes on **9** leads to the formation of the two regioisomeric alcohols **10** and **11** (Scheme 5). Results are gathered in Table III.



Scheme 4

Addition of crotyl chloride **8c** or 3-chlorobutene **8d** to $SmCp_2$ followed by reaction with cyclohexanone gives after hydrolysis a mixture of the two isomeric alcohols **10** and **11**. The same ratio of the two isomers is obtained in both cases (entries 4 and 5). This suggests the involvement of the same intermediate probably a species with an η^3-allyl structure **9c** as shown in Scheme 4. This proposal is not only based on study of the regioselectivity of the reaction but also relies on results of literature. Evans reported that the action of Cp^*_2Sm on olefins forms $Cp^*_2Sm(\eta^3\text{-allyl})$ complexes and determined their X-ray structures[36]. Other η^3-allyl lanthanide derivatives have been also described[37,21].

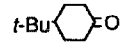
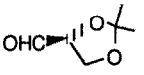
By action of **9c** on cyclohexanone (entry 4) the branched alcohol **10** is the major isomer. Same reaction is completely selective in the case of complex **9b** (entry 3). Regioselectivity in favour of the branched isomer is commonly observed with most organometallic allylic reagents[38-41]. However by the use of allyl cerium reagents Cohen obtained the inverse selectivity[42]. In Barbier type conditions with SmI_2 the reaction product was a mixture of the two isomers with the linear one predominant[35].



9a $R^4 = H$
9b $R^4 = Ph$
9c $R^4 = CH_3$

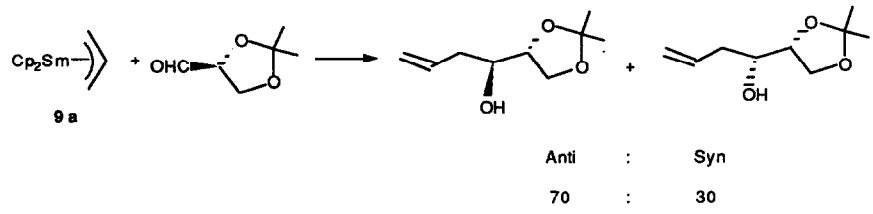
Scheme 5

Table III : Reaction of allyl samarium compounds **9** towards ketones and aldehydes.

Entry	9	3	t°C	10+11[a,b]	10 : 11[c]
1	**9a**		- 20	94	
2	**9a**	PhCHO	- 20	75	
3	**9b**		- 40	72	> 100:1
4	**9c**[d]		- 30	52	4:1
5	**9c**[e]		- 30	57	4:1
6	**9a**		-40	71	

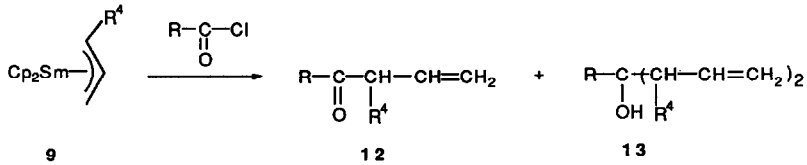
[a] % Isolated yield. [b] $SmCp_2$/**8**/**3** : 5/2/2, solvent THF. [c] Measured by ^1H NMR. [d] Prepared from **8c**. [e] Prepared from **8d**.

Stereoselectivity of the reactions of isopropylidene-(D)-glyceraldehyde with preformed η^3-allyl samarium **9a** or with a mixture of allyl chloride and $SmCp_2$ in Barbier type conditions has also been examined. Under Barbier type conditions only reduction or pinacolisation of the aldehyde was observed. Reaction of **9a** with isopropylidene glyceraldehyde at -30°C yields a mixture of the two diastereoisomeric alcohols *anti : syn* in a 70 : 30 ratio (Scheme 6). Performing the reaction at -50°C or changing the solvent for toluene does not affect the ratio of isomers. The diastereoselectivity is the same than with allyl zinc compounds at -78°C and slightly better than with allyl magnesium compounds[43,44].



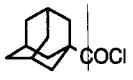
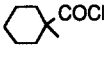
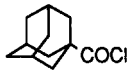
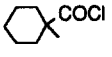
Scheme 6

The allyl samarium complexes **9** also react with acid chlorides (Scheme 7, Table IV). With **9a** a tertiary alcohol **13** is selectively formed in high yield at -20°C. The reaction is very sensitive to temperature and to the steric hindrance of the reactants as in the reaction of benzyl samarium compounds **4** on acid chlorides. With **9b** and **9c** the reaction is chemio and regioselective and yields ketones **12** as the most substituted isomer if acid chlorides with bulky substituents are used. β,γ-unsaturated ketones are obtained without isomerisation into α,β-unsaturated ketones.



Scheme 7

Table IV : Reaction of allyl samarium compounds **9** towards acid chlorides.

Entry	9	RCOCl	t°C	12[a,b]
1	**9a**	$C_8H_{17}COCl$	- 20	0[c]
2	**9b**		- 50	55[d]
3	**9b**	*t*-BuCOCl	- 50	44[d]
4	**9b**		- 50	47[d]
5	**9c**		- 50	77
6	**9c**		- 30	40[e]

[a] % Isolated yield. [b] $SmCp_2$/**8**/**5** : 5/2/2. [c] 65% Isolated yield in **13**. [d] Regioselectivity measured by ^1H NMR > 100 : 1. [e] 25% Isolated yield in **13** (mixture of diastereoisomers).

Conclusion

We have set up an easy method for the formation of benzylic and allylic samarium derivatives starting from divalent $SmCp_2$. As in reactions forming acylsamarium species from acid chlorides we observe a stabilisation of the organometallic species by the use of the cyclopentadienyl ligand[9]. The new organometallic derivatives possess interesting properties for potential synthetic applications. Noteworthy they react with enolisable ketones and ketoalcohols and show a high 1,2 selectivity towards α,β-unsaturated compounds. Reactions of allyl samarium complexes on ketones or acid chlorides present regioselectivity in favour of the more substituted isomers affording in the latter case an efficient route to β,γ-unsaturated ketones. The scope of the reactivity of alkyl halides with $SmCp_2$ is under investigation.

Experimental section

General.

A Bruker AM 200 NMR spectrometer operating at 200 MHz for ^1H and 50.4 MHz for ^{13}C was used for determining spectra with tetramethylsilane as the internal standard, in $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane . Infrared spectra were recorded neat and are reported in cm^{-1}. Mass spectra (MS)(70 eV) data were determined on a Ribermag R-10 gas chromatograph/mass spectrometer. GC analyses were performed with a 25 m BP 1 capillary column connected with a computing integrator.

THF solutions of SmI_2 and $SmCp_2$ in suspension in THF were prepared according to the previously reported procedures[1,9]. Alternatively, commercial solutions of SmI_2 (Strem, Aldrich) were used. Unless otherwise stated all organic compounds were commercially available and distilled prior to use. 1-Methylcyclohexyl carboxylic acid chloride was obtained from 1-methylcyclohexyl carboxylic acid by the usual procedure[45]. Isopropylidene glyceraldehyde was prepared by oxidation of diisopropylidene mannitol by $NaIO_4$ according to a described procedure[46]. All the reactions were carried out under argon atmosphere. Silica gel 60 (230-400 mesh) was used for flash chromatography.

General procedure for the preparation of the organometallics 1

In a typical experiment a solution of 2 mmol of the benzylic chloride $ArCH_2Cl$ in 20 ml of THF was added slowly at room temperature to 5 mmol of $SmCp_2$ in suspension in 75 ml of THF. After 45 min of reaction, the purple color of $SmCp_2$ disappeared and the solution became brown limpid. Treatment of a sample of 1 ml of the solution by a few drops of D_2O followed by analysis by GC and GC/MS permitted to check complete formation of organometallics **1b** and **1c**.

^1H NMR spectrum of complex 1b

0.5 mmol of $SmCp_2$ was prepared as usual. THF was then evaporated under vacuum. In a glovebox 2 ml of deuterated benzene and 0.2 mmol of 4-*t*-butylbenzylchloride were added to the purple powder. After 15 min the suspension was filtrated and NMR spectrum immediately recorded. *^1H NMR :* δ : 12.8 (br s, 10 H), 11.0 (br s, 2 H), 7.35-7.15 (m, 5 H), 1.8 (br s, 4 H), 1.15 (s, 9 H), 0.5 (br s, 4 H).

Synthesis of alcohols 4.

Alcohol **4l** : α-Tetralone (292 mg, 2 mmol) was added by syringe at room temperature to the brown solution containing 2 mmol of organometallic **1b** in 100 ml THF. The solution turned orange-yellow in a few minutes. After hydrolysis with HCl 0.1N, extraction with Et_2O, the solution was washed with water, brine and dried over $MgSO_4$. The crude product was purified by flash chromatography on a silica column with

eluent hexane : ethyle acetate, 50 : 50. A yellow solid (472 mg) was isolated and its structure was determined by GC/MS, ^{1}H NMR and elemental analysis.

All alcohols **4** were prepared and purified by a similar procedure and analyzed by GC, GC/MS and ^{1}H NMR. The oily products were homogeneous and they showed a single spot by TLC on silica gel, single peak by GC. Their purity was checked by ^{1}H NMR. Isolated yields are listed in Table I.

1-phenyl-2-octanol : 4a

^{1}H NMR : δ : 7.25 -7.07 (m, 5 H), 3.8-3.6 (m, 1 H), 2.8-2.6 (m, 2 H), 1.72 (s, 1 H), 1.6- 1.4 (m, 10 H), 0.9 (t, 3 H). *MS (m/e) :* 206 (M^+, 2), 121 (26), 115 (36), 92 (24), 91 65), 85 (52), 77 (11), 71 (23), 57 (18), 55 (17).

1-(4-tertiobutyl)phenyl-2-butanol : 4b

^{1}H NMR : δ : 7.25 (d, 2 H), 7.07 (d, 2 H), 3.55 (m, 1 H), 2.70-2.43 (m, 2 H), 1.57 (s, 1 H), 1.55-1,38 (m, 2 H), 1.23 (s, 9 H), 0.92 (t, 3 H). *MS (m/e) :* 206 (M^+, 5.2), 191 (1.9), 148 (24.6), 133 (100), 117 (13), 105 (14.5), 92 (49.5), 77 (5.8), 57 (73.5).

1-(4-tertiobutyl)phenyl-2-octanol : 4c

^{1}H NMR : δ : 7.35-7.15 (m, 4 H), 3.8-3.6 (m, 1 H), 2.8-2.6 (m, 2 H), 1.74 (s, 1 H), 1.6-1.4 (m, 10 H), 1.30 (s, 9 H), 0.9 (t, 3 H). *MS(m/e) :* 262 (M^+, 1.2), 161 (1.2), 148 (35.6), 147 (8.6), 133 (100), 115 (3), 105 (6.5), 92 (23.3), 91 (12.7), 57 (32.5), 55 (17.8).

1-(4-tertiobutyl)phenyl-2,3,3-trimethyl-2-butanol : 4d

^{1}H NMR : δ : 7.4-7.1 (m, 4 H), 2.75 (s, 2 H), 1.30 (s, 9 H), 1.24 (s, 3 H), 0.93 (s, 9 H). *MS (m/e) :* 248 (M^+, 71), 148 (25), 147 (100), 133 (22), 105 (42), 92 (18), 91 (22), 77 (15), 57 (9).

1-(2,5-dimethyl)phenyl-2-butanol : 4e

^{1}H NMR : δ : 7.08-6.90 (m, 3 H), 3.73 (m, 1 H), 2.87-2.55 (m, 2 H), 2.29 (s, 3 H), 2.27 (s, 3 H), 1.65 (s, 1 H), 1.62-1,55 (m, 2 H), 1.03 (t, 3 H). *MS (m/e) :* 178 (M^+, 0.5), 176 (34.2), 119 (80), 91 (17.3), 77 (12.1), 57 (100).

1-(4-tertiobutyl)phenyl-2-tertiobutyl-3,3-dimethyl-2-butanol : 4g

^{1}H NMR :δ : 7.35-7.15 (m, 4 H), 3.05 (s, 2 H), 1.35 (s, 18 H), 1.12 (s, 9 H). *IR ν :* 3600, 2850, 1480, 1390. *MS (m/e) :* 290 (M^+, 1), 234 (3), 178 (1), 177 (9), 159 (10), 143 (18), 91 (73), 87 (58), 85 (10), 69 (5), 57 (100).

1-(4-tertiobutyl)benzyl-2,2,6,6-tetramethyl-1-cyclohexanol : 4i

^{1}H NMR : δ : 7.28 (m, 4 H), 2.97 (s, 2 H), 1.72-1.55 (m, 6 H), 1.31 (s, 9 H), 1.21 (s, 6 H), 0.88 (s, 6 H). *MS (m/e) :* 302 (M^+, 18), 218 (10), 155 (39), 148 (93), 133 (100), 97 (76), 91 (28), 83 (34), 69 (50), 59 (92), 57 (88), 43 (72), 41 (60). *Anal.* Calcd for $C_{21}H_{34}O$:.C, 83.38; H, 11.33. Found : C, 83.57; 11.5.

1-(4-tertiobutyl)phenyl-2-methyl-3-penten-2-ol : 4j

^{1}H NMR : δ : 7.30 (d, 2 H), 7.10 (d, 4 H), 5.61-5.55 (m, 2 H), 2.78 (m, 2 H), 1.70 (d, 3 H), 1.32 (s, 9 H), 1.27 (d, 3 H). *MS (m/e) :* 214 (M-H_2O, 6), 199 (13), 157 (35), 148 (28), 133 (58), 85 (100), 67 (18), 57 (24), 43 (18). *Anal.* Calcd for $C_{16}H_{24}O$:.C, 82.6; H, 10.4. Found : C, 82.3; 10.53.

1-(4-tertiobutyl)phenyl-3-7-dimethyl-6-octen-2-ol : 4k

^{1}H NMR : δ : 7.33 (d, 2H), 7.13 (d, 2 H), 5.11 (m, 1 H), 3.91 (m, 1 H), 2.85-2.73 (m, 2 H), 2.65-2.50 (m, 2 H), 2.08-1.90 (m, 3 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.33 (s, 9 H), 0.92 (dd, 3 H). *MS (m/e) :* 302 (M^+, 20), 148 (36), 133 (100), 92 (26), 81 (35), 69 (39), 57 (68), 41 (32).

1-(4-tertiobutyl)benzyl-1,2,3,4-tetrahydro-1-naphtol : 4l

^{1}H NMR : δ : 7.29 (d, 2 H), 7.40-7.10 (m, 6 H), 3.11 (m, 2 H), 2.35 (m, 2 H), 2.05-1.87 (m, 4 H), 1.37 (s, 9 H). *MS (m/e) :* 276 (M-H_2O, 85), 261 (64), 219 (100), 148 (17), 147 (56), 129 (75), 128 (58), 117 (20), 91 (65), 77 (8), 57 (13). *Anal.* Calcd for $C_{21}H_{26}O$:.C, 85.6; H, 8.9. Found : C, 85.26; H, 8.88.

2-(4-tertiobutyl)benzyl-1,2,3,4-tetrahydro-2-naphtol : 4m

^1H NMR : δ : 7.35 (d, 2 H), 7.24-7.0 (m, 6 H), 3.10-2.65 (m, 6 H), 2.07-1.70 (m, 2 H), 1.6 (s, 1 H), 1.35 (s, 9 H). *MS (m/e) :* 276 (M-H_2O, 10), 261 (4), 219 (6), 148 (56), 147 (28), 133 (100), 129 (44), 117 (26), 91 (35), 77 (8), 57 (25), 41 (11).

1-(4-tertiobutyl)phenyl-2-methyl-2,5-pentanediol : 4n

^1H NMR : δ : 7.35 (d, 2 H), 7.15 (d, 2 H), 3.68 (t, 2 H), 2.76 (dd, 2 H), 2.13 (m, 1 H), 1.80-1.55 (m, 4 H), 1.31 (s, 9 H), 1.28 (s, 3 H). *MS (m/e) :* 232 (M-H_2O, 75), 217 (61), 147 (51), 133 (72), 129 (41), 117 (19), 91 (58), 77 (9), 57 (12), 41 (9).

1-(4-tertiobutyl)phenyl-2-methyl-2-propanol : 4o

^1H NMR : δ : 7.33 (d, 2 H), 7.13 (d, 2 H), 2.75 (s, 2 H), 1.32 (s, 9 H), 1.22 (s, 6 H). *IR : ν :* 3300, 3000-2925, 1470, 1365. *MS (m/e) :* 206 (M^+, 5), 148 (23), 147 (100), 133 (21), 119 (8), 105 (41), 92 (20), 91 (21), 77 (16), 57 (14).

1-(4-tertiobutyl)phenyl-2-phenyl-3,3,3-trifluoro-2-propanol : 4p

^1H NMR : δ : 7.55 (m, 2 H), 7.37 (m, 3 H), 7.22 (d, 2 H), 6.91 (d, 2 H), 3.40 (s, 2 H), 1.26 (s, 9 H). *MS (m/e) :* 322 (M^+, 3), 148 (43), 147 (100), 133 (29), 119 (10), 117 (20), 105 (37), 92 (19), 91 (21), 77 (19), 57 (13).

General procedure for preparation of ketones 6 :

Ketone 6b : The brown solution containing 2 mmol of organometallic **1b** in 100 ml THF is cooled down to -20°C. Then 2,2-dimethyl propanoyl chloride (2 mmol, 241mg) are added rapidly by syringe. The solution turned orange-yellow in a few minutes and was maintained at low temperature for one hour before hydrolysis and treatment as indicated previously for alcohols **4**. The crude product was purified by flash chromatography on a silica column with eluent hexane : ethyle acetate, 80 : 20. A yellow oil (213 mg) was isolated and its structure was determined by GC/MS and ^1H NMR.

All ketones **6** were prepared and purified by a similar procedure and analyzed by GC, GC/MS and ^1H NMR. The oily products are homogeneous and they showed a single spot by TLC on silica gel, single peak by GC. Their purity was checked by ^1H NMR. Isolated yields are listed in Table II.

1-(4-tertiobutyl)phenyl-3,3-dimethyl-2-butanone : 6b

^1H NMR : δ : 7.35-7.05 (m, 4 H), 3.73 (s, 2 H), 1.27 (s, 9 H), 1.17 (s, 9 H). *MS (m/e) :* 232 (M^+, 12.7), 147 (17.6), 133 (11.7), 117 (10), 85 (27.6), 57 (100).

4-tertiobutylbenzyl cyclohexyl ketone : 6c

^1H NMR : δ : 7.32 (d, 2 H), 7.12 (d, 2 H), 3.70 (s, 2 H), 2.47 (m, 1 H), 1.42-1.12 (m, 10 H), 1.30 (s, 9 H). *MS (m/e) :* 258 (M^+, 6.4), 147 (9.6), 133 (6.4), 117 (16.1), 111 (100), 105 (6.4).

2,5-dimethylbenzyl cyclohexyl ketone : 6d

^1H NMR : δ : 7.08-6.88 (m, 3 H), 3.72 (s, 2 H), 2.48 (m, 1 H), 2.30 (s, 3 H), 2.18 (s, 3 H), 1.4-1.1 (m, 10 H). *MS (m/e) :* 230 (M^+, 5.4), 119 (8), 111 (16.9), 105 (2.8), 91 (5.5), 83 (100), 77 (4.2), 55 (25).

1-(4-tertiobutyl)phenyl-3,3,3-trifluoropropanone : 6e

^1H NMR : δ : 7.27 (d, 2 H), 7.08 (d, 2 H), 3.94 (s, 2 H), 1.28 (s, 9 H). *MS (m/e) :* 244 (M^+, 3), 175 (21), 147 (82), 133 (61), 117 (36), 97 (41), 91 (76), 85 (62), 77 (29), 69 (33), 57 (52).

General procedure for synthesis of alcohols 10 and 11 and ketones 12 :

A solution of 2 mmol of the allylic chloride **8** in 20 ml of THF was added slowly at low temperature to 5 mmol of $SmCp_2$ in suspension in 75 ml of THF. After 1 h of reaction, the purple color of $SmCp_2$ disappeared and the solution became brown limpid. Ketone, aldehyde or acid chloride (2 mmol) were then added. Reaction mixture turned rapidly yellow and after one hour was hydrolysed, treated and purified as indicated above for alcohols **4** and ketones **6**. Isolated yields in alcohols **10** + **11** and in ketones **12** are listed respectively in Table III and IV.

1-adamantyl 1-phenyl-2-propenyl ketone :

^1H NMR : δ : 7.28 (m, 5 H), 6.22-6.14 (m, 1 H), 5.07 (m, 2 H), 4.88 (d, 1 H), 2.62 (m, 1 H), 2.02 (m, 3 H), 1.68 (m, 6 H), 1.32 (m, 6 H). *IR : v:* 3020, 2910, 1703, 1640, 1460. *MS (m/e) :* 280 (M^+, 0.2), 163 (12.3), 136 (11.4), 135 (100), 93 (11.3), 91 (6.7), 79 (14.4), 55 (4.3).

2,2-dimethyl-4-phenyl-6-hexen-3-one :

^1H NMR : δ : 7.30 (m, 5 H), 6.40-6.08 (m, 1 H), 5.12-5.0 (m, 2 H), 4.87 (d, 1 H), 1.10 (s, 9 H). *IR : v :* 3020, 2960, 1700, 1635, 1480. *MS (m/e) :* 202 (M^+, 0.8), 118 (7), 117 (20), 115 (17.4), 91 (6.1), 85 (31.4), 65 (3.4), 57 (100).

1-methylcyclohexyl 1-phenyl-2-propenyl ketone :

^1H NMR : δ : 7.40-7.15 (m, 5 H), 6.42-6.08 (m, 1 H), 5.32-5.0 (m, 2 H), 4.85 (d, 1 H), 2.1-1.8 (m, 4 H), 1.6-1.2 (m, 6 H), 1.07 (s, 3 H). *MS (m/e) :* 125 ($(C_6H_{10})Me(CO)$, 13), 118 (7), 117 (Ph-CH=CH_2, 5.6), 116 (4.3), 115 (5.6), 98 (8.5), 97 (98), 55 (100).

1-adamantyl 1-methyl-2-propenyl ketone :

^1H NMR : δ : 6.1-5.7 (m, 1 H), 5.12-4.92 (m, 2 H), 3.77 (m, 1 H), 2-1.5 (m, 15 H), 1.12 (d, 3 H). *MS (m/e) :* 163 ($C_{10}H_{15}CO$, 6), 136 (11.7), 135 (100), 107 (11), 93 (28), 91 (20), 81 (11), 77 (24), 67 (15), 55 (24).

1-methylcyclohexyl 1-methyl-2-propenyl ketone :

^1H NMR : δ : 6.1-5.7 (m, 1 H), 5.13-4.92 (m, 2 H), 3.74 (q, 1 H), 1.7-1.3 (m, 10 H), 1.18 (d, 3 H), 0.95 (s, 3 H). *MS (m/e) :* 180 (M^+, 0.2), 125 (8.4), 98 (8.8), 97 (100), 81 (4), 69 (8), 55 (90).

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