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Generation and Reactivity of Allylic and Benzylic Samarium Compounds Using Diiodosamarium in Tetrahydropyran.

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Abstract : *Diiodosamarium prepared in THP reduces allylic iodides and bromides at 0 or -15 °C to give organosamarium compounds which are stable under these conditions. These allylic samarium compounds react with many functionalities including the keto group of keto esters. Benzylic samarium compounds were prepared similarly from benzylic bromides.* © 1997 Elsevier Science Ltd.

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].

$$RX \; + \; 2\,SmI_2 \xrightarrow{THF} RSmI_2 \; + \; XSmI_2 \qquad [1]$$

On the other hand, stable allyl and benzylsamarium compounds can be prepared in THF by using $SmCp_2$[3] or $Sm(OTf)_2$/ LiOTf[4] as reducing agent. We wish to report here that stable allylsamariums and benzylsamariums are easily prepared according to eq. [1] with SmI_2 in tetrahydropyran (THP) instead of THF, without the Wurtz coupling reaction as exclusively observed in THF[5]. 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 $RC(O)SmI_2$[6]. The competitive coupling to give samarium-enediolates could be avoided, allowing the use of acylsamariums as nucleophilic reagents (eg formation of α-ketols by addition to aldehydes). We found that isolable allylsamarium species are also formed in THP at 0 or -15°C by the action of SmI_2 on allylic iodides. The presence of organometallics species was established by quenching with D_2O and product analysis (Table I). 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. The organometallics prepared from crotylbromide reacts with 2-octanone providing a similar product in 76% yield after a one hour reaction time (Scheme 1).

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) (Scheme 2).

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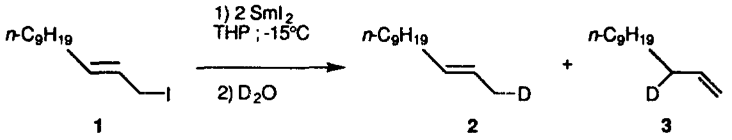
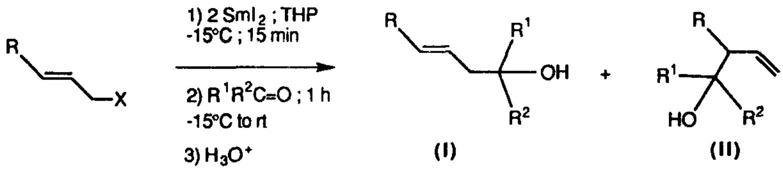
Table 1: Deuteration of Allylic Samarium Species.



t (min) [a]	Yield % of 2 (deuteration %)	Yield % of 3 (deuteration %)
15	33 (17)	67 (85)
30	52 (<10)	48 (65)
60	84 (<10)	16 (27)

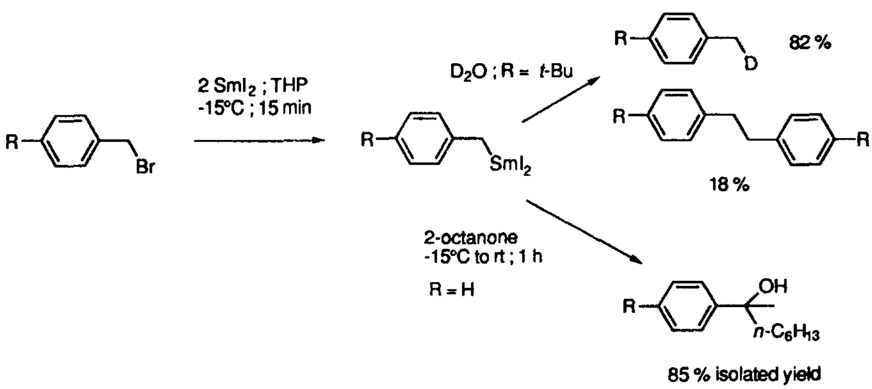
a) Dropwise addition of 1 in 10 min, then standing time t (min) before deuterolysis.



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

X = Br ; R = CH_3 ; $R^1 = CH_3$; $R^2 = n$-C_6H_{13} ; (I): 76 % (isolated yield), (II): 7 %

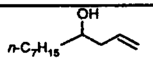
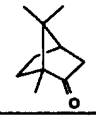
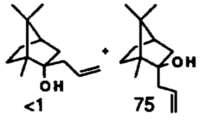
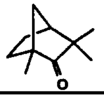
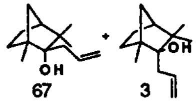
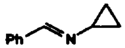
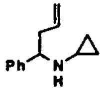
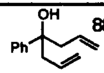
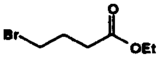
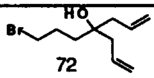
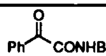
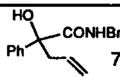
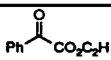
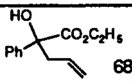
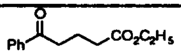
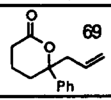
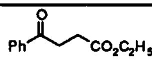
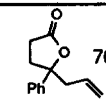
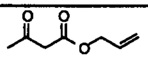
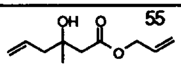
Scheme 1: Preparation and Reactions of Allylic Samarium Species.



Scheme 2: Preparation and Reactions of Benzylic Samarium Species.

The usefulness of the present methodology is established by the various examples listed in Tables 2 and 3.

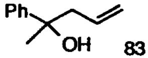
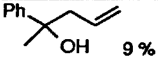
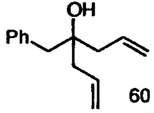
Table 2 : Reaction of Allylsamarium Diiodide in THP on Various Functional Groups

Substrate	Reaction time ^{a} (h)	allyliodide/Substrate	Products, isolated yields %
n-$C_7H_{15}CHO$	0.25	1:0.5	 75
	4^{b}	1:0.5	 <1 + 75
	4^{b}	1:0.5	 67 + 3
	4^{b}	1:0.5	 62
$PhCO_2C_2H_5$	2	1:0.45	 88
	1.5	1:0.4	 72
	2	1:0.75	 75
	2	1:0.9	 68
	15	1:0.5	 69
	15	1:0.5	 70
	3	1:0.75	 55

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.

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[7] . The allylation is very stereoselective both on camphor and fenchone. The sequential procedure (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).

Table 3: Reactions of Allylsamarium Diiodide (Prepared at 0°C in THP from 2 eq. 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	 9 %[b] 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.

We are currently studying the possibility of generating other classes of stable organosamariums (eg. alkylsamariums) in THP in order to extend the scope of the reaction.

Acknowledgments.

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