

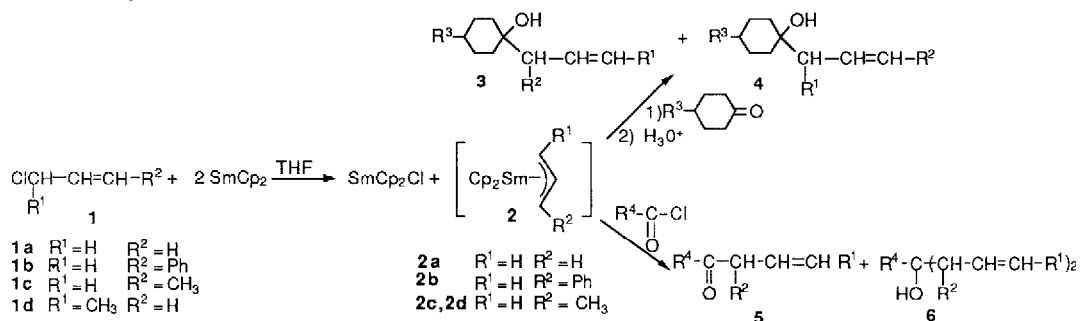
SYNTHESIS AND REACTIVITY OF ALLYL SAMARIUM COMPLEXES

J. Collin, C. Bied, H.B. Kagan*.

Laboratoire de Synthèse Asymétrique Associé au CNRS, Institut de Chimie Moléculaire d'Orsay.
 Université Paris-Sud, 91405 Orsay, France.

Summary : Allyl chlorides react with SmCp_2 to afford an allyl samarium intermediate, the η^3 -allyl structure of which has been tentatively assigned upon its reactivity with ketones. Synthesis of β,γ -unsaturated ketones have been also performed by reacting allyl samarium compounds with acid chlorides.

Lanthanides (III) alkyl complexes are usually prepared from some Ln (III) compounds^{1,2}. In the course of syntheses involving SmI_2 , alkyl samarium complexes have never been characterized^{3,4}. Similarly reaction of bis pentamethylcyclopentadienyl samarium (II) on alkyl halides in most cases do not lead to isolable alkyl complexes^{5,6}. We reported previously that SmCp_2 , which has different properties from SmI_2 and SmCp^*_2 , reacts in THF with benzylic halides to form benzylic samarium complexes^{7,8}. We now extend this reaction to allylic chlorides.



When allylic chlorides are added to a purple suspension of samarium dicyclopentadienide in THF maintained at low temperature, the reaction mixture turns brown. Further reaction with ketones leads to the obtention of alcohols. Results are reported in following table and experimental part in note⁹. Reaction between cinnamyl chloride **1b** or crotyl chloride **1c** and SmCp_2 (at -20°C or -30°C respectively) followed by introduction of cyclohexanone allows obtention in high yield of homoallylic alcohol preferentially as the more substituted isomer **3**. This is in contrast with product distribution in Barbier-type conditions with SmI_2 (a mixture of the two alcohols with linear isomer in major amount was obtained)¹⁰. This selectivity for the branched product similar with the one observed for most organometallics¹¹⁻¹³ is in favour of the formation of an organosamarium species **2**. Incorporation of deuterium by quenching of **2b** with deuterated water is also indicative of the presence of an organometallic species. Obtention of homoallylic alcohols **3** and **4** with the same diastereoisomers ratio for the reactions of crotyl chloride **1c** and 3-chloro-1-butene **1d** on SmCp_2 followed by addition of cyclohexanone is consistent with formation of a common intermediate (**2c** identical to **2d**) probably η^3 -allyl samarium. Stable η^3 -allyl bis pentamethylcyclopentadienyl complexes of neodymium, lanthanum¹ as well as samarium¹⁴ have been already described. Transmetalation reactions on allyl

magnesium, lithium or tin have been used for the preparation of allyl lanthanides; they react with 1,2 selectivity on α,β unsaturated carbonyl compounds but their structures have not been determined^{15,17}

TABLE: Synthesis of alcohols **3** and **4** or ketones **5** from some allyl chlorides and SmCp₂

R ¹	R ²	R ³	R ⁴	T°C	%(3+4) ^{a,b}	3:4 ^c	%(5) ^{a,e}
H	H	<i>t</i> -Bu		-20	94 ^d		
H	Ph	H		-40	72	>100:1	
H	CH ₃	H		-30	52	4:1	
CH ₃	H	H		-30	57	1:4	
H	H		C ₈ H ₁₇	-20			0 ^f
H	Ph		1-Adamantyl	-50			55 ^g
H	Ph		<i>t</i> -Bu	-50			44 ^g
H	Ph		1-Methylcyclohexyl	-50			47 ^g
H	CH ₃		1-Adamantyl	-30			77 ^h
H	CH ₃		1-Methylcyclohexyl	-30			40 ⁱ

^a Isolated yield; ^b SmCp₂/1/4-*t*-butylcyclohexanone or cyclohexanone 5/2/2; ^c measured by GC and NMR, ^d 1:1 mixture of *cis-trans* diastereoisomers, ^e SmCp₂/1/ acid chloride 5/2/2, ^f 65% isolated yield in **6**; ^g regioselectivity >100:1 ^h contaminated with 10% of α,β -unsaturated ketone corresponding to linear isomer, ⁱ 25% of **6** as a mixture of diastereoisomers have been isolated.

Intermediate allyl samarium complexes **2** react with *acid chlorides* as indicated in table above. Addition of nonanoyl chloride on **2a** yields only tertiary alcohol **6**. Reaction of complexes **2b** and **2c** at low temperatures (-50°C, -30°C) with acid chlorides which have a tertiary substituted carbon in α position to the carbonyl group produces β,γ -unsaturated ketones **5** as the major products¹⁸. Regioselectivity is the same than for reaction of allylic complexes **2** on ketones.

We are currently looking to the properties of various allylsamarium complexes now easily available from SmCp₂.

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- (9) In a typical experiment, a solution of cinnamyl chloride (2 mmol, 0.28 mL) in 10 mL THF is added dropwise at -50°C to SmCp₂ (5 mmol) in suspension in 75 mL of THF. After one hour, the purple solution turns brown-green. Ketone or acid chloride (2 mmol) are then added and the solution becomes yellow within a few minutes. After two hours the reaction mixture is hydrolysed and treated as previously described⁷
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- (18) For the reaction of acid chlorides on benzylic samarium complexes, bulky substituents in the acid chloride and use of low temperature also selectively afford benzyl ketones⁸.

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