π-Allyl Lanthanoid Ate Complex as a New Highly 1,2-Regioselective Allyl Transfer Agent for α,β-Unsaturated Carbonyl Compounds

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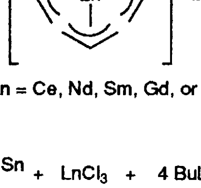
The π-allyl lanthanoid ate complex (**1**), which was prepared *in situ* from tetra-allyltin, the lanthanoid trichloride, and n-butyl-lithium in tetrahydrofuran (THF), reacts smoothly with α,β-unsaturated carbonyl compounds (**3**)—(**11**) with a high degree of 1,2-regioselectivity to give 3-hydroxy-1,5-dienes (**12**)—(**20**) in good to excellent yields.

Allylmetal compounds are important allyl transfer agents which transform carbonyl compounds to synthetically useful homoallylic alcohols.[1] Various types of allylmetal compound have been developed and the different metallic species lead to different selectivities in organic synthesis. For example, allyltrimethylsilane leads to 1,4-regioselective allylation of α,β-enones in the presence of titanium tetrachloride,[2] crotyltributyltin allows their use for highly diastereoselective addition to aldehydes,[3] and allylchromium compounds add to aldehydes chemoselectively.[4] Allyl-lanthanoid complexes should also be promising allylmetal compounds leading to unique and selective allyl transfer reactions, since organolanthanoid compounds have a characteristic reactivity which differs in some respects from that of conventional reagents.[5] However, studies on the reactivity of π-allyl-lanthanoid complexes with organic molecules are limited;[6,7a] alkyl-lanthanoid halide σ-complexes have been shown to function as efficient nucleophiles in their regio- and stereo-selective addition to carbonyl compounds.[7]

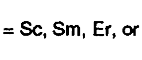
Complexes (**1**)[8] and (**2**) (cp = cyclopentadienyl)[9] are typical π-allyl-lanthanoid complexes which have been isolated and their structure determined. In our studies of lanthanoid complexes in organic synthesis, we were interested in the easily prepared π-allyl-lanthanoid ate complex (**1**) and explored its use as an allyl transfer agent. We now report that complex (**1**) reacts smoothly with α,β-unsaturated carbonyl compounds (**3**)—(**11**) with a high degree of 1,2-regioselectivity to give 3-hydroxy-1,5-dienes (**12**)—(**20**) in good to excellent yields.[10]

As complex (**1**) is highly air- and moisture-sensitive and pyrophoric, we used it in tetrahydrofuran (THF) solution without isolation. Complex (**1**) was readily prepared in THF at ambient temperature under nitrogen by transmetallation of tetra-allyltin,[11] with the anhydrous lanthanoid trichloride and n-butyl-lithium (4 equiv.).[8] Reactions were carried out at 0 °C or room temperature by adding an organic substrate to the coloured homogeneous THF solution which contained (**1**), tetrabutyltin, and lithium chloride.

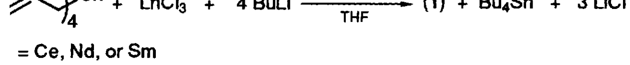
Treatment of chalcone (**3**) with allyl-lithium[12] gave a mixture of 1,2- and 1,4-adducts in a ratio of 40 : 60, showing an almost complete lack of selectivity (Table 1, run 1). However, the π-allyl lanthanoid ate complex (**1**) showed a dramatic improvement in regioselectivity; the ratio of 1,2- to 1,4-products was 75 : 25 (run 2). With both linear and cyclic α,β-enones such as benzylideneacetone (**4**) and cyclohex-2-enone (**9**), (**1**) was superior in giving not only higher 1,2-regioselectivities but also higher yields than allyl-lithium. The results of the reaction of (**1**) with the α,β-enones (**3**)—(**11**) are summarized in Table 1. The selectivity and yields were independent of the lanthanoid metal used (Ce, Nd, or Sm) (Table 1, runs 8, 9, and 11—13). Besides the high regioselectivity, the advantages of this reaction are the mild conditions (0 °C to room temp.) and simplicity. One method for



(**1**) Ln = Ce, Nd, Sm, Gd, or Dy



(**2**) Ln = Sc, Sm, Er, or Ho

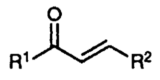


= Ce, Nd, or Sm

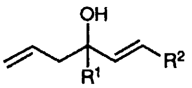
Table 1. Reaction of the π-allyl-lanthanoid ate complex (**1**) with α,β-unsaturated carbonyl compounds (**3**)—(**11**) to give the products (**12**)—(**20**).[a]

Run	α,β-Unsaturated carbonyl compound	Ln in (1)	Yield (%)[b]	Isomer ratio[c] (1,2 : 1,4)
1[d]	Chalcone (**3**)	—[e]	99	40 : 60
2[d]	(**3**)	Ce	90	75 : 25
3	Benzylideneacetone (**4**)	—[e]	80	100 : 0
4	(**4**)	Ce	84	100 : 0
5	Methyl vinyl ketone (**5**)	–[e]	47	100 : 0
6	(**5**)	Ce	64	100 : 0
7	Cyclopent-2-enone (**8**)	—[e]	72	89 : 11
8	(**8**)	Ce	82	97 : 3
9	(**8**)	Nd	77	100 : 0
10	Cyclohex-2-enone (**9**)	—[e]	64	84 : 16
11	(**9**)	Ce	96	99 : 1
12	(**9**)	Nd	93	100 : 0
13	(**9**)	Sm	98	100 : 0
14[d]	Isophorone (**10**)	Ce	94	100 : 0
15[d]	(**10**	Nd	99	100 : 0
16[d]	L-Carvone (**11**)	Ce	95	100 : 0
17[f]	Cinnamaldehyde (**6**)	Ce	99	100 : 0
18[f]	Crotonaldehyde (**7**)	Ce	99	100 : 0

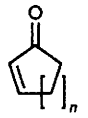
[a] General procedure: a hexane solution of n-butyl-lithium (1.6 M; 1 ml) was added slowly at room temperature to a suspension of the anhydrous lanthanoid trichloride (0.4 mmol) and tetra-allyltin (0.4 mmol) in THF (5 ml) under nitrogen. The solution became homogeneous and coloured (Ce: violet, Nd: yellow–green, Sm: orange) within 10 min and was stirred for 1 h.[8] To the resulting solution was added a THF solution (5 ml) of (**3**) (1.6 mmol) at 0 °C or room temperature by a syringe. The colour of the solution faded and the solution was stirred at 0 °C or room temperature for 1 h. After usual work-up, GLC analysis showed the presence of the corresponding 1,2-adduct (**4**) as the major product with tetrabutyltin and a small amount of 1,4-adduct. The isomer ratio of 1,2 to 1,4-adduct was determined by GLC. The product was isolated by column chromatography on silica gel; hexane eluted tetrabutyltin and then hexane–diethyl ether (5 : 1) eluted the 1,2-adduct. The ^{1}H NMR and IR spectra, and analytical data were consistent with the structures assigned. Reactions in Table 1 were carried out at 0 °C unless noted otherwise. [b] Isolated total yield of 1,2- and 1,4-adducts. [c] Determined by GLC. [d] Reaction was carried out at room temperature. [e] Allyl-lithium was used. [f] Reaction temperature was −78 °C.



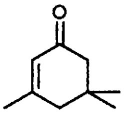
(3) $R^1 = R^2 = Ph$
(4) $R^1 = Me, R^2 = Ph$
(5) $R^1 = Me, R^2 = H$
(6) $R^1 = H, R^2 = Ph$
(7) $R^1 = H, R^2 = Me$



(12) $R^1 = R^2 = Ph$
(13) $R^1 = Me, R^2 = Ph$
(14) $R^1 = Me, R^2 = H$
(15) $R^1 = H, R^2 = Ph$
(16) $R^1 = H, R^2 = Me$



(8) $n = 1$
(9) $n = 2$



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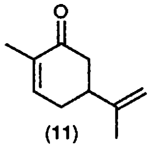
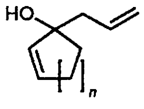
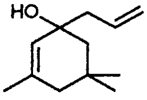


(11)



(17) $n = 1$
(18) $n = 2$



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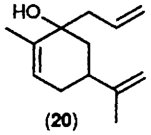

(20)

preparation of allyl-lanthanoid reagents from allyl sulphides requires strong bases and seems to be of limited utility.[7a]

The high degree of 1,2-regioselectivity in the reaction of (**1**) with α,β-enones is consistent with the alkylation by alkyl-lanthanoid σ-complexes[7a—c,f] and reduction by the combination of $NaBH_4$[13] or $LiAlH_4$[14] with lanthanoid trichlorides. The 1,2-regioselective allylation may be rationalized by the strong oxophilicity and hardness of lanthanoid metal species.[15] Finally, complex (**1**) also added to α,β-enals such as cinnamaldehyde (**6**) and crotonaldehyde (**7**) with exclusive 1,2-selectivity without contamination by any side reactions at −78 to 0 °C (runs 17 and 18).

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