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REACTIONS OF ORGANOLANTHANOID σ COMPLEXES WITH α,β-UNSATURATED CARBONYL COMPOUNDS. SELECTIVE 1,2-ADDITION

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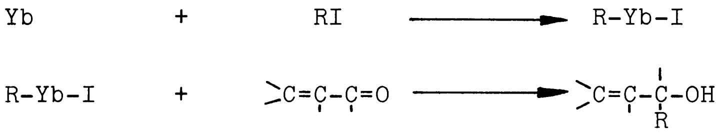
Organoytterbium iodide σ complexes (RYbI) react with α,β-unsaturated carbonyl compounds such as acrolein, methyl vinyl ketone, benzalacetone, chalcone, and 2-cyclohexen-1-one to give 1,2-addition products selectively. This high selectivity is explained in terms of the HSAB theory.

The complexes of type RLnI of the lanthanoids (Ln) such as Ce, Sm, Eu, and Yb were first reported by Evans et al.1) We have reported the reactions of Pr, Nd, Gd, Dy, Ho, and Er with organic halides2) and some applications of RLnI σ complexes to organic synthesis.3,4) As part of our interest in utilizing RLnI complexes for organic synthesis, we have investigated the reactions of RYbI (R=Ph, Me) with α,β-unsaturated carbonyl compounds. In this communication, we wish to report the reactions of RYbI σ complexes with α,β-unsaturated carbonyl compounds such as acrolein, methyl vinyl ketone, benzalacetone, chalcone, and 2-cyclohexen-1-one, to give 1,2-addition products selectively, which is sharp contrast to the Grignard reagent.



$$\mathrm{Yb} + \mathrm{RI} \longrightarrow \mathrm{R{-}Yb{-}I}$$

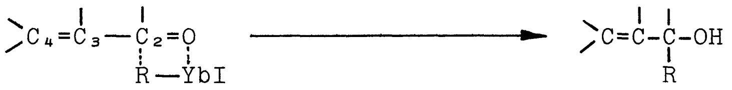
$$\mathrm{R{-}Yb{-}I} + {>}\mathrm{C{=}C{-}C{=}O} \longrightarrow {>}\mathrm{C{=}C{-}}\overset{|}{\underset{\mathrm{R}}{\mathrm{C}}}\mathrm{{-}OH}$$

Typical experimental procedure is as follows. Yb (0.6 mg atom) and a magnetic stirring bar were placed in a 50-ml centrifuge tube and the tube was sealed with a cerum cap. After the tube was dried by heating under a stream of nitrogen, 3 ml of THF, which was freshly distilled under nitrogen from sodium benzophenone ketyl, was added by a syringe. Then iodobenzene (0.90 mmol) in 0.3 ml of THF was added to the tube at -30°C in 5 min. After almost all Yb reacted with iodobenzene, the mixture was stirred for additional 1.5 h, and then α,β-unsaturated carbonyl compounds (0.50 mmol) in THF (0.3 ml) was added to the resulting dark brown solution of RYbI at -30°C. The reaction mixture was stirred overnight at room temperature and then hydrolyzed with aqueous NH_4Cl and 2 N HCl, and the products were extracted with ether. The products were identified by comparison with authentic samples. The results are summarized in Table 1 which also contains those with the Grignard reagent for comparison. As shown in the table, RYbI complexes give the 1,2-addition products exclusively except run 4. On the other hand, the Grignard reagents give mixtures of 1,2- and 1,4-addition products and in the case of chalcone, give the 1,4-addition product as a main product by a steric factor. It is of much interest that RYbI complexes give 1,2-addition products selectively although the atomic radius of Yb is larger than that of Mg. This unique regioselectivity can be explained by the hard and soft acids and bases (HSAB) theory. From the HSAB theory, the lanthanoid complexes (RYbI) are harder than the Grignard reagents, and in the conjugate enone system C_2 (carbonyl carbon) is harder than C_4.[5] Thus the attack of RYbI is enhanced at the hard site, i.e., C_2, to give 1,2-addition products selectively.

Table 1. Reactions of RYbI with α,β-Unsaturated Carbonyl Compounds

Run	RYbI	Carbonyl compd	Product and Yield, %[a] 1,2-Additn	1,4-Additn	Grignard reagent 1,2-Additn :1,4-Additn
1	PhYbI	Acrolein[b]	66	0	–
2	PhYbI	Methyl vinyl ketone[c]	37[d]	0	–
3	PhYbI	Benzalacetone[e]	43	0	88 : 12[f]
4	PhYbI	Chalcone[e]	50[g]	10	6 : 94[f]
5	MeYbI	2-Cyclohexen-1-one[e]	39	0	72 : 28[h]

[a] GLC yields based on the carbonyl unless otherwise noted. [b] Yb (0.5 mg atom), PhI (0.75 mmol), and the aldehyde (0.50 mmol). [c] Yb (0.5 mg atom), PhI (0.75 mmol) and the ketone (0.50 mmol). [d] Based on Yb. [e] Yb (0.6 mg atom), RI (0.90 mmol), and the ketone (0.50 mmol). [f] E. P. Kohler, Am. Chem. J., 38, 511 (1907); J. Am. Chem. Soc., 55, 1073 (1933). [g] Determined by NMR. [h] F. C. Whitmore, G. W. Pedlow, J. Am. Chem. Soc., 63, 758 (1941).



These results clearly show that organoytterbium σ complexes (RYbI) have a unique regioselectivity toward α,β-unsaturated carbonyl compounds in sharp contrast to the Grignard reagent.

References

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