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REACTIONS OF PHENYLYTTERBIUM σ COMPLEX WITH CARBONYL COMPOUNDS: A NEW GRIGNARD-TYPE REAGENT HAVING UNUSUAL REACTIVITY TOWARD ESTERS AND KETONES

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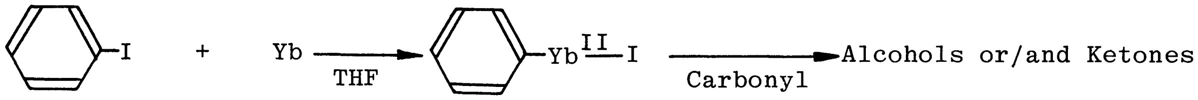
Phenylytterbium iodide has been found to react with ketones, aldehydes, esters, and nitriles to give alcohols and/or ketones. The reactions with esters at low temperature give ketones as main products, and the reactivity of esters to Ph-Yb-I is higher than that of ketones in contrast to the Grignard reaction.

Although elements of the rare earths series, having f orbitals, and their derivatives have been widely used in inorganic chemical fields,[1] they have received only scarce attention from synthetic organic chemists. However, their high coordinative ability with many functional groups, and contribution of f orbitals to σ and π bonds[2] should result in modifications of the steric and electronic environment of the reactive site of a molecule, and therefore their use for synthetic purposes seems to be promising.

With the exception of cerium(IV), which is used as an oxidation agent, and use of europium derivatives as shift reagents in nmr spectroscopy, few reports may be available concerning the use of organolanthanides in organic chemistry.[3-7]

Lanthanides are usually found in the trivalent state. But some divalent compounds have been isolated.[8] Deacon and Tuong reported that diorganoytterbium(II) compounds, prepared from ytterbium metal and diorganomercurials, reacted with carbonyl compounds to give rise to alcohols.[9] Kagan et al. reported on the reactions of lanthanide diiodides with ketones and organic halides to afford alcohols and alkanes.[3a] Evans et al. have found in their pioneering work that the rare earth elements such as europium, ytterbium, and samarium readily react with alkyl and aryl iodides to give divalent compounds R-M^{II}-I in THF and that they undergo Grignard-type reactions.[10] But, of carbonyl compounds, only benzophenone was used to test the reaction with Ph-Yb-I. We are interested in the reactions of lanthanides for the aim of exploring new C-C bond forming reactions, and investigated the reactions of phenylytterbium iodide (Ph-Yb-I), prepared from ytterbium metal ($4f^{14}$) and phenyl iodide in THF at low temperature, with a variety of carbonyl compounds, to find its unique reactivity.

We herein report on the results of the reactions of Ph-Yb-I with ketones, aldehydes, esters, and nitriles in comparison with the Grignard reaction.



In a standard procedure, 0.5 mmol of ytterbium powder and a magnetic stirring bar were placed in a 50-ml centrifuge tube under air and the tube was sealed with a serum cap. After the tube was dried by heating under nitrogen, 3 ml of THF, which was freshly distilled under nitrogen from sodium benzophenone ketyl, was added by a syringe. Then 0.75 mmol of iodobenzene in 0.3 ml of THF was added slowly to the tube at -20°C during 5-10 min. After a short induction period (10-30 min), ytterbium started to react with the iodide, and then to the resulting phenylytterbium iodide, 0.5 mmol of the ketone (or ester or nitrile) in THF (0.5 ml) was added at -20°C and the solution was hydrolyzed with 2N-HCl, and the products were extracted with ether. The results are listed in Table I, and the data in the table show that Ph-Yb-I reacts with ketones, aldehydes, and nitriles just as Grignard reagents. Table II summarizes the reactions with esters such as methyl benzoate and methyl phenylacetate. It became apparent that Ph-Yb-I readily reacts also with esters. Characteristic is that the reaction affords considerable amounts of ketones besides alcohols, and especially at low temperature, ketones as main products. Usually the Grignard reagents give alcohols predominantly when they react with esters. In fact, 1,1-diphenylethanol was formed predominantly from the reaction of Ph-Mg-I and ethyl acetate. This suggested to us that esters are more reactive than ketones toward Ph-Yb-I. In order to confirm this point we performed the competitive reactions between methyl benzoate and acetophenone.[11] From this reaction benzophenone, which was derived from the ester, was formed in 34% yield based on Yb metal together with 17% of 1,1-diphenylethanol which was derived from the ketone. This result clearly

Table I. Reactions of Ph-Yb-I with Ketones, Aldehydes, and Nitriles[a]

Run	Ketone	Product and Yield,[b] %		
		Alcohol	Ketone	Total %
1	CH_3COPh	78	–	78
2	PhCOPh	18	–	18[c]
3	$PhCH_2COPh$	21	–	21
4	C_2H_5CHO	58	–	58
5	$(CH_3)_2CHCHO$	36	–	36
6	PhCHO	62	–	62[d]
7	CH_3CN	–	8	8[d]
8	PhCN	–	7	7[d]
9	$PhCH_2CN$	–	4	4

a) Reactions were carried out using Yb (0.5 mmol), THF (3 ml), PhI (0.75 mmol), and ketones (0.5 mmol) initially at -20°C and r.t. overnight and then at reflux for 2 h unless otherwise noted. b) Yields are based on Yb metal and determined by GLC. c) Triphenylmethane was also formed in 3% yield. d) Reactions were carried out using Yb (0.6 mmol) and PhI (0.5 mmol), and yields are based upon PhI.

Table II. Reactions of Ph-Yb-I with Esters[a]

Run	Yb	PhI	Ester (RCOOR')		Product and Yield,[b] %			Selectivity[c]	
	mmol	mmol	R (0.5 mmol)	R'	Alcohol	Ketone	Total	Ketone	Alcohol
1	1	1.5	Ph	CH_3[d]	50	12	62[e]	30	70
2	0.5	0.75	Ph	CH_3[f]	16	14	30[g]	58	42
3	1	1.5	$PhCH_2$	CH_3[d]	55	2	57	7	93
4	0.5	0.75	$PhCH_2$	CH_3[f]	15	10	25	57	43

a) Ph-Yb-I was prepared in situ at -20°C. b) Yields are based on Yb metal and determined by GLC. c) Calculated as follows: selectivity of ketone = 100×2×Yield of ketone/(Yield of alcohol + 2×Yield of ketone), selectivity of alcohol=100×Yield of alcohol/(Yield of alcohol + 2×Yield of ketone), in runs 1 and 2, the yield of triphenylmethane was also added to that of alcohols. d) After addition of esters the mixture was stirred at r.t. overnight and then refluxed for 2 h. e) Triphenylmethane was also formed in 6% yield. f) After addition of esters the mixture was stirred at -20°C overnight. g) Triphenylmethane was also formed in 4% yield.

shows that Ph-Yb-I has a peculiar tendency to react with the ester better than the ketone. Contrary to this, for example Ph-Mg-I gave triphenylcarbinol predominantly when it was allowed to react with benzophenone and ethyl acetate competitively. That Ph-Yb-I gives rise to more ketones as main products than alcohols when reacted with esters at low temperature, and the reactivity of esters is higher than that of ketones, is in sharp contrast to the Grignard reactions.

As shown above, the reaction of the phenylytterbium(II) compound is unique and should have a potential utility for organic synthesis. Studies are currently underway on the effects of reaction conditions, reactivities of other aryl- and alkyllanthanides, and applications to asymmetric synthesis.

References

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11) The competitive reaction was carried out at -20°C overnight charging an equimolar amount (0.5 mmol) of acetophenone and methyl benzoate in THF (0.3 ml) to a Ph-Yb-I solution prepared from Yb (0.5 mmol) and PhI (0.75 mmol) in THF (3 ml), and the products were analyzed by vpc.

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