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REACTIONS OF PHENYLYTTERBIUM σ COMPLEX WITH BENZOYL CHLORIDE AND METHYL BENZOATE: A SELECTIVE KETONE SYNTHESIS

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Phenylytterbium iodide (Ph-Yb-I) has been found to react with benzoyl chloride to give both triphenylcarbinol and benzophenone. When Ph-Yb-I is added inversely to benzoyl chloride, especially in the presence of $FeCl_3$, the ketone is obtained selectively in modest yields in contrast to the Grignard reaction.

Only a few reports are available on the organic reactions with lanthanide metals, having f orbitals, and their derivatives in spite of their relatively abundant occurrence in nature.1) However, their high coordinative ability and contribution of f orbitals to σ and π bonds should result in unique reactivity in the organic reactions.

We have reported that Ph-Yb-I reacts with a variety of ketones, aldehydes, esters, and nitriles to give alcohols and ketones.2) We have found that Ph-Yb-I reacts with benzoyl chloride to give both triphenylcarbinol and benzophenone, and that the inverse addition of Ph-Yb-I to benzoyl chloride in the presence of $FeCl_3$ affords the ketone, benzophenone, selectively.

We herein report on the results of the reactions of Ph-Yb-I with benzoyl chloride and methyl benzoate in comparison with the Grignard reaction.

When benzoyl chloride or methyl benzoate was added to a THF solution of Ph-Yb-I, both triphenylcarbinol and benzophenone were obtained as major products.3) (Table I, runs 1,2,3,4,17,18,and 19) in contrast to the Grignard reaction which gave the alcohol predominantly.4) Contrary to this, if Ph-Yb-I was added inversely to benzoyl chloride, benzophenone was obtained as a main product in ca. 80% selectivity (runs 5,6,and 7). Furthermore, the table shows that addition of small amounts of $FeCl_3$5) and inverse addition of Ph-Yb-I result in the selective formation of benzophenone (runs 11,12,13,14,15, and 16), and that CuCl excerts the less effect on the selectivity than $FeCl_3$.6) In the case of the reaction with Ph-Mg-I, benzoyl chloride gave benzophenone selectively under the same reaction conditions, but the yield became very low. Inverse addition of Ph-Yb-I to methyl benzoate also increases the selectivity of the ketone (run 20), but $FeCl_3$ is not effective in this case (run 21). The high selectivity of the ketone observed above might be attributed partly to the larger ionic radius of Yb^{2+} (0.93 Å)1b) than that of Mg^{2+} (0.65 Å)7) which makes the Yb reagent less reactive than the Grignard reagent toward bulky benzophenone.

These results clearly shows that Ph-Yb-I has a unique reactivity toward benzoyl chloride and methyl benzoate in sharp contrast to the Grignard reaction. The scope and mechanism of this selective ketone synthesis are currently being studied.

Table I. Reactions of Ph-Yb-I with Benzoyl Chloride or Methyl Benzoate[a]

Run	PhCOX mmol	THF ml	Temp °C	Additive mg	Product and Yield,[b] %				Selectivity[c]	
					Ph_2CO	Ph_3COH	Ph_3CH	Total	Ketone	Alcohol
1	X=Cl, 0.5	3	r.t.[d]	—	19	36	3	58	49	51
2	0.5	3	r.t.[e]	—	19	34	3	56	51	49
3	0.5	3	-20	—	16	32	1	49	49	51
4	0.5	3	-20[f]	—	15	28	3	46	49	51
5	1	6	r.t.	—	34	15	1	50	81[g]	19
6	1	6	-20	—	24	8	5	37	79[g]	21
7	1	6	-20[f]	—	26	11	3	40	80[g]	20
8	1	6	-20	CuCl(1.5)	26	13	5	44	75[g]	25
9	1	6	-20	CuCl(9.0)	27	13	6	46	74[g]	26
10	1	6	-20	$FeCl_3$(4.5)	27	8	2	37[h]	84[g]	16
11	1	6	-20	$FeCl_3$(20)	24	4	–	28[i]	92[g]	8
12	1	6	-20	$FeCl_3$(50)	21	1	–	22[j]	99[g]	1
13	1	6	-20	CuCl(10) + $FeCl_3$(50)	22	1	–	23[k]	99[g]	1
14	1	6	-20[f]	$FeCl_3$(50)	23	1	–	24[k]	99[g]	1
15	0.5	6	-20	$FeCl_3$(50)	21	1	–	22[k]	99[g]	1
16	0.5	6	-20	$FeCl_3$(25)	25	3	–	28[k]	94[g]	6
17	X=OMe 0.5	3	r.t.[d]	—	12	50	6	68	30	70[l]
18	0.5	3	-20	—	14	16	4	34	58	42[l]
19	0.5	3	-20[f]	—	14	25	4	43	49	51
20	1	6	-20	—	13	11	6	30	61[g]	39
21	1	6	-20	$FeCl_3$(50)		no reaction				

a) Reactions were carried out using Yb(0.5 mmol) and PhI (0.75 mmol) initially at -20°C and the mixture was stirred overnight at -20°C unless otherwise noted. 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), and the yield of triphenylmethane was also added to that of alcohols. d) After stirring at r.t. overnight the mixture was refluxed for 2 h. e) The mixture was stirred at r.t. overnight. f) Reaction time: 2 days. g) Ph-Yb-I was added inversely into the carbonyls. h) Biphenyl was also formed in 5% yield. i) Biphenyl was also formed in 7% yield. j) Biphenyl was also formed in 13% yield. k) Biphenyl was also formed in 9% yield. l) From ref. 2.

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