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Ytterbium Metal Mediated Synthesis of Symmetrical and Unsymmetrical Pinacols from Carbonyl Compounds

Zhaomin HOU, Kan TAKAMINE, Yuzo FUJIWARA,* and Hiroshi TANIGUCHI
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka 812

Reaction of aromatic aldehydes and ketones with ytterbium metal gives the corresponding pinacols in high yields. Cross-coupling reaction of benzophenone with other carbonyl compounds to produce unsymmetrical pinacols is also described.

We have recently shown that lanthanoid metals have unique reactivity toward organic compounds. For example, ytterbium metal (Yb) can selectively reduce the C-C multiple bonds conjugated with aromatic rings,[1] and the reaction of nitro-compounds with samarium metal (Sm) gives the corresponding azoxy-compounds in high yields.[2] In continued efforts to develop lanthanoid mediated organic reactions, we have found that Yb metal causes reductive coupling of carbonyl compounds. In this paper, we describe the Yb metal mediated reaction of carbonyl compounds which constitutes a new convenient method for synthesis of symmetrical and unsymmetrical pinacols.

A typical experiment was carried out as follows (run 1, Table 1). To 173 mg of Yb metal (1 mmol) was added 2 μl of CH_3I by a syringe under nitrogen atmosphere, and the metal was then warmed slightly by dryer to activate Yb metal. Addition of 2 cm^3 of THF gave a colored slurry (light-yellow) to which 2 cm^3 of HMPA was introduced. Benzophenone (364 mg, 2 mmol) in THF (2 cm^3) was then added by a syringe and the color of the solution immediately turned dark blue. The mixture was then stirred at room temperature for 10 min and finally a purple solution (opaque) was obtained. Usual work-up followed by chromatographic purification (silica gel) gave the reductive coupling product, benzopinacol (177.5 mg, 97%, mp 185-187 °C[3]). Some representative results are summarized in Eq.1 and Table 1. It is interesting to

note that the reaction of 0.5 equiv. of Yb metal with benzophenone gives benzopinacol(**1**) selectively (run 1) whereas 1 equiv. of Yb results in the sole formation of benzohydrol(**2**) (run 2).[4] The reaction of 2-octanone with Yb did not occur under the same reaction conditions (run 8).

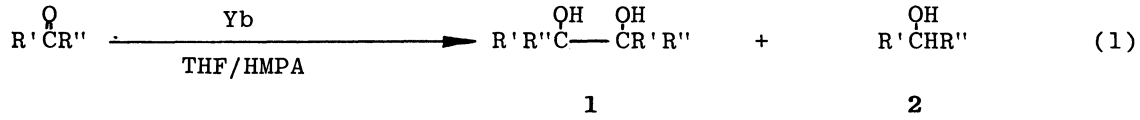
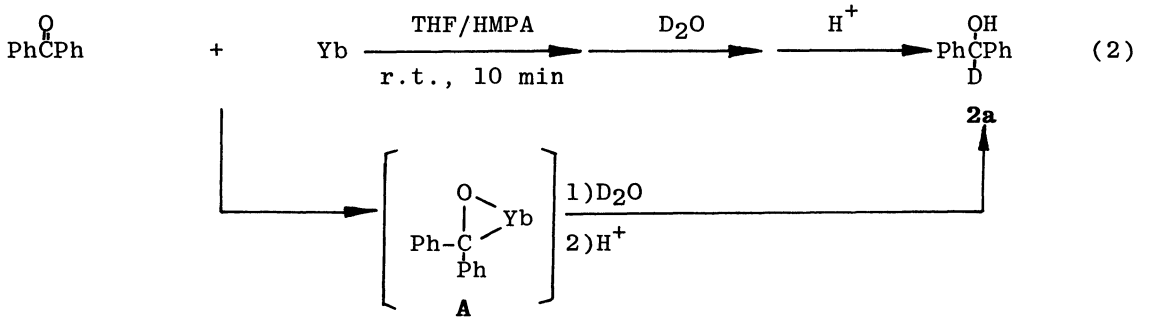


Table 1. Reaction of Carbonyl Compounds with Yb Metal[a)]

Run	R'	R"	Yb : R'COR" (mmol)	Reaction time	Product and Yield/%[b)] **1**	**2**
1	Ph	Ph	1 : 2	10 min	97	-
2	Ph	Ph	1 : 1	10 min	-	98
3	Ph	Me	1 : 2	5 h	73	-
4	p-CNC_6H_4	Me	1 : 1	3 h	58	-
5	p-$MeOC_6H_4$	Me	1 : 1	4 h	71	-
6	p-$MeOC_6H_4$	H	1 : 1	7 h	99	-
7	2-Naphthyl	Me	1 : 2	2 h	96	-
8	n-C_6H_{13}	Me	1 : 1	18 h	-[c)]	-

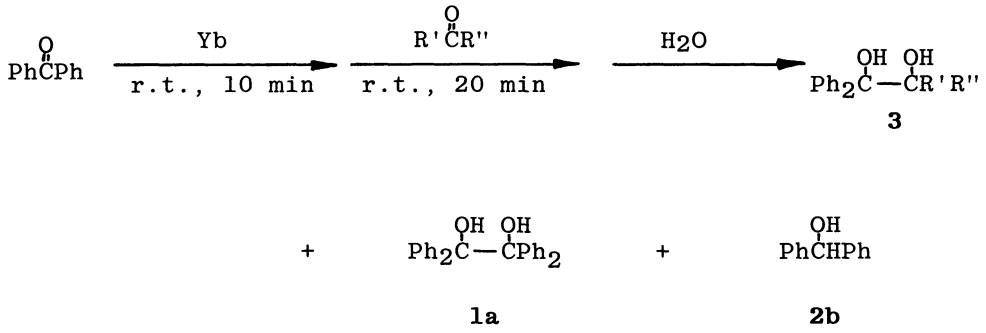
a) All reactions were carried out at room temperature in THF (4 cm^3)/HMPA (2 cm^3).
b) Isolated yields. All products gave satisfactory ^{1}H-NMR and IR spectral data.
c) The starting substrate was recovered.

It was also found that after the reaction of 1 equiv. of Yb with benzophenone (run 2), treating the reaction mixture with D_2O gave the corresponding C-deuteriated reduction product(**2a**, mp 64-65 °C; M^+=185) (Eq.2). This result indicates that in



this reaction, an intermediate like (**A**) which has a C-Yb bond, might exist before hydrolysis.

Based on this result, we tried the synthesis of unsymmetrical pinacols from benzophenone and other carbonyl compounds utilizing the intermediate(**A**). The results are summarized in Eq.3 and Table 2.



(3)

Table 2. Reductive Cross-coupling of Benzophenone with Other Carbonyl Compounds[a)]

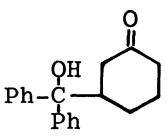
Run	R'	R''	Product and Yield/%[b)]		
			3	**1a**	**2b**
1	Me	Me	56	25	-
2	n-C_6H_{13}	Me	90	-	8
3	$-(CH_2)_5-$		90	-	9
4	$-(CH_2)_3-CH=CH-$		37[c)]	-	37

a) Yb : PhCOPh : R'COR'' = 2 : 1 : 1 (mmol), THF: 4 cm^3, HMPA: 2 cm^3.

b) Isolated Yields. All products gave satisfactory spectral data (^{1}H-NMR and IR), and the new compounds also gave satisfactory analytical data.

c) 3-(Diphenylhydroxymethyl)cyclohexanone(**4**) was also formed in 26% yield.

One can see from Table 2 that in the case of 2-octanone and cyclohexanone (runs 2 and 3), the corresponding unsymmetrical pinacols(**3**) are formed in excellent yields, although these alkyl carbonyl compounds themselves do not undergo coupling reaction with Yb metal under the same reaction conditions (run 8, Table 1). The reaction of benzophenone with 2-cyclohexene-1-one gave a mixture of 1,2- and 1,4-addition products(**3** and **4**) together with benzohydrol(**2b**). These cross-coupling products would be derived from nucleophilic addition of (**A**) to the carbonyl compounds(R'COR''), which indicates that the intermediate(**A**)



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derived from benzophenone and Yb metal appears to be a new nucleophilic reagent for introduction of a diphenylhydroxymethyl group.

The present method for pinacol synthesis has some notable characteristics which were not observed previously.[5,6] Of lanthanoid elements low-valent cerium and samarium were reported to cause the reductive coupling reaction of carbonyl compounds,[5b,5c] however cerium metal was unreactive toward the carbonyl compounds.[5b] Cross-coupling reaction between different carbonyl compounds is thought to be difficult and few reports could be found.[6c] Formation of an intermediate which acts as a nucleophilic reagent has been first observed in the present reaction by using Yb metal. Furthermore, the simplicity and the high yields of this method make it competitive with other ways of pinacol formation.

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References

1) Z. Hou, H. Taniguchi, and Y. Fujiwara, Chem. Lett., 1987, 305.

2) Z. Hou, Y. Fujiwara, and H. Taniguchi, submitted to J. Chem. Soc.,Chem. Commun.

3) W. E. Bachmann, J. Am. Chem. Soc., 55, 1179 (1933).

4) If no HMPA was used, benzopinacol was still formed as a main product even though 1 equiv. of Yb metal was used.

5) For lanthanoid mediated pinacol formation, see: a) G. B. Deacon and T. D. Tuong, J. Organomet. Chem., 205, C4 (1981); b) T. Imamoto, T. Kusumoto, Y. Hatanaka, and M. Yokoyama, Tetrahedron Lett., 23, 1353 (1982); c) J. L. Namy, J. Souppe, and H. B. Kagan, ibid., 24, 765 (1983).

6) a) T. Mukaiyama, T. Sato, and J. Hanna, Chem. Lett., 1973, 1041; b) J. E. McMurry and M. P. Fleming, J. Am. Chem. Soc., 96, 4708 (1974); c) E. J. Corey, R. L. Danheiser, and S. Chadrasekaran, J. Org. Chem., 41, 260 (1976).

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