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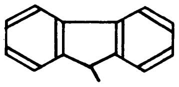
REACTIONS OF METHYLYTTERBIUM IODIDE WITH ACTIVE HYDROGEN COMPOUNDS

Kazuhiro YOKOO, Yasushi KIJIMA, Yuzo FUJIWARA,* and Hiroshi TANIGUCHI
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka 812

Methylytterbium iodide (CH_3YbI) has been found to react with active hydrogen compounds such as phenylacetylene and fluorene to give phenylpropynoic acid and fluorenol in modest yields. The reactivity of CH_3YbI to these active hydrogen compounds is far higher than that of CH_3MgI.

Utilization of lanthanoid metals to organic synthesis is an interesting problem. We reported some reactions of organolanthanoids (RLnI) with ketones, aldehydes, ethers, and acid chlorides.$^{1)}$ In order to further explore the reactivity of RLnX, we have investigated the reactions of RLnI with active hydrogen compounds in comparison with those of the Grignard reagent. We find that CH_3YbI reacts with active hydrogen compounds (RH) like phenylacetylene and fluorene to give intermediates, RYbI, which give the corresponding carboxylic acids or alcohols in modest yields when treated with CO_2 or O_2, respectively. In this communication we wish to report the reactions of CH_3YbI with RH such as phenylacetylene, fluorene, and triphenylmethane.

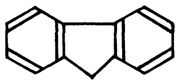
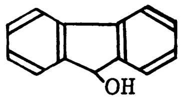
$$CH_3YbI \quad + \quad RH \xrightarrow[THF]{} RYbI \xrightarrow[\text{or } O_2]{CO_2} RCOOH \quad \text{or} \quad ROH$$

R: PhC≡C-, , Ph_3C-

Typical experimental procedure is as follows. Yb (0.5 mg-atom) and a magnetic stirring bar were placed in a 50-ml centrifuge tube and the tube was sealed with serum cap. After the tube was dried by heating under a stream of nitrogen, 1.5 ml of THF, which was freshly distilled under nitrogen from sodium benzophenone ketyl, was added by a syringe. Then iodomethane (0.6 mmol) was added in 20 min to the tube at -20 °C, and the mixture was stirred at -20 °C for 1 h, to form a red brown CH_3YbI solution. To the tube containing the CH_3YbI solution, phenylacetylene (0.25 mmol) was added by a syringe and the mixture was stirred at -20 °C for 2 h. After the addition of ca. 18 ml of THF, CO_2 was bubbled through the solution at -20 °C for 2 h. The resulting mixture was hydrolyzed with aq. NH_4Cl and 2 M HCl and then aq. $NaHCO_3$ was added. After the addition of ether the water layer was separated and treated with conc HCl, and the product was extracted with ether. Usual work-up gave phenylpropynoic acid in 50% yield. In a similar manner as described above, fluorene and triphenylmethane were allowed to react with CH_3YbI, followed by bubbling of O_2, instead of CO_2, to afford fluorenol and triphenylcarbinol in 40 and

1% yields, respectively. The results are summarized in Table 1 which also contains those with CH_3MgI performed at room temperature in ether.

Table 1. Reactions of CH_3YbI with Active Hydrogen Compounds

Active hydrogen compound	Treatment	Product	Yield/%a)	
			M=Yb b)	M=Mg c)
PhC≡CH	CO_2	PhC≡CCOOH	50	17
	O_2		40	trace
Ph_3CH	O_2	Ph_3COH	1d)	1d)
Ph_2CH_2	O_2	Ph_2CHOH	0d)	0d)

a)Based on the active hydrogen compound and determined by NMR unless otherwise noted. b)Reaction temp: -20 °C. c)Reaction temp: room temp. d) GLC yields based on the active hydrogen compound.

As is apparent from Table 1, CH_3YbI can react with active hydrogen compounds (RH) to give RYbI, the alkyl-exchanged intermediates which further react with CO_2 or O_2 affording carboxylic acids or alcohols. Phenylacetylene (pKa 18.5)2) is the most reactive toward CH_3YbI and triphenylmetane (pKa 31.5)2) gives only 1% yield of triphenylcarbinol, and diphenylmethane (pKa 33)2) fails to react. That CH_3YbI reacts with phenylacetylene to give phenylpropynoic acid in 50% yield even at -20 °C while CH_3MgI gives only 17% yield at room temperature3) clearly indicates the far higher reactivity of CH_3YbI than CH_3MgI, the corresponding Grignard reagent.

The results reported here constitute the one of the unique properties of RYbI1,4) and provide a convenient synthetic tool.

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References

1) T. Fukagawa, Y. Fujiwara, K. Yokoo, and H. Taniguchi, Chem. Lett., 1981, 1771; T. Fukagawa, Y. Fujiwara, and H. Taniguchi, ibid., 1982, 601; K. Yokoo, Y. Yamanaka, T. Fukagawa, H. Taniguchi, and Y. Fujiwara, ibid., 1983, 1301; K. Yokoo, Y. Fujiwara, T. Fukagawa, and H. Taniguchi, Polyhedron, 2, 1101 (1983).

2) A. J. Gordon and R. A. Ford, "The Chemist's Companion," John Wiley & Sons, New York (1972).

3) Usually reactions of the Grignard reagents with acetylenes are performed at elevated temperature: K. H. Meyer and P. Strenli, Helv. Chim. Acta, 20, 1179 (1937). Furthermore, the reaction of CH_3MgI with phenylacetylene under the same reaction conditions as those with CH_3YbI, gave only 2% yield of phenylpropynoic acid.

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