Tetrahedron Letters, Vol. 34, No. 8, pp. 1321-1322, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Hydroperfluoroalkylation of Alkenes Using R_fI/ $YbCl_3$(cat.) /Zn System

Yu Ding* , Gang Zhao and Weiyuan Huang

Shanghai Institute of Organic Chemistry Academia Sinica,
345Lingling Lu, Shanghai 200032, China

Abstract: Hydroperfluoroalkylation of alkenes using R_fI/YbCl3(cat.)/Zn system in good yields is described.

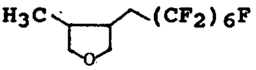
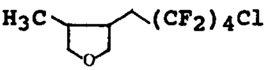
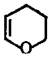
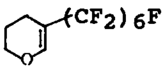
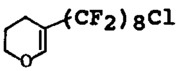
The f-block metals and its compounds as catalysts have been used in organic reaction[1]. Recently, Fujiwara et al reported reductive coupling of α,β- unsaturated carbonyl compounds by Yb metal or $YbCl_3$/Zn[2]. Although perfluoroalkylation of carbon-carbon multiple bonds has been reported by means of the transition metals or bimetal redox system as catalysts[3], such as Zn, $BrCo(dmgH)_2$/Zn etc., there have been few methods of the direct hydroperfluoroalkylation of alkenes. Herein, we describe a facile method for the reductive addition of perfluoroalkyl iodides to alkenes promoted by $YbCl_3$(cat.)/Zn system in THF affording hydroperfluoroalkylated product in rather good yield.

$$\underset{\mathbf{1}}{R_fI} + \underset{\mathbf{2}}{CH_2{=}CHR} \xrightarrow[\text{THF. 50-76}^\circ\text{C}]{YbCl_3\text{(cat.)/Zn}} \underset{\mathbf{3}}{R_fCH_2CH_2R}$$

General procedure is as follows: To a mixture of perfluoroalkyl iodide (10mmol), alkene(10mmol) and anhydrous $YbCl_3$(0.5mmol) in THF(10ml) was added Zn dust(5-10mmol). The mixture was stirred for 5-10 min at 50-76°C. Then, the reaction was quenched with dil. HCl and the organic layer was extracted with ether. Usual workup gave the hydrofluoroalkylated product in good yields.

The reaction of perfluoroalkyl iodides with alkenes in THF was summarized in Table. Alkenes bearing functional groups, including ester, hydroxyl, and phosphonate, could be tolerated under the reaction conditions. The reaction was completed by using $YbCl_3$(cat.) and less than a stoichiometric amount of Zn powder within a few min. However, we found that the reaction did not occur in EtOH or benzene.

Table $YbCl_3$(cat.)/Zn promoted hydroperfluoroalkylation of alkenes.[a]

Entry No.	R_fI 1	Alkene 2	Time (min.)	Adduct 3	yield[b] (%)
1	$F(CF_2)_6I$	$CH_2{=}CHCH_2OAc$	6	$F(CF_2)_6(CH_2)_3OAc$	95
2	$F(CF_2)_6I$	diallyl ether	5	 cis/trans=1:2.4[c]	90
3	$Cl(CF_2)_4I$	diallyl ether	5	 cis/trans=1:2.2[c]	93
4	$Cl(CF_2)_6I$		6		88
5	$Cl(CF_2)_8I$		6		90
6	$F(CF_2)_6I$	allyl alcohol	7	$F(CF_2)_6(CH_2)_3OH$	56
7	$F(CF_2)_6I$	$CH_2{=}CHCH_2PO(OEt)_2$	10	$F(CF_2)_6(CH_2)_3PO(OEt)_2$	60
8	$Cl(CF_2)_8I$	1-Octene	10	$Cl(CF_2)_8CH_2CH_2C_6H_{13}$	58

a: Molar ratio **1**:**2**:$YbCl_3$:Zn=1:1:0.05:0.5(1). b: Isolated yield based on **2**. c: Cis/trans ratio determined by GC-MS and ^1H NMR

The possible mechanism is shown in scheme 1:

Scheme 1

$$YbCl_3 + Zn \longrightarrow [\text{ low-valent Yb such as } YbCl_2 \text{ }]$$

$$R_fI \xrightarrow{YbCl_2} [R_fI]^{\overline{\cdot}} \longrightarrow R_f\cdot + I^-$$

$$R_f\cdot + CH_2{=}CHR \longrightarrow R_fCH2\dot{C}HR \xrightarrow{THF} R_fCH_2CH_2R$$

References:

1. Tsutsui, M.; Ely, N.; Dubois, R. Acc. Chem. Res. **1976**, 9, 217.
2. Takaki, K.; Nagase, K.; Beppu, F.; Shindo, T,; and Fujiwara, Y. Chem. Lett. **1991**, 1665-1672
3. a) Q. Y. Chen, Z. Y. Yang and Z. M. Qiu. Kexue Tongbao. **1987**, 593.
   b) Tomoya kitazume and Nobuo Ishikawa, Chem. Lett. **1982**, 1453-1454.
   c) C. M . Hu and Y. L. Qiu. Tetrahedron Lett., **1991**, 4001-4002.

(Received in China 27 October 1992)