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$LnCl_3$(cat.)/Zn promoted Hydroperfluoroalkylation of α,β - Unsaturated Esters With Perfluoroalkyl Iodides

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Summary: $LnCl_3$(cat.)/Zn system has been found to cause hydroperfluoroalkylation of α,β - unsaturated esters with perfluoroalkyl iodides in high yields as compared with the reaction with Zn alone.

It is well known that the addition of perfluoroalkyl radical R_f. to α,β- unsaturated esters was troublesome[1]. Recently, Hu has reported the hydroperfluoroalkylation of acrylate with perfluoroalkyl iodides in the presence of catalytic amount of bromo(pyridine) cobaloxime (Ⅱ) and excess of zinc powder in EtOH[2]. However, it is still desirable to develop a better means for introducing a fluoroalkyl group to organic molecules. In this communcation, we would like to describe the hydroperfluoroalkylation of α,β- unsaturated esters with perfluoroalkyl iodides by $LnCl_3$(cat.)/Zn in THF.

$$R_fI + R_1CH{=}CR_2COOR_3 \xrightarrow[\text{THF, } 50\text{-}76\,^{\circ}C]{LnCl_3\text{(cat.)/Zn}} R_fR_1CHCHR_2COOR_3$$

R_1, R_2 = H, CH_3.
R_3= CH_3, C_2H_5.

Typical procedure: Into a mixture of $LnCl_3$(0.5 mmol), α,β- unsaturated ester(10 mmol), and perfluoroalkyl iodides(10 mmol) in THF(10 ml) was added zinc dust(5-10 mmol). The mixture was stirred for 5-10 min. at 50-76°C. Dil. HCl quenched the reaction, the reaction mixture was extracted three times with ether, and the combined organic phases were washed with aq. $NaHCO_3$, aq. $Na_2S_2O_4$ and aq. NH_4Cl, dried over Na_2SO_4, filtered and evaporated. Distillation or flash column chromatography gave hydroperfluoroalkylated product in good yield.

The reaction proceeded smoothly in a few min in THF, but if EtOH or benzene as solvent , the adduct was not detected. The results using

$LnCl_3$(cat.)/Zn system are summarized in Table.

Table: $LnCl_3$(cat.)/Zn promoted hydroperfluoroalkylation of α,β-unsaturated esters with perfluoroalkyl iodides.

Entry	$LnCl_3$	R_fI	α,β-unsaturated ester	yield(%)[a,b]
1	$SmCl_3$	$Cl(CF_2)_8I$	CH_2=CHCOOEt	76
2	$SmCl_3$	$Cl(CF_2)_8I$	CH_2=CHCOOMe	75
3	$SmCl_3$	$Cl(CF_2)_8I$	CH_2=CCH_3COOMe	80
4	$SmCl_3$	$Cl(CF_2)_4I$	E-CH_3CH=CHCOOMe	65
5	$DyCl_3$	$Cl(CF_2)_8I$	CH_2=CCH_3COOMe	78
6	$DyCl_3$	$Cl(CF_2)_4I$	CH_2=CHCOOEt	75
7	$DyCl_3$	$F(CF_2)_6I$	CH_2=CHCOOEt	74
8	$DyCl_3$	$F(CF_2)_8I$	CH_2=CHCOOEt	70
9	YCl_3	$Cl(CF_2)_8I$	CH=CCH_3COOMe	78
10	YCl_3	$Cl(CF_2)_6I$	CH_2=CHCOOEt	70
11	YCl_3	$Cl(CF_2)_4I$	CH_2=CHCOOMe	65
12	YCl_3	$F(CF_2)_8I$	CH_2=CHCOOEt	60

a) Isolated yield after flash column chromatography or distillation.

b) All compounds gave satisfactory IR., ^1H NMR., ^{19}F NMR. and MS.

In all cases, the reaction was completed with $LnCl_3$(cat.)/Zn system in a few min. It was found that the $LnCl_3$/Zn system gave hydroperfluoroalkylated product in higher yield than Zn alone did[2]. Although the reaction mechanism is not clear at present, the reaction may involve a radical mechanism, since $YbCl_3$(cat.)/Zn could cause the R_f. addition to diallyl ether and resulted in tetrahydrofuran derivative.[3]

References:

1. a, Y.F. Zhang, L.Lu and W.Y. Huang. Act. Chimia. Sinica. (Engl. Ed.) 376(1989).
   b, A. Roger, New J. Chem. **13**, 543(1989).
   c, C. J. Boookes, P. L. Coe, D. M. Owen, A. E. Pedler and J. C. Tatlo J. Chem. Soc., Chem. Commun., 323(1974).
   d, Y. Maki and K. Inukai, J. synth. Org. Chem., **34**, 722(1976).
   e, A. Battais, B. Boutevin, J. P. Hugon and Y. Pietrasanta, J. Fluorine Chem., **16**, 397(1980)
2. C. M. Hu and Y. L. Qiu, Tetrahedron Lett., **32**, 4001(1991).
3. Y. Ding, G. Zhao and W.Y. Huang, Tetrahedron lett., to be published.

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