

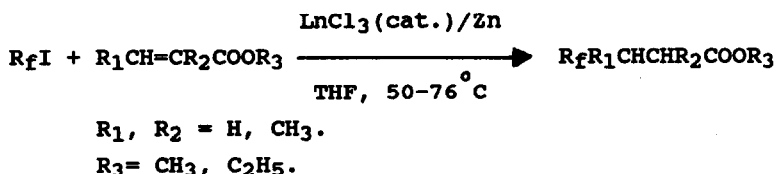
LnCl₃(cat.)/Zn promoted Hydroperfluoroalkylation of α,β -Unsaturated Esters With Perfluoroalkyl Iodides

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Summary: LnCl₃(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 troublesome¹. Recently, Hu has reported the hydroperfluoroalkylation of acrylate with perfluoroalkyl iodides in the presence of catalytic amount of bromo(pyridine) cobaloxime (III) and excess of zinc powder in EtOH². However, it is still desirable to develop a better means for introducing a fluoroalkyl group to organic molecules. In this communication, we would like to describe the hydroperfluoroalkylation of α,β -unsaturated esters with perfluoroalkyl iodides by LnCl₃(cat.)/Zn in THF.



Typical procedure: Into a mixture of LnCl₃(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. NaHCO₃, aq. Na₂S₂O₄ and aq. NH₄Cl, dried over Na₂SO₄, 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

$\text{LnCl}_3(\text{cat.})/\text{Zn}$ system are summarized in Table.

Table: $\text{LnCl}_3(\text{cat.})/\text{Zn}$ 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	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{CH}_2=\text{CHCOOEt}$	76
2	SmCl_3	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{CH}_2=\text{CHCOOMe}$	75
3	SmCl_3	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{CH}_2=\text{CCH}_3\text{COOMe}$	80
4	SmCl_3	$\text{Cl}(\text{CF}_2)_4\text{I}$	$\text{E}-\text{CH}_3\text{CH}=\text{CHCOOMe}$	65
5	DyCl_3	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{CH}_2=\text{CCH}_3\text{COOMe}$	78
6	DyCl_3	$\text{Cl}(\text{CF}_2)_4\text{I}$	$\text{CH}_2=\text{CHCOOEt}$	75
7	DyCl_3	$\text{F}(\text{CF}_2)_6\text{I}$	$\text{CH}_2=\text{CHCOOEt}$	74
8	DyCl_3	$\text{F}(\text{CF}_2)_8\text{I}$	$\text{CH}_2=\text{CHCOOEt}$	70
9	YCl_3	$\text{Cl}(\text{CF}_2)_8\text{I}$	$\text{CH}=\text{CCH}_3\text{COOMe}$	78
10	YCl_3	$\text{Cl}(\text{CF}_2)_6\text{I}$	$\text{CH}_2=\text{CHCOOEt}$	70
11	YCl_3	$\text{Cl}(\text{CF}_2)_4\text{I}$	$\text{CH}_2=\text{CHCOOMe}$	65
12	YCl_3	$\text{F}(\text{CF}_2)_8\text{I}$	$\text{CH}_2=\text{CHCOOEt}$	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 $\text{LnCl}_3(\text{cat.})/\text{Zn}$ system in a few min. It was found that the LnCl_3/Zn system gave hydroperfluoroalkylated product in higher yield than Zn alone did². Although the reaction mechanism is not clear at present, the reaction may involve a radical mechanism, since $\text{YbCl}_3(\text{cat.})/\text{Zn}$ could cause the R_f addition to diallyl ether and resulted in tetrahydrofuran derivative.³

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