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PRELIMINARY NOTE

Iron-Catalyzed Addition Reaction of Fluoroalkyl Iodides to Alkenes

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SUMMARY:

Fluoroalkyl iodides react with alkenes in the presence of catalytic amounts of iron to give the corresponding adducts in good yields, the influence of solvent on the reaction is discussed and a SET initiated radical chain mechanism is proposed.

Recently, we have found that addition of fluoroalkyl iodides to carbon-carbon multiple bonds could be catalyzed by copper[1], Raney-nickel[2] as well as palladium[3] and platinum[4] complexes. Now we wish to report the addition of fluoroalkyl iodides to alkenes in the presence of catalytic amounts of iron(7 mol%) in DMF to afford the adducts in good yields which would be more convenient and economical as compared with other methods of fluoroalkylation of alkenes.

$$R_fI + CH_2{=}CR^1R^2 \xrightarrow[\text{DMF, } N_2]{\text{Fe}} R_fCH_2CIR^1R^2$$

The representative results are listed in Table I.

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TABLE I

Reaction of fluoroalkyl iodides with alkenes in the presence of iron[a]

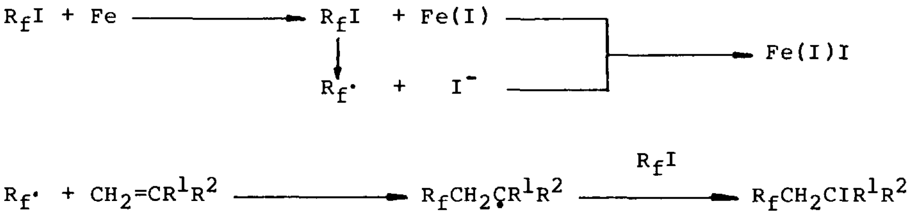
R_fI	Alkene	t(h)	Conv.(%)[b]	Yield(%)[c]
$Cl(CF_2)_6I$	$C_5H_{11}CH=CH_2$	2	100	79
$Cl(CF_2)_6I$	$C_4H_9CH=CH_2$	2	100	73
$Cl(CF_2)_2I$		5	89	92
$Cl(CF_2)_4I$	$MeEtC=CH_2$	5	48	73[b]
$Cl(CF_2)_4I$		2	92	97
$Cl(CF_2)_4I$	$C_5H_{11}CH=CH_2$	2	95	92
$Cl(CF_2)_4I$	$C_4H_9CH=CH_2$	2	100	85
$CF_3(CF_2)_2I$		5	90	90

[a] All the reactions were carried out under nitrogen; Alkene: R_fI=2:1; Reaction temperature: 80°C; Fe: 7 mol%.

[b] Determined by ^{19}F-NMR.

[c] Isolated yield unless specified otherwise. All the products showed spectral data(^1H- and ^{19}F-NMR,IR and Mass) and elemental analyses in accord with the assigned structures.

Oxygen in air inhibited this reaction completely, addition of free radical inhibitor, e.g. 3 mol% of 2-nitro-2-nitrosopropane decreased the conversion of R_fI to 10% as compared with that of control(100%) in the reaction of $Cl(CF_2)_6I$ with 1-heptene, the presence of single electron transfer scavenger, e.g. 10 mol% of p-dinitrobenzene decreased the conversion of R_fI to 9%. Furthermore, diallyl ether(DAE) could trap the fluoroalkyl radical generated in this reaction system to afford tetrahydrofuran derivative. All these results seem to show that the reaction may involve a SET initiated free radical chain mechanism as follows:



The existence of a bit of water in the solvent showed little influence on the conversion and yield. If acetone was used as solvent instead of DMF, the yield was also excellent as shown in Table II.

TABLE II

The influence of solvent on the reaction of $Cl(CF_2)_6I$ with 1-heptene[a]

Solvent	t(h)	Conversion(%)[b]	Yield(%)[b]
DMF(dry)	2	100	98
DMF(C.P.)	4	91	90
Acetone(C.P.)[c]	4	90	100

a. Alkene:R_fI=2:1; Reaction temperature: 80°C; Fe: 7 mol%.
b. Determined by ^{19}F-NMR.
c. The reaction mixture was placed in a sealed tube.

The operational details of a typical experimental procedure are outlined below for the fluoroalkylation of 1-hexene.

A mixture of 1-iodo-4-chloro-perfluorobutane(0.91g, 2.5 mmol), 1-hexene(0.42g, 5 mmol), dry DMF(0.5 ml) and acid-treated iron powder(9.8mg, 0.175 mmol) was stirred at 80°C for 2h under nitrogen, ^{19}F-NMR spectrum showed that the reaction was complete. Distillation in vacuo gave 1-(4-chloro-perfluorobutyl)-2-iodo-hexane 0.95g(85%).

Fluoroalkylation of alkynes with R_fI could also be accomplished under catalysis of iron to afford E isomer of adducts, e.g. phenylacetylen reacted with $Cl(CF_2)_4I$ in the presence of 20 mol% of iron in DMF for 5.5 h at 80°C gave E isomer(without Z isomer) of adduct in the yield of 95% with the conversion of 45% of R_fI.

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