

Received: February 12, 1988; accepted: February 24, 1988

PRELIMINARY NOTE

Addition Reactions of F-Alkyl Iodides to Carbon-Carbon Double Bonds Promoted by Metallic Tin(0)-Metal Salt Systems

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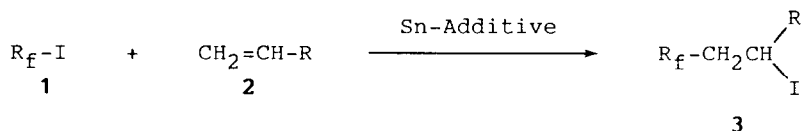
Summary

F-Alkyl iodides readily reacted with a variety of alkenes in methanol at room temperature under the influence of metallic tin(0)-silver(I) acetate or metallic tin(0)-copper(I) chloride to afford the corresponding addition products, F-alkylated iodides, in good to excellent yields. This addition reaction was also promoted by the use of a metallic tin(0)-aluminium(0) reagent, though gentle heating was necessary for allowing the reaction to proceed.

The addition of F-alkyl halides to carbon-carbon multiple bonds is well recognized to be a useful and fundamental reaction for the synthesis of fluorine-containing compounds. This reaction can be attained under various conditions, for example, thermal [1], photo-irradiated [2], transition [3] or typical metal-mediated [4], electrochemical [5], and biochemical [6] conditions. However, it is still quite valuable to develop new methods or reagents for the addition of F-alkyl halides, because the methods reported so far still have some drawbacks, such as severe reaction conditions, low yields of the products, or undesired side-reactions.

In the course of our studies [3f, 4b] to explore novel reagents for effecting such a reaction, we have found that a

metallic tin(0)-silver(I) acetate or metallic tin(0)-copper(I) chloride reagent can efficiently promote the addition of F-alkyl iodides to a variety of alkenes under extremely mild conditions.



In the present study, commercially available tin(0) powder was washed [7] successively with dilute hydrochloric acid, methanol, and diethyl ether, and was dried under vacuum prior to use. When F-butyl iodide (1 mmol) was treated with 1-octene (2 mmol) in the presence of activated tin(0) powder (1 mmol) and two drops of sulfuric acid (0.1 N) in diethyl ether (5 mL)-water (0.5 mL) at 30 °C, the corresponding addition product 3[†] was obtained in 78% yield (Run 1), along with a small amount of the reduction product, 1-hydril-F-butane. The use of a trace quantity of the acid was found to be essential for suppressing the formation of 1-hydril-F-alkane, R_f-H (Runs 1 and 2): no sulfuric acid resulted in the substantial formation of the reduction products.

Other additives than the acid were extensively examined in order to avoid the acidic conditions, which often make the scope of the reaction limited. Among the additives employed, silver(I) acetate and copper(I) chloride were the most efficient additives for the present reaction. Thus, F-alkyl iodides (1) smoothly underwent the addition to various alkenes (2) under neutral conditions at room temperature by using a combination of metallic tin(0)-silver(I) acetate or -copper(I) chloride [8] to give the corresponding F-alkylated iodides (3)[†] in good to excellent yields. The representative results of the reaction are summarized in Table 1.

Several features are noted as follows. (i) Methanol is

[†] The spectroscopic (IR, MS, ¹H and ¹⁹F NMR) and analytical data pertaining to all the products were consistent with the assigned structures.

TABLE 1

The Addition of \underline{F} -Alkyl Iodides to Alkenes Promoted by Using Metallic Tin(0)

Run	R_f	R	Additive	Solvent	Temp °C	Yield ^a %
1	$\underline{n-C}_4F_9$	$CH_3(CH_2)_5$	H^{+b}	Et_2O-H_2O	30	78
2		$CH_3CO(CH_2)_2$	H^{+b}	Et_2O-H_2O	30	73
3		$HOCH_2$	AgOAc	MeOH	rt	73
4		$HO(CH_2)_2$	AgOAc	MeOH	rt	71
5		$HO(CH_2)_4$	AgOAc	MeOH	rt	81
6	$\underline{n-C}_6F_{13}$	$CH_3(CH_2)_5$	AgOAc	MeOH	rt	71
7		$CH_3(CH_2)_5$	CuCl	MeOH	rt	75
8		$(CH_3)_2CHCH_2$	CuCl	MeOH	rt	62
9		$CH_3CO(CH_2)_2$	AgOAc	MeOH	rt	67
10		$CH_3CO(CH_2)_2$	CuCl	MeOH	rt	66
11		$(EtOCO)_2CHCH_2$	AgOAc	MeOH	rt	56
12	$\underline{n-C}_4F_9$	$CH_3(CH_2)_5$	Al	Et_2O-H_2O	30	82
13		$PhCH_2$	Al	Et_2O-H_2O	refl.	60
14		diallyl ether	$Al-H^{+b}$	Et_2O-H_2O	refl.	70 ^c

^a Yields are of pure isolated products.

^b Two drops of 0.1N sulfuric acid were added.

^c 3-(1,1-Dihydril- \underline{F} -pentyl)-4-iodomethyltetrahydrofuran was obtained.

the most suitable solvent. (ii) Some functionalities such as hydroxyl (Runs 3-5), ketone (Runs 2,9 and 10), and ester groups (Run 11) are compatible with the reaction. (iii) The yields of the products **3** are generally high (56-81%). (iv) The reaction conditions are very mild (room temperature, 24 h).

The reaction of \underline{F} -hexyl iodide with 1-octene (Run 6) is described as the typical procedure. To a mixture of acid-

washed tin(0) powder (1 mmol) and silver(I) acetate (0.15 mmol) in methanol (1.5 mL) were added F-hexyl iodide (1 mmol) and 1-octene (1.5 mmol) under an argon atmosphere. The whole was stirred at room temperature for 24 h and then was diluted with diethyl ether. This mixture was filtered through a Celite 545 bed and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel to give analytically pure **3** in 71% yield. The reactions using copper(I) chloride as the additive were conducted in 6 mL of methanol (Runs 7, 8, and 10).

Moreover, the combined use of metallic tin(0)-aluminium(0) could also be found to be effective for the addition of F-alkyl iodides to alkenes, as shown in Table 1 (Runs 12-14). Thus, the treatment of F-butyl iodide with 1-octene in the presence of tin(0) (1 equiv.) and aluminium(0) (1 equiv.) in diethyl ether-water under heating gave the product **3** in 82% yield. In the case of diallyl ether (Run 14), intramolecular cyclization occurred to afford a good yield of an F-alkylated tetrahydrofuran derivative.

The method described herein is quite unique and unprecedented, and provides an efficient access to various fluorine-containing compounds.

Further studies on the applications of these reactions as well as their mechanism are in progress.

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