Addition of R_FI ($C_nF_{2n+1}I$; $n = 4, 6, 8$) to allyl alcohol catalyzed by zinc in different solvents: application to the synthesis of *F*-alkyl epoxypropanes

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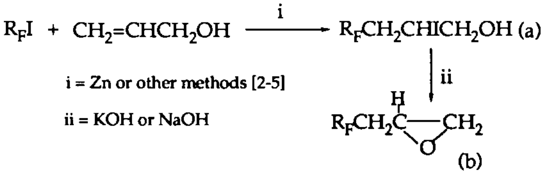
Abstract

The addition of R_FI to allyl alcohol catalyzed by zinc in different solvents has been studied. The adduct $R_FCH_2CHICH_2OH$ readily gives the corresponding *F*-alkyl epoxypropane.

F-Alkyl epoxypropanes are intermediates in the synthesis of polyacrylates containing perfluoro pendant chains and present striking surface properties (very low surface tensions) [1]. These compounds are synthesized by reaction of perfluoroalkyl iodides R_FI with allyl alcohol according to eqn. (1):



(1)

This addition can be realized by different methods: UV irradiation [2], radical initiator [3], oxidation–reduction couple [4] or electrochemical reduction [5]. We show here that this reaction can be carried out very readily using zinc powder as a catalyst (Table 1).

The reaction may be performed with small quantities of zinc. As such, it is very selective and gives good yields but is slow (5d) (expt. A, Table 1). This time length can be reduced (3–5 h) by the use of larger amounts of metal and low polarity solvents (expts. D and E).

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TABLE 1

Addition of R_FI to allyl alcohol catalyzed by zinc in different solvents[a]

Expt.	Solvent[b]	$C_6F_{13}I$ [g (mol)]	Allyl alcohol [g (mol)]	Zinc[c] [g (mol)]	Reaction time (h)	Product (a) (% mol)[d]
A	no solvent	22.3 (0.05)	3.9 (0.05)	0.327 (0.005)	120	95
B	n-hexane	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	18	68
C	toluene	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	12	64
D	dichloromethane	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	6	77
E	chloroform	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	5	70
F	acetone	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	5	44
G	water	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	no reaction	
H	tetrahydrofuran	22.3 (0.05)	3.9 (0.05)	3.27 (0.05)	15	63

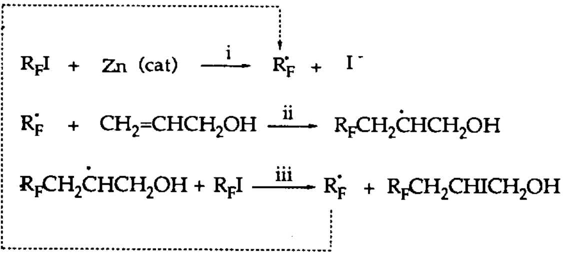
[a] All reactions were carried out at 30 °C. It should be noted that at 80 °C this reaction gave numerous by-products arising from the Wurtz reaction. Such addition–reduction, addition–dimerization or addition–elimination products reduced the selectivity of the addition compound to 40%.

[b] Used in 20 ml quantities.

[c] Purchased from Atochem Co. Ltd.

[d] Obtained on a Varian EM 360 spectrometer.

A radical mechanism may be proposed according to eqn. (2):



$$R_FI + Zn\ (cat) \xrightarrow{i} R_F^{\bullet} + I^-$$

$$R_F^{\bullet} + CH_2{=}CHCH_2OH \xrightarrow{ii} R_FCH_2\dot{C}HCH_2OH \qquad (2)$$

$$R_FCH_2\dot{C}HCH_2OH + R_FI \xrightarrow{iii} R_F^{\bullet} + R_FCH_2CHICH_2OH$$

This mechanism seems to be confirmed by the fact that when R_FBr and R_FCl are used under the same conditions, no addition to the C—C double bond occurs and no reaction is observed. Carbon–chlorine bonds are too strong to allow the formation of the $R_F^{\bullet}$ radical by abstraction of halogen in stage (iii) of eqn. (2). However, in the presence of zinc powder as a catalyst, addition of R_FI to olefins such as vinyl and allyl acetates [6], allylamine, vinyl acetic ester and allyl nitrile can be performed even in chlorinated solvents [7]. The reactivity of these olefins differs from that of ethyl acrylate and acrylonitrile. These compounds react with R_FI only if acid is added (HCl, acetic or propionic acid) to the medium, when an addition–reduction product is obtained [8]. From this observation, it appears that the electrophilic radical $R_F^{\bullet}$ reacts with the C—C double bonds which are electron-rich. This explains the reactivity with allyl compounds where the methylene group acts as a screen against the inductive effect of electroattractive groups such as CN or CO_2R.

It is known that zinc metal can emit electrons from its surface, although to our knowledge this phenomenon has yet to be quantified. However, the experimental observations described in this paper suggest that the electrons involved in the reaction depend on the specific surface area of zinc and hence on the quantity of metal employed. Radical additions of R_FI to alkenes catalyzed by metals have been carried out by Chen and Yang [9], although reaction of R_FI with allyl alcohol in the presence of zinc has not been described hitherto [10].

The typical experimental procedure for step i of eqn. (1) was as follows. $C_6F_{12}I$ (22.3 g, 0.05 mol) and 2.9 g of $H_2C{=}CHCH_2OH$ (0.05 mol) were added to a dispersion of 3.27 g of zinc (0.05 mol) in 5 ml of solvent. As the temperature of the medium increased, a further 15 ml of solvent was added slowly to the system. The reaction was followed by ^{19}F NMR spectroscopy. Stage ii of eqn. (1) was then accomplished by treating the crude product a, after removal of the zinc by filtration, with a concentrated solution (or even better a dispersion) of KOH in CH_2Cl_2 for 1 h to yield the corresponding epoxide b. The epoxide was distilled and compared with authentic samples (yields: $R_F{=}C_4F_9$, 67%; $R_F{=}C_6F_{13}$, 65%; $R_F{=}C_8F_{17}$, 62%).

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