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The effect of triphenylphosphine on ring-opening of aliphatic epoxides with potassium fluoride–poly(hydrogen fluoride)

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Abstract

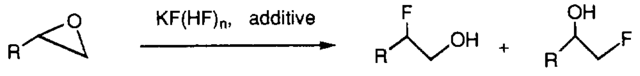
The ring-opening reaction of aliphatic epoxides with potassium fluoride–poly(hydrogen fluoride) is enhanced by a catalytic amount of triphenylphosphine. It is assumed that phosphonium fluoride species formed from triphenylphosphine work as fluorinating agents in this reaction. © 1997 Elsevier Science S.A.

Keywords: Potassium fluoride–poly(hydrogen fluoride); Fluorinating agent; Ring opening; Epoxides; Triphenylphosphine

1. Introduction

Potassium fluoride–poly(hydrogen fluoride) ($KF(HF)_n$) salts are easy-to-handle solid reagents which are easily prepared from potassium fluoride and anhydrous hydrogen fluoride [1]. From the viewpoint that they are poly(hydrogen fluoride) species, they are expected to be solid alternatives to anhydrous hydrogen fluoride or amine–HF, which are effective nucleophilic fluorinating agents [2]. Recently, we have demonstrated the utility of $KF(HF)_n$ as nucleophilic fluorinating agents for the first time [3,4]. When $KF(HF)_n$ is used for ring-opening reactions of epoxides and for halofluorination of alkenes, the reactions proceed in a regio- and stereoselective manner to afford the corresponding fluorohydrins and halofluorides respectively. Especially, the stereoselectivity of the ring-opening reaction is quite unique, namely the reaction proceeds via predominantly cis-addition of hydrogen fluoride to the epoxide.

Concerning this ring-opening of epoxides, however, the substrate is limited only to aromatic epoxides, such as styrene oxide. If aliphatic epoxides are reacted with $KF(HF)_n$, the yields of corresponding fluorohydrins are very low [3]. In this study, we investigate the ring-opening of aliphatic epoxides with $KF(HF)_n$ and find that a catalytic amount of triphenylphosphine enhances this reaction.



1 2 3

a : R = $C_{10}H_{21}$ -

b : R = $PhOCH_2$ -

Scheme 1.

2. Results and discussion

The reaction of 1-dodecene oxide (**1a**) with KH_2F_3 was initially attempted (Scheme 1). Without additives, although the ring-opening reaction proceeded at 80°C, the yields of corresponding fluorohydrins (**2a** and **3a**) were very low because of undesirable side reactions such as polymerization (Table 1, entry 1). However, the yield was improved when the reaction was carried out in the presence of a catalytic amount of trialkylphosphine (entry 2). And when triphenylphosphine (Ph_3P) was used as an additive, the fluorohydrins were obtained in 64% yield (entry 3).

The effect of Ph_3P on the reaction using other $KF(HF)_n$ or substrates was examined. When **1a** was reacted with $K_2H_5F_7$, the ring-opening reaction proceeded at room temperature, but the combined yield of **2a** and **3a** was only 12% (entry 5). If a catalytic amount of Ph_3P was used as an additive, the yield was improved to 44% (entry 6). And although the reaction of phenyl glycidyl ether (**1b**) with KH_2F_3 did not proceed at all (entry 7), the reaction proceeded

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Table 1
The effect of phosphines on the ring-opening of aliphatic epoxides [a]

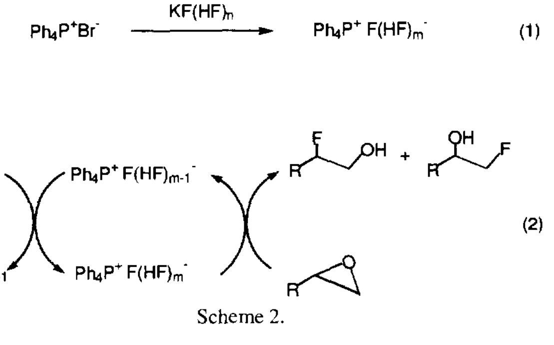
Entry	Substrate	KF(HF)$_n$	Additive	Time (h)	Products (**2**+**3**)	
					Yield [b] (%)	Selectivity [b] (**2**:**3**)
1	**1a**	KH$_2$F$_3$	–	32	9 [c]	84:16
2	**1a**	KH$_2$F$_3$	n-Bu$_3$P	72	40	73:27
3	**1a**	KH$_2$F$_3$	Ph$_3$P	72	64	69:31
4	**1a**	KH$_2$F$_3$	Ph$_4$P$^+$Br$^-$	45	66	68:32
5	**1a**	K$_2$H$_5$F$_7$	–	7	12 [d]	92:8
6	**1a**	K$_2$H$_5$F$_7$	Ph$_3$P	3	44	80:20
7	**1b**	KH$_2$F$_3$	–	32	0 [e]	
8	**1b**	KH$_2$F$_3$	Ph$_3$P	72	33 [f]	79:21

[a] Epoxide (1 mmol), KF(HF)$_n$ (5 mmol), and an additive (0.1–0.2 mmol) were stirred at 80 °C in 1,2-dichloroethane.
[b] Yield and selectivity were determined by ^{19}F-NMR of the crude product (C$_6$H$_5$CF$_3$ was used as internal standard).
[c] The substrate (ca. 30%) was recovered.
[d] The reaction was conducted at room temperature.
[e] The substrate (100%) was recovered.
[f] The substrate (ca. 45%) was recovered.

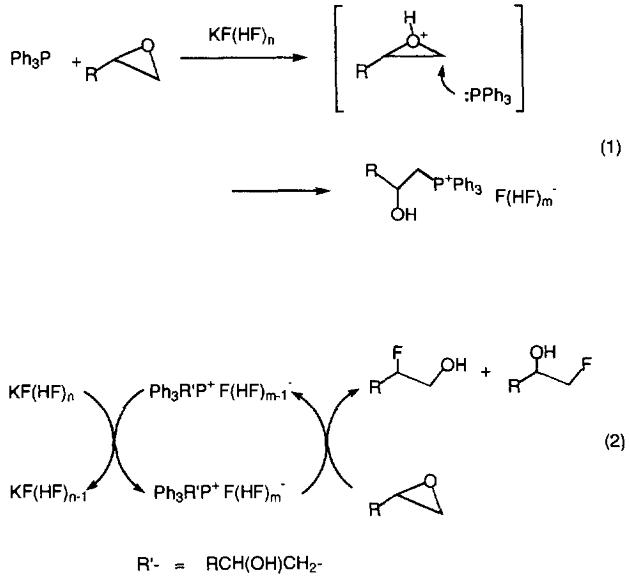
in the presence of a catalytic amount of Ph$_3$P and afforded **2b** and **3b** in 33% yield (entry 8).

To consider the mechanism of this reaction, the reaction of **1a** with KH$_2$F$_3$ was attempted in the presence of a catalytic amount of tetraphenylphosphonium bromide (Ph$_4$P$^+$Br$^-$) (entry 4). As a result, the corresponding fluorohydrins were obtained in 66% yield and the regioselectivity **2a**:**3a** was 68:32, which was almost the same result as the reaction using Ph$_3$P (entry 3). This result suggests that the mechanism of the reaction using Ph$_3$P is similar to that using Ph$_4$P$^+$Br$^-$.

It has been reported that tetraphenylphosphonium fluoride species, such as Ph$_4$P$^+$HF$_2^-$, form from Ph$_4$P$^+$Br$^-$ and hydrogen fluoride [5], and that these phosphonium fluorides work as nucleophilic fluorinating agents [5,6]. Consequently, it is assumed that the ring-opening of epoxides with KH$_2$F$_3$ in the presence of a catalytic amount of Ph$_4$P$^+$Br$^-$ proceeds via formation of tetraphenylphosphonium fluoride species such as Ph$_4$P$^+$F(HF)$_m^-$ and that fluorination with the phosphonium fluoride follows, as shown in Scheme 2. Similarly, ring-opening reactions in the presence of Ph$_3$P would also proceed by fluorination with phosphonium fluoride species. It is known that ring-opening of epoxides with Ph$_3$P in the presence of acid readily occurs to form β-hydroxyalkyltriphenylphosphonium salts [7]. Consequently, in the case of the ring-opening of epoxides with KF(HF)$_n$ in the presence of a catalytic amount of Ph$_3$P, it is assumed that β-hydroxyalkyltriphenylphosphonium fluoride species such as RCH(OH)CH$_2$–Ph$_3$P$^+$F(HF)$_m^-$ are formed from epoxide, Ph$_3$P, and KF(HF)$_n$. RCH(OH)CH$_2$–Ph$_3$P$^+$F(HF)$_m^-$ then fluorinates more epoxide to form RCH(OH)CH$_2$–Ph$_3$P$^+$F(HF)$_{m-1}^-$, and RCH(OH)CH$_2$–Ph$_3$P$^+$F(HF)$_m^-$ is regenerated with KF(HF)$_n$ (Scheme 3).



Scheme 2.



Scheme 3.

3. Experimental details

A typical experimental procedure is as follows. To KH$_2$F$_3$ (5 mmol) in a Teflon® (PFA) vessel was added a solution of the epoxide (1 mmol) and an additive (0.1–0.2 mmol) in 1,2-dichloroethane (5 ml). The reaction mixture was stirred at 80 °C for a period indicated in Table 1, and quenched with aqueous sat. NaHCO$_3$. After the usual work up, yields and selectivity of the products were determined by ^{19}F-NMR of the crude product ($C_6H_5CF_3$ was used as internal standard). The products were purified and identified by comparison of their IR, ^{1}H-NMR, and ^{19}F-NMR spectra with those of authentic samples [8–10].

4. Conclusion

We have demonstrated the effect of triphenylphosphine on ring-opening reactions of aliphatic epoxides with $KF(HF)_n$. A catalytic amount of triphenylphosphine enhances this reaction and it has been suggested that phosphonium fluoride species form from triphenylphosphine, $KF(HF)_n$, and epoxide, and act as fluorinating agents in this reaction.

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