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Heterogeneous fluorination of allylic halides by the combination of lead fluoride and a sodium salt

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Abstract

The composite solid reagent consisting of lead(II) fluoride and a small amount of sodium bromide has been found to facilitate the fluorination of allylic halides in acetonitrile to afford a mixture of the corresponding and rearranged fluorides in the ratio of 1:1 to 1:2. Such allylic rearrangement is not observed when KF/18-crown-6 or tetrabutylammonium fluoride are employed.

Keywords: Heterogeneous fluorination; Allylic halides; Lead fluoride; Sodium salts; NMR spectroscopy

1. Introduction

With an increased understanding of the specific behavior of organofluorine compounds, the selective introduction of fluorine into organic molecules has become of considerable importance [1]. To date much effort has been expended in developing more efficient fluorinating reagents which are organic solvent-soluble [2]. In contrast, we have studied novel solid–liquid interfacial fluorination methodologies whereby combinations of metal fluorides are used in the solid state in organic solvents [3,4]. We have observed recently that the combined use of lead(II) fluoride with a small amount of a sodium salt accelerates the heterogeneous substitution reaction of substituted benzyl halides to the corresponding fluorides in acetonitrile [5]. In this paper, we report that the NaBr/PbF_2 reagent exhibits an interesting reactivity towards the fluorination of allylic halides.

2. Results and discussion

The heterogeneous fluorination of 1-bromo-2-butene (**1-Br**) with the NaBr/PbF_2 solid reagent proceeded smoothly in acetonitrile at 90 °C over 5 h to give an 80% total yield of two fluorinated products, 1-fluoro-2-butene (**1-F**) and 3-fluoro-1-butene (**3-F**) formed via allylic rearrangement in a 1:2 ratio. In contrast, the use of well-known fluorinating reagents such as KF/18-crown-6, KF/CaF_2 [3] or tetrabutylammonium fluoride did not induce this rearrangement as the results listed in Table 1 show. As far as we know, fluoride substitution with allylic rearrangement has scarcely been observed previously except for an example using AgF [6].

The use of lead(II) fluoride alone, which was less reactive towards fluorination, gave the rearrangement product in the same ratio as that of the composite fluoride reagent (Table 1, entry 2). This indicates that the allylic rearrangement was induced by lead fluoride itself.

The fluorination of 1-chloro-2-butene (**1-Cl**) with the NaBr/PbF_2 reagent also proceeded to give the same ratio of products (**1-F/3-F** = 1:2) as for **1-Br**. Variation of halides in the substrates did not affect the regio-

Table 1
Fluorination of 1-bromo-2-butene (**1-Br**) [a]

Entry No.	Fluoride reagent	Molar ratio [b]	Reaction conditions	Total yield (%) [c]	**1-F/3-F**
1	NaBr/PbF_2	0.1:2.5	90 °C, 5 h	80	31:69
2	PbF_2	2.5	90 °C, 24 h	37	32:68
3	KF/CaF_2	2.0:6.0	90 °C, 38 h	83	98:2
4	KF/18-crown-6	2.0:0.2	90 °C, 48 h	86	97:3
5	$Bu_4NF \cdot xH_2O$	2.0	r.t., 4 h	83	82:18

[a] Reactant contained 15% of **3-Br**.
[b] Molar ratio relative to 1 mmol of **1-Br**.
[c] Determined by GC methods.

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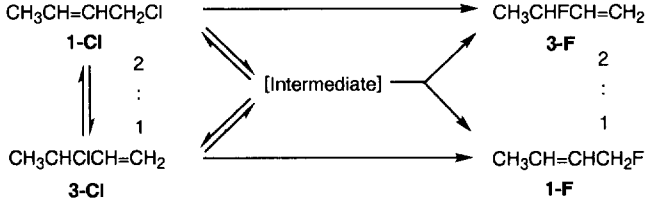
selectivity. In order to compare with this reaction, the fluorination of 3-chloro-1-butene (**3-Cl**) was carried out under the same reaction conditions. Table 2 shows the reactant product distribution in the two reactions as monitored by GC methods. Both **1-Cl** and **3-Cl** were found to be rapidly isomerized to an equilibrium mixture consisting of 70% **1-Cl** and 30% **3-Cl**, followed by displacement to give the fluorides in the reverse ratio of ca.30% **1-F** and 70% **3-F**. No isomerization of the fluorinated products could be confirmed under the reaction conditions employed. The results suggest an S_N2' type substitution of these allylic substrates by the solid NaBr/PbF_2 reagent. Another possibility might be the presence of a common intermediate, such as a cationic species formed from the two substrates presumably on the surface of the solid reagent. There is no simple experimental differentiation between these processes (Scheme 1).

Fluoride substitutions of various allylic bromides or chlorides accompanied by allylic rearrangement have been observed in solid–liquid two-phase reactions with NaBr/PbF_2 or NaBr/NaF/PbF_2 composite reagents as summarized in Table 3 [1]. The products were mostly mixture of **1-F** and **3-F**. If those products were stable in the reaction mixture, allylic rearrangements of the substrates would take place prior to fluoride substitution

Table 2
Fluorination of 1-chloro-2-butene (**1-Cl**) and 3-chloro-1-butene (**3-Cl**) using NaBr/PbF_2 reagent [a]

Reactant (**1-Cl**/**3-Cl**)	Time (h)	Reactant/product distribution [b]				**1-Cl**/**3-Cl**	**1-F**/**3-F**
		1-Cl	**3-Cl**	**1-F**	**3-F**		
1-Cl	5	54	24	6	12	69:31	33:67
(99.8:0.2)	24	27	11	12	31	71:29	27:73
	48	7	3	13	46	71:29	22:78
3-Cl	2	60	31	2	3	67:33	
(13:87)	6	45	21	11	18	68:32	38:62
	24	15	7	18	44	69:31	29:71

[a] In $CH_3(CH_2)_2CN$ at 90 °C.
[b] Determined by GC methods.



Scheme 1.

[1] The composite lead fluoride reagent containing NaF exhibited a lower reactivity but occasionally gave higher yields of products through suppression of the decomposition of reactants and/or products than observed with the NaBr/PbF_2 reagent.

or allylically conjugated cationic species would intervene; however, the allylic isomerizations of the substrates were not completely surveyed.

As far as our composite reagent is concerned, it has already been confirmed by powder X-ray diffractometry that some chemical interaction between the two solids PbF_2 and NaBr takes place, forming a trace amount of new inorganic compound [5], which may be the cause of the enhanced reactivity. Further mechanistic investigation of fluorination on the solid surface of the composite reagent is currently under way.

3. Experimental details

^1H, ^{13}C and ^{19}F NMR spectra were recorded using a Bruker WM-360 instrument at 360, 90 and 339 MHz, respectively. Tetramethylsilane was used as internal reference standard for ^1H and ^{13}C NMR spectra and *p*-chlorofluorobenzene (δ −116.25 ppm) for ^{19}F NMR spectra. Analytical GC was performed using a Shimazu 14A gas chromatograph with a 2-m glass column packed with 10% silicone DC-550 on Chromosorb W.

Most of the organic and inorganic materials were available commercially and used without further purification. PbF_2 was supplied by the Morita Kagaku Kogyo Co., Ltd. [5]. 1-Bromo-2-octene (containing 33% of 3-bromo-1-octene), 1-bromo-2-decene (containing 11% of 3-bromo-1-decene) and myrtenyl chloride were prepared by bromination [7] and chlorination [8] of the corresponding alcohols.

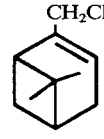
3.1. Preparation of the composite lead fluoride reagent

A solid mixture of PbF_2 powder (5 mmol) and 4 mol% of NaBr (0.2 mmol) or a mixture of PbF_2 powder (5 mmol), NaBr (0.2 mmol) and NaF (2 mmol), which had been dried over P_2O_5 at 160 °C under vacuum for several hours, was suspended in acetonitrile at 90 °C for 24–72 h. The heterogeneous mixture could be used directly in the reaction or stored after removal of the solvent and vacuum drying.

3.2. Fluorination using the composite lead fluoride reagent

Typical reaction procedures are described in following examples. For the fluorination of 1-bromo-2-butene (Table 1, entry 1; Table 3, entry a), to the NaBr/PbF_2 reagent (0.2:5.0 mmol) in butyronitrile prepared as described above contained in a 20 ml test tube fitted with a rubber septum was added 1-bromo-2-butene (2 mmol). *p*-Chlorofluorobenzene was then added as an internal standard for product analyses of the mixture. The heterogeneous mixture was stirred at 90 °C for 5 h. GC analysis of the reaction solution showed the

Table 3
Solid–liquid two-phase fluorination using the $NaBr/PbF_2$ or $NaBr/NaF/PbF_2$ reagent [a]

Entry	Substrate	Temp. (°C)	Time (h)	1-F (%)	3-F (%)	Total (%)	1-F/3-F
a	$CH_2=CHCH_2Br$ [b]	90	72	31		31	
b	$CH_3CH=CHCH_2Br$ [b]	90	5	25	55	80	31:69
c	$CH_3CH=CHCH_2Cl$	90	72	21	58	79	26:74
d	$CH_3CHClCH=CH_2$	90	48	18	51	69	26:74
e	$CH_3CH_2CH=CHCH_2Br$	90	17	26	38	64	41:59
f	$(CH_3)_2C=CHCH_2Br$	r.t. [c]	120	31	25	56	56:44
g	$CH_3(CH_2)_4CH=CHCH_2Br$ [b]	90	4	22	20	42	52:48
h	$CH_3(CH_2)_6CH=CHCH_2Br$ [b]	90	4	29	25	54 (43)	54:46
i		90	24	28	26	54 (36)	52:48
j	$PhCH=CHCH_2Br$	90	5	65	3	68 (50)	96:4

[a] Substrate (2 mmol), $NaBr/NaF/PbF_2$ reagent (molar ratio 0.2:2.0:5.0) in CH_3CN or $CH_3(CH_2)_2CN$. Yields determined by GC or ^{19}F NMR methods and isolated yields shown in parentheses.
[b] $NaBr/PbF_2$ reagent (molar ratio 0.2:5.0) used.
[c] At 90 °C, isoprene was obtained as the main product.

product distribution to be **3-F** (55%), **1-F** (25%), the diene (2%), **3-Br** (2%) and **1-Br** (3%). The yields of **3-F** and **1-F** were confirmed by ^{19}F NMR spectroscopy. ^{19}F NMR ($CDCl_3/CH_3CH_2CH_2CN$) δ: −170.34 (m, **3-F**); −207.72 (t, $J_{HF}=47.5$ Hz, **1-F**$_{trans}$); −212.88 (t, $J_{HF}=47.4$ Hz, **1-F**$_{cis}$) ppm.

For the fluorination of myrtenyl chloride (Table 3 entry i), myrtenyl chloride (2.0 mmol) was added to the $NaBr/NaF/PbF_2$ reagent (0.2:2.0:5.0 mmol) in CH_3CN contained in a 30 ml test tube fitted with a Teflon-lined screw cap. The heterogeneous mixture was stirred at 90 °C for 24 h. The solid materials were filtered off, washed with pentane and the solvents removed in vacuo. The residue was purified by preparative TLC on silica gel using pentane as an eluent to give a 36% yield of a mixture of **3-F** and **1-F**; colorless oil. ^{19}F NMR ($CDCl_3$) δ: −136.27 (dm, $J_{HF}=51.5$ Hz, **3-F**); −213.36 (td, $J_{HF}=47.6$, 7.8 Hz, **1-F**) ppm. The two products were separated in part by preparative TLC. Compound **1-F**: ^{13}C NMR ($CDCl_3$) δ: 21.02, 26.07, 31.30, 31.48, 38.00, 40.68, 42.95, 85.23 (d, $J_{CF}=162.4$ Hz, CH_2F); 122.61 (d, $J_{CF}=13.4$ Hz, =CH); 144.02 (d, $J_{CF}=14.7$ Hz, >C=) ppm. ^1H NMR ($CDCl_3$) δ: 4.70 (dm, $J_{HF}=47.6$ Hz, 2H, CH_2F) ppm. Compound **3-F**: ^{13}C NMR ($CDCl_3$) δ: 21.96, 25.86, 27.66, 33.22 (d, $J_{CF}=22.0$ Hz, CH_2CHF); 39.09, 40.68, 50.04, 88.44 (d, $J_{CF}=167.2$ Hz, CHF); 115.51, 149.65 (d, $J_{CF}=11.0$ Hz, >C=) ppm. ^1H NMR ($CDCl_3$) δ: 5.09 (dd, $J_{HF}=51.2$ Hz, $J=6.9$ Hz, 1H, CHF) ppm.

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