Poly-4-vinylpyridinium Poly(Hydrogen Fluoride): A Solid Hydrogen Fluoride Equivalent Reagent[1]

George A. Olah,* Xing-Ya Li, Qi Wang, G.K. Surya Prakash

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, USA

Received 19 March 1992; revised 2 November 1992

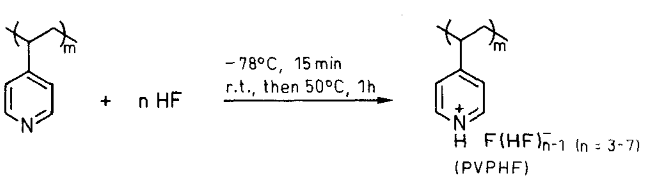
Poly-4-vinylpyridinium poly(hydrogen fluoride) (PVPHF), containing 35–60 % hydrogen fluoride by weight, was prepared as a solid hydrogen fluoride equivalent reagent. PVPHF with 60 % hydrogen fluoride by weight was found to be a versatile fluorinating agent for the hydrofluorination and bromofluorination of alkenes and alkynes, fluorination of alcohols as well as other fluorination reactions. Low hydrogen fluoride content PVPHF (3 equivalents of hydrogen fluoride to 1 equivalent of 4-vinylpyridine unit) was also found to be an efficient reagent for bromofluorination of alkenes in the presence of 1,3-dibromo-5,5-dimethylhydantoin. Fluorosulfonic acid-modified PVPHF showed enhanced reactivities for the fluorination of secondary alcohols.

Exhaustive growth in the applications of organofluorine compounds have led to the development of a variety of new and convenient fluorinating reagents.[2] The 30 % pyridine–70 % hydrogen fluoride system, has been shown to be a versatile ambient temperature fluorinating agent[3] and its utilization for a wide variety of fluorination reactions has been explored in our laboratory.[4] More recently, this reagent was also used for the preparation of *gem*-difluoro compounds[5] and *gem*-trifluorination.[6] Whereas the reagent and subsequently developed related ones[7] represent convenient liquid forms of anhydrous hydrogen fluoride, some difficulties remain and a solid equivalent reagent will be advantageous.

The preparation and use of a polymer supported hydrogen fluoride reagent was first reported by Zupan and co-workers[8,9] but only with limited success. In a preliminary communication,[1b] we reported an effective polymeric fluorinating agent, poly-4-vinylpyridinium poly(hydrogen fluoride) (PVPHF), prepared from poly-4-vinylpyridine and hydrogen fluoride. The reagent contains 60 % by weight of hydrogen fluoride and is found to be a general purpose solid fluorinating agent, showing substantial advantages of easy handling and convenient workup. We now report in detail the preparation, modification, properties and reactions of these solid hydrogen fluoride equivalent reagents as well as its limitations.

Preparation and Properties of PVPHF

The reagent can be conveniently prepared either by adding condensed anhydrous hydrogen fluoride (AHF) or by condensing AHF into a bottle containing the commercially available cross-linked poly-4-vinylpyridine (PVP, in bead form), which was cooled to −78 °C (Scheme 1). No solvents were used in the above reaction.



Scheme 1

As the reaction between PVP and hydrogen fluoride, especially at the beginning, is highly exothermic, the first one third of hydrogen fluoride should be introduced very slowly and the bottle should be shaken regularly to keep the reaction smooth. After reaction, the polymer beads become considerably swollen. The ratio of poly-4-vinylpyridine and hydrogen fluoride is variable and the stability of the complex depends on their relative ratio. PVPHF containing 41 % of polyvinylpyridine and 59 weight % of hydrogen fluoride, referred to as PVPHF (40/60) (about 7 equivalents of hydrogen fluoride to one equivalent of 4-vinylpyridine unit), is a dry solid stable up to 50 °C (see Table 1).

Table 1. Thermal Stability of PVPHF (40% PVP/60% HF, mole ratio: 1 : 7)

Temp. (°C)	Time (h)	Weight (%)	
		PVP	HF
20	0	40.5	59.5
50	1	40.8	59.2
50	2	40.9	59.1
50	3	41.1	58.9

No loss of hydrogen fluoride was observed when the PVPHF (40/60) beads are stored in a closed bottle at room temperature. However, the beads fume slightly when exposed to air as the poly(hydrogen fluoride) forms hydrated hydrogen fluoride (and therefore should be handled and stored under nitrogen atmosphere). Under constant current of nitrogen flow, the PVPHF with 7 moles of hydrogen fluoride per vinylpyridine unit loses about 3 moles of hydrogen fluoride in 20 hours at room temperature. The orange to brown colored PVPHF (40/60) changed to yellowish beads with mole ratio of hydrogen fluoride : vinyl pyridine equal to about 4 [59 % PVP and 41 % HF by weight and referred to as PVPHF

Table 2. Loss of HF in PVPHF Under Constant Nitrogen Flow (Initial Composition: PVP, 11.564 g; HF, 15.192 g)

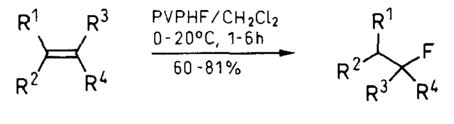
Time (h)	Weight of PVPHF (g)	Mole Ratio of HF : PVP
0	26.756	6.91
20	20.734	4.17
40	19.727	3.71
65	18.901	3.34
90	18.623	3.21
160	18.381	3.10
240	18.033	2.94
528	17.293	2.60

(60/40)], which is quite stable and loses hydrogen fluoride very slowly under nitrogen flow until the hydrogen fluoride/vinylpyridine molar ratio reaches about 3 in one week (see Table 2).

The yellowish 1:3 (vinyl pyridine: hydrogen fluoride) complex, containing about 64 % PVP and 36 % hydrogen fluoride by weight [referred to as PVPHF (64/36)], is very stable and does not fume when exposed to air. Ordinary laboratory glassware can be used for the reactions involving this complex. The low hydrogen fluoride content PVPHF can be directly prepared by reacting calculated amounts of condensed AHF with PVP beads.

Hydrofluorination of Alkenes and Alkynes

The hydrofluorination of alkenes and alkynes with PVPHF (40/60) can be conveniently carried out at atmospheric pressure in polyethylene bottles or flasks (Scheme 2).



Scheme 2

We first studied the solvent effect on hydrofluorination of alkenes with cyclododecene as substrate. The results are listed in Table 3.

Table 3. Solvent Effect on the Fluorination of Cyclododecene with PVPHF (40/60) at Room Temperature

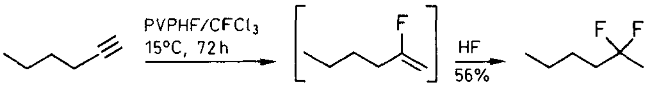
Solvent	Yield of Cyclododecyl Fluoride (%)			
	3 h	6 h	24 h	48 h
CH_2Cl_2	54	60	55	
$CHCl_3$		52	50	
$CF_2ClCFCl_2$		30		41
CCl_4		12		
Hexane		13	21	

Various solvents, such as dichloromethane, chloroform, carbon tetrachloride, 1,1,2-trichlorotrifluoroethane (Freon 113), trichlorofluoromethane and hexane can be used as the reaction medium. Dichloromethane was found to be the most efficient and convenient one. No hydrofluorination takes place, however, in tetrahydrofuran, which has been successfully used as solvent for the reactions of alkenes and alkynes with liquid hydrogen fluoride/pyridine reagent.[4]

The reaction was carried out by suspending PVPHF in dichloromethane containing the substrates to be fluorinated and the mixture was stirred magnetically at or below room temperature. After the reaction was completed the solid reagent is simply removed by filtration. Products were obtained after the removal of the solvent in good to excellent yield. Results are given in Table 4.

Cycloalkenes and branched alkenes can be readily hydrofluorinated. However, no hydrofluorination occurred with dodecene and only the starting material was recovered. When *cis*-stilbene was treated with PVPHF in dichloromethane, a mixture of *cis*- and *trans*-stilbenes was obtained without detectable amount of fluorinated products.

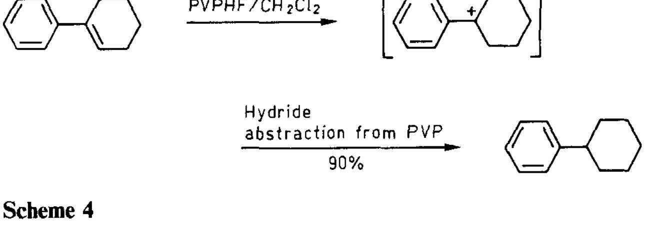
When alkynes, such as 1-hexyne and 3-hexyne, was reacted with PVPHF (40/60) under similar conditions, the formation of both monofluorinated alkenes and difluoroalkanes was observed at the beginning of the reaction. Monofluoroalkenes are probably intermediate products, which were slowly converted to difluoroalkanes under prolonged reaction time (Scheme 3).



Scheme 3

Dimerization has been observed with some acid-sensitive alkenes. Thus α-methylstyrene, when treated with PVPHF (40/60) in dichloromethane, gave predominantly the dimer with some trimer.

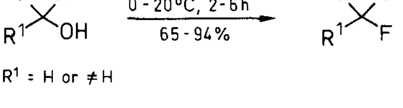
Surprisingly, all attempts to hydrofluorinate 1-phenylcycloalkenes failed. Under the reaction conditions, 1-phenylcyclohexene, 1-phenylcyclopentene and 2-phenyl-2-norbornene were converted to the corresponding cycloalkanes, i.e., phenylcyclohexane, phenylcyclopentane and 2-phenylnorbornane, respectively, in very high yields. PVPHF (polymer backbone) seemingly acts as a hydride donor in this ionic hydrogenation reaction (Scheme 4).



Scheme 4

Fluorination of Secondary and Tertiary Alcohols.

Tertiary alcohols are readily fluorinated with PVPHF (40/60) (Scheme 5).

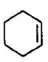
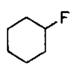
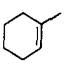
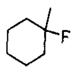
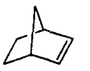
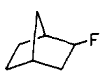
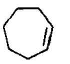
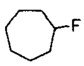
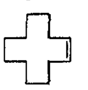
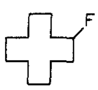
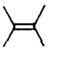
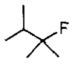
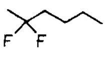
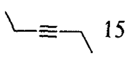
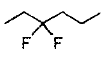


Scheme 5

The fluorination of secondary alcohols, however, was generally more sluggish except in the case of cycloalkanols, such as 2-adamantanol and cycloheptanol, which gave the corresponding fluorides in good yield. (Table 5). Impurities, especially water, drastically retards the reaction and decrease the yields of the fluorides. Therefore, the alcohol used must be freshly distilled.

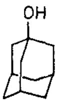
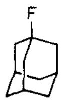
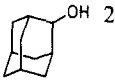
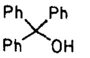
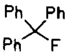
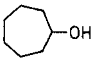
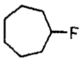
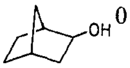
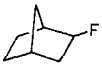
It is known that dehydration and carbocationic rearrangement or oligomerization are the common side reactions encountered when replacing the OH groups of an alcohol

Table 4. Hydrofluorination of Alkenes and Alkynes with PVPHF (40/60)[1b]

Substrate	Temp. (°C)	Time (h)	Product	Yield (%)	mp (°C) or bp (°C)/Torr found	reported	^{13}C NMR (CDCl$_3$/TMS) δ, J (Hz)	^{19}F NMR [CDCl$_3$/CFCl$_{3(ext)}$] δ, J (Hz)
	20	2		76	42–44/100	102–104/760[4]	22.7 (d, $J_{C,F} = 7.4$), 25.0, 32.2 (d, $^{2}J_{C,F} = 19$), 91.3 (d, $^{1}J_{C,F} = 170$)	-174 (m)
	0	1		80	58–61/100	–[a]	22.3, 25.2, 27.3 (d, $^{2}J_{C,F} = 25$), 37.1 (d, $^{2}J_{C,F} = 22$), 94.4 (d, $^{1}J_{C,F} = 166$)	-147 (br s)[b]
	0	1		79[c]	–	–	–	–
	20	1		81[c]	–	–	–	–
	20	6		60	50–52	50–52[16]	20.6 (d, $J_{C,F} = 7.2$), 23.3, 23.4, 23.9, 24.2, 30.0 (d, $^{2}J_{C,F} = 21$), 92.5 (d, $^{1}J_{C,F} = 164$)	-176 (m)
	15	6		72	80–83/760	–[d]	17.4 (d, $^{3}J_{C,F} = 6.2$), 23.8 (d, $^{2}J_{C,F} = 25$), 37.3 (d, $^{2}J_{C,F} = 22$), 98.1 (d, $^{1}J_{C,F} = 167$)	-140 (septet doublet, $^{3}J_{H,F} = 21$, $^{3}J_{H,F} = 12$)[e]
	15	72[f]		56	84–87/760	85–87/760[4]	13.8, 22.5, 23.2 (t, $^{2}J_{C,F} = 28$), 24.9 (t, $^{3}J_{C,F} = 4.1$), 37.7 (t, $^{2}J_{C,F} = 25$), 124.4 (t, $^{1}J_{C,F} = 237$ Hz)	-91 (sextet, $^{3}J_{H,F} = 17.4$)
	15	72[f]		59	84–87/760	84–86/760	6.6 (t, $^{3}J_{C,F} = 6$), 13.9, 15.8 (t, $^{3}J_{C,F} = 5.4$), 29.5 (t, $^{2}J_{C,F} = 26$), 38.0 (t, $^{2}J_{C,F} = 25$), 125.5 (t, $^{1}J_{C,F} = 240$)	-100 (quintet, $^{3}J_{H,F} = 16.5$)

[a] Not reported in Ref. 14.
[b] Lit[14] $\delta = -152$.
[c] See Table 5 spectral data.
[d] Not reported in Ref. 15.
[e] Lit.[15] $\delta = -139.9$.
[f] CFCl$_3$ was used as solvent for the convenience of separation.

Table 5. Fluorination of Alcohols with PVPHF (40/60)[1b]

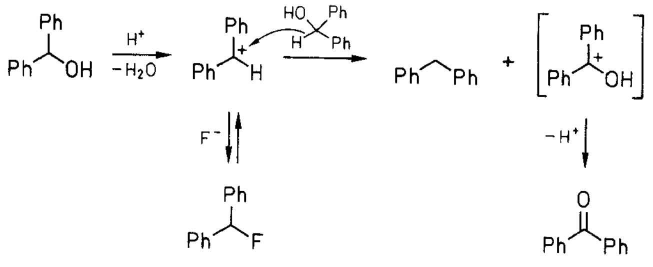
Substrate	Temp. (°C)	Time (h)	Product	Yield (%)	mp (°C) or bp (°C)/Torr found	reported	^{13}C NMR (CDCl$_3$/TMS)[a] δ, J (Hz)	^{19}F NMR [CDCl$_3$/CFCl$_{3(ext)}$][b] δ, J (Hz)
	20	2		95	207–209	210[3a]	31.4 (d, $^{3}J_{C,F} = 9.4$), 35.9, 42.7 (d, $^{2}J_{C,F} = 17$), 94.1 (d, $^{1}J_{C,F} = 183$)	-129 (s)
	20	6		88	253–255	254–255[4]	27.0 (d, $J_{C,F} = 17$), 31.4, 32.8 (d, $J_{C,F} = 18$), 35.7 (d, $J_{C,F} = 8.8$), 37.2, 37.8, 95.6 (d, $^{1}J_{C,F} = 177$)	-174 (dd, $^{2}J_{H,F} = 50.6$, $^{3}J_{H,F} = 5.3$)
	0	2		77	102–104	103–104[4]	101.3 (d, $^{1}J_{C,F} = 174$), 127.8, 127.9, 128.1, 143.2 (d, $^{2}J_{C,F} = 24$)	-126 (s)
	20	6		67	62–64/100	70–71/200[4]	21.7 (d, $J_{C,F} = 9.5$), 28.3, 34.6 (d, $^{2}J_{C,F} = 21$), 94.4 (d, $^{1}J_{C,F} = 166$)	-164 (m)
	0	2		65	56–58	56–59[4]	22.5, 28.1, 34.7, 34.9, 39.9 (d, $^{2}J_{C,F} = 19$), 42.0 (d, $^{2}J_{C,F} = 19$), 96.1 (d, $^{1}J_{C,F} = 181$)	-161 (m)

[a] Measured at 50.29 MHz.
[b] Measured at 188.18 MHz.

with fluorine using hydrogen fluoride as the fluorinating agent. Some of these complications also occurred with PVPHF (40/60). For example, attempts to fluorinate cyclododecanol and 2,5-dimethylhexan-2-ol led to the formation of dehydration products, i.e., cyclododecene and 2,5-dimethylhex-2-ene, respectively, while the corresponding fluorides were only the minor product. When 1-phenylethanol was reacted with PVPHF (40/60), dimer and trimers of styrene were obtained as the major products.

An unusual redox disproportionation reaction was observed with diphenylmethanol and 9-hydroxyxanthene, forming corresponding ketones and hydrocarbons. Fluorination products were detected only at the beginning of the reaction and disappeared within half an hour. Since diphenylmethanol reacts with liquid pyridinium poly(hydrogen fluoride) giving fluorodiphenylmethane in high yield, this redox disproportionation reveals some differences in reactivity of the polymeric vs liquid reagents.

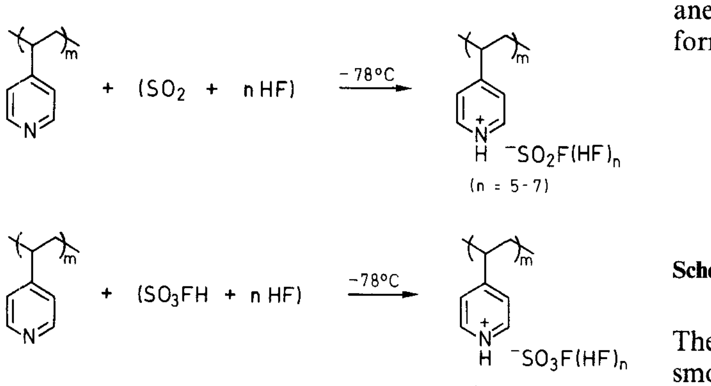
The mechanism may involve an equilibrium between diphenylfluoromethane and diphenylmethyl cation followed by hydride abstraction from diphenylmethanol (Scheme 6).



Scheme 6

Modification of PVPHF with Fluorosulfonic Acid: An Improved Fluorinating Agent for Secondary Alcohols

Although tertiary alcohols are readily transformed into the corresponding fluorides, the fluorination of secondary alcohols met only with limited success. Considering the fact that small amounts of water can drastically decrease the reactivity of PVPHF and that an equimolar amount of water forms as the result of fluorination of alcohols, the presence of a dehydrating agent was expected to increase the reactivity of PVPHF. Indeed fluorosulfonic acid and sulfur dioxide have been found to modify the reactivity of the PVPHF reagent.



Scheme 7

The molar ratio of vinyl pyridine to fluorosulfonic acid or sulfur dioxide varied from 1 : 0.2 to 1 : 1. A comparison of the reactivity of PVPHF and its modified forms is given in Table 6.

Both sulfur dioxide and fluorosulfonic acid significantly increase the fluorinating ability of PVPHF for secondary alcohols. However, the reactivity of the PVPHF/sulfur dioxide complex deteriorates upon storage, whereas no significant change of the reactivity of PVPHF/fluorosulfonic acid complex was observed in several months. Therefore fluorosulfonic acid is more suitable for modifying PVPHF. The modified reagent with a mole ratio of unit vinylpyridine: hydrogen fluoride: fluorosulfonic acid equal to 1 : 6 : 0.5 showed satisfactory reactivity for the fluorination of secondary alcohols as well as for the hydrofluorination of alkenes. A 1 : 1 : 1 complex of unit vinylpyridine, hydrogen fluoride and fluorosulfonic acid shows little reactivity for fluorination of secondary

Table 6. Fluorination with PVPHF and its Modified Reagents

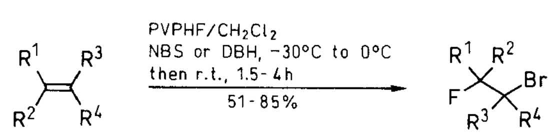
Alcohols	Reagent	Time (h) (r.t.)	Product	Yield (%)
cyclohexanol	PVPHF (40/60)	72	cyclohexyl fluoride	8
	PVPHF-SO_2 (1 : 7 : 0.5)[a]	6	cyclohexyl fluoride	34
cyclododecanol	PVPHF (40/60)	24	cyclododecene	30
			cyclododecyl fluoride	trace
	PVPHF/SO_3HF (1 : 6 : 0.5)[a]	6	cyclododecene	15
			cyclododecyl fluoride	60
Ph_2CHOH	PVPHF (40/60)	2	Ph_2CHF	0
			Ph_2CH_2	60[b]
			$Ph_2C{=}O$	40[b]
	PVPHF/SO_3HF (1 : 6 : 0.5)[a]	1	Ph_2CHF	88[b]
			Ph_2CH_2	5[b]
			$Ph_2C{=}O$	7[b]

[a] Mole ratio of PVP : HF : SO_2 or SO_3HF.

[b] Relative GC peak ratio.

Bromofluorination of Alkenes

When alkenes were added to a stirred suspension of *N*-bromosuccimide (NBS) or 1,3-dibromo-5,5-dimethylhydantoin (DBH) and PVPHF (40/60) in dichloromethane the corresponding vicinal bromofluoroalkanes were formed in good yields (Scheme 8) (Table 7).



Scheme 8

The bromofluorination reaction generally proceeds smoothly at room temperature. Branched alkenes react much faster and the reaction can also be carried out at low temperature (− 30 °C). The common side reactions for hydrofluorination of alkenes and fluorination of alcohols, e.g. dimerization and rearrangement, are either absent or negligible for the bromofluorination even when acid-sensitive alkenes like styrene was reacted. It seems that bromofluorination is much faster than dimerization or rearrangement of the alkenes.

Besides vicinal bromofluoroalkanes, addition products of NBS to the double bonds were also isolated when *trans*-4-octene and cycloheptene, respectively, were reacted. When the reaction was carried out at − 30 °C using catalytic amount of PVPHF, the NBS adduct became the major product (Scheme 9).

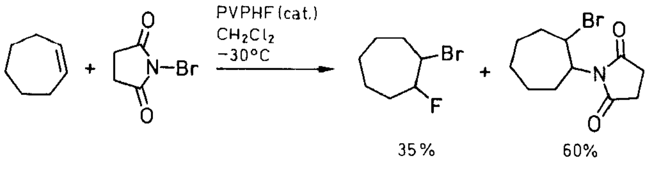
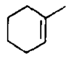
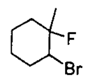
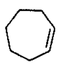
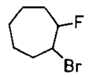
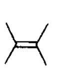
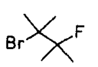
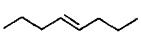
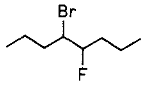
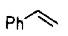
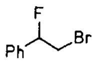
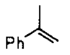
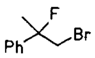
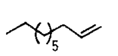
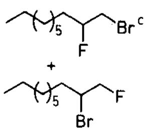


Table 7. Bromofluorination of Alkenes

Substrate	Temp. (°C)	Time (h)	Product		Yield (%)
	0	1[a]			75
	0–20	72[a]			70
	0	1[a]			81
	0–20	72[a]			72
	0	1[b]			78
	0	1[b]			71
	0–20	2[b]		[c]	76 8

[a] Reagent: NBS/PVPHF (40/60).

[b] Reagent: DBH/PVPHF (60/40).

[c] bp 91–93 °C/1 Torr (Lit.[4] bp 95–98 °C/1 Torr).
^{13}C NMR (CDCl$_3$/TMS): δ = 14.1, 22.6, 24.7, 29.2, 29.3, 29.4, 31.8, 33.2, 33.8 (d, $^2J_{C,F}$ = 22 Hz), 92.1 (d, $^1J_{C,F}$ = 174 Hz).
^{19}F NMR [CDCl$_3$/CFCl$_{3(ext)}$]: δ = − 178 (m).
For the spectral data of rest of the products, see Table 8.

The succinimidyl group can be replaced by fluorine when treated with PVPHF in dichloromethane but the reaction proceeds very slowly. At room temperature, it took 3 days to convert 2-succinimidylbromocycloheptane into *vic*-bromofluorocycloheptane in 70% yield. It thus seems that these adducts are not the necessary intermediates in the bromofluorination reaction but side products formed by a parallel reaction pathway.

Ionic addition of NBS to alkenes has not yet been well established although addition products of alkenes with *N*-halosuccinimides have been obtained by a radical process.[10] Our results show that ionic addition of NBS to disubstituted alkenes is a facile process, but no corresponding adducts of NBS to tri- or tetrasubstituted alkenes were found.

It is noteworthy that the very stable PVPHF with hydrogen fluoride/vinyl pyridine ratio of 4 or 3 works equally well for bromofluorination as does the reagent with hydrogen fluoride/vinylpyridine ratio of 7. This is in contrast to the hydrofluorination and the fluorination of alcohols, in which only the high hydrogen fluoride-content reagent, i.e. PVPHF (40/60), works well. The bromofluorinations with low hydrogen fluoride-content reagent, namely PVPHF (64/36), were found to proceed much more efficiently with 1,3-dibromo-5,5-dimethylhydantoin compared to *N*-bromosuccinimide, in terms of both reaction time and yield.

As shown in Table 8, both aromatic and aliphatic alkenes were bromofluorinated in good yields. The reaction also took place no matter where the double bond was located. The only complication we encountered was in the case of 1-methylcyclohexene, where allylic bromination occurred at 0 °C. The extent of allylic bromination was reduced by lowering the reaction temperature and shielding the reaction vessel from light but it could not be completely eliminated. Increasing the content of hydrogen fluoride in PVPHF also suppresses this side reaction.

The use of low hydrogen fluoride-content PVPHF for halofluorinations appears extremely attractive since this reagent, as mentioned above, is very stable and does not corrode laboratory glassware. Compared to the recently reported applications of low hydrogen fluoride-content ammonium polyhydrogen fluorides[11,12] and the polymer supported hydrogen fluoride developed by Zupan and co-workers,[9] PVPHF reagents have shown general applicability for halofluororination of a wide range of alkenes and simplifies the workup procedure. Spent polyvinylpyridine can be easily collected and recycled.

Poly-4-vinylpyridinum polyhydrogen fluorides containing 35–60% by weight of hydrogen fluoride has been prepared by reacting poly-4-vinylpyridine with anhydrous hydrogen fluoride at low temperature without using solvent. PVPHF (40/60) is stable up to 50 °C. It is a general purpose fluorinating agent with a reactivity similar to that of liquid pyridinium polyhydrogen fluoride reagent. Hydrofluorination and bromofluorination of alkenes and alkynes and fluorination of tertiary alcohols proceed satisfactorily with this reagent, but fluorination of secondary alcohols met with only limited success. Fluorosulfonic acid and sulfur dioxide have been used to modify the reagent. The fluorosulfonic acid-modified PVPHF fluorinates secondary alcohols more efficiently to fluorides. Low hydrogen fluoride-content PVPHF (3 to 4 hydrogen fluoride per vinylpyridine unit) is an efficient fluorinating agent for the bromofluorination of alkenes in the presence of 1,3-dibromo-5,5-dimethylhydantoin. Its good stability and ease of handling and workup make it a convenient reagent for halofluorination.

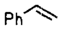
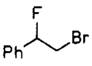
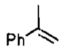
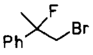
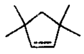
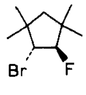
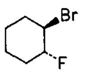
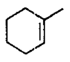
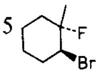
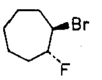
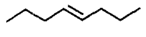
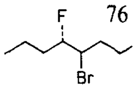
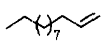
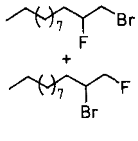
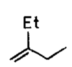
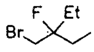
The advantages of using a solid hydrogen fluoride reagent are significant. By using the new solid reagent, products can be easily separated from the reagent by simple filtration. Recovered spent polyvinylpyridine reagents can be readily regenerated by washing with water, drying and retreatment with hydrogen fluoride.

Polymer beads of poly-4-vinylpyridine supplied by Reilly Tar and Chemical Co., and Sybron Chemicals Inc., have been used for the preparation of PVPHF. Both polymers have similar properties and reactivity, but the polymer beads from Sybron had better mechanical strength. Anhydrous hydrogen fluoride (99.9 %) was obtained from Matheson Gas Products.

Poly-4-vinylpyridinium Poly(Hydrogen Fluoride):

Method A: Cross-linked poly-4-vinylpyridine (10 g) (Sybron Chemicals, bead), pre-dried at 120 °C under vacuum for 4 h, was placed under N_2 into a 100 mL polyethylene bottle cooled to − 78 °C. To it was added portionwise condensed anhydr. HF (16 g) with constant shaking, during a period of 15 min. The first ⅓ of the HF should be added slowly to avoid vigorous reaction. After warming gradually to r.t., the bottle was kept at 50 °C under N_2 for 1 h. The resulting orange to brown colored dry solid contains 59 % by weight HF and 41 % polyvinylpyridine (about 7 equiv of HF to each equiv of vinylpyridine unit); yield: 24.5 g. The low HF-content

Table 8. Bromofluorination of Alkenes Using DBH/PVPHF (64/36)

Substrate	Reaction Conditions	Product	Yield[a] (%)	bp (°C)/ Torr	Molecular Formula[b] or Lit. bp (°C)/Torr	^{13}C NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{19}F NMR [$CDCl_3$/ $CFCl_{3(ext)}$]	MS *m/z* (%)
	0°C, 0.5 h r.t., 2 h		71	72–75/1	65/1.5[20]	34.2 (d, $^2J_{C,F} = 28$), 92.6 (d, $^1J_{C,F} = 177$), 125.7, 128.5, 129.0, 137.0 (d, $^2J_{C,F} = 20$)	−174 (ddd, $^2J_{H,F} = 47$, $^3J_{H,F} = 25$, $^3J_{H,F} = 16.5$	–
	0°C, 0.5 h r.t., 2 h		73	96–98/3	54–55/0.15	25.3 (d, $^2J_{C,F} = 22$), 40.3 (d, $^2J_{C,F} = 28$), 94.7 (d, $^1J_{C,F} = 177$), 123.4 (d, $^3J_{C,F} = 9.6$), 128.2, 128.5, 141.5 (d, $^2J_{C,F} = 20$)	−148 (tq, $^3J_{H,F} = 22$, $^3J_{H,F} = 18$)	–
	0°C, 0.5 h r.t., 3 h		85[c]	70–71/5	$C_9H_{16}BrF$ (223.2)	24.9 (d, $^3J_{C,F} = 12$), 27.3, 28.7, 29.9, 36.9 (d, $^3J_{C,F} = 6.2$), 37.5 (d, $^2J_{C,F} = 17$), 52.0 (d, $^3J_{C,F} = 3.4$), 63.3 (d, $^2J_{C,F} = 19$), 104.6 (d, $^1J_{C,F} = 195$)	−200 (m)	224 (0.1), 222 (0.1), 209 (0.1), 207 (0.1), 189 (0.24), 187 (0.24), 168 (1.1), 166 (1.2), 149 (5.3), 147 (5.3), 143 (23), 123 (12.1), 109 (2.1), 107 (2.1), 97 (11.4), 87 (100)
	0°C, 0.5 h r.t., 3.5 h		83	80–82/16	76–77/15	22.54 (d, $J_{C,F} = 8$), 24.7, 31.0 (d, $^2J_{C,F} = 20$), 34.5 (d, $^3J_{C,F} = 2.7$), 52.3 (d, $^2J_{C,F} = 20$), 93.8 (d, $^1J_{C,F} = 180$)	−168 (m)	182 (2.2), 180 (2.4), 101 (28.9), 81 (100)
	−30°C, 0.5 r.t., 1.5 h		51[d]	78–81/10	–[e]	23.6 (d, $^2J_{C,F} = 24$), 33.1 (d, $J_{C,F} = 3.7$), 34.4, 34.8, 37.0 (d, $^2J_{C,F} = 22$), 57.0 (d, $^2J_{C,F} = 26$), 95.2 (d, $^1J_{C,F} = 172$)	−137 (br s)	–
	0°C, 0.5 h r.t., 3 h		70	70–71/3	70–73/3.5[18]	20.7, 24.7, 27.2, 31.3 (d, $^2J_{C,F} = 21$), 33.8 (d, $^3J_{C,F} = 6.1$), 56.2 (d, $^2J_{C,F} = 24$), 98.2 (d, $^1J_{C,F} = 176$)	−160 (m)	–
	0°C, 0.5 h r.t., 3 h		76	60–62/15	$C_8H_{16}BrF$ (211.2)	13.5, 13.9, 18.4, 20.7, 34.5 (d, $^2J_{C,F} = 21$), 35.7 (d, $^3J_{C,F} = 3.5$), 56.4 (d, $^2J_{C,F} = 22$), 94.9 (d, $^1J_{C,F} = 176$)	−179 (m)	168 (0.02), 166 (0.03), 149 (0.04), 147 (0.04), 137 (0.5), 135 (0.5), 131 (0.3), 111 (22), 69 (100), 55 (89), 41 (55)
	0°C, 0.5 h r.t., 4 h		74[f,g]	99–101/1	$C_{12}H_{24}BrF$ (267.3)	14.1, 22.7, 24.66, 24.74, 29.3, 29.4, 29.5, 29.6, 31.9, 33.4 (d, $^2J_{C,F} = 21$), 33.7 (d, $^2J_{C,F} = 26$), 92.0 (d, $^1J_{C,F} = 175$)	−178 (m)	248 (M^+-HF, 0.1), 246 (0.1), 191 (0.3), 175 (0.7), 162 (2.6), 148 (5.5), 125 (6.8), 111 (28), 97 (51), 83 (40.4), 69 (36.5), 57 (63.3), 55 (52.1), 43 (100)
	0°C, 0.5 h r.t., 2 h		68[h]	75–77/16	$C_6H_{12}BrF$ (183.1)	7.3 (d, $^3J_{C,F} = 6$), 28.1 (d, $^2J_{C,F} = 23$), 35.5 (d, $^2J_{C,F} = 31$), 96.9 (d, $^1J_{C,F} = 175$)	−156 (m)	184 (0.1), 182 (0.1), 155 (3.5), 153 (4.9), 135 (3.3), 133 (3.4), 109 (3.4), 107 (4.4), 89 (100), 88 (32.5), 73 (51.6), 69 (85.6)

---

[a] Isolated yield.

[b] Satisfactory microanalyses obtained: C ± 0.52, H ± 0.31.

[c] ^1H NMR ($CDCl_3$/TMS): $\delta = 1.01$ (d, 3H, $J = 3.8$ Hz), 1.07 (s, 6H), 1.19 (s, 3H), 1.67 (d, 2H, $^4J_{H,F} = 4.0$ Hz), 4.05 (dd, 1H, $^3J_{H,F} = 14.6$ Hz, $^3J_{H,H} = 9.5$ Hz), 4.65 (dd, 1H, $^2J_{H,F} = 53$ Hz, $^3J_{H,H} = 9.5$ Hz).

[d] Contaminated with 10% of the corresponding allylic bromide.

[e] Not reported in Ref. 19.

[f] ^1H NMR ($CDCl_3$/TMS): $\delta = 0.9$ (t, 3H, $J = 6$ Hz), 1.2–1.8 (br, 18H), 3.49 (dd, 2H, $^3J_{H,F} = 21$ Hz, $^3J_{H,H} = 6$ z), 4.63 (dm, 1H, $^2J_{H,F} = 53$ Hz).

[g] 10% of the isomeric 2-bromo-1-fluorododecane was also isolated.

[h] 0.93 (t, 6H, $^3J_{H,H} = 7.6$ Hz), 1.80 (dq, 4H, $^3J_{H,F} = 19.4$ Hz, $^3J_{H,H} = 7.6$ Hz), 3.46 (d, 2H, $^3J_{H,F} = 15.6$ Hz).

PVPHF, 64% of PVP and 36% of HF, was also prepared by this procedure.

Method B: Instead of reacting the PVP beads with condensed liquid HF, the desired amount of HF was condensed directly into the bottle containing the PVP beads. Compared to Method A this procedure is easier to control at the early stage of the reaction.

Stability of PVPHF:

Thermal Stability: PVPHF (40/60) (25.88 g) was placed into a 75 mL polyethylene bottle. The bottle was connected through a 3 mm (o. d.) tube to a N_2 line to keep the pressure in the bottle equal to the atmospheric pressure. The bottle containing PVPHF was heated at 50 °C and weighed periodically to measure the loss of HF. The results are given in Table 1.

Stability under Constant Nitrogen Stream: PVPHF (26.76 g) having mole ratio of HF : vinyl pyridine unit equal to 6.91 was placed into a 125 mL polyethylene bottle. A constant N_2 flow (rate 300 mL/min) was allowed to pass through the bottle. The loss of HF was determined by periodic weighing. The results are listed in Table 2.

Fluorination of Alcohols with PVPHF (40/60), 1-Fluoroadamantane; Typical Procedure:

To a 30 mL polyethylene bottle containing PVPHF (2.6 g) (41% polyvinylpyridine-59% HF by wt) and CH_2Cl_2 (10 mL) was added at r. t. 1-adamantanol (0.93 g, 6.1 mmol). The bottle was filled with N_2, capped and stirred magnetically at r. t. for 2 h. The polymer was removed by filtration and washed with CH_2Cl_2. The combined filtrate was washed with 3% aq $NaHCO_3$ solution (15 mL), and H_2O (20 mL) and subsequently dried (Na_2SO_4). Removal of the solvent afforded 1-fluoroadamantane; yield: 0.90 g (95% yield); colorless crystals; mp 207–209 °C ($MeOH/CCl_4$) (Lit.[3a] mp 210 °C) (Table 5).

Hydrofluorination of Alkenes and Alkyne and the Effect of Solvent on the Preparation of Cyclododecyl Fluoride:

By a similar procedure, cyclododecene was allowed to react with PVPHF (40/60) at r. t. in different solvents. The yields of cyclododecyl fluoride are given in Table 3.

Bromofluorination Using NBS/PVPHF (40/60), 2-Bromo-3-fluoro-2,3-dimethylbutane; Typical Procedure:

To a stirred suspension of NBS (1.04 g, 5.8 mmol) and PVPHF (40/60) (3.0 g) in CH_2Cl_2 (15 mL) in a polyethylene bottle was added dropwise a solution of 2,3-dimethyl-2-butene (0.48 g, 5.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After reacting at r. t. for another 0.5 h, the mixture was worked up as described previously. The organic solution was chromatographed through a short silica gel column (eluent: hexane). Removal of the solvent at 0 °C gave 2-bromo-3-fluoro-2,3-dimethylbutane; yield: 0.79 g (85%); mp 84–86 °C (Lit.[17] mp 87–89 °C).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 23.5$ (d, $^2J_{C,F} = 24$ Hz), 29.4, 67.6, 97.8 (d, $^1J_{C,F} = 176$ Hz).

^{19}F NMR [$CDCl_3/CFCl_{3(ext)}$] $\delta = -147$ (octet, $^3J_{H,F} = 21$ Hz).

Bromofluorination Using DBH/PVPHF (64/36), 1-Bromo-2-fluorocyclohexane; Typical Procedure:

To a stirred suspension 1,3-dibromo-5,5-dimethylhydantoin (1.14 g, 4 mmol) and PVPHF (64/36) (2.0 g) in CH_2Cl_2 (15 mL) in a polyethylene bottle was added dropwise a solution of cyclohexene (0.49 g, 6.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After reacting at 0 °C for 0.5 h and at r. t. for another 3.5 h, the mixture was filtered and the polymer was washed with CH_2Cl_2 (3 × 1 mL). The filtrate was washed with H_2O, 3% aq $NaHCO_3$ solution (15 mL), H_2O (20 mL), dried ($MgSO_4$) and distilled; yield: 0.90 g (83%); bp 80–82 °C/16 Torr (Lit.[11] bp 76–77 °C/15 Torr).

Preparation of PVP/HF/FSO_3H Complexes:

The procedure is similar to that of Method A for the preparation of PVPHF except that, instead of condensed HF, a mixture of HF and FSO_3H pre-prepared at −78 °C was used to react with PVP at −78 °C.

Support of our work by the National Science Fundation is gratefully acknowledged.

(1) (a) Synthetic Methods and Reactions. Part 169. For Part 168, see:
Olah, G.A.; Wu, A.; Farooq, O. *Synthesis* **1991**, 1179.
(b) A preliminary report appeared, see: Olah, G.A.; Li, X.Y. *Synlett* **1990**, 267.

(2) *Synthetic Fluorine Chemistry*; Olah, G.A.; Chambers, R.D.; Prakash, G.K.S., Eds.; Wiley Interscience: New York, 1992.

(3) (a) Hirschmann, R.F.; Miller, R.; Wood, J.; Jones, R.E, *J. Am. Chem. Soc.* **1956**, *78*, 4956.
(b) Bergstrom, C.G.; Nicholson, R.T.; Dodson, R.M. *J. Org. Chem.* **1963**, *28*, 2633.

(4) Olah, G.A.; Welch, J.T.; Vankar, Y.D.; Nojima, M.; Kerekes, I.; Olah, J.A. *J. Org. Chem.* **1979**, *44*, 3872, and references cited therein.

(5) (a) Sondej, S.C.; Katzenellenbogen, J.A. *J. Org. Chem.* **1986**, *51*, 3508.
(b) Prakash, G.K.S.; Reddy, V.P.; Li, X.Y.; Olah, G.A. Synlett **1990**, 594.
(c) Jeko, J.; Timar, T.; Jaszberenyi, J. Cs. *J. Org. Chem.* **1991**, *56*, 6748.

(6) (a) Matthews, D.P.; Whitten, J.P.; McCarthy, J.R. *Tetrahedron Lett.* **1986**, *27*, 4861.
(b) Olah, G.A.; Wang, Q.; Li X.-Y.; Prakash, G.K.S., unpublished results.

(7) For review, see:
(a) Yoneda, N. *Tetrahedron*, **1991**, *47*, 5329.
(b) Olah, G.A.; Li, X.Y. In *Synthetic Fluorine Chemistry*. Olah, G.A.; Chambers, R.D.; Prakash, G.K.S. Eds.; Wiley Interscience: New York, 1992, pp 163–204.

(8) Zupan, M.; Sket, B.; Johar, Y. *J. Macromol. Sci.-Chem.* **1982**, *A17*, 759.

(9) (a) Gregorcic, A.; Zupan, M. *J. Fluorine Chem.* **1984**, *24*, 291.
(b) Gregorcic, A.; Zupan, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3083.

(10) Day, J.C.; Katsaros, M.G.; Kocher, W.D.; Scott, A.E.; Skell, P.S. *J. Am. Chem. Soc.* **1978**, *100*, 1950.

(11) Alvernhe, G.; Laurent, A.; Haufe, G. *Synthesis* **1987**, 562.

(12) For examples, see:
(a) Kuroboshi, M.; Hiyama, T. *Tetrahedron Lett.* **1991**, *32*, 1215.
(b) Kuroboshi, M.; Hiyama, T. *Synlett* **1991**, 185.
(c) Haufe, G.; Alvernhe, G.; Laurent, A. *J. Fluorine Chem.* **1990**, *46*, 83.
(d) Camps, F.; Chamorro, E.; Gasol, V.; Guerrero, A. *J. Org. Chem.* **1989**, *54*, 4294.
(e) Muehlbacher, M.; Poulter, C.D. *J. Org. Chem.* **1988**, *53*, 1026.

(13) Skell, P.S.; Day, J.C. *Acc. Chem. Res.* **1978**, *11*, 381, and the references cited therein.

(14) Weigert, F.J. *J. Org. Chem.* **1980**, *45*, 3476.

(15) Yoneda, N.; Abe, T.; Fukuhara, T.; Suzuki, A. *Chem. Lett.* **1983**, 1135.

(16) Schneider, H.J.; Thomas, F. *Tetrahedron* **1976**, *32*, 2005.

(17) Olah, G.A.; Bollinger, J.M. *J. Am. Chem. Soc.* **1967**, *89*, 4745.

(18) Hashimoto, T.; Prakash, G.K.S.; Shih, J.G.; Olah, G.A. *J. Org. Chem.* **1987**, *52*, 931.

(19) Camps, F.; Chamorro, E.; Gasol, V.; Guerrero, A. *J. Org. Chem.* **1989**, *54*, 4294.

(20) Hamman, S. *J. Fluorine Chem.* **1989**, *45*, 377.