Fluoro Olefins. VII. Preparation of Terminal Vinyl Fluorides

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The synthetic scope of the reactions of several aldehydes and ketones with fluoromethylenetriphenylphosphorane, $(C_6H_5)_3P{=}CHF$, either pregenerated via the dehydrohalogenation of fluoromethyltriphenylphosphonium iodide with *n*-butyllithium in THF at −78°, or better generated in situ via the dehalogenation of fluoroiodomethyltriphenylphosphonium iodide with zinc–copper couple in DMF at 0°, was studied in detail. In addition several methods of preparation of the phosphonium salts which served as the precursors to the designated ylide were investigated.

Vinyl fluorides are generally synthesized by (1) nucleophilic substitution reactions on fluoro olefins; (2) dehalogenation of saturated halofluorocarbons; and (3) dehydrohalogenation of saturated halofluorocarbons.[2a] These methods, however, are normally accompanied by unfavorable side reactions and/or involve multistep procedures employing poorly accessible starting materials. The Wittig reaction of fluoromethylenetriphenylphosphorane with a carbonyl moiety offers a simple, one-step synthetic tool to terminal H–F olefins.

At present, two reports have appeared in the literature which describe the fluoromethylene ylide route to vinyl fluorides. Rabinowitz[3] has claimed that the reaction of a trialkylphosphine with a dihalofluoromethane in the presence of a carbonyl compound afforded the corresponding fluoromethylene olefin and a *gem*-dihalide, the latter product formed from the reaction of a dihalophosphorane with the aldehyde or ketone.

$$2R_3P + CHFXY + 2R'C(O)R'' \longrightarrow R'C(R'){=}CHF + 2R_3PO + R'C(R'')XY$$

These reactions presumably proceed through the intermediacy of a fluorohalomethyltrialkylphosphonium salt which is subsequently dehalogenated by additional phosphine generating the ylide and a phosphorane.[4] In our hands this method of approach was unsuccessful as a method of preparation of vinyl fluorides. Schlosser and Zimmermann[5,6] have recently reported that some aldehydes and a steroid could be successfully fluoroolefinated via the Wittig reaction employing fluoromethylenetriphenylphosphorane pregenerated at temperatures below −50°.

$$R_3P + CHFXY \longrightarrow [R_3\overset{+}{P}CHFX]Y^- \xrightarrow{R_3P} \begin{matrix} R_3P{=}CHF \\ + \\ R_3PXY \end{matrix}$$

Results and Discussion

Fluoromethylenetriphenylphosphorane, pregenerated from the reaction of *n*-butyllithium and fluoromethyltriphenylphosphonium iodide in THF at Dry Ice temperatures, reacted readily with a variety of carbonyl compounds representing most structural groups, affording the corresponding vinyl fluorides in fair yields (approximately 10–30% via GLC analysis). Treatment of these reaction mixtures with potassium *tert*-butoxide at 0° or room temperature resulted in significant increases of the desired products. It appears that the intermediate betaines form strong complexes with lithium salts which inhibit their cyclization into oxaphosphetanes that precede betaine collapse into olefin and phosphine oxide.[7]

The reactions reported here were carried out by simply adding a freshly standardized[8] solution of *n*-butyllithium in hexane dropwise to a stirred slurry of fluoromethyltriphenylphosphonium iodide in THF cooled to approximately −78°. The generation of the ylide was believed to coincide with the color changes of the slurry; that is, initially it was a faint canary yellow which gradually darkened into a deep brownish-red upon completion of the addition. The reaction mixture was then stirred for 30 min at −78° before being quenched with an aldehyde or ketone. Stirring was continued for approximately 2 hr at −78° and then for 1.5 hr at room temperature. When very active carbonyl compounds were employed (i.e., fluorinated aldehydes and ketones) the reaction mixture was cooled in an ice–water slush bath before the betaine was decomposed with potassium *tert*-butoxide. The results of these reactions are summarized in Table I.

Table I
Synthesis of Fluoro Olefins via the Reaction of Pregenerated Fluoromethylenetriphenylphosphorane with Carbonyl Compounds

Product	GLC yield,[a] %	Cis:trans
$C_6H_5C(CF_3){=}CHF$	28.3[b]	39:61
	50.4[c]	46:54
$C_6H_5C(CH_3){=}CHF$	48.8	49:51
$(C_6H_5)_2C{=}CHF$	46.8	
$c\text{-}C_6H_{10}{=}CHF$	69.3	
$C_6H_5CH{=}CHF$	43.5	44:56[d]
$n\text{-}C_6H_{13}CH{=}CHF$	25.7	48:52
$C_6H_5C(CF_3){=}CHF$	48.0	49:51[e]

[a] GLC yields based on thermal conductivity corrections relative to an appropriate standard. [b] Betaine decomposition for 42 hr at 28°. [c] Betaine decomposition for 2 hr at 0°. [d] Isomers were not completely separable by GLC; the isomer ratio was determined by employing an integrated ^1H NMR spectrum of the isomer mixture. [e] Ylide was pregenerated by reaction with $LiN[CH(CH_3)_2]_2$ in place of BuLi.

The present olefination technique did exhibit three major limitations: (1) the ylide precursor (i.e., fluoromethyltriphenylphosphonium iodide) could only be prepared from triphenylphosphine and the poorly accessible fluoroiodomethane; (2) *n*-butyl substitution products of the desired olefins were formed during these reactions in fair yields (14–23%); and (3) the stable betaine–lithium salt complex necessitated the employment of potassium tert-butoxide to catalyze betaine collapse into olefin and phosphine oxide.

Fluoromethylenetriphenylphosphorane was also found to be sufficiently stable when generated under similar conditions at 0°, for it could be trapped 40 min later with an activated ketone. In an identical reaction conducted at room temperature (28°), however, no olefins were produced when the ylide was quenched 20 min after its pregeneration.

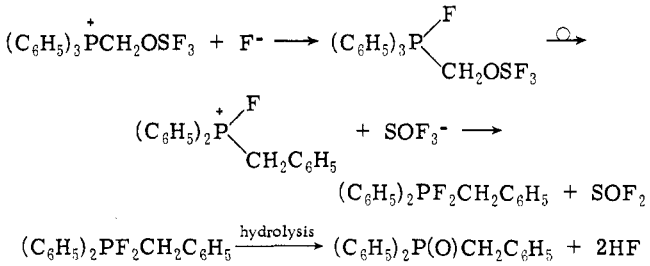
Fluoromethyltriphenylphosphonium iodide was isolated in 86% yield from the reaction of triphenylphosphine with

fluoroiodomethane. However, this methylene halide could only be prepared in yields of approximately 20% from the reaction of mercuric fluoride and methylene iodide, the major reaction product being methylene fluoride, formed in yields as high as 67%. Schlosser[5] has recently reported that this phosphonium salt could be synthesized by the reaction of perchloryl fluoride with salt-free methylenetriphenylphosphorane. However, the employment of elaborate safety precautions in the event of spontaneous ignition or detonation of perchloryl fluoride reaction mixtures limits the scale of such reactions and detracts from their usefulness.

Several other synthetic routes to a fluoromethyltriphenylphosphonium salt have been unsuccessfully investigated in this laboratory. The ease associated with the preparation of hydroxymethyltriphenylphosphonium chloride[9,10] and its conversion into the corresponding halomethyl derivatives when treated with thionyl chloride[10] or phosphorus tribromide[11,12] lead to the attempted fluorination of this salt with sulfur tetrafluoride. In each reaction conducted in this study the isolated organic product, as determined by ^{1}H NMR spectroscopy, was a chloromethyltriphenylphosphonium salt. A fluoromethyl derivative was detected (~1% yield) in the product from only one reaction which was conducted in the presence of sodium fluoride and a very large excess of sulfur tetrafluoride.

The observed reaction product was apparently formed by the chloride ion displacement of $^-OSF_3$ in the intermediate generated during the initial reaction between sulfur tetrafluoride and the phosphonium salt. In an attempt to avoid this side reaction, the less nucleophilic bifluoride and fluoroborate derivatives of hydroxymethyltriphenylphosphonium chloride were prepared via analogous methods and treated with sulfur tetrafluoride. Unexpectedly, the major reaction product was benzyldiphenylphosphine oxide, although low yields (<20%) of a fluoromethyltriphenylphosphonium salt could be detected in some of the product mixtures in addition to small amounts of the chloromethyl derivative.

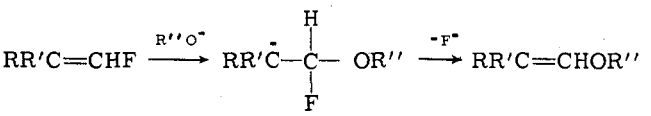
Benzyldiphenylphosphine oxide could conceivably be produced during these reactions by fluoride ion attack on phosphorus in the initial reaction intermediate followed by subsequent rearrangement to benzyldifluorodiphenylphosphorane. Hydrolysis of this latter compound during the work-up of the products would afford the observed phosphine oxide. Recent observations in this laboratory[13] have indicated that positive four-coordinated organophosphorus compounds react with fluoride ion forming a fluorophosphorane, which can then expel the most stable phosphorus ligand as a carbanion ($C_6H_5^-$ in this case). The chloromethylphosphonium salt presumably arises from chlorine-containing impurities in the gaseous fluorinating reagent.



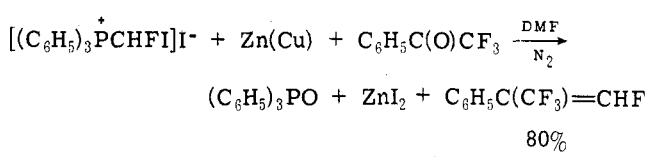
The attempted fluoride ion displacement of iodide and of chloride in their respective halomethyltriphenylphosphonium salts resulted in the isolation of a methyltriphenylphosphonium salt in the former case and unreacted starting material in the latter. Apparently the carbon–iodine bond was thermally cleaved in the reaction involving iodomethyltriphenylphosphonium iodide and the organic radical that was produced abstracted a hydrogen atom from the solvent. The carbon–chlorine bond in the chloromethylphosphonium salt was evidently resistant to thermal cleavage as well as displacement by fluoride ion.

The second major limitation of the described fluoroolefination technique is the significant formation of *n*-butyl derivatives of the vinyl fluorides. Although *n*-butyllithium is expected to be capable of reacting with fluoro olefins to afford the observed by-products,[14] the presence of an organolithium reagent could not be detected by quenching an aliquot of an ylide solution with ethylene bromide prior to the addition of a carbonyl compound. It appears, therefore, that the observed by-products are formed from the reaction of the carbonyl compounds with *n*-butylmethylenetriphenylphosphorane generated from the reaction of a base with an *n*-pentyltriphenylphosphonium salt formed from the displacement of fluoride ion in fluoromethyltriphenylphosphonium iodide by *n*-butyllithium. Although this pathway would not normally be expected to compete with proton abstraction in the ylide generation sequence, the fact that fluorine destabilizes adjacent carbanionic sites[2b] and that the lithium–fluorine bond is stronger than the carbon–fluorine bond,[15] could assist fluoride ion displacement. In an attempt to avoid this problem, lithium diisopropylamide was employed as the base in place of *n*-butyllithium (cf. Table I). The yield of vinyl olefin and the cis:trans ratio of products were similar to the *n*-butyllithium method of generation and did not appear to offer any significant advantage.

The necessity to employ potassium *tert*-butoxide in this reaction sequence to assist in the decomposition of the intermediate betaine–lithium salt complexes is potentially the most severe limitation to this synthetic method, for terminal fluoro olefins are known to be very susceptible to nucleophilic substitution by alkoxides.[14,16] This fact is dramatically demonstrated in the lower yield of 1-hydro-2-phenylperfluoropropene obtained when the corresponding betaine–lithium halide complex was treated with the alkoxide for 42 hr at 28° vs. 2 hr at 0° (cf. Table I).



A synthetic fluoroolefination technique has been developed that completely avoids the use of basic materials in any step of the reaction sequence, thus eliminating the formation of n-butyl derivatives of the vinyl fluorides and the potential consumption of the fluoro olefins by alkoxides. In the presence of activated carbonyl compounds the zinc–copper couple catalyzed dehalogenation of fluoroiodomethyltriphenylphosphonium iodide, readily prepared from the reaction of triphenylphosphine with fluorodiiodomethane,



afforded good yields of the corresponding H–F olefins. These results are summarized in Table II.

The fact that acetophenone reacted poorly under these conditions when, in fact, it readily reacted with the pregenerated fluoromethylene ylide at lower temperatures suggested that a "free ylide" is not the olefinating agent during the in situ method of vinyl fluoride formation. It appears that the olefinating agent is a complex of ylide and

Table II
Synthesis of Fluoro Olefins via the Reaction of Carbonyl Compounds with Fluoromethylenetriphenylphosphorane Generated In Situ

Product	GLC yield,[a] %	Cis:trans
$C_6H_5C(CF_3)=CHF$	79.9	52:48
$C_6H_5CH=CHF$	52.4	41:59[b]
$C_6F_5CH=CHF$	65.0	54:46
n-$C_6H_{13}CH=CHF$	54.4	43:57
$C_6H_5C(CH_3)=CHF$	12.0	57:43

[a] GLC yields based on thermal conductivity corrections relative to an appropriate standard. [b] Isomers were not completely separable by GLC; the isomer ratio was determined by employing an integrated normalized ^1H NMR spectrum of the isomer mixture.

$$[(C_6H_5)_3\overset{+}{P}CHFI]I^- + Zn(Cu) \longrightarrow \begin{matrix}(C_6H_5)_3P{=}CHF\cdots ZnI_2 \\ \Downarrow \\ [(C_6H_5)_3\overset{+}{P}CHFZnI]I^-\end{matrix}$$

zinc iodide which is not as reactive as the "free ylide". Mercury halide complexes of nonstabilized ylides have been reported in the literature, some of which have also demonstrated olefinating capabilities at elevated temperature.[17,18] It is suggested that nonactivated carbonyl compounds could be satisfactorily fluoroolefinated using the pregeneration procedure described previously, for the consumption of the resulting olefin by reaction with potassium *tert*-butoxide in the betaine decomposition sequence should be minimal under carefully controlled conditions.

In addition to the decreased reactivity of the fluoroolefinating species generated by this technique, very reactive halogenated carbonyl compounds that are capable of reacting to an appreciable extent with the dehalogenating agent cannot be satisfactorily employed. For example, *sym*-dichlorotetrafluoroacetone was completely consumed during its attempted in situ fluoroolefination but no olefinic products were detected via GLC analysis of the reaction mixture. An unsuccessful attempt was made to develop a procedure in which the fluoroolefinating agent could be pregenerated at 0° via the salt dehalogenation sequence so that the reaction of zinc–copper couple with very reactive carbonyl compounds could be avoided. However, it appears that in the absence of a carbonyl compound the fluoroolefinating reagent is not appreciably stable, for only a 16% yield of 1-hydro-2-phenylperfluoropropene was realized when a reaction mixture of fluoroiodomethyltriphenylphosphonium iodide and zinc–copper couple was quenched with α,α,α-trifluoroacetophenone 90 min after initiating the reaction. A similar reaction conducted in the presence of the carbonyl compound afforded an 80% yield of the product.

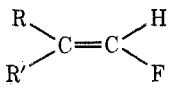
The olefins synthesized during the course of this study were isolated by distillation and/or preparative GLC techniques and characterized by ir, NMR (^1H and ^{19}F), and mass spectral analysis. When possible the spectra of the products were compared to those of authentic samples or to those reported in the literature.

The observed cis:trans isomer ratios of the H–F olefins synthesized by the reaction of unsymmetrical carbonyl compounds with fluoromethylenetriphenylphosphorane, either pregenerated at −78° or generated in situ, were consistently close to unity. Although the method of ylide generation apparently affects the isomer ratio in the reactions involving α,α,α-trifluoroacetophenone and acetophenone, this observation appears to be an artifact attributed to the preferential consumption of the cis isomer by potassium *tert*-butoxide in the betaine decomposition sequence of the pregenerated olefination technique. The fact that neither isomer is predominantly formed suggests that the equilibrium normally established between the diastereomeric erythro and threo betaines in the presence of lithium salts[19] is insignificant and that the electrostatic replusions between the groups attached to the carbonyl carbon atoms and the hydrogen and fluorine atoms of the ylide are similar. The structural assignments and physical constants for the H–F olefins are shown in Table III.

The ir spectra of all of the compounds synthesized in this study are typical and will not be described in detail. Spectra of the H–F olefins generally exhibit very strong C=C stretching vibrations between 5.96 and 6.02 μm with the exception of that for 1,1-diphenyl-2-fluoroethylene, which occurred at 6.11 μm (cf. Table III). The n-butyl derivatives showed a similar but much weaker vibration from 5.87 to 6.25 μm.

The ^1H and ^{19}F NMR spectra of the olefinic compounds normally exhibited first-order spectra with characteristic chemical shifts and coupling constants. The vinyl fluorine resonances occurred between ϕ^* 108.8 and 142.3 ppm in the ^{19}F NMR spectra and exhibited geminal HCF coupling constants between 77.6 and 88.0 Hz. The magnitude of the HCF coupling is consistent with the values reported pre-

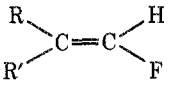
Table III
Structural Assignments, Physical Constants, and Infrared Data for H–F Olefins of the Type



Registry no.	R	R′	Isomer	Bp, °C (mm)	$n^{20}D$	λ, C=C, μm
55904-26-2	C_6H_5	CF_3	Cis	163 (745)	1.4460	5.98
55904-27-3	CF_3	C_6H_5	Trans	149 (745)	1.4456	5.96
55904-28-4	CH_3	C_6H_5	Cis		1.5223	6.00
55904-29-5	C_6H_5	CH_3	Trans		1.5185	5.99
390-75-0	C_6H_5	C_6H_5			1.5902	6.11
16416-47-0				119 (746)	1.4397	5.98
20405-78-1	H	C_6H_5	Cis		1.5259[a]	6.02[a]
20405-77-0	C_6H_5	H	Trans			
55904-30-8	H	C_6F_5	Cis	152 (745)	1.4338	5.97
55904-31-9	C_6F_5	H	Trans	152 (745)	1.4392	6.00
32814-16-7	H	n-C_6H_{13}	Cis	135 (742)[b]	1.4021[b]	5.98
32814-17-8	n-C_6H_{13}	H	Trans		1.4003	5.97

[a] Recorded for a cis:trans (41:59) mixture. [b] Recorded for a cis:trans (32:68) mixture.

Table IV
^1H and ^{19}F Nuclear Magnetic Resonance Data[a] for H–F Olefins of the Type



Chemical shifts				Coupling constants, Hz				
R	R′	H	F	J_{HCF}	$J_{H,R}$	$J_{H,R'}$	$J_{F,R}$	$J_{F,R'}$
C_6H_5	CF_3	6.42	112.2	80.1		0		24.7
CF_3	C_6H_5	7.04	124.1	77.9	1.8		8.0	
CH_3	C_6H_5	6.62	124.9	84.3	1.6		5.0	
C_6H_5	CH_3	6.88	132.7	85.4		1.6		3.8
C_6H_5	C_6H_5	6.88	128.7	83.4				
		6.39	142.3	88.0	1.1	1.1	*b*	*b*
H	C_6H_5	6.53	123.0	79.5	5.4		44.0	
C_6H_5	H	7.10	130.5	79.8		11.4		17.9
H	C_6F_5	6.77	108.8	80.4	5.4	~0.5	40.3	*c*
C_6F_5	H	7.47	111.9	81.0	0.7	11.6	*c*	19.6
H	n-C_6H_{13}	6.45	130.9	85.1	4.8	1.4	42.6	1.7
n-C_6H_{13}	H	6.50	130.6	85.4	1.2	11.2	2.0	19.3

[a] ^1H and ^{19}F NMR chemical shifts are reported on the δ and ϕ^* scales using internal references Me_4Si and $CFCl_3$, respectively. Similar coupling constants for a compound from the ^1H and ^{19}F spectra were averaged and are given in hertz. [b] Nondetectable. [c] Variable and not unequivocally determined.

viously for terminal fluoro olefins.[20-23] When applicable, cis and trans isomer assignments were made on the basis of the magnitude of the coupling of the terminal hydrogen and fluorine atoms with the groups (H, R, or R′) on the vicinal carbon atom. The coupling constants reported in the literature for the following designated cis and trans configurations agreed with the values for similar cases observed in this investigation (cf. Table IV): HC=CH;[23,24] HC≡CF;[22,23,25] HC=CCH$_2$;[23] FC=CCH$_2$;[23] CH$_2$CH=;[23] HC=CCF$_3$;[24,26] and FC=CCF$_3$.[22,27,28]

Each olefin was also characterized by mass spectral analysis. All of the mass spectra exhibited molecular ions coincident with those calculated for the respective compounds.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 21 spectrophotometer using a neat film of sample, and calibrated vs. a 0.07-mm polystyrene film. Proton NMR spectra were obtained with approximately 10% (w/v) solutions on a Varian A-60 spectrometer and are reported in δ values downfield from an internal standard of tetramethylsilane. Fluorine NMR spectra were obtained with approximately 10% (w/w) solutions on a Varian HA-100 spectrometer at 94.1 MHz and are reported in ϕ^* values upfield from an internal standard of trichlorofluoromethane. Analytical GLC analyses were obtained on a Hewlett-Packard Model 5750 dual column gas chromatograph equipped with 10 ft × 0.25 in. stainless steel columns using helium as a carrier gas. Product yields were determined from comparisons of the relative areas under peaks vs. an appropriate standard, corrected for thermal conductivity differences. Column A was packed with 15% w/w silicone gum rubber, column B with 15% w/w Carbowax 20M, and column C with 10% w/w FS-1265 fluorosilicone rubber. Preparative GLC analyses were obtained with a Varian Aerograph Model 700 gas chromatograph equipped with 10 ft × 0.50 in. stainless steel columns using helium as a carrier gas. Column D was packed with 30% w/w Carbowax 20M, column E with 30% w/w QF-1 fluorosilicone rubber, and column F with 30% w/w silicone gum rubber. All column packings were supported on 80–100 mesh acid-washed Chromosorb P. Carbon and hydrogen analyses were obtained in this laboratory. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6 mass spectrometer operated at 70 eV by Dr. Donald A. Wiebe in this department.

Fluoroiodomethane and Methylene Fluoride. The apparatus employed consisted of a 500-ml two-necked round-bottomed flask equipped with a magnetic stirring bar, a Fieser solid addition apparatus, and a water-cooled Friedrichs condenser connected to two traps cooled in ice and in liquid nitrogen followed by a connection to a vacuum pump. The apparatus was dried at 110° prior to use and assembled while warm under a continuous nitrogen flow to exclude moisture. The flask was charged with 599.4 g (2.238 mol) of methylene iodide and the solid addition apparatus with 78.4 g (0.328 mol) of mercuric fluoride. The pressure within the apparatus was reduced to 12–17 mm and the flask was heated with an oil bath at 62–69° while the fluorinating agent was *slowly* added to the rapidly stirred methylene iodide over a 13-hr period. Upon completion of the addition the reaction mixture was allowed to stir for an additional 10 hr at the prescribed conditions. The reaction was terminated and the liquid nitrogen cooled trap was sealed at one end as the other end was connected to a previously weighed trap cooled in a Dry Ice–isopropyl alcohol slush bath. As the liquid nitrogen cooled trap was slowly allowed to warm to 0°, 11.5 g of a volatile material distilled out of this trap and into the trap cooled to −78°. The ir spectrum of this material was identical with that reported for methylene fluoride in the literature,[29] yield 0.221 mol (67.4%) based on mercuric fluoride.

The nonvolatile product (21.3 g, 20.3% crude yield) was combined with two other similarly prepared product mixtures and distilled at atmospheric pressure through a 24-in. Nester-Faust Teflon spinning band column. A total of 68.1 g of pure fluoroiodomethane was obtained, bp 53.2–53.7° (lit.[30] bp 53.4°), $n^{20}D$ 1.4974 (lit.[30] nD 1.4910). The ^1H NMR spectrum (neat) exhibited a doublet at δ 6.35 (J_{HCF} = 49.1 Hz). The ^{19}F NMR spectrum (CCl_4) showed a triplet at ϕ^* 191.3 ppm (J_{FCH} = 48.8 Hz).

Fluoromethyltriphenylphosphonium Iodide. A 1-l. one-necked round-bottomed flask fitted with a water-cooled reflux condenser and a magnetic stirring bar was charged with 111.7 g (0.426 mol) of triphenylphosphine, 68.1 g (0.426 mol) of fluoroiodomethane, and 550 ml of dry benzene. The resulting solution was refluxed for 64 hr with moderate stirring. Upon completion of the reaction the white insoluble phosphonium salt was collected on a sintered glass funnel, washed with hot benzene (3 × 200 ml), and dried in a vacuum desiccator at 0.1 mm for 12 hr, yield 154.2 g (0.365 mol, 85.7%), mp 168.4–169.5° dec (reported[5] for fluoromethyltriphenylphosphonium iodide, 169–171°). The ^1H NMR spectrum ($CDCl_3$) consisted of a doublet (2 H) at δ 6.84 (J_{HCF} = 44.8, J_{HCP} = 0 Hz) and a complex multiplet (15 H) located at δ 7.54–8.16, peaking at δ 7.78. The ^{19}F NMR spectrum ($CHCl_3$) exhibited a doublet of triplets at ϕ^* 243.6 ppm (J_{FCP} = 58.0, J_{FCH} = 45.8 Hz).

Fluoriodomethyltriphenylphosphonium Iodide. A black 500-ml one-necked round-bottomed flask, equipped with a water-cooled reflux condenser and a magnetic stirring bar, was charged with 104.4 g (0.398 mol) of triphenylphosphine and 165 ml of reagent grade methylene chloride. Fluorodiiodomethane (111.6 g 0.390 mol), previously prepared by the method described by Hine,[31] was shaken with elemental mercury immediately prior to use and then filtered directly into the reaction mixture. The re-

sulting solution was moderately stirred while being heated at 58–60° for 46 hr. Upon completion of the reaction the warm slurry was filtered through a sintered glass funnel and the light canary yellow phosphonium salt was washed with hot methylene chloride (2 × 150 ml) and then with hot benzene (100 ml) before being dried in vacuo over phosphorus pentoxide, yield 123.4 g (0.225 mol, 57.7%, 25.4% based on $CHFI_2$), mp 168.8–172.0° dec. The ^1H NMR spectrum (saturated in DMSO-d_6) consisted of an unresolved multiplet at δ 7.62–8.21, peaking at δ 7.86 (15 H), and a doublet of doublets (1 H) at δ 9.19 (J_{HCF} = 44.8, J_{HCP} = 7.8 Hz). The ^{19}F NMR spectrum of this sample exhibited a doublet of doublets at ϕ^* 184.4 ppm (J_{FCP} = 66.0, J_{FCH} = 45.5 Hz).

Anal. Calcd for $C_{19}H_{16}FI_2P$: C, 41.64; H, 2.94. Found: C, 40.16; H, 3.15.

α,α,α-Trifluoroacetophenone. This polyfluorinated ketone was prepared in 57.3% yield by the method of Dishart and Levine.[32]

Zinc–Copper Couple. Zinc–copper couple was prepared by the method of Le Goff.[33]

General Procedure for the Synthesis of Vinyl Fluorides via Pregenerated Fluoromethylenetriphenylphosphorane. The apparatus consisted of a 200-ml three-necked round-bottomed flask equipped with a magnetic stirring bar, a glass stopper, a constant-pressure addition funnel fitted with a nitrogen inlet, and a water-cooled reflux condenser topped with a T joint leading to a mineral oil bubbler. The apparatus was flushed with nitrogen, flame dried, and allowed to cool to room temperature while deaeration with nitrogen was continued.

A typical preparative reaction using the synthesis of 1-hydro-2-phenylperfluoropropene, $C_6H_5C(CF_3)$=CHF, as an example proceeded as follows. The flask was charged with 6.44 g (0.015 mol) of fluoromethyltriphenylphosphonium iodide and 80 ml of dry THF containing 1.12 g (0.012 mol) of toluene. The glass stopper was replaced with a rubber septum and the nitrogen inlet on top of the addition funnel was replaced with a glass stopper. However, the nitrogen atmosphere was maintained throughout the system by connecting the previously exposed T joint atop the condenser to the inert gas source. The slurry of phosphonium salt and solvent was moderately stirred while cooled in a Dry Ice–isopropyl alcohol slush bath. During this cooling process the addition funnel was charged with 10.0 ml (0.015 mol) of 1.53 *N* *n*-butyllithium in hexane. Any appreciable amount of hydrolysis of the organolithium reagent was avoided by maintenance of a constant sweep of nitrogen over the addition funnel when the stopper was removed and by transferring the base via a pipette under a dry nitrogen atmosphere. The base was added dropwise over a 23-min period. Upon completion of the addition, the reaction mixture was stirred for 25 min at −78°. At the end of this period a 1.0-ml aliquot of the reaction mixture was withdrawn under a nitrogen atmosphere and added to 1.0 ml of ethylene bromide with the evolution of heat. GLC analysis of the resulting mixture (column B) indicated that no *n*-butyl bromide was formed, suggesting that all of the *n*-butyllithium had reacted with the phosphonium salt. The reaction was continued for an additional 25 min at −78° and then 3.36 g (0.0193 mol) of α,α,α-trifluoroacetophenone was added. The reaction between the ylide and the carbonyl compound was allowed to proceed for 2 hr at −78° and then for 1.5 hr at room temperature. The reaction mixture was then cooled in ice. Potassium *tert*-butoxide (MSA Research, 1.57 g, 0.0140 mol) was added and the mixture was stirred for 2 hr at 0°. At the end of this period GLC analysis (column B) indicated that 1-hydro-2-phenylperfluoropropene was formed in 50.4% yield (cis:trans 46:54). In addition to the desired products, 17.4% of 1,1,1-trifluoro-2-phenylheptene-2 was also formed (cis:trans 39:61) and some higher boiling materials.

The dark reaction mixture was centrifuged and decanted, and the precipitate was washed with small portions of THF. The decantates were combined and washed with saturated aqueous sodium chloride solutions (3 × 100 ml) until the aqueous layer was neutral to litmus paper. The dried (anhydrous magnesium sulfate) and filtered organic material was concentrated by removal of the solvent through a 6-in. Vigreux column. The residue was flash distilled at reduced pressure through a short-path distillation apparatus and two fractions were collected in Dry Ice cooled receivers. Preparative GLC analysis of fraction I on column D at 136° afforded pure samples of *cis*- and *trans*-1-hydro-2-phenylperfluoropropene. Pure samples of *cis*- and *trans*-1,1,1-trifluoro-2-phenylheptene-2 were isolated from fraction II by preparative GLC analysis on column D at 178°.

General Procedure for the Synthesis of Vinyl Fluorides via Fluoromethylenetriphenylphosphorane Generated in Situ. The apparatus consisted of a 200-ml three-necked round-bottomed flask equipped with a magnetic stirring bar, a Schlenk solids addition tube, a glass stopper, and an air-cooled reflux condenser topped with a T joint connected to a nitrogen source and to a mineral oil bubbler. The assembled apparatus was simultaneously deaerated with nitrogen and flame dried and then allowed to cool to room temperature while a slow sweep of nitrogen was maintained.

A typical preparative reaction using the synthesis of α,β-dihydrohexafluorostyrene, C_6F_5CH=CHF, as an example proceeded as follows. Fluoroiodomethyltriphenylphosphonium iodide (27.41 g, 0.0500 mol), purified pentafluorobenzaldehyde (Peninsular ChemResearch, 9.80 g, 0.05 mol), toluene (3.00 ml, 2.60 g, 0.0282 mol), and 150 ml of dry DMF were placed into the reaction flask. The flask was cooled to 0° as the Schlenk solids addition tube was charged with 4.90 g (0.0750 g-atom) of zinc–copper couple. The cold solution was rapidly stirred as the couple was added in one portion. The reaction was allowed to proceed for 45 min at 0°, at which time GLC analysis on column C indicated that all of the carbonyl compound had been consumed. The reaction mixture was stirred for 45 min and then filtered with nitrogen pressure through a Schlenk fritted funnel. An aliquot of the filtrate was withdrawn and analyzed on column C vs. a standard solution of α,β-dihydrohexafluorostyrene and toluene in ether, yield 65.0% (cis:trans 54:46).

The apparatus was rinsed with ether (2 × 50 ml) and the washes were passed through the funnel. The organic materials were combined and added to 75 ml of water with the evolution of heat. The mixture was steam distilled and upon completion of the distillation the flask appeared to be etched. The distillate was saturated with sodium chloride and extracted with ether (3 × 100 ml). The extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated by removal of the solvent through a 6-in. Vigreux column. The residue was then flash distilled at reduced pressure through a short-path distillation apparatus. GLC analysis of the distillate on column C indicated that the trans isomer was significantly consumed during the work-up procedures (cis:trans 80:20), presumably owing to its susceptibility to hydrolysis. Pure samples of *cis*- and *trans*-α,β-dihydrohexafluorostyrene were isolated from the flash distillate by preparative GLC analysis on column E at 90°.

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Registry No.—Fluoroiodomethane, 373-53-5; methylene fluoride, 75-10-5; fluoromethyltriphenylphosphonium iodide, 28096-32-4; triphenylphosphine, 603-35-0; fluoroiodomethyltriphenylphosphonium iodide, 55904-32-0; fluorodiiodomethane, 1493-01-2; α,α,α-trifluoroacetophenone, 434-45-7; fluoromethylenetriphenylphosphorane (uncharged species), 28096-33-5; fluoromethylinetriphenylphosphorane (charged species), 28096-34-6; pentafluorobenzaldehyde, 653-37-2.

References and Notes

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A Rapid Method of Preparation of Phospholanium Perchlorates via Intramolecular Cyclizations of 4-Hydroxybutylorganophosphines[1]

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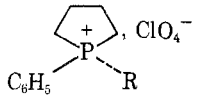
A rapid synthetic procedure for the preparation of phospholanium perchlorates in high yield has been developed. The process involves the cleavage of tetrahydrofuran by lithium organophosphides, affording 4-hydroxybutylorganophosphines, which are then intramolecularly cyclized in an aqueous solution. The following phospholanium salts (very tediously prepared by other methods) have been obtained by this procedure: methylphenyl-, ethylphenyl-, *n*-propylphenyl-, *n*-butylphenyl-, and diphenylphospholanium perchlorate. Evidence is also presented to show that cleavage of THF by diethylphenylphosphine and lithium metal afforded not only the expected diethyl-4-hydroxybutylphosphine, but also ethyl-4-hydroxybutylphenylphosphine. Confirmation of this was obtained in the form of subsequent intramolecular cyclization of these phosphines to the corresponding diethylphospholanium perchlorate and ethylphenylphospholanium perchlorate. Extension of this synthetic procedure to tetrahydropyran also afforded the desired phosphorinanium perchlorate in good yield.

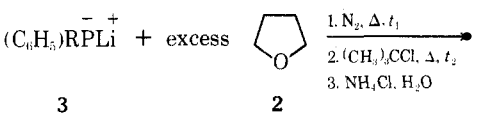
Historically, phospholanium salts have been prepared by quaternization of a selected phospholane with an alkyl halide.[3] Although the quaternization procedures generally afforded the desired salts in high yield, major drawbacks to this approach have been centered around the synthesis of the initial phospholanes,[4] which have been recently reviewed.[3,5,6] In order to alleviate this necessity of first preparing the phospholane, we have developed a process involving the cleavage of a cyclic ether by lithium organophosphides to yield γ-hydroxyalkylorganophosphines, which were intramolecularly cyclized to the desired alkylphenylphospholanium salts **1** in high yield. The initial step



1

R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, C_6H_5

in the synthetic sequence involved the cleavage of tetrahydrofuran **2** by a lithium alkylphenylphosphide **3**, generated in situ from the corresponding diphenylalkylphosphines and lithium metal,[7] to yield the necessary alkyl-4-hydroxybutylphenylphosphines **4**.



3 **2**

$(C_6H_5)RP(CH_2)_4OH$

4

R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, C_6H_5

This cleavage of cyclic ethers **5** by alkali organophosphides **6** has been previously shown to afford the corresponding γ-hydroxyalkylorganophosphines **7**, although the yields reported were quite variable.[8-15] A variety of substituted cyclic ethers such as propylene oxide, styrene oxide, and cyclohexene oxide have also been utilized.[8] Most of the alkali organophosphides **6** studied have been symmetric, i.e., the organic substituents of the phosphide have been dimethyl,[13] diethyl,[8] diphenyl, etc.[8,11] In the present work, the lithium organophosphides **3** have been *dissymmetric*, except in the case of the diphenyl derivative, and have afforded the dissymmetric 4-hydroxybutylalkylphenylphosphines **4** (Table I). The cleavage of tetrahydrofuran by

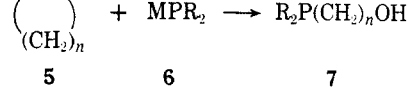
Table I
Preparation of 4-Hydroxybutylalkylphenylphosphines 4 via Lithium Organophosphides and Tetrahydrofuran

$(C_6H_5)RP(CH_2)_4OH$

4

R	t_1, hr[a]	t_2, hr[b]	Bp, °C (mm)	Yield, %	Registry no.
CH_3	12	12	87–89 (0.10)	86	55759-63-2
C_2H_5	12	24	121–124 (0.15)	86	54807-90-8
n-C_3H_7	48	12	126–128(0.35)	73	55759-64-3
n-C_4H_9	48	12	135–137 (0.10)	78	55759-65-4
C_6H_5	48	12	160–164 (0.20)	73	7526-70-7

[a] Time of reflux before addition of $(CH_3)_3CCl$. [b] Time of reflux after addition of $(CH_3)_3CCl$.



5 **6** **7**

n = 2, 3, 4, 5 M = Li, K
R = dialkyl or diaryl