Registry No. (±)-**1**, 2437-95-8; (±)-**2**, 111821-60-4; (±)-**4a**, 6627-72-1; (±)-**4a** (acetate), 36386-52-4; (±)-**4b**, 24393-70-2; (±)-**4b** (acetate), 17283-45-3; (±)-**5a**, 36386-49-9; (±)-**5a** (acetate, 111821-74-0; (±)-**5b**, 111821-62-6; (±)-**5b** (acetate), 111773-53-6; (±)-**7**, 111821-63-7; (±)-**7** (ketone), 110012-74-3; (±)-**8**, 111821-64-8; (±)-**8**-2-*endo*-*d*, 111821-72-8; (±)-**8**-2-*endo*-*d* (methyl xanthate), 111773-51-4; (±)-**9**, 111821-65-9; (±)-**9** (ketone), 111821-71-7; (±)-**10**, 111821-66-0; (±)-**10** (*p*-brosylate), 111773-45-6; (±)-**10** (ketone), 52363-25-4; (±)-**11**, 111821-67-1; (±)-**12**, 111821-68-2; (±)-**13**, 111821-69-3; (±)-**14**, 70223-30-2; (±)-**14** (ketone), 30469-48-8; (±)-**14** (ketone tosylhydrazone), 111773-46-7; (±)-**14**-3,3-d_2 (ketone), 111821-73-9; (±)-**15**, 70223-29-9; (±)-**15**-3,3-d_2, 111793-88-5; (±)-**15**-3,3-d_2 (methyl xanthate), 111773-52-5; (±)-**16**, 111773-44-5; (±)-**16** (unlabeled), 82764-88-3; (±)-**17**, 111821-61-5; (±)-**18**, 111793-87-4; **19**, 29031-17-2; **19** (ketone), 4722-54-7; **20**, 29031-18-3; (±)-**21**, 111821-70-6; (±)-α-terpinenyl acetate, 10581-37-0; (±)-limonene, 7705-14-8; norbornene, 498-66-8; cyclohexene, 110-83-8; (±)-B-pinene, 23089-32-9; (±)-5,5-dimethyl-2-*exo*-deuterio-2-*endo*-norbornanol, 111773-47-8; (±)-5,5-dimethyl-2-*exo*-deuterio-2-*endo*-norbornyl methyl xanthate, 111773-48-9; (±)-deuterioapocyclene, 111773-49-0; (±)-apocyclene, 111773-50-3.

Supplementary Material Available: Preparative procedures, necessary constants, and spectral data for **2**, **5b**, and **10**–**18**; Table V showing the ^1H and ^{13}C NMR parameters of **7**–**13** and **21**; Scheme III showing pathways to products from α-pinene; Figure 5 showing ^{13}C NMR spectra of C-1 regions of borneol (**4a**); and Figure 6 showing the EI mass spectra of authentic β-nopinol (**14**) and of the product corresponding to the peak labeled a in Figure 1 (7 pages). Ordering information is given on any current masthead page.

Fluorinated Phosphoranium Salts: Syntheses and Mechanisms of Formation, Hydrolysis, and Halogenation

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Triphenylphosphine and/or tri-*n*-alkylphosphines (R = Et, Bu, Oc) react with fluorotrihalomethanes in a three-to-one ratio to produce fluorinated phosphoranium salts in excellent yields. The solvents utilized exclusively for the preparation of these ylides are methylene chloride, benzonitrile, and *o*-chlorotoluene. Hydrolysis of the fluorinated phosphoranium salts takes place under mild reaction conditions to produce an equivalent of phosphine oxide and (fluoromethyl)phosphonium salt. Halogenation of the fluorinated phosphoranium salts was shown to be an almost quantitative reaction to produce the corresponding (dihalofluoromethyl)phosphonium salt and dihalophosphorane. The mechanism of formation of fluorinated phosphoranium salt is a series of halophilic reactions similar to that of non-fluorine-containing phosphoranium salts. The hydrolysis of phosphoranium salts is explained by attack by hydroxide ion on the most positively charged phosphorus of the newly formed bis phosphonium salt; the stability of the ejected ylide is secondary to the formation of the strongest phosphorus–oxygen bond. Halogenation occurs by initial abstraction of positive halogen by the fluorinated phosphoranium salt to produce the bis phosphonium salt, followed by attack by halide ion on the phosphonium center, resulting in ejection of the more stable halofluoromethylene ylide.

Introduction

In 1961 Ramirez[2] reported the first synthesis of a phosphoranium salt. The name was coined because the molecule comprised both the phosphorane and phosphonium moieties. The synthetic sequence began with the

$$[Ph_3P^+–C^-H–P^+Ph_3]Br^-$$
1

preparation of methylene bis(triphenylphosphonium bromide) from 2 mol of triphenylphosphine and 1 mol of methylene bromide. Treatment of the bis phosphonium salt with aqueous sodium carbonate afforded the phosphoranium salt 1. Subsequent to this initial report, the syntheses of a variety of phosphoranium salts have appeared in the literature,[3-22] most of which have been prepared by the reaction of a tertiary phosphine with a halogenated methane. The general structure of phosphora-

Table I. Solvents and Solubilities

	solubilities[a]			
	$[Bu_3P^+–C^-F–P^+Bu_3]X^-$			
solvent (bp, °C)	$CFCl_3$	$CFBr_3$	Bu_3PCl_2	Bu_3PBr_2
methylene chloride (40)	S (95%)	S (92%)	S	S
benzonitrile (191)	S (94%)	S (91%)	S	IS
o-chlorotoluene (158)	S (92%)	S (91%)	S	IS
acetonitrile (82)	S (91%)	S (93%)	S	IS
dioxane (101)	S (90%)	S (89%)	S	IS

[a] ^{19}F NMR yield vs hexafluorobenzene (HFB): S = soluble; IS = insoluble—solid present which is not detected by ^{31}P NMR analysis.

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nium salts is given by **2**.

$$[R_3P^+-C^-X-P^+R_3]X^-$$
2

X = H, Cl, Br, I; R = alkyl, aryl

The synthetic utility of phosphoranium salts has been primarily limited to the preparation of carbodiphosphoranes by reaction with either a strong base (potassium[2]) or a strong halophilic agent (tris(dimethylamino)phosphine[15-17]).

There have been no reports of successful Wittig-type reactions of **2** with carbonyl compounds.[12,23,24] Two possible reasons for this lack of reactivity are (1) steric hindrance about the carbanionic center and/or (2) the carbanionic center (when X = Cl or Br) is very weakly nucleophilic and is not capable of Wittig-type reactions. In order to increase the reactivity of the ylide one could place a carbanion destabilizing group on the central carbon atom. An ideal choice would be fluorine due to its well-known destabilization of α-carbanions and its minimal steric hindrance.[25]

In our laboratories fluorinated phosphonium and bis phosphonium salts have been synthesized and shown to be useful precursors of ylides, carbenes, and methide ions.[26,27] The logical extension of this series would include fluorinated phosphoranium salts as well.

$[R_3P^+-CFY_2]X^-$	$[R_3P^+-CFY-P^+R_3]2X^-$	$[R_3P^+-C^-F-P^+R_3]X^-$
X = Cl, Br, H	Y = H, F	X = Cl, Br, BF_4
X = Cl, Br, BF_4	X = Cl, Br	

Results and Discussion

Synthesis. Our interest in the mechanism of formation of fluorinated phosphonium and bis phosphonium salts eventually led to the synthesis of fluorinated phosphoranium salts. Tri-*n*-butylphosphine reacts with the appropriate *F*-halomethane in a variety of solvents (other than triglyme or diethyl ether) to produce the fluorinated phosphoranium salt **3** (eq 1). The solubilities of the phosphoranium salt and the corresponding dihalophosphorane (X = Cl or Br) were determined in each solvent system by ^{31}P NMR spectroscopy and are located in Table I.

$$3Bu_3P + CFX_3 \xrightarrow{\text{solvent}} [Bu_3P^+-C^-F-P^+Bu_3]X^- + Bu_3PX_2 \quad (1)$$
3

X = Cl or Br

The fluorine-containing phosphoranium salt was soluble in all of the solvent systems explored. Selective removal of the unwanted dihalophosphorane was often necessary for further synthetic applications. Attempts to convert the soluble dichlorophosphorane into phosphine oxide via reaction with 1,2-epoxybutane failed. However, nitrogen-pressurized Schlenk filtration could be employed to remove the insoluble dibromophosphorane from the solution which contained the soluble phosphoranium salt. All attempts to isolate the fluorinated phosphoranium salt failed, affording mostly the protonated phosphoranium salt. In comparison, the chlorinated phosphoranium salt prepared by Appel and co-workers can be isolated without protonation.[12,17-21]

The phosphoranium salt can be prepared from either fluorotribromomethane or fluorotrichloromethane. Utilization of the less reactive, although less expensive and commercially available, fluorotrichloromethane was a high priority. Therefore the development of solvent systems which would utilize fluorotrichloromethane and allow for the facile isolation of the newly formed compounds was explored.[23,24]

Three solvent systems (methylene chloride, benzonitrile, and *o*-chlorotoluene) have been optimized in order to produce excellent yields of the fluorinated phosphoranium salt **3**. This optimization has reduced the byproducts **4** and **5**, which arise from abstraction of a proton from the solvent or from the alkyl groups. These protonated phosphonium salts are usually present in less than 8% yield (4% each) based on the starting methane.

$$[Bu_3P^+-CFH-P^+Bu_3]X^- \qquad [Bu_3P^+-CFHX]X^-$$
4 **5**

After having demonstrated the convenient synthesis of the fluorinated phosphoranium salt **3**, it was of interest to determine the generality of this synthetic procedure. A variety of alkyl and aryl tertiary phosphines were utilized in the formulation of these generalities.

Straight- and branched-chain trialkylphosphines were reacted with fluorotrichloromethane. The reactions of the straight-chain phosphines were similar to those of tri-*n*-butylphosphine, producing fluorinated phosphoranium salts (eq 2). However, the identifiable reaction products

$$3R_3P + CFCl_3 \xrightarrow{CH_2Cl_2} [R_3P^+-C^-F-P^+R_3]Cl^- \quad (2)$$
(85–95% ^{19}F NMR)

R = Et, *n*-Bu, *n*-Oc

from the branched trialkylphosphines were the reduced phosphonium salts **6** and **7** and not the expected fluorinated phosphoranium salt (eq 3). Abstraction of a proton

$$3R_3P + CFCl_3 \xrightarrow{CH_2Cl_2} [R_3P^+-CFHCl]Cl^- + [R_3P^+-CFH_2]Cl^- \quad (3)$$
6 **7**

R = *i*-Pr, *t*-Bu

by a reaction intermediate was the major pathway producing these reduced phosphonium salts. From these data it was evident that α-branching of the alkyl group does not allow for phosphoranium salt formation.

The above reactions (eq 2 and 3) were carried out at 0 °C in methylene chloride. The exotherms were easily controlled in all cases except tri-*tert*-butylphosphine, in which an extreme exotherm was observed, resulting in a very dark brown solution, which contained **7** as the major product. This exotherm was controlled by cooling the system to −78 °C and then slowly warming to room tem-

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Table II. ^{19}F, ^{31}P, and ^{13}C NMR Data for *F*-Phosphoranium Salts

phosphoranium salt	^{19}F, ppm[a]	^{31}P, ppm[b]	^{13}C, ppm[c]
$[Bu_3P^+–C^-F–P^+Bu_3]Br^-$	−283.8 (t)	26.6 (d)	91.85 (d,t)
	$J(F,P)$ = 42 Hz		$J(C,F)$ = 164 Hz
			$J(C,P)$ = 108 Hz
$[Et_3P^+–C^-F–P^+Et_3]Cl^-$	−288.8 (t)	32.6 (d)	
	$J(F,P)$ = 41 Hz		
$[Ph_3P^+–C^-F–P^+Ph_3]Br^-$	−262.8 (t)	20.5 (d)	86.6 (t,d)
	$J(F,P)$ = 49 Hz		$J(C,P)$ = 180 Hz
			$J(C,F)$ = 136 Hz
$[Ph_3P^+–C^-F–P^+Bu_3]Br^-$	−268.4 (d,d)	14.9 (d,d) (PPh_3)	88.0 (d,d,d)
		29.9 (d,d) (PBu_3)	
	$J(F,PBu_3)$ = 39 Hz		$J(C,PPh_3)$ = 176 Hz
	$J(F,PPh_3)$ = 49 Hz		$J(C,F)$ = 138 Hz
	$J(PPh_3,PBu_3)$ = 65 Hz		$J(F,PBu_3)$ = 114 Hz
$[Ph_3P^+–C^-F–P^+Et_3]Br^-$	−271.4 (d,d)	15.4 (d,d) (PPh_3)	
		36.2 (d,d) (PEt_3)	
	$J(F,PEt_3)$ = 39 Hz		
	$J(F,PPh_3)$ = 49 Hz		
	$J(PPh_3,PEt_3)$ = 70 Hz		
$[Ph_3P^+–C^-F–P^+Oc_3]Br^-$	−269.0 (d,d)	15.3 (d,d) (PPh_3)	
		30.4 (d,d) (POc_3)	
	$J(F,POc_3)$ = 41 Hz		
	$J(F,PPh_3)$ = 47 Hz		
	$J(PPh_3,POc_3)$ = 67 Hz		

[a] Chemical shift relative to internal $CFCl_3$. [b] Chemical shift relative to external 10% H_3PO_4. [c] Chemical shift of carbanionic carbon relative to internal TMS. Spin relaxer $Cr(DPM)_3$ (approximately 75 mg) was used in all cases.

perature. The same reaction products were produced, however, with the ratio of **7** to **6** reversed. This reversal may be explained by the decrease in temperature, which slowed the formation of **7** from salt **6** with excess phosphine.

It was also of interest to determine if this procedure was utilizable with the less nucleophilic triarylphosphines. Triphenylphosphine does not react with fluorotrichloromethane in any solvent utilized in this study. However, when the more reactive fluorotribromomethane is allowed to react with triphenylphosphine in THF, a tan precipitate forms, which is phosphonium salt **8**.[28]

$$[Ph_3P^+CFBr_2]Br^-$$
8

When methylene chloride was used in place of THF, the fluorinated phosphoranium salt **9** was obtained in greater than 95% yield as determined by ^{19}F NMR spectroscopy relative to hexafluorobenzene, HFB (eq 4). Schlenk filtration of the heterogeneous reaction mixture removed the dibromotriphenylphosphorane. This procedure allowed for exchange of the counter anion (eq 5).

$$3Ph_3P + CFBr_3 \xrightarrow{CH_2Cl_2} [Ph_3P^+–C^-F–P^+Ph_3]Br^- + Ph_3PBr_2 \quad (4)$$
9

$$[Ph_3P^+–C^-F–P^+Ph_3]Br^- + NaBF_4 \rightarrow [Ph_3P^+–C^-F–P^+Ph_3]BF_4^- + NaBr \quad (5)$$

Substitution at the ortho position of the phenyl group introduced sufficient steric hindrance to retard the formation of the fluorinated phosphoranium salt when fluorotribromomethane was reacted with ortho-substituted triarylphosphines (eq 6). The major products were

$$3Ar_2Ar'P + CFBr_3 \xrightarrow{CH_2Cl_2} [Ar_2Ar'P^+CFBr_2]Br^- + [Ar_2Ar'P^+CFHBr]Br^- \quad (6)$$
10 **11**

Ar = Ar′ = *o*-$CH_3OC_6H_4$; Ar = C_6H_5, Ar′ = *o*-$CH_3C_6H_4$

phosphonium salts **10** and **11**. In the case of the less hindered phosphine, (*o*-methylphenyl)diphenylphosphine, the major product was the (bromofluoromethyl)-phosphonium salt **11**. Phosphonium salt **10** was the major product when tris(*o*-methoxyphenyl)phosphine was allowed to react with fluorotribromomethane in methylene chloride.

The above data allow one to generalize concerning the scope of fluorinated phosphoranium salt formation. Utilization of only straight-chain trialkylphosphines or triphenylphosphine permitted these special ylides to be formed in excellent yields. The ^{19}F, ^{31}P, and ^{13}C NMR spectroscopic data for the fluorinated phosphoranium salts are tabulated in Table II.

After the successful syntheses of the alkyl and aryl fluorinated phosphoranium salts, attention was turned to the synthesis of mixed fluorinated phosphoranium salts.

Entry into the mixed salts was accomplished by utilizing the easily prepared (dibromofluoromethyl)triphenylphosphonium bromide (**8**).[28] Tri-*n*-butylphosphine was added dropwise to a suspension of **8** in methylene chloride at 0 °C, which within minutes became homogeneous. This reaction mixture contained the mixed fluorinated phosphoranium salt **12b** as determined by ^{19}F and ^{31}P NMR spectroscopy (eq 7). The mixed fluorinated phosphoranium salt **12b** was formed in an 81% yield as determined by ^{19}F NMR spectroscopy based on the internal standard HFB. The formation of 15% **13** and 4% **14b** was revealed

$$[Ph_3P^+CFBr_2]Br^- + 2R_3P \rightarrow$$
8

$$[Ph_3P^+–C^-F–P^+R_3]Br^- + [Ph_3P^+CFH_2]Br^- + [Ph_3P^+–CFH–P^+R_3]2Br^- \quad (7)$$
12a, R = Et; **b**, R = *n*-Bu; **c**, R = *n*-Oc — **13** — **14a**, R = Et; **b**, R = *n*-Bu; **c**, R = *n*-Oc

by their characteristic signals in the ^{19}F and ^{31}P NMR spectra. The observed reduced compounds were triphenylphosphonium salt derivatives. The corresponding reduced tri-*n*-butylphosphonium salts were not detected by NMR spectroscopy. Utilization of tri-*n*-octylphosphine in the above procedure afforded the mixed fluorinated phosphoranium salt **12c** in a 60% yield based on HFB.

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The reduced byproducts were **13** (20%) and **14c** (20%). Similarly, when triethylphosphine was allowed to react with **8**, 60% of the corresponding mixed fluorinated phosphoranium salt **12a** was formed relative to HFB. The only reduced byproduct was **14a**, which formed in a 40% yield.

Spectroscopic and chemical methods were used to characterize the phosphorus-containing substances. ^{19}F, ^{31}P, and ^{13}C NMR analyses were employed to provide information concerning the structure of the fluorinated phosphoranium salts (Table II and supplementary material). Spectroscopic information indicated that the fluorinated phosphoranium salts were never prepared free of impurities. Several attempts to isolate the fluorinated phosphoranium salts resulted in increased amounts of the reduced impurity. Therefore analytical elemental analysis could not be employed.

Hydrolysis. Hydrolysis of fluorinated phosphoranium salts was best performed in two steps: (1) protonation of the ylide **15** with anhydrous HCl(g) to yield fluoromethylene bis phosphonium salt **16** (eq 8), followed by (2) cleavage of **16** with 10% NaOH to produce (fluoromethyl)phosphonium salt **17** and phosphine oxide (eq 9).

$$\underset{\textbf{15a, R = } n\text{-Bu}\\ \textbf{b, R = Ph}}{[R_3P^+\text{–}C^-F\text{–}P^+R_3]X^-} + HCl(g) \rightarrow \underset{\textbf{16a (>95\%)}\\ \textbf{b (>95\%)}}{[R_3P^+\text{–}CFH\text{–}P^+R_3]2X^-} \quad (8)$$

$$\underset{\textbf{16a, R = } n\text{-Bu}\\ \textbf{b, R = Ph}}{[R_3P^+\text{–}CFH\text{–}P^+R_3]2X^-} \xrightarrow{OH^-(aq)} \underset{\textbf{17a (>90\%)}\\ \textbf{b (>90\%)}}{[R_3P^+\text{–}CFH_2]X^-} + R_3PO \quad (9)$$

On the basis of the ylide, the yields of the salts were quantitative, as determined by ^{19}F NMR spectroscopy relative to the internal standard HFB. To confirm the structural assignment of **16a**, the NMR sample was spiked with fluoromethylene bis phosphonium salt **16a**;[29] only the fluorine signal for **16a** was enhanced. The above salts were not isolated. However, in subsequent work by Wiemers,[30] salt **17b** has been isolated and utilized as an inexpensive route[31-33] to the fluoromethylene ylide **18**. Attempted isolation of salt **17a** resulted in an oil which could not be crystallized.

Hydrolysis of the fluorinated phosphoranium salts was also performed by the addition of an equimolar amount of water; hydrolysis of the dihalophosphorane (which is not shown in the equations) generated HX in situ. Subsequent addition of base to this mixture produced (fluoromethyl)phosphonium salt **17** in a quantitative yield. The yield of fluoromethylene bis phosphonium salt **16b**, however, was affected by the addition of a large excess of water, which promoted a cleavage reaction and yielded **17b**. It was found that **16a** is more resistant to hydrolysis by water than **16b**.

Fluorinated phosphoranium salts prepared from two different phosphines were subjected to protonation via addition of HCl(g) (eq 10). Protonation of ylide **12** to produce fluoromethylene bis phosphonium salt **14** was essentially quantitative as determined by ^{19}F NMR spectroscopy (HFB internal standard).

$$\underset{\textbf{12a, R = Et, R' = Ph}\\ \textbf{b, R = } n\text{-Bu, R' = Ph}\\ \textbf{c, R = } n\text{-Oc, R' = Ph}}{[R_3P^+\text{–}C^-F\text{–}P^+R'_3]X^-} + HCl(g) \rightarrow \underset{\textbf{14a (>96\%)}\\ \textbf{b (>96\%)}\\ \textbf{c (>96\%)}}{[R_3P^+\text{–}CFH\text{–}P^+R'_3]2X^-} \quad (10)$$

Base hydrolysis of **14b** produced the two expected (fluoromethyl)phosphonium salts **17a** and **17b** in a ratio of 2.2:1, respectively (eq 11). The combined yield of the

$$\underset{\textbf{14b}}{[Ph_3P^+CFHP^+Bu_3]2X^-} \xrightarrow{NaOH} \underset{\textbf{17a (62\%)}}{[Bu_3P^+CFH_2]X^-} + \underset{\textbf{17b (28\%)}}{[Ph_3P^+CFH_2]X^-} \quad (11)$$

two salts was >90% (based on **14b**) as determined by ^{19}F NMR spectroscopy relative to HFB. In order to confirm the assignments, the NMR sample was spiked with an authentic sample of (fluoromethyl)phosphonium salt **17b**;[34] only the signal for **17b** was enhanced.

The observed selectivity of hydrolysis of **14b** can be accounted for primarily by the susceptibility of the phosphonium center to nucleophilic attack by hydroxide ion to produce phosphine oxide and not the relative stability of the newly formed fluoromethylene ylide. Inductive effects play a primary role, as the electron-withdrawing nature of the phenyl groups enhance the positive charge on the triphenylphosphonium center, which is preferentially attacked by hydroxide ion to produce triphenylphosphine oxide and the less stable tri-*n*-butylphosphonium fluoromethylene ylide **19** (eq 12). Therefore, the relative stability of the generated ylide is secondary to inductive effects which direct the initial attack of hydroxide on the mixed bis phosphonium salt (eq 13).

$$\underset{\textbf{14b}}{[Ph_3P^+CFHP^+Bu_3]2X^-} \xrightarrow{^-OH} Ph_3PO + \underset{\textbf{19}}{Bu_3P^+\text{–}C^-FH} \quad (12)$$

$$\underset{\textbf{14b}}{[Ph_3P^+CFHP^+Bu_3]2X^-} \xrightarrow{^-OH} Bu_3PO + \underset{\textbf{18}}{Ph_3P^+\text{–}C^-FH} \quad (13)$$

Halogenation. Appel[10] reported that treatment of chlorinated phosphoranium salt **20** with elemental chlorine produced the (trichloromethyl)phosphonium salt **21** and dichlorophosphorane **22** (eq 14). Treatment of the reaction mixture with 1,2-epoxybutane, followed by addition of diethyl ether, converted **22** into triphenylphosphine oxide, thus allowing convenient isolation of **21**.

$$\underset{\textbf{20}}{[Ph_3P^+\text{–}C^-Cl\text{–}P^+Ph_3]Cl^-} + 2Cl_2 \rightarrow \underset{\textbf{21}}{[Ph_3P^+CCl_3]Cl^-} + \underset{\textbf{22}}{Ph_3PCl_2} \quad (14)$$

In our investigation, fluorinated phosphoranium salt **15b** reacted with elemental chlorine to produce a homogeneous reaction mixture which contained 62% (dichlorofluoromethyl)phosphonium salt **23** and 32% (bromochlorofluoromethyl)phosphonium salt **24**, as determined by ^{19}F NMR analysis relative to HFB (eq 15). The bromine-

$$\underset{\textbf{15b}}{[Ph_3P^+\text{–}C^-F\text{–}P^+Ph_3]X^-} + 2Cl_2 \rightarrow \underset{\textbf{23}}{[Ph_3P^+CFCl_2]X^-} + \underset{\textbf{24}}{[Ph_3P^+CFClBr]X^-} + Ph_3PCl_2 \quad (15)$$

containing salt is accounted for by the inability to quantitatively remove bromide ion from the reaction mixture by anion exchange with tetrafluoroborate. Thus, reaction of bromide ion with elemental chlorine results in formation of BrCl, which provides a source of positive bromine. The ^{19}F NMR spectrum of the isolated solid (**23** and **24**) revealed two doublets at δ –61.8 (d, J(F,P) = 83 Hz) and –65.1 (d, J(F,P) = 80 Hz) in a ratio of 63:37, respectively. The absorptions were assigned as arising from the (dichlorofluoromethyl)triphenylphosphonium salt **23** and

(29) An authentic sample was prepared by the reaction of 3 mol tri-*n*-butylphosphine with 1 mol of trichlorofluoromethane in diethyl ether according to the procedure reported by Kesling in ref 27.

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(33) Burton, D. J.; Greenlimb, P. E. *J. Fluorine Chem.* **1973**, *3*, 447.

(34) An authentic sample was prepared by Greenlimb. Greenlimb, P. E. Ph.D. Thesis, University of Iowa, 1972. Procedure also described in ref 30.

(bromochlorofluoromethyl)triphenylphosphonium salt **24**, respectively.[35]

The fluorinated phosphoranium salt **15b** was re-formed by addition of a sample of the isolated solid to an NMR sample tube containing triphenylphosphine in methylene chloride. It is interesting to note that triphenylphosphine readily reacts with (dichlorofluoromethyl)phosphonium salt, but does not react with fluorotrichloromethane.

Addition of elemental bromine to fluorinated phosphoranium salt **15b** resulted in a heterogeneous reaction mixture which contained (dibromofluoromethyl)-phosphonium salt **8** and dibromotriphenylphosphorane. The insoluble dibromotriphenylphosphorane did not react with 1,2-epoxybutane. The ^{19}F and ^{31}P NMR spectroscopic data are consistent with those reported by Vander Haar.[28] This preparation of **8** was not pursued, since an easier preparation has already been described.[28]

Fluorinated phosphoranium salt **15a** reacts with elemental chlorine or bromine at 0 °C in methylene chloride to produce a homogeneous reaction mixture which contains the (dihalofluoromethyl)phosphonium salt **25** in >90% yield (based on methane) as determined by ^{19}F NMR spectroscopy relative to internal standard HFB (eq 16). All attempts to isolate **25** free of dihalophosphorane have been unsuccessful.

$$[Bu_3P^+-C^-F-P^+Bu_3]X^- + 2X_2 \rightarrow [Bu_3P^+CFX_2]X^- + Bu_3PX_2 \quad (16)$$
15a → **25a**, X = Cl; **b**, X = Br

Hydrolysis of **25a** and **25b** was carried out by the addition of water to each of the NMR sample tubes containing the above reaction mixtures and resulted in the conversion of the phosphonium salts into the corresponding dihalofluoromethanes and phosphine oxide (eq 17).

$$[Bu_3P^+CFX_2]X^- + Bu_3PX_2 + H_2O \rightarrow CHFX_2 + Bu_3PO \quad (17)$$
25

X = Cl or Br

Tri-*n*-butylphosphine was added to an NMR sample tube which contained a fresh aliquot of the (dibromofluoromethyl)tri-*n*-butylphosphonium salt **25b**. The fluorinated phosphoranium salt **15a** was re-formed in greater than 75% yield (based on methane), as determined by ^{19}F NMR analysis relative to HFB. Attempts to study formation of mixed phosphoranium salts starting from **25** were unsuccessful due to the presence of the dichlorotri-*n*-butylphosphorane which intercepts the intermediate ylide **19** to generate bis phosphonium salt **26** (eq 18–20). Subsequent removal of positive halogen from **26** results in the formation of **15a** (eq 20).

$$[Bu_3P^+CFX_2]X^- + Ph_3P \rightarrow Bu_3P^+-C^-FX + Ph_3PX_2 \quad (18)$$
19

$$Bu_3P^+ - C^-FX + Bu_3PX_2 \text{ (excess)} \rightarrow [Bu_3P^+-CFX-P^+Bu_3]2X^- \quad (19)$$
26

$$[Bu_3P^+-CFX-P^+Bu_3]2X^- + Ph_3P \rightarrow [Bu_3P^+-C^-F-P^+Bu_3]X^- \quad (20)$$
15a

Fluorinated phosphoranium salt **14b** reacts with elemental bromine to produce only (dibromofluoromethyl)-triphenylphosphonium salt **8** and dibromotri-*n*-butylphosphorane, as observed by ^{19}F and ^{31}P NMR spectroscopy.

Halogenation of fluorinated phosphoranium salts can occur by the following steps: (1) initial abstraction of positive halogen by the ylide to produce halofluoromethylene bis phosphonium salt **27** (eq 21), followed by (2) nucleophilic attack by halide ion on either the central carbon atom or one of the phosphonium centers (eq 22).

$$[Ph_3P^+-C^-F-P^+Bu_3]Br^- + 2Br_2 \rightarrow [Ph_3P^+-CFBr-P^+Bu_3]2Br^- \quad (21)$$
14b → **27**

$$[Ph_3P^+-CFBr-P^+Bu_3]2Br^- \rightarrow Ph_3P^+-C^-FBr + Bu_3PBr_2 \quad (22)$$
28

$$Ph_3P^+-C^-FBr + Br_2 \rightarrow [Ph_3P^+CFBr_2]Br^- \quad (23)$$
8

If halide attacks the central carbon atom, trivalent phosphorus must be ejected from the molecule. There is no data at the present time to indicate that when halogenation takes place, tri-*n*-butylphosphine should be ejected in preference to triphenylphosphine. On the other hand, attack of halide ion on the tri-*n*-butylphosphonium center would result in ejection of the more stable halofluoromethylene ylide **28**. Based on the cleavage data of **14b**, it is probable that halide ion attacks the tri-*n*-butylphosphonium center to eject the more stable halofluoromethylene ylide and dihalophosphorane. This selectivity of cleavage is in contrast to hydrolysis, where the hydroxide ion attacks the more positive triphenylphosphonium center to generate the less stable tri-*n*-butylphosphonium fluoromethylene ylide. The difference can be attributed to formation of a strong phosphorus–oxygen bond in contrast to the weaker phosphorus–halogen bond. Also, in the halogenation reaction there is the possibility of nucleophilic attack by the newly formed fluoromethylene ylide on the dihalophosphorane to generate starting materials.

Mechanistic Aspects. The formation of reduced phosphonium salts in the preparation of the fluorinated phosphoranium salts was first posited to occur by the abstraction of a proton from the reaction medium (triglyme) by the fluorinated phosphoranium salt.[27] However, after the successful synthesis of the fluorinated phosphoranium salt it was found that the ylide was stable in ethereal solvents for short periods of time, without protonation. Therefore there must be, within the reaction system, an intermediate which is more basic than the fluorinated phosphoranium salt. Once protonated, this intermediate is utilized in the formation of reduced products (illustrated below).

$$[R_3P^+-CFH-P^+R_3]2X^- \qquad [R_3P^+-CFHX]X^- \qquad [R_3P^+-CFH_2]X^-$$

R = alkyl or aryl

The mechanism of formation of phosphoranium salts is directly applicable to the formation of fluorinated phosphoranium salts. The currently accepted mechanism for phosphoranium salt formation is a series of positive halogen abstractions by tertiary phosphine (eq 24–27).[10,11] Positive halogen is removed from the halo-*F*-methane by phosphine to generate an ion pair which rearranges to the more stable phosphonium salt. Attack of the second mole

(35) Van Hamme, M. J.; Burton, D. J.; Greenlimb, P. E. *Org. Magn. Reson.* **1978**, *11*, 275. Utilizing the method of Van Hamme the ^{19}F chemical shifts and $J(F,P)$ coupling constants calculated for the (dichlorofluoromethyl)triphenylphosphonium salt and the (bromochlorofluoromethyl)triphenylphosphonium salt were within 10% of the observed values.

(36) Van Hamme, M. J. Ph.D. Thesis, University of Iowa, 1973.

of tertiary phosphine on the halo-*F*-methyl group of the phosphonium salt generates the halofluoromethylene ylide **29** and dihalophosphorane. Nucleophilic attack on the dihalophosphorane by **29** produces the halofluoromethylene bis phosphonium salt **27**. In the last step, the third equivalent of tertiary phosphine removes a halogen cation from **30** to produce the fluorinated phosphoranium salt.

$$R_3P + CFX_3 \rightarrow [R_3P^+\text{–}X]CFX_2^- \rightarrow [R_3P^+\text{–}CFX_2]X^- \quad (24)$$

$$[R_3P^+\text{–}CFX_2]X^- + R_3P \rightarrow \underset{\mathbf{29}}{R_3P^+\text{–}C^-FX} + R_3PX_2 \quad (25)$$

$$R_3P^+\text{–}C^-FX + R_3PX_2 \rightarrow \underset{\mathbf{30}}{[R_3P^+\text{–}CFX\text{–}P^+R_3]2X^-} \quad (26)$$

$$[R_3P^+\text{–}CFX\text{–}P^+R_3]2X^- + R_3P \rightarrow [R_3P^+\text{–}C^-F\text{–}P^+R_3]X^- \quad (27)$$

According to the above mechanism two species other than the fluorinated phosphoranium salt are capable of accepting a proton, the ion pair and the fluoromethylene ylide **29**. The ion pair was not believed to be the species protonated, because (halo-*F*-methyl)phosphonium salts have been prepared in ethereal solvents.[28] Therefore it seemed advisable to focus attention on the fluoromethylene ylide **29** as the intermediate which undergoes protonation.

The scheme in eq 28–30 is a possible reaction pathway for the formation of these reduced products. The proton source has not been identified, however, the solvent and/or the alkyl groups attached to phosphorus are suspected.

$$R_3P^+\text{–}C^-FX + H^+ \rightarrow [R_3P^+\text{–}CFHX]X^- + R_3P \rightarrow \underset{\mathbf{31}}{R_3P^+\text{–}C^-FH} \quad (28)$$

$$R_3P^+\text{–}C^-FH + R_3PX_2 \rightarrow \underset{\mathbf{32}}{[R_3P^+\text{–}CFH\text{–}P^+R_3]2X^-} \quad (29)$$

$$[R_3P^+\text{–}CFH\text{–}P^+R_3]2X^- + R_3P^+\text{–}C^-FH \rightarrow [R_3P^+\text{–}C^-F\text{–}P^+R_3]X^- + [R_3P^+\text{–}CFH_2]X^- \quad (30)$$

Protonation of the halofluoromethylene ylide **29** produces a reduced phosphonium salt, which subsequently reacts with phosphine, generating the fluoromethylene ylide **31** (eq 28). Nucleophilic attack by **31** on the dihalophosphorane produces the fluoromethylene bis phosphonium salt **32** (eq 29). Depending upon the phosphine utilized, transylidation may take place, to produce the fluorinated phosphoranium salt and the (fluoromethyl)phosphonium salt (eq 30).

For the above scheme to be considered an acceptable reaction pathway, it was necessary to substantiate that (1) the ylide was stable in triglyme and diethyl ether, (2) the fluoromethylene ylide **31** was nucleophilic enough to attack the dihalophosphorane, and (3) the fluoromethylene ylide **31** was capable of undergoing a transylidation reaction with the fluoromethylene bis phosphonium salt **32**.

The stability of the fluorinated phosphoranium salt in triglyme and diethyl ether was established as follows. The fluorinated phosphoranium salt was prepared in methylene chloride, followed by removal of the solvent under reduced pressure and addition of diethyl ether or triglyme to the resulting solid. Analysis of this solution by ^{19}F and ^{31}P NMR spectroscopy revealed almost no protonation of the fluorinated phosphoranium salt in these solvents after approximately 30 min.

The nucleophilicity of the fluoromethylene ylide **31** was established by Kesling[27] in the following manner: 2 mol of tri-*n*-butylphosphine and 1 mol of fluorodiiodomethane resulted in formation of the fluoromethylene bis phosphonium salt and the (fluoroiodomethyl)phosphonium salt in a 70/30 ratio, respectively (eq 31). The bis phosphonium salt was reported by Kesling to be present in a 47% yield relative to the internal standard benzotrifluoride.

$$2Bu_3P + CFI_2H \rightarrow \underset{70\%}{[Bu_3P^+\text{–}CFH\text{–}P^+Bu_3]2I^-} + \underset{30\%}{[Bu_3P^+CFIH]I^-} \quad (31)$$

Kesling proposed that the mechanism of formation was similar to that of the phosphoranium salt. The first step involves formation of reduced phosphonium salt (eq 32). The second mole of phosphine removes the second iodine cation, forming fluoromethylene ylide (eq 33). This important step demonstrates that phosphine reacts with reduced phosphonium salts to generate fluoromethylene ylides. Rapid nucleophilic attack by this ylide on the diiodophosphorane forms the fluoromethylene bis phosphonium salt (eq 34). This nucleophilic substitution is not surprising, as one would expect fluoromethylene ylides to be more reactive than the corresponding dichloromethylene ylides, since α-fluorines are known to destabilize carbanions.[25] The (fluoromethyl)tri-*n*-butylphosphonium salt which would arise from transylidation was not detected by NMR spectroscopy.

$$Bu_3P + CFI_2H \rightarrow [Bu_3P^+CFIH]I^- \quad (32)$$

$$[Bu_3P^+CFIH]I^- + Bu_3P \rightarrow Bu_3P^+\text{–}C^-FH + Bu_3PI_2 \quad (33)$$

$$Bu_3P^+\text{–}C^-FH + Bu_3PI_2 \rightarrow [Bu_3P^+\text{–}CFH\text{–}P^+Bu_3]2I^- \quad (34)$$

Transylidation products were detected when employing the triarylphosphonium moiety. Therefore, a reaction incorporating (bromofluoromethyl)triphenylphosphonium bromide **33** was utilized to establish transylidation.[28] It was found that the reaction of **33** with tri-*n*-butylphosphine produced the expected transylidation products **34** (40%) and **35** (60%), as revealed by ^{19}F and ^{31}P NMR spectroscopy. Product formation arises from abstraction of positive bromine from the initial phosphonium salt **33** to generate the fluoromethylene ylide (eq 35). Nucleophilic attack by this ylide on the dibromophosphorane produces the mixed bis phosphonium salt (eq 36). Subsequent reaction of the bis phosphonium salt with the fluoromethylene ylide produces the observed transylidation products (eq 37).

$$\underset{\mathbf{33}}{[Ph_3P^+CFBrH]Br^-} + Bu_3P \rightarrow Ph_3P^+\text{–}C^-FH + Bu_3PBr_2 \quad (35)$$

$$Ph_3P^+\text{–}C^-FH + Bu_3PBr_2 \rightarrow [Ph_3P^+\text{–}CFH\text{–}P^+Bu_3]2Br^- \quad (36)$$

$$[Ph_3P^+\text{–}CFH\text{–}P^+Bu_3]2Br^- + Ph_3P^+\text{–}C^-FH \rightarrow \underset{\mathbf{34}\ (40\%)}{[Ph_3P^+\text{–}C^-F\text{–}P^+Bu_3]Br^-} + \underset{\mathbf{35}\ (60\%)}{[Ph_3P^+\text{–}CFH_2]Br^-} \quad (37)$$

The rationalization for the occurrence of transylidation in reactions illustrated in eq 35–37 and not in reactions depicted in eq 32–34 is a difference in ylide stability and therefore reactivity. The difference occurs in the ability of the R groups attached to the phosphorus to stabilize the fluoromethylene ylide. The triphenyl fluoromethylene ylide is more stable than the tri-*n*-butyl fluoromethylene ylide due to the electron-withdrawing effect of the phenyl rings. This stability results in a lower reactivity, which allows for separation of the ylide and dihalophosphorane. Once separated transylidation can occur. On the other hand, the tri-*n*-butyl ylide, being less stable and therefore more reactive, rapidly reacts with the dihalophosphorane

before the two species can separate, not allowing transylidation to occur.

Conclusion

It has been shown that triphenylphosphine and/or tri-*n*-alkylphosphines react with fluorotrihalomethanes in a three-to-one ratio to produce fluorinated phosphoranium salts in excellent yields. The solvent systems utilized exclusively for the preparation of these ylides are methylene chloride, benzonitrile, and *o*-chlorotoluene. The choice of solvent is dependent upon subsequent reactions of the ylide.

Hydrolysis of fluorinated phosphoranium salts takes place under mild reaction conditions. The best results are obtained when hydrolysis is carried out as a two-step process involving protonation by HCl(g), followed by treatment with dilute NaOH. The mixed fluorinated phosphoranium salt, when hydrolyzed, exhibits selectivity in forming the (fluoromethyl)tri-*n*-butylphosphonium salt preferentially. The more important step in hydrolysis of the mixed fluorinated phosphoranium salt is attack at the more positively charged phosphorus to produce a strong P–O bond and not generation of the more stable intermediate ylide.

Halogenation of fluorinated phosphoranium salts was shown to be an almost quantitative reaction to produce the corresponding (dihalofluoromethyl)phosphonium salts and dihalophosphorane. 1,2-Epoxybutane quickly and selectively removes dichlorotriphenylphosphorane from the reaction mixture; dibromotriphenylphosphorane, however, did not react with 1,2-epoxybutane.

The mechanism of formation of the fluorinated phosphoranium salts is a series of halophilic reactions which is similar to that of other non-fluorine-containing phosphoranium salts. This mechanism has led to the understanding of the origin of the protonated byproducts which are a minor component of every fluorinated phosphoranium salt preparation. These protonated byproducts arise from the intermediate halofluoromethylene ylides.

Experimental Section

Preparation of $[R_3P^+–C^-F–P^+R_3]Cl^-$ (R = Bu or Et). A 250-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 150 mmol of tri-*n*-alkylphosphine and 60 mL of solvent (methylene chloride or benzonitrile). The flask and contents were cooled to <5 °C with an ice bath. To the cold solution was added 50 mmol (6.9 g, 4.7 mL) of fluorotrichloromethane by syringe in one portion. The solution was stirred at <5 °C for 1 h and at room temperature for 3 h. The resulting solution was light yellowish green. The ^{19}F and ^{31}P NMR spectral data, listed in Table II, indicated the formation of the fluorinated phosphoranium salt in 85–95% yield.

Preparation of $[Bu_3P^+–C^-F–P^+Bu_3]BF_4^-$ in *o*-Chlorotoluene. A 250-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 150 mmol (30.3 g, 37.4 mL) of tri-*n*-butylphosphine and 70 mL of *o*-chlorotoluene. The flask and contents were cooled to <5 °C with an ice bath. To the cold solution was added 50 mmol (13.5 g, 4.9 mL) of fluorotribromomethane by syringe at such a rate as to maintain the temperature below 10 °C. A creamy white precipitate formed immediately. Upon completion of methane addition the precipitate turned light yellow. This very thick mixture was stirred vigorously for 4 h at room temperature. ^{19}F NMR analysis revealed the ylide present in 91% yield relative to HFB. The precipitate was filtered by a nitrogen-pressurized Schlenk funnel (coarse frit) to leave a yellow solution, which contained the ylide in 86% yield relative to HFB. The ^{19}F and ^{31}P NMR spectral data are listed in Table II.

To the filtered ylide solution prepared above was added 150 mmol (16.5 g) of anhydrous sodium tetrafluoroborate. The mixture was stirred under a nitrogen atmosphere for 4 h. Nitrogen-pressurized Schlenk filtration (fine frit) of the heterogeneous mixture yielded a light yellow-to-tan solution. ^{19}F and ^{31}P NMR spectroscopy indicated the presence of the anion-exchanged ylide in 82% yield based on the starting methane.

Preparation of $[Ph_3P^+–C^-F–P^+Ph_3]BF_4^-$ in Methylene Chloride. A 250-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 90 mmol (23.6 g) of triphenylphosphine and 50 mL of methylene chloride. The flask and contents were cooled to <5 °C with an ice bath. To the cold solution was added 30 mmol (8.1 g, 2.9 mL) of fluorotribromomethane by syringe in one portion. The solution was stirred at <5 °C for 1 h and at room temperature for 7 h, yielding a heterogeneous solution containing a tan precipitate. The dibromotriphenylphosphorane was removed by nitrogen-pressurized Schlenk filtration (coarse frit), yielding a tan homogeneous solution containing the ylide.

Anion exchange with tetrafluoroborate resulted in a tan solution which contained the anion exchanged ylide in 90% as determined by ^{19}F NMR analysis.

Preparation of $[Ph_3P^+–C^-F–P^+R_3]Br^-$ in Methylene Chloride (R = Et, Bu, or Oc). A 25-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 4 mL of methylene chloride via syringe. To this solvent was added 2.3 mmol (dibromofluoromethyl)triphenylphosphonium bromide (1.2 g) via a solids addition tube. The flask and contents were cooled to <5 °C with an ice bath. To the cold solution was added 4.6 mmol of tri-*n*-alkylphosphine by syringe in a dropwise manner. The solution was stirred at 0 °C for 1 h and at room temperature for 3 h. The resulting homogeneous solution was light yellowish brown. The ^{19}F and ^{31}P NMR spectra revealed the formation of the mixed fluorinated phosphoranium salt in a 60–81% yield. Table II contains the ^{19}F, ^{13}C, and ^{31}P NMR data for the mixed ylide.

Reaction of $(o\text{-}MeOC_6H_4)_3P$ with $CFBr_3$. A 25-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 3 mmol (1.1 g) of tris(*o*-methoxyphenyl)phosphine and 3 mL of methylene chloride. The flask and contents were cooled to <5 °C with an ice bath. To the cold solution was added 1 mmol (0.3 g, 0.1 mL) of fluorotribromomethane by syringe in one portion. The solution was stirred at <5 °C for 1 h and at room temperature for 12 h, yielding a brown homogeneous solution. ^{19}F and ^{31}P NMR spectroscopy revealed the following doublets; ^{19}F NMR δ –60.2 (d, J(F,P) = 99 Hz), –63.8 (d, J(F,P) = 95 Hz); ^{31}P NMR δ 6.06 (d, J(P,F) = 97 Hz), 60.9 (d, J(P,F) = 97 Hz. One of these doublets corresponds to $[(o\text{-}MeO\text{-}C_6H_4)_3P^+–CFBr_2]Br^-$. The other doublet could correspond to a (dibromofluoromethyl)phosphonium salt where an aryl group has been modified by ether cleavage. Other bands in the NMR spectrum were identified as the reduced salt $[(o\text{-}MeOC_6H_4)_3P^+–CFBrH]Br^-$.

Reaction of $(o\text{-}MeC_6H_4)Ph_2P$ with $CFBr_3$. A 25-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 3 mmol (0.83 g) of *o*-tolyldiphenylphosphine and 3 mL of methylene chloride. The flask and contents were cooled to <5 °C with an ice bath. To the cold solution was added 1 mmol (0.3 g, 0.1 mL) of fluorotribromomethane by syringe in one portion. The solution was stirred at <5 °C for 1 h and at room temperature for 8 h, yielding a brown homogeneous solution. ^{19}F and ^{31}P NMR spectroscopy revealed the formation of $[(o\text{-}MeC_6H_4)Ph_2P^+–CFBr_2]Br^-$ (^{19}F NMR δ –75.3 (d); ^{31}P NMR δ 33.4 (d, J(P,F) = 74 Hz)) and $[(o\text{-}MeC_6H_4)\text{-}Ph_2P^+–CFHBr]Br^-$ (major) (^{19}F NMR δ –1.61 (d,d); ^{31}P NMR δ 26.1 (d, J(P,F) = 70 Hz, J(F,H) = 40 Hz)).

Reaction of $[Ph_3P^+–CFHBr]Br^-$ with Bu_3P in Methylene Chloride. A 25-mL three-neck flask equipped with a magnetic stirring bar, septum, and nitrogen tee was charged with 3 mL of methylene chloride via syringe. To this solvent was added 2.6 mmol (bromofluoromethyl)triphenylphosphonium bromide[28] (1.2 g) via a solids-addition tube. The flask and contents were cooled to <5 °C with an ice bath. To the solid solution was added 2.6 mmol (0.7 mL) of tri-*n*-butylphosphine by syringe in a dropwise manner. The resulting homogeneous brown solution was stirred at <5 °C for 1 h. ^{19}F and ^{31}P NMR spectroscopy revealed the formation of 40% $[Ph_3P^+–C^-F–P^+Bu_3]Br^-$ and 60% $[Ph_3P^+\text{-}CFH_2]Br^-$ relative to HFB.

Reaction of $[Bu_3P^+–C^-F–P^+Bu_3]Cl^-$ with H_2O. To an ice-cold reaction mixture containing 5 mmol of the title phospho-

ranium salt was added 5 mmol (0.9 g) of water via syringe. To the solution was added 1 mmol (0.19 g) of HFB. ^{19}F and ^{31}P NMR analyses were consistent with the presence of the fluoromethylene bis phosphonium salt. ^{19}F NMR spectroscopy revealed the quantitative formation of the reduced ylide relative to the internal standard hexafluorobenzene (HFB). Subsequent addition of excess water produced no change in the NMR spectra.

Formation of $[Bu_3P^+–CFH_2]Cl^-$. To the above reaction mixture containing the fluoromethylene bis phosphonium salt was added 10% NaOH until the reaction mixture was slightly basic (red litmus, indicator). The ^{19}F and ^{31}P NMR spectra were consistent with the fluoromethyl tri-*n*-butylphosphonium salt. ^{19}F NMR analyses revealed a 90–93% yield (based on methane) of the (fluoromethyl)phosphonium salt, relative to the internal standard HFB.

Reaction of $[Ph_3P^+–C^-F–P^+Ph_3]Br^-$ with HCl(g). Into an ice cold reaction mixture containing 5 mmol of the title phosphoranium salt was bubbled HCl(g) for several minutes. ^{19}F and ^{31}P NMR analyses were consistent with the proposed structure. ^{19}F NMR spectroscopy revealed the quantitative formation of the reduced ylide relative to the internal standard HFB. The fluoromethylene bis phosphonium salt was then treated with base as described below.

Reaction of $[Ph_3P^+–C^-F–P^+Ph_3]Br^-$ with H_2O. To an ice-cold reaction mixture containing 5 mmol of the title phosphoranium salt was added 5 mmol (0.9 g) of water via syringe, followed by 1 mmol (0.19 g) of HFB. ^{19}F and ^{31}P NMR analyses were consistent with the formation of fluoromethylene bis phosphonium salt. ^{19}F NMR spectroscopy revealed the quantitative formation of the reduced ylide relative to the internal standard hexafluorobenzene (HFB). Subsequent addition of excess water produced no change in the yield of bis phosphonium salt.

Formation of $[Ph_3P^+–CFH_2]X^-$. To the above reaction mixture containing the fluoromethylene bis phosphonium salt was added 10% NaOH until slightly basic, as determined by red litmus. ^{31}P NMR analysis was consistent with the (fluoromethyl)triphenylphosphonium salt. ^{19}F NMR analysis revealed a 90–92% yield (based on methane) of the (fluoromethyl)-phosphonium salt, relative to the internal standard HFB. To the NMR sample tube containing the (fluoromethyl)phosphonium salt was added an authentic sample of (fluoromethyl)phosphonium salt prepared by Greenlimb.[34] Only the ^{31}P and ^{19}F NMR signals which corresponded to the (fluoromethyl)phosphonium salt increased.

Reaction of $[Ph_3P^+–C^-F–P^+R_3]Br^-$ with HCl(g) (R = Et, Bu, or Oc). Into an ice-cold reaction mixture containing 3.7 mmol of the title mixed phosphoranium salt was bubbled HCl(g) for several minutes. ^{19}F and ^{31}P NMR analyses were consistent with the proposed structure. ^{19}F NMR spectroscopy revealed the quantitative formation of the reduced ylide relative to the internal standard HFB. The fluoromethylene bis phosphonium salt was then treated with base as described below.

Treatment of $[Ph_3P^+–CFH–P^+Bu_3]2X^-$ with 10% NaOH. To the above reaction mixture containing the title fluoromethylene bis phosphonium salt was added 10% NaOH until the reaction mixture was slightly basic (red litmus, indicator). ^{19}F NMR analysis revealed the formation of $[Ph_3P^+CFH_2]X^-$ and $[Bu_3P^+CFH_2]X^-$ in a ratio of 1:2.2 for a total yield of 90% (based on fluoromethylene bis phosphonium salt), relative to the internal standard HFB. To the NMR sample tube containing the above reaction mixture was added authentic (fluoromethyl)triphenylphosphonium salt prepared by Greenlimb.[34] Only the ^{31}P and ^{19}F NMR signals which corresponded to the reduced ylide increased.

Reaction of $[Ph_3P^+–C^-F–P^+Bu_3]Br^-$ with H_2O. To an ice-cold reaction mixture containing 3.7 mmol of the title mixed phosphoranium salt was added via syringe an excess of water. ^{19}F NMR analysis revealed the formation of a 1:1.8 mixture of (fluoromethyl)tri-*n*-butylphosphonium salt and (fluoromethyl)-triphenylphosphonium salt. ^{19}F NMR spectroscopy revealed the quantitative formation of the reduced salts (based on ylide), relative to the internal standard HFB.

Reaction of $[Bu_3P^+–O^-F–P^+Bu_3]Cl^-$ with Cl_2. To an ice-cold reaction mixture containing 15 mmol of the title phosphoranium salt was added chlorine gas via the dry ice/2-propanol condenser, until the solution turned to a light yellow, indicating the presence of a slight excess of elemental chlorine. The reaction mixture was stirred at room temperature for 1 h, followed by the addition of 1.7 mmol (0.3261 g) of HFB. ^{19}F and ^{31}P NMR analyses revealed the formation of the (dichlorofluoromethyl)phosphonium salt in >81% yield (based on methane), as determined by ^{19}F NMR spectroscopy, relative to HFB.

Hydrolysis of $[Bu_3P^+–CFCl_2]Cl^-$. Water was added to the NMR sample tube containing the above reaction mixture. ^{19}F NMR analysis indicated the formation of dichlorofluoromethane [δ −80.3 (d, J(H,F) = 54 Hz)] (47% ^{19}F NMR yield) and trichlorofluoromethane (53% ^{19}F NMR yield)—a product which resulted from the reaction of dichlorofluoromethide ion with excess elemental chlorine.

Reaction of $[Bu_3P^+–CFCl_2]Cl^-$ with Bu_3P. Tri-*n*-butylphosphine was added to an NMR sample tube which contained a fresh aliquot of the (dichlorofluoromethyl)phosphonium salt reaction mixture. ^{19}F and ^{31}P NMR analyses, after 1 h, revealed the re-formation of the fluorinated phosphoranium salt in 53% yield (based on methane), as determined by ^{19}F NMR analysis, relative to HFB. The (fluoromethyl)tri-*n*-butylphosphonium salt was present in a 45% yield as determined by ^{19}F NMR analysis.

Reaction of $[Bu_3P^+–C^-F–P^+Bu_3]Br^-$ with Br_2. An ice-cold reaction mixture containing 15 mmol of the title phosphoranium salt was charged with 33 mmol (5.3 g, 1.7 mL) of bromine. The reaction mixture was stirred at room temperature for 1 h, and then 2.2 mmol (0.4177 g) of HFB was added. ^{19}F and ^{31}P NMR analyses revealed the formation of the (dibromofluoromethyl)-phosphonium salt in >85% yield (based on methane), as determined by ^{19}F NMR spectroscopy, relative to HFB.

Hydrolysis of $[Bu_3P^+–CFBr_2]Br^-$. Water was added to the NMR sample tube containing an aliquot of the above reaction mixture. ^{19}F NMR analysis indicated the formation of dibromofluoromethane [δ −83.9 (d, J(H,F) = 51 Hz)] (54% yield, based on methane, ^{19}F NMR).

Reaction of $[Bu_3P^+–CFBr_2]Br^-$ with Bu_3P. Tri-*n*-butylphosphine was added to an NMR sample tube which contained a fresh aliquot of the (dibromofluoromethyl)phosphonium salt reaction mixture. ^{19}F and ^{31}P NMR analyses, after 1 h, revealed the re-formation of the fluorinated phosphoranium salt in 75% yield (based on methane), as determined by ^{19}F NMR analysis, relative to HFB.

Reaction of $[Ph_3P^+–C^-F–P^+Ph_3]Br^-$ with Br_2. An ice-cold reaction mixture containing 15 mmol of the title phosphoranium salt was slowly charged with 33 mmol (5.3 g, 1.7 mL) of bromine. The reaction mixture was stirred at room temperature for 1 h. ^{19}F and ^{13}P NMR analyses revealed the formation of the (dibromofluoromethyl)phosphonium salt. 1,2-Epoxybutane (15 mmol, 0.9 g) was added to the reaction mixture via syringe in one portion. The reaction mixture was stirred for 4 h. ^{31}P NMR analysis revealed that the dibromotriphenylphosphorane was slowly being converted into phosphine oxide. After 48 h the solid was isolated by nitrogen-pressurized Schlenk filtration (coarse frit) and dried in vacuo.

Into an NMR sample tube was placed 0.0647 g of the isolated solid along with 0.5 mL of methylene chloride and 0.04 mmol of benzotrifluoride (BTF). 75 μL of 5% NaOH was added via syringe. ^{19}F NMR analysis of the resulting homogeneous reaction mixture revealed the presence of dibromofluoromethane in a 40% yield relative to the internal standard BTF. It was extrapolated that the isolated solid was 40% (dibromofluoromethyl)triphenylphosphonium bromide.

Reaction of $[Ph_3P^+–C^-F–P^+Ph_3]BF_4^-$ with Cl_2. To an ice-cold reaction mixture containing 15 mmol of the title phosphoranium salt was added chlorine gas via a dry ice/2-propanol condenser until the solution turned light yellow, indicating the presence of a slight excess of elemental chlorine. The reaction mixture was stirred at room temperature for 1 h. To this mixture, 20 mmol (1.4 g, 1.7 mL) of 1,2-epoxybutane was added dropwise by syringe. The mixture was stirred for 4 h, and then 4 mmol (0.46 mL) of HFB was added by syringe in one portion. ^{19}F NMR analysis revealed the formation of (dichlorofluoromethyl)-phosphonium salt in 62% yield plus (bromochlorofluoromethyl)phosphonium salt in 32% yield (based on methane), relative to HFB.[35] Addition of diethyl ether precipitated a white solid. The solid was filtered via nitrogen-pressurized Schlenk filtration (coarse frit) to yield 6.3 g of the solid. ^{19}F and ^{31}P NMR

analyses revealed two sets of doublets in the ratio of 64:36, which were assigned to the (dichlorofluoromethyl)phosphonium salt and the (bromochlorofluoromethyl)phosphonium salt, respectively.

Reaction of $[Ph_3P^+-CFClX]Y^-$ with Ph_3P. Triphenylphosphine was added to an NMR sample tube which contained methylene chloride and a small amount of the solid which was isolated in the previous procedure. ^{19}F and ^{31}P NMR analyses, after 1 h, revealed the re-formation of the fluorinated phosphoranium salt.

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Registry No. 3 (X = Cl), 84195-43-7; 3 (X = BF_4), 111635-51-9; 8, 81962-38-1; 10, 111635-56-4; **12a** (X = Br), 111635-53-1; **12b** (X = Br), 111635-54-2; **12c** (X = Br), 111635-55-3; **15a** (X = Br), 88410-13-3; **15b** (X = BF_4), 111635-52-0; **15b** (X = Br), 88410-12-2; **17a** (X = Cl), 111635-58-6; **23** (X = BF_4), 111635-61-1; **24** (X = BF_4), 111689-14-6; **25a**, 111635-57-5; **25b**, 111635-59-7; $[Et_3P^+C^-FP^+Et_3]Cl^-$, 111635-49-5; $[Ph_3{}^+PC^-FHBr]Br^-$, 111635-62-2; $CFCl_3$, 75-69-4; $CFBr_3$, 353-54-8; Bu_3P, 998-40-3; Ph_3P, 603-35-0; $(o\text{-}MeOC_6H_4)_3P$, 4731-65-1; $(o\text{-}MeC_6H_4)Ph_2P$, 5931-53-3; $[(o\text{-}MeOC_6H_4)_3P^+CFBr_2]Br^-$, 111902-72-8; $[(o\text{-}MeOC_6H_4)_3P^+CHFBr]Br^-$, 111902-73-9; $[(Ph_3P^+CFH_2]Br^-$, 111902-74-0; $[(Bu_3P^+CHFP^+Bu_3]Cl^-OH^-$, 111902-75-1; $[(Ph_3P^+CHFP^+Ph_3]Br^-Cl^-$, 111902-76-2; $[Ph_3P^+CHFP^+Et_3]Br^-Cl^-$, 111902-77-3; $[Ph_3P^+CHFP^+Bu_3]Br^-Cl^-$, 111902-78-4; $[Ph_3P^+CHFP^+Oc_3]Br^-Cl^-$, 111902-79-5; $[Ph_3P^+CHFP^+Ph_3]Br^-OH^-$, 111902-80-8.

Supplementary Material Available: Spectroscopic data for the compounds described in the Experimental Section (5 pages). Ordering information is given on any current masthead page.

4*H*-Pyran and Pyrylium Hemispherands: Partly Preorganized Ionophores with Reactive Molecular Cavities

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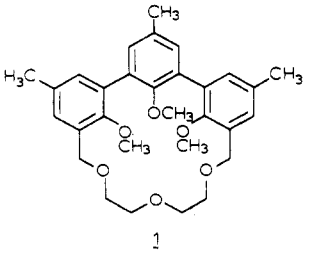
The synthesis and reactivity of a 2,6-diaryl-substituted pyrylium cation incorporated in an 18-membered macrocycle (**3a,b**) has been studied. Hemispherands with a central pyridine (**4a,b**) and with alkyl- or phenyl-substituted pyridinium ions (**5a,b**) were obtained by reaction with ammonium acetate or primary amines. The reactivity of the pyrylium 4-methyl group was demonstrated by converting **3b** into the corresponding 4-methylenepyran derivative **6** or novel pyrylium hemispherands **3c,d**. The pyrylium hemispherands **3a,b** were prepared through the 4*H*-pyran hemispherands **2a,b** in a linear synthesis starting from **7a,b**. The stable bis(hydroxymethyl) derivative **12b** gave the hemispherand **3b** in 65% yield. The X-ray crystal structures of the sodium picrate complexes of **1**, **2b**, and **4c** have been determined and compared with the crystal structures of the free ligands (**1**, **4c**). These structures reveal that the conformational changes upon complexation are reflected in the binding free energies ($-\Delta G°$) of the hemispherands with alkali picrates, measured via two-phase partition ($H_2O/CDCl_3$).

Introduction

Host–guest chemistry can be based on two major principles, viz. complementarity between host and guest and preorganization of the host. Good examples of the complementarity principle are the complexes of uronium (urea)[1] and guanidinium[2] cations with 27–30-membered crown ethers. The preorganization approach has been demonstrated by the complexation of alkali and ammonium cations by the fully preorganized spherands.[3] Molecular cavities of synthetic hosts can also be *partially* organized prior to complexation, e.g., by incorporating meta-coupled anisyl units[4] or anisyl units in combination with cyclic urea units.[5] Molecular models of these hemispherands, the prototype of which is **1**, show that the



1

electron pairs of the anisyl oxygen atoms must converge onto the cavity, and this will cause a substantial O–O repulsion. Besides, the cavity is partly deshielded from solvent molecules by the diverging oxygen methyl groups. Contrarily, the bridging poly(ethylene glycol) is conformationally rather mobile. These hemispherands appeared to be attractive molecules for a systematic study of the effect of preorganization on the structure-binding relationship with alkali and ammonium cations[5] and with neutral molecules, e.g., malononitrile.[6] Studies with hemispherands in which the central anisyl unit of **1** has been substituted for methoxycyclohexane,[7] pyridine, or a

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