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Synthetic and mechanistic aspects of the reactions between bromodifluoromethyltriphenylphosphonium bromide and dibromofluoromethyltriphenylphosphonium bromide and trialkylphosphites

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Dedicated to Professor Dennis Curran.

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ABSTRACT

Bromofluoromethyltriphenylphosphonium bromides react with trialkylphosphites in two distinct ways. Bromodifluoromethyltriphenylphosphonium bromide undergoes a rapid exchange reaction with trialkylphosphites to give the corresponding bromodifluoromethylphosphonates in good to excellent yields. A similar exchange reaction also occurred with an analogous diethoxyphenylphosphonite to give the corresponding ethoxyphenylphosphinate. Mechanistically, the exchange process involves the formation of difluorocarbene *via* dissociation of the intermediate difluoromethylene ylide, capture of the difluorocarbene by the trialkylphosphite to give $[(RO)_3\overset{+}{P}\overset{-}{C}F_2]$, which captures bromine followed by dealkylation to the product, bromodifluoromethylphosphonate. The equilibria involved in the multi-step mechanism are all shifted to the phosphonate product by the final dealkylation step. In contrast, the dibromofluoromethyltriphenylphosphonium bromide does not under exchange reactions with trialkylphosphite. The phosphite serves as a halophilic reagent to abstract Br from the dibromofluoromethylphosphonium salt to generate the bromofluoromethylene ylide, which can easily be trapped *in situ* with aldehydes or ketones to give good yields of the *E*/*Z*-bromofluoroalkenes. No dissociation of the bromofluoromethylene ylide was observed.

1. Introduction

The preparation of difluoromethylene ylides *via* the reaction of tertiary phosphines and dibromodifluoromethane is a well-established reaction, and when this reaction is carried out in the presence of an aldehyde or ketone the resultant Wittig reaction produces the 1,1-difluoroalkene [1].

$$2R_3P: + CF_2Br_2 + >C{=}O \rightarrow >{=}CF_2 + R_3PO + R_3PBr_2 \quad (1)$$

Mechanistic studies suggest that the intermediate phosphonium salt is not formed by an S_N2 process but involves difluorocarbene as an intermediate (Eq. (2)) [1,2]. Subsequent halophilic attack on the intermediate phosphonium salt generates the difluoromethylene

$$R_3P: + CF_2Br_2 \longrightarrow [\overset{+}{R_3P}Br][CF_2Br]^-$$

$$[CF_2Br]^- \longrightarrow :CF_2 + Br^-$$

$$R_3P: + :CF_2 \rightleftharpoons [\overset{+}{R_3P}\text{-}\overset{-}{C}F_2] \quad (2)$$

$$[\overset{+}{R_3P}\text{-}\overset{-}{C}F_2] + [\overset{+}{R_3P}Br] \longrightarrow [\overset{+}{R_3P}CF_2Br] + R_3P:$$

$$\text{overall Rx: } R_3P: + CF_2Br_2 \longrightarrow [\overset{+}{R_3P}CF_2Br]Br^-$$

ylide and the dibromophosphorane (Eq. (3))[1]. The intermediate difluoromethylene ylide is

$$[\overset{+}{R_3P}CF_2Br]Br^- + R_3P: \rightleftharpoons [\overset{+}{R_3P}\overset{-}{C}F_2] + R_3PBr_2 \quad (3)$$

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unstable and rapidly dissociates into difluorocarbene and tertiary phosphine (Eq. (4))[1,2]. Thus when an isolated phosphonium salt is reacted with a *different* tertiary phosphine, the

$$[R_3\overset{+}{P}\overset{-}{C}F_2] \rightleftharpoons R_3P: + [:CF_2] \quad (4)$$

difluorocarbene can be captured by either tertiary phosphine to give a mixture of bromodifluoromethylphosphonium salts (Eq. (5)) [1,3]. The percentage of the two bromodifluoromethylphosphonium salts varies with the nucleophilicity of the tertiary phosphines, solvent and temperature [2,3]. When a bromodifluoromethyltrialkylphosphonium salt is reacted with an identical tertiary trialkylphosphine that is part of the phosphonium salt, the

$$[Ph_3\overset{+}{P}CF_2Br]Br^- + (p\text{-}CH_3C_6H_4)_3P: \underset{70\,^\circ C,\ 48\ h}{\overset{\text{triglyme}}{\rightleftharpoons}} [Ph_3\overset{+}{P}CF_2Br]Br^- + [p\text{-}CH_3C_6H_4)_3\overset{+}{P}CF_2Br_2]Br^- \quad (5)$$

7% 93%

exchange reaction is an invisible reaction and generates no new products. However, the intermediate difluoromethylene ylide could also attack the intermediate bromotrialkylphosphonium cation to produce a bisphosphonium salt (Eq. (6)) [1,4]. This bisphosphonium salt formation is unique for trialkylphosphine derivatives. When the corresponding triarylphosphonium salts, $(Ar_3\overset{+}{P}CF_2Br)Br^-$, and trisdimethylaminophosphonium salts $[(Me_2N)_3\overset{+}{P}CF_2Br]Br^-$.

$$[Bu_3\overset{+}{P}CF_2Br]Br^- + Bu_3P: \longrightarrow [Bu_3\overset{+}{P}\overset{-}{C}F_2] + [Bu_3\overset{+}{P}Br]Br^- \longrightarrow [Bu_3\overset{+}{P}CF_2\overset{+}{P}Bu_3]2Br^- \quad (6)$$

86%

were utilized, no *stable* bisphosphonium salt formation was observed [4]. When fluorotrihalomethanes, such as $CFCl_3$ and $CFBr_3$, are employed in reactions with trialkylphosphines, the intermediate bisphosphonium salt can react further to give fluorine-containing phosphoranium salts (Eq. (7)) [4,5–7]. Thus, a wide variety of reactions are possible for the reaction of tertiary phosphines with fluorohalomethanes.

$$Bu_3P: + CFBr_3 \xrightarrow[RT]{CH_2Cl_2} [Bu_3\overset{+}{P}CFBr\overset{+}{P}Bu_3]2Br^- \xrightarrow{Bu_3P} [Bu_3\overset{+}{P}\overset{-}{C}F\overset{+}{P}Bu_3]Br^- + Bu_3PBr_2 \quad (7)$$

92%

2. Results and discussion

2.1. Reaction of bromodifluoromethyltriphenylphosphonium salts with trialkylphosphites

Our initial goals in this research were to determine: (1) if trialkylphosphites could undergo exchange reactions with bromodifluoromethyltriarylphosphonium salts and would the phosphite compete with the triarylphosphine (from dissociation of the difluoromethylene ylide; (2) would the intermediate (from halophilic attack on the phosphonium) salt undergo substitution of bromide ion to produce a mixed phosphonium–phosphonate product.

Bromodifluoromethyltriphenylphosphonium bromide (**1**) is known to react with potassium fluoride to produce difluorocarbene [8]. Thus, in an attempt to demonstrate that triethylphosphite (**2**) was capable of intercepting [:CF_2], a small scale exploratory reaction between (**1**), KF, and (**2**) was carried out in triglyme at room temperature in the presence of an equivalent amount of tetramethylethylene (TME) (Eq. (8)). The major product was observed to be bromodifluoromethylphosphonate (**3**) in 74% yield (^{19}F vs. $PhCF_3$). Traces of the

$$[Ph_3\overset{+}{P}CF_2Br]Br^- + KF + (EtO)_3P + \text{TME} \xrightarrow[RT]{\text{triglyme}} (EtO)_2P(O)CF_2Br \quad (8)$$

(**1**) (**2**) (**3**)

(74% ^{19}F NMR yield)

difluoromethylphosphonate, $(EtO)_2P(O)CF_2H$, as well as 1,1-difluorotetramethylcyclopropane, were also detected. Surprisingly, no ^{19}F NMR signals were observed for the expected by-product, Ph_3PF_2. Thin layer chromatography of the reaction mixture (50% $CHCl_3$, hexane) revealed a component in the mixture with an identical R_f value to Ph_3P. The ^{31}P NMR spectrum of the reaction mixture also showed a singlet, $\delta = 5.98$, which agreed well with the reported chemical shift of Ph_3P [Lit. $\delta = 5.9$] [9].

Hydrolysis of (**1**) is also known to proceed *via* a difluorocarbene intermediate [10]. Therefore, we attempted the reaction of (**1**), (**2**) and H_2O in triglyme at room temperature. The **only** product observed in the ^{19}F NMR spectrum of the reaction mixture was CF_2BrH arising from the reaction between (**1**) and H_2O above. Since; reactions in triglyme were heterogenous, the above reaction was repeated in $CHCl_3$ in which (**1**) is entirely soluble. The addition of (**2**) to the solution of (**1**) in $CHCl_3$ caused an exothermic reaction. The addition of H_2O to this reaction mixture had no effect, since the exchange reaction had *already* occurred (Eq. (9)). Since the exchange product (**3**) was formed in both reactions described above in Eqs. (8) and (9)

$$(\mathbf{1}) + (\mathbf{2}) \xrightarrow[RT]{CHCl_3} \underset{48\%(^{19}F)}{(\mathbf{3})} \xrightarrow{H_2O} \text{no change} \quad (9)$$

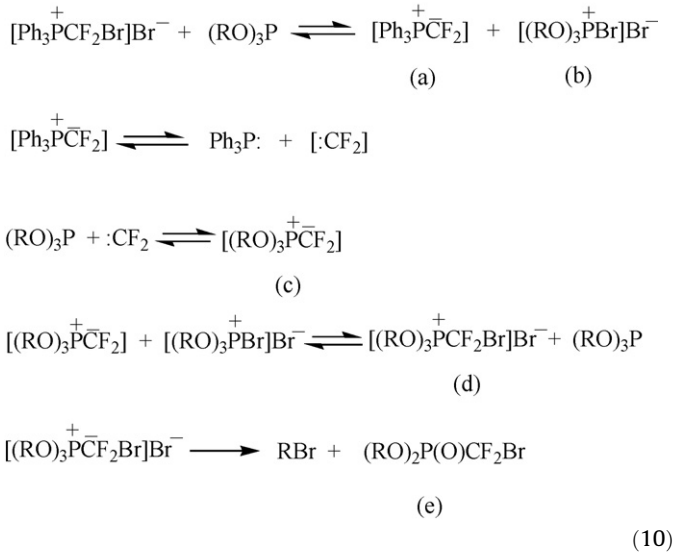
it was obvious that neither KF nor H_2O actually participated in the exchange reaction. It was also obvious that no equilibrium reaction, similar to that described in Eq. (5), had occurred since no (**1**) was detected at the completion of these reactions.

In order to determine the best reaction conditions to afford the exchanged phosphonate (**2**), the reaction between (**1**) and (**2**) was carried out in several solvents. The yields of (**3**) ranged from moderate (32% CH_3CN), (48% $CHCl_3$), (54% DMF) to excellent (92% CH_2Cl_2). In triglyme, the reaction was very slow in the absence of adequate mixing. The lower yields in $CHCl_3$, CH_3CN and DMF can be ascribed to the formation of $[Ph_3\overset{+}{P}CF_2H]Br^-$, which was observed spectroscopically as a major by-product in these solvents and which most likely is formed by protonation of the intermediate ylide.

In order to evaluate the potential scope of this exchange process, (**1**) was reacted with a variety of trialkylphosphites in CH_2Cl_2 at room temperature. These results are summarized in Table 1.

The exchange product from the reaction with trimethylphosphite (entry 1) reacts further (dealkylation) with the co-product to give the phosphonium–phosphonate salt. The products from reaction with *n*-Bu, and *i*-Bu phosphonates (entries 4 and 5) were identified spectroscopically by comparison with the bromodifluoromethylphosphonates previously prepared in this laboratory *via* the Michaelis–Arbuzov reaction [11]. Triphenylphosphite (entry 8) did not react with (**1**) at room temperature. When the triphenylphosphite reaction was heated at reflux, several minor products were observed in the ^{19}F NMR spectrum of the reaction mixture; however, none of them were the desired diphenylbromodifluoromethylphosphonate. A surprising result was obtained with $(ClCH_2CH_2O)_3P$ (entry 6). This phosphite is inert under the Michaelis–Arbuzov conditions [11]; however, in the exchange process, the ^{19}F NMR spectroscopic data indicated that the exchange reaction had afforded the bromodifluoromethylphosphonate. When diethylphenylphosphonite (entry 7) was employed in the exchange reaction, a 79% (^{19}F NMR yield vs. $PhCF_3$) of ethylphenyl bromodifluoromethylphosphinate was produced. The spectroscopic properties of the phosphinate were identical to a sample previously prepared from diethylphenylphosphonite and CF_2Br_2 [12].

Mechanistically, the following explanation is the most plausible to explain the exchange reaction (Eq. (10)). Halophilic attack on the phosphonium salt by the phosphite generates the

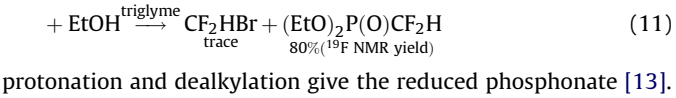


(10)

phosphonium ylide (a) and bromotrialkoxyphosphonium bromide (b). Dissociation of the ylide produces tertiary phosphine and difluorocarbene, which is subsequently captured by either the tertiary phosphine (reverse reaction) or the phosphite. The phosphite trapped intermediate (c) abstracts bromine from (b) to afford the bromodifluoromethyltrialkoxyphosphonium bromide (d), which on dealkylation provides the bromodifluoromethylphosphonate (e). Mechanistically, the process is similar to the exchange of the bromodifluoromethyl group between bromodifluoromethyltriarylphosphonium bromide and tertiary phosphines (Eq. (5), Ref. [2]). However, one major difference is that the dealkylation reaction of $[(RO)_3\overset{+}{P}CF_2Br]Br^-$ is an irreversible process and shifts all equilibria to the formation of the bromodifluoromethylphosphonate. Thus, the *only* bromodifluoromethyl product of the exchange process is the phosphonate.

A similar mechanism occurs with dialkoxyphenylphosphonites to give the corresponding alkoxyphenylphosphinate. Likewise the expected reaction of $[Ph_3\overset{+}{P}CF_2I]I^-$ with $(EtO)_3P$ in CH_2Cl_2 gave a 60% ^{19}F NMR yield of $(EtO)_2P(O)CF_2I$.

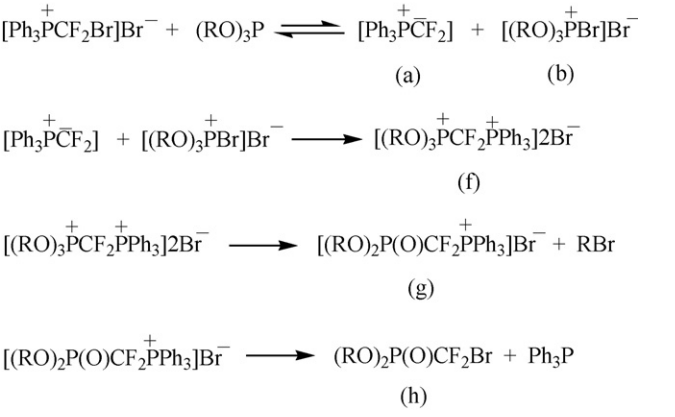
Ethanol reacts with (**1**) to extrude [:CF_2] (similar to the reaction of (**1**) with H_2O [10]) and affords CF_2HBr and the product of carbene insertion, $CH_3CH_2OCF_2H$ in a 74/26 ratio [4]. When the reaction between (**1**) and (**2**) is carried out in triglyme containing ethanol, the only observed products (detected by ^{19}F NMR) were CF_2HBr (trace) and $(EtO)_2P(O)CF_2H$ (Eq. (11)). This result is a clear indication that (**2**) has successfully trapped [:CF_2] to give $[(RO)_3\overset{+}{P}CF_2]$, which on



(11)

protonation and dealkylation give the reduced phosphonate [13].

An alternative mechanism for the exchange process is outlined below (Eq. (12)). The



(12)

Table 1
Exchange reaction of (**1**) with trialkylphosphites

$[Ph_3\overset{+}{P}CF_2Br]Br^-_{(1)} + (RO)\ 3P_{(2)} \xrightarrow[RT]{CH_2Cl_2} (RO)_2P(O)CF_2Br_{(3)}$

Entry	R	% Yield[a]
1	CH_3	60[b]
2	C_2H_5	92 (67)
3	*i*-Pr	85 (68)
4	*n*-Bu	86
5	*i*-Bu	94
6	CH_2ClCH_2	61
7	$PhP(OEt)_2$	79[c]
8	Ph	No Rx.

[a] ^{19}F NMR yield vs. $PhCF_3$ internal standard, values in parentheses are isolated yield based on phosphite.
[b] Product reacts further to give $[Ph_3\overset{+}{P}CH_3][\bar{O}_2P(OCH_3)(CF_2Br)]$ as the observed dealkylation product.
[c] Product is the phosphinate $PhP(O)OEt(CF_2Br)$.

initially formed ylide (step 1, identical to step 1 in Eq. (10)) could conceivably react with the trialkoxyphosphonium cation to generate a bisphosphonium salt (f) (step 2), which on dealkylation (step 3) would afford the phosphonium phosphonate salt (g). The last step (step 4) would be a second attack by bromide on the difluoromethylene carbon of (g) with the elimination of triphenylphosphine. This mechanistic sequence is considered unlikely for the following reasons: (1) we have studied in detail the attack at various sites of $(RO)_2P(O)CF_2Br$ compounds [12]. The only position that was inert to attack by a variety of reagents and nucleophiles was the difluoromethylene carbon; (2) all attempts in this work to produce a mixed salt of the type, $[Ph_3\overset{+}{P}CF_2P(O)(OEt)_2]Br^-$ were unsuccessful; and (3) Kesling [4] was successful in generating (in solution) the mixed salt, $[Bu_3\overset{+}{P}CF_2P(O)(OEt)_2]Br^-$, *via* the reaction between $[Bu_3\overset{+}{P}CF_2Br]Br^-$ and $(EtO)_3P$ [14]. This bis salt is very stable and there was no evidence that it decomposed to Bu_3P and the phosphonate. Although the triphenyl analog has not yet been prepared, it seems unlikely that its behavior would be significantly different from the tributyl bisphosphonium phosphonate in this respect. Thus, we feel that this alternative mechanistic interpretation is less plausible than the mechanism outlined in Eq. (10).

2.2. Reaction of dibromofluoromethyltriphenylphosphonium salts with trialkylphosphites

The hydrolysis of $[Ph_3\overset{+}{P}CF_2Br]Br^-$ and $[Ph_3\overset{+}{P}CFBr_2]Br^-$ with H_2O are significantly different. Hydrolysis of the bromodifluoromethyl salt in the presence of a radioactive isotope of bromide or sodium iodide gave unequivocal evidence that the mechanism for this reaction proceeds through a difluorocarbene intermediate [10]. On the other hand, hydrolysis of the dibromofluoromethyl salt in the presence of a radioactive isotope of bromide gave evidence that the mechanism of this reaction proceeds *via* the dibromofluoromethide ion and *not via* a bromofluorocarbene intermediate [15]. Likewise, we have observed that difluoromethylene ylides readily dissociate into tertiary phosphine and difluorocarbene (Eq. (4), [2]), whereas the corresponding bromofluoromethylene ylide is more stable, and we have not observed any dissociation in our detailed investigations of this ylide. Thus, it was of interest to us to determine if a similar exchange reaction occurs when dibromofluoromethylphosphonium salts were reacted with trialkylphosphites.

When $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (**4**) was treated with triethylphosphite (**2**) in CH_2Cl_2, the phosphonium salt was rapidly consumed but only traces of fluorine containing products were detected by ^{19}F NMR analysis of the reaction mixture. When the same reaction was carried out in the presence of trifluoroacetophenone, (*E*)- and (*Z*)-2-phenyl-1-bromotetrafluoropropene were formed in excellent isolated yield (Eq. (13)) [16]. When the reaction between (**4**) and (**2**) was

$$\underset{(\mathbf{4})}{[Ph_3\overset{+}{P}CFBr_2]Br^-} + \underset{(\mathbf{2})}{(EtO)_3P} \longrightarrow [Ph_3\overset{+}{P}\overset{-}{C}FBr] + [(EtO)_3\overset{+}{P}Br]Br^-$$

$$[Ph_3\overset{+}{P}\overset{-}{C}FBr] + CF_3C(O)Ph \longrightarrow \underset{78\%}{PhC(CF_3)=CFBr}$$

$$E/Z = 55/45 \qquad (13)$$

carried out in the presence of TME, no bromofluorocyclopropane [17] was detected by ^{19}F NMR analysis of the reaction mixture. When (**4**) and (**2**) were reacted in the presence of CF_3CH_2OH, a 71% (^{19}F NMR yield) of the reduced phosphonium salt was produced (Eq. (14)).

$$(\mathbf{4}) + (\mathbf{2}) \xrightarrow{CF_3CH_2OH} \underset{71\%(^{19}F\ NMR)}{[Ph_3\overset{+}{P}CFHBr]Br^-} \qquad (14)$$

In this case the intermediate ylide was intercepted by the alcohol and protonated.

In order to test the generality of this route to bromofluoro olefins, a series of aldehydes and ketones were reacted with (**4**) and (**2**), and these results are summarized in Table 2. As noted in our earlier work [1,18,19] the fluorine-containing ketones were the most reactive substrates, and cyclopentanone gave mainly protonation of the ylide *via* the enol of the ketone. These reactions are clean, the solvent easily removed, and the products easily isolated. This alternative route to bromofluoroolefins compliments the earlier reported work [1].

Table 2
Synthesis of bromofluoroolefins by dehalogenation of (**4**) with (**2**)

$$\underset{(\mathbf{4})}{[Ph_3\overset{+}{P}CFBr_2]Br^-} + \underset{(\mathbf{2})}{(EtO)_3P} + RC(O)R' \xrightarrow{CH_2Cl_2} R(R')C=CFBr$$

R	R′	% Yield[a]	*Z*/*E*
Ph	CF_3	78	55/45
Ph	CF_3CF_2	58	38/62
Ph	CF_2Cl	75	51/49
Ph	H	54	45/55
Ph	CH_3	55	43/57
$-CH_2CH_2CH_2CH_2-$		17	–
$-(CH_2)_5-$		61	–

[a] Isolated yield based on the carbonyl component.

3. Experimental

3.1. General experimental procedures

The ^{19}F NMR spectra were recorded on a Varian HA-100 Spectrometer operated at 94.075 MHz in the HR (non-lock) mode. The ^{19}F NMR spectra were obtained as 10–15% (w/v) solutions of a pure compound in $CDCl_3$ or as aliquots of reaction mixtures vs. an internal standard of $CFCl_3$. Chemical shifts are reported in ppm upfield of $CFCl_3$. Spectra were internally calibrated by the audio side band technique. Quantitative measurements were carried out by integration relative to an internal standard ($C_6H_5CF_3$). Routine ^1H NMR spectra were obtained as 10–15% (w/v) solutions of a pure compound in $CDCl_3$ or, occasionally, as aliquots of reaction mixtures vs. an internal standard of TMS on a Varian A-60 analytical NMR spectrometer. Chemical shift values are reported in ppm downfield of TMS. ^{13}C NMR spectra were obtained as 15% (w/v) solutions in a suitable deuterated solvent (usually $CDCl_3$), which also provided the lock signal, on a Bruker HX-90E Spectrometer operated at 22.63 MHz vs. TMS as internal standard. In all cases, broad band proton decoupling was employed to simplify the spectra. Chemical shift values are reported in ppm downfield from TMS. ^{31}P NMR spectra were obtained as 15% (w/v) solutions of a pure compound in a suitable deuterated solvent (usually $CDCl_3$) which also provided the lock signal or approximately 50/50 mixtures of a reaction mixture. The ^{31}P NMR Spectra were obtained on a Bruker HX-90E Spectrometer operated at 36.435 MHz vs. 85% H_3PO_4 as the external standard. In most cases, broad band proton decoupling was employed to simplify the spectra. When P–H coupling information was desired, the instrument was operated in the gated decoupled mode which retained nearly the full NOE and still yielded accurate coupling data. Chemical shift values are reported in ppm vs. H_3PO_4. Mass spectra were obtained on a Hitachi-PerkinElmer RMU-6E Mass Spectrometer operated at 70 eV. Analytical GLC were carried out on either an F&M Dual

Column Gas Chromatograph Model 700, or when it was desired to collect a sample for mass spectral or C, H, N analysis on an F&M Dual Column Research Chromatograph Model 5750. Both instruments were equipped with TCD. The columns utilized in this work were as follows: column A was a 10 ft × 0.25 in. column packed with 20% (w/w) Carbowax 20 M on 80–100 mesh Chromosorb P. Column B was a 10 ft × 0.25 in. column packed with 20% (w/w) SE-30 on 80–100 mesh Chromosorb P. Column C was a 6 ft × 0.25 in. column packed with 5% (w/w) SE-30 on 80–100 mesh Chromosorb P. Infrared spectra were obtained as thin films between NaCl plates in the case of liquid samples or as KBr pellets for solid samples on a Beckman IR-20A Infrared Spectrometer. C, H, N analyses were carried out by service personnel of this department on a PerkinElmer 240 (automated) Elemental Analyzer. All melting points were obtained in capillaries on a Thomas–Hoover Unimelt apparatus and are uncorrected. All bp were determined during fractional distillation and are uncorrected.

Potassium fluoride (J.T. Baker, anhydrous) was dried at 250 °C/0.5 mm Hg for 18 h and stored in a desiccator. Alternatively, KF was placed in an evaporating dish and heated to ~450 °C with a Bunsen burner. After breaking up of the initial crust which formed, the finely divided salt was heated for 1 h at 450 °C and transferred to a weighed container while still hot. Triglyme (Ansul Ether 161) and other glymes were purified by distillation from a sodium benzophenone ketyl and stored in brown bottles over 4 Å molecular sieves. Diethyl ether was dried and stored over sodium wire in a brown bottle until used. Methylene chloride was refluxed overnight over P_2O_5, distilled at atmospheric pressure and stored in a brown bottle over 4 Å molecular sieves.

Trichlorofluoromethane (Freon 11) and dibromodifluoromethane (Freon 12B2) were obtained commercially and used as obtained. Trifluoroethanol was obtained commercially and stored over 4 Å molecular sieves. Trimethyl, triethyl, tributyl and triisobutyl phosphites were obtained from commercial vendors, distilled from sodium metal under vacuum and stored in brown bottles over 4 Å molecular sieves. Triisopropyl, triphenyl, and tris-2-chloroethyl phosphites were obtained commercially and used as obtained. Diethylphenylphosphonite was prepared from Et_3N, EtOH, and phenyldichlorophosphine in 59% yield (bp 70–73°/0.3 mm Hg) by the literature procedure. Tribromofluoromethane was prepared by the method of Birchall and Haszeldine [20] and stored in a refrigerator over copper wire. The salts, $[Ph_3\overset{+}{P}CF_2Br]Br^-$, $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $[Ph_3\overset{+}{P}CF_2H]Br^-$, and $[Ph_3\overset{+}{P}CF_2I]I^-$ were prepared by previously described methods from this laboratory [1]. The phosphonates employed for comparison purposes (spectroscopically) were prepared by the previously described method from this laboratory [11].

3.2. Solvent survey for the exchange reaction between $(EtO)_3P$ and $[Ph_3\overset{+}{P}CF_2Br]Br^-$

In these reactions, the phosphonium salt was placed into a weighed NMR tube, the appropriate solvent added and a stoichiometric amount of triethyl phosphite added *via* a syringe. The reaction with the phosphite was instantaneous in all solvents, except triglyme. The yields of the exchanged product, $(EtO)_2P(O)CF_2Br$ were determined by ^{19}F NMR vs. $PhCF_3$ internal standard. *Results*: (solvent, % yield $(EtO)_2P(O)CF_2Br$: $CHCl_3$ (48%), CH_3CN (32%), DMF (54%), CH_2Cl_2 (92%) [21], TG (slow).

3.3. Large scale exchange reaction between $[Ph_3\overset{+}{P}CF_2Br]Br^-$ and $(EtO)_3P$

Into an apparatus which was equipped for simple distillation was charged $[Ph_3\overset{+}{P}CF_2Br]Br^-$ (11.8 g, 0.025 mol) and 30 ml dry CH_2Cl_2. After the salt completely dissolved, $(EtO)_3P$ (4.15 g, 0.025 mol) was slowly syringed into the homogeneous solution. A very slight exotherm occurred and the solution assumed a light yellow–brown color. The reaction was complete after 10 min as shown by the total absence of the salt in the ^{19}F NMR spectrum of the reaction solution. The solution was distilled to remove most of the CH_2Cl_2 and ethyl bromide. The ^1H NMR of the distilled material showed a triplet, $\delta = 1.62$ and quartet, $\delta = 3.42$ for the EtBr, and these peaks were enhanced upon the addition of an authentic sample of EtBr to the NMR tube. The remaining solution was then distilled through a short path distillation apparatus to yield 4.45 g (67%) of $(EtO)_2P(O)CF_2Br$ (bp 67.5–69.5°/0.6 mm Hg). The residue remaining in the flask was recrystallized from methanol (35 ml) to yield 4.2 g (65%) of a solid identified as triphenylphosphine (mp 79–80°), mixed mp with authentic Ph_3P, 79–81 °C. The infrared spectrum of this solid material was identical to the reported spectrum for Ph_3P. Repetition of this reaction on a smaller scale afforded a yield (^{19}F NMR vs. $PhCF_3$) of 92%. The ^{19}F, ^{31}P, and ^{13}C NMR data for the $(EtO)_2P(O)CF_2Br$ prepared in this reaction was identical to the data for $(EtO)_2P(O)CF_2Br$ prepared *via* the Michaelis–Arbuzov method [11,12,22].

3.4. Preparation of $[(CH_3)_2CHO)]_2P(O)CF_2Br$

Similar to the procedure described in Section 3.3, $[Ph_3\overset{+}{P}CF_2Br]Br^-$ (14.2 g, 0.030 mol), 50 ml dry CH_2Cl_2 and 6.45 g $[(CH_3)_2CHO)_3P]$ (0.03 mol) gave (after distillation) 6.0 g (68% of $[(CH_3)_2CHO)]_2P(O)CF_2Br$ (bp 75°/2 mm Hg). An aliquot of the reaction mixture showed an 85% ^{19}F NMR yield (vs. $PhCF_3$) of the bromodifluoromethyldiisopropylphosphonate [23].

3.5. Small scale exchange reaction between $[Ph_3\overset{+}{P}CF_2Br]Br^-$ and $(RO)_3P$ (Table 1)

The small-scale exchange reactions cited in Table 1 were all NMR scale reactions and were carried out in an identical manner. The reaction with trimethyl phosphite will be described in detail as an illustrative example. The phosphonium salt, $[Ph_3\overset{+}{P}CF_2Br]Br^-$ (0.38 g, 0.0008 mol) was added to an NMR tube, then 0.5 ml dry CH_2Cl_2 was added to dissolve the phosphonium salt. To this solution was added $(MeO)_3P$ (0.1 g, 0.0008 mol). The addition of the phosphite caused precipitation of the salt which then rapidly dissolved to give a clear, yellow–brown solution. Benzotrifluoride (0.04 g, 0.00027 mol) was added and the ^{19}F NMR spectrum recorded. ^{19}F NMR (ppm): $d = -55.3$ (d, $^2J_{PF} = 67$ Hz), 60% ^{19}F NMR yield of $\left[Ph_3\overset{+}{P}CH_3\right]^-[O_2P(OMe)CF_2Br]$. The identity of this compound was confirmed by spiking the sample with a solution of the phosphonium–phosphonate salt in CH_2Cl_2 prepared by the reaction between $(MeO)_2P(O)CF_2Br$ [11] and Ph_3P. No new peaks were detected.

3.6. Reaction of $[Ph_3\overset{+}{P}CF_2Br]Br^-$ and $(ClCH_2CH_2O)_3P$

A 50 ml flask fitted with a condenser and glass tee was charged with $[Ph_3\overset{+}{P}CF_2Br]Br^-$ (2.7 g, 0.0057 mol), 20 ml CH_2Cl_2 and $(ClCH_2CH_2O)_3P$ (1.54 g, 0.0057 mol). The salt was soluble in CH_2Cl_2, and the addition of the phosphite had no visible effect. The solution was then heated to reflux overnight; then $PhCF_3$ (0.27 g, 0.0019 mol) was added as an internal standard. In addition to a small amount of reduced phosphonium salt, the only other fluorine-containing product detected in the ^{19}F NMR spectrum of the reaction mixture was a doublet at $\delta = -62.2$ ($^2J_{PF} = 96$ Hz) in 61% (^{19}F) yield consistent with the formation of $(ClCH_2CH_2O)_2P(O)CF_2Br$.

3.7. Reaction of $[Ph_3\overset{+}{P}CF_2Br]Br^-$, $(EtO)_3P$ and CH_3CH_2OH in triglyme

To a 5 mm NMR tube was added $[Ph_3\overset{+}{P}CF_2Br]Br^-$ (0.12 g, 0.00026 mol), triglyme (0.5 ml), $(EtO)_3P$ (0.0042 g, 0.00026 mol) and CH_3CH_2OH (0.034 g, 0.00077 mol). The NMR tube was allowed to stand, with occasional shaking, for 2 days, at the end of which time the solution was homogenous. $PhCF_3$ (0.025 g, 0.00017 mol) was added and the ^{19}F NMR spectrum showed a signal at $\delta = -136.4$ (dd) for $(EtO)_2P(O)CF_2H$ in 80% ^{19}F NMR yield; identical to the ^{19}F NMR spectrum of $(EtO)_2P(O)CF_2H$ previously prepared in this laboratory [12].

3.8. General procedure for the reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$ and $(EtO)_3P$ in presence of an aldehyde or ketone [24]

A 100 ml, 3-necked round bottom flask was equipped with a septum, constant pressure addition funnel and a glass tee leading to source of nitrogen and a mineral oil bubbler. The flask was charged with $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (15.9 g, 0.03 mol), dry CH_2Cl_2 (45 ml) and trifluoroacetophenone (5.22 g, 0.03 mol). The suspension was cooled in an ice bath; $(EtO)_3P$ (4.98 g, 003 mol) in 20 ml CH_2Cl_2 was then added dropwise slowly *via* the constant addition funnel. After the addition of $(EtO)_3P$ was completed, the homogeneous solution was examined by ^{19}F NMR and found to contain some unreacted ketone. Therefore, an additional 4 g (0.0075 mol) of the phosphonium salt was added to the solution and additional $(EtO)_3P$ (1.25 g, 0.0075 mol) in CH_2Cl_2 (5 ml) added dropwise to entirely consume the ketone. The solvent (CH_2Cl_2) was then distilled at atmospheric pressure. When most of the CH_2Cl_2 had been removed, water (20 ml) was added to the remaining reaction mixture, and the residue steam distilled; approximately 100 ml of distillate was collected. The aqueous layer was separated and extracted with 50 ml of ether. The organic layers were combined, washed with 5% NaOH (2× 15 ml) and H_2O (2× 50 ml) and dried over anhydrous $MgSO_4$. The ether was removed *via* rotary evaporation at reduced pressure and the residue distilled through a short path distillation apparatus to yield 6.3 g (78%, based on ketone) of (*E*)- and (*Z*)-1-bromo-2-phenyl-F-propene (bp 83.5°/42 mm Hg) *Z*/*E* = 55/45, ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -55.7$ (q, $^4J_{FF} = 13$ Hz, *Z* vinyl F); $\delta = -58.3$ (m, *E* vinyl F); $\delta = -59.8$ (overlap of CF_3 groups) ^1H NMR ($CDCl_3$) ppm: $\delta = 7.38$ (m). The ^{19}F NMR spectra were in agreement with those reported by Vander Haar [18,19].

3.8.1. Reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $(EtO)_3P$ and $CF_3CF_2C(O)C_6H_5$

In a similar manner (cf. 3.8) $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (19.9 g, 0.037 mol), $(EtO)_3P$ (6.23 g, 0.037 mol) and $CF_3CF_2C(O)C_6H_5$ (5.88 g, 0.03 mol) afforded 5.6 g (58% of (*E*)- and (*Z*)-1-bromo-2-phenyl-F-1-butene (bp 55–59°/5.5 mm Hg) *Z*/*E* = 38/62. ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -54.6$ (tq, $^4J_{FF} = 27$ Hz, $^5J_{FF} = 11$ Hz, (*E*)-vinyl F); $\delta = -83.9$ (dt, $^5J_{FF} = 12$ Hz, $^3J_{FF} = 3$ Hz, (*E*)-CF_3); $\delta = -109.6$ (dq, $^4J_{FF} = 27$ Hz, $^3J_{FF} = 3$ Hz, (*E*)-CF_2); $\delta = -46.0$ (t, $^4J_{FF} = 8$ Hz, (*Z*)-vinyl F); $\delta = -82.5$ (t, $^3J_{FF} = 3$ Hz, (*Z*)-CF_3); $\delta = -111.0$ (dq, $^4J_{FF} = 8$ Hz, $^3J_{FF} = 3$ Hz, (*Z*)-CF_2). This ^{19}F NMR data for these isomers was in good agreement to that reported by Vander Haar [18,19].

3.8.2. Reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $(EtO)_3P$ and $CF_2ClC(O)C_6H_5$

In a similar manner (cf. 3.8) $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (19.9 g, 0.037 mol), $(EtO)_3P$ (6.23 g, 0.037 mol) and $CF_2ClC(O)C_6H_5$ (5.72 g, 0.03 mol) afforded 6.4 g (75%) of (*E*)- and (*Z*)-1-bromo-2-phenyl-3-chloro-F-propene (bp 66–70°/2.2 mm Hg) *Z*/*E* = 51/49. The wash procedure in this case consisted of 5% NaOH (3× 40 ml) and H_2O (3× 50 ml). ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -46.5$ (d, $^4J_{FF} = 29$ Hz, (*E*)-CF_2Cl); $\delta = -46.7$ (d, $^4J_{FF} = 11$ Hz, (*Z*)-CF_2Cl); $\delta = -57.4$ (t, $^4J_{FF} = 29$ Hz, (*E*)-vinyl F); $\delta = -57.4$ (t, $^4J_{FF} = 11$ Hz, (*Z*)-vinyl F); ^1H NMR ($CDCl_3$) (ppm): $\delta = 7.41$ (s). This spectral data was in close agreement with the data for these isomers reported by Vander Haar [18,19].

3.8.3. Reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $(EtO)_3P$ and C_6H_5CHO

In a similar manner (cf. 3.8) $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (19.9 g, 0.037 mol), $(EtO)_3P$ (6.23 g, 0.037 mol) and C_6H_5CHO (3.18 g, 0.03 mol) in CH_2Cl_2 were reacted. The ^{19}F NMR spectrum after the addition of the phosphite still showed some unreacted phosphonium salt, so additional $(EtO)_3P$ (0.96 g, 0.006 mol) was added slowly *via* syringe to the reaction mixture. The phosphonium salt was completely consumed. The wash procedure in this case consisted of $NaHSO_3$ (40%, 2× 30 ml) and H_2O (2× 30 ml). The yield of (*E*)- and (*Z*)-1-bromo-1-fluoro-2-phenylethene was 3.25 g (54%) (bp 78–82°/8 mm Hg) *Z*/*E* = 45/55. ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -65.9$ (d, $^3J_{HF} = 15$ Hz, (*Z*)-F); $\delta = -68.4$ (d, $^3J_{HF} = 33$ Hz, (*E*)-F); ^1H NMR ($CDCl_3$) (ppm): $\delta = 5.97$ (d, $^3J_{HF} = 34$ Hz, (*E*)-H); $\delta = 6.66$ (d, $^3J_{HF} = 15$ Hz, (*Z*)-H); $\delta = 7.2$–7.6 (m). This spectral data was in good agreement with the data for this compound reported by Vander Haar [18,19].

3.8.4. Reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $(EtO)_3P$ and $CH_3C(O)C_6H_5$

In a similar manner (cf. 3.8) $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (19.9 g, 0.037 mol), $(EtO)_3P$ (6.23 g, 0.037 mol), and $CH_3C(O)C_6H_5$ (3.6 g, 0.03 mol) afforded a mixture of the (*E*)- and (*Z*)-isomer of (*E*)- and (*Z*)-1-bromo-1-fluoro-2-phenylpropene (3.53 g, 55%) and unreacted acetophenone (0.6 g, 17%); bp 55–64°/1.3 mm Hg). The wash procedure in this case consisted only of H_2O (3× 50 ml) *Z*/*E* = 43/57. ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -75.2$ (overlapping quartets, $^4J_{HF} = 3$ Hz, (*Z*)-F, $^4J_{HF} = 4$ Hz, (*E*)-F); ^1H NMR ($CDCl_3$) (ppm): $\delta = 2.06$ (δ, $^4J_{HF} = 4$ Hz, (*Z*)-CH_3), $\delta = 2.06$ (d, $^4J_{HF} = 3$ Hz, (*E*)-CH_3), $\delta = 7.36$ (s), $\delta = 2.57$ (CH_3, acetophenone). These values are in good agreement with those reported by Vander Haar [18,19].

3.8.5. Reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $(EtO)_3P$ and cyclopentanone

In a similar manner (cf. 3.8) $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (19.9 g, 0.037 mol), $(EtO)_3P$ (6.23 g, 0.037 mol), and cyclopentanone (2.52 g, 0.03 mol) were reacted in CH_2Cl_2. After complete addition of the phosphite some phosphonium salt still remained, so additional phosphite (0.97 g, 0.006 mol) was added to the reaction mixture to completely consume the phosphonium salt. The wash procedure in this case consisted of $NaHSO_3$ (40%, 3× 35 ml) and water. The yield of 1-bromo-1-fluoromethylenecyclopentane was 0.9 g (17%) bp 37.5–38.5°/8 mm Hg. ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -78.3$ (bs), lit. $\delta = -74.9$ (m) [19]. ^1H NMR ($CDCl_3$) (ppm): $\delta = 1.5$ and 2.0–2.5 (complex multiplets in 1:1 ratio; ^{13}C NMR ($CDCl_3$) (ppm): $\delta = 26.1$ (s), 27.4 (s), 29.2 (s), 31.6 (s)—ring carbon and $\delta = 124.8$ (d, $^1J_{CF} = 312$ Hz, $\underline{C}FBr$), $\delta = 123.9$ (d, $^2J_{CF} = 13$ Hz, $\underline{C} = CFBr$); IR: 5.91 μm (C=C), lit. 5.98 μm [19]. This olefin is unstable and decomposes on standing.

3.8.6. Reaction of $[Ph_3\overset{+}{P}CFBr_2]Br^-$, $(EtO)_3P$ and cyclohexanone

In a similar manner (cf. 3.8) $[Ph_3\overset{+}{P}CFBr_2]Br^-$ (26.6 g, 0.05 mol), $(EtO)_3P$ (8.31 g, 0.05 mol) and cyclohexanone (3.92 g, 0.04 mol) afforded 4.7 g (61%) of 1-bromo-1-fluoromethylenecyclohexane (bp 61.5–63.5°/12 mm Hg). The wash procedure consisted of $NaHSO_3$ (40% 3× 35 ml) and water. ^{19}F NMR ($CDCl_3$) (ppm): $\delta = -82.6$ (bs); ^1H NMR ($CDCl_3$) (ppm): $\delta = 1.4$–1.6 and 1.9–2.4 (broad singlets, ratio 6:4); IR: 5.97 μm (C=C), mass spectrum (*m*/*e*, relative intensity): 194 (22), 192 (26), 153 (26), 151 (29), 113 (53), 94 (43), 68 (100), 41 (32), 39 (48).

4. Conclusions

Bromofluoromethylphenylphosphonium halides react with trialkylphosphites in two distinct ways. Bromodifluoromethyltriphenylphosphonium halides undergo a rapid exchange reaction with trialkylphosphites to give the corresponding bromodifluoromethylphosphonates. A similar exchange reaction also occurred

with an analogous dialkoxyphenylphosphonite. Mechanistically, the exchange process involves formation of difluorocarbene *via* dissociation of the intermediate difluoromethylene ylide, capture of the difluorocarbene by the trialkylphosphite to give $[(RO)_3\overline{P}CF_2]$, which captures bromine followed by dealkylation to produce the bromodifluoromethylphosphonate. The equilibria involved in the multi-step mechanism are all shifted to the phosphonate product by the final dealkylation step. This method provides a rapid clean entry to bromodifluoromethylphosphonates or phosphinates from a common intermediate. The yields are equal or better than the Michaelis–Arbuzov methodology [18] and the reaction is especially useful for volatile phosphites due to the mild reaction conditions (RT). In contrast to the bromodifluoromethylphosphonium salt, dibromofluoromethyltriphenylphosphonium bromide does not undergo exchange reactions with trialkylphosphites. The phosphite serves as a halophilic reagent to abstract Br from the dibromofluoromethylphosphonium salt to generate the bromofluoromethylene ylide, which can easily be trapped with aldehhydes or ketones *in situ* to give *E*/*Z*-bromofluoroalkenes. This approach gives yields as good or better than those from $R_3P/CFBr_3$ or metal dehalogenation of dibromofluoromethylphosphonium salts [1,18,19]. It also avoids the formation of R_3PBr_2 as a by-product, which can react with aldehyde substrates to decrease the yield of the bromofluoroolefin. It also works well with ketones, such as $C_6H_5C(O)CF_2Cl$, which reacts readily with Zn or Zn/Cu, again lowering the yield of the olefinic product.

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