THE JOURNAL OF Organic Chemistry

VOLUME 48, NUMBER 7 APRIL 8, 1983

Ylide–Carbene Chemistry. Synthesis of 1,1-Difluoro-1-alkenes[1]

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Received June 29, 1982

The reaction between nonstabilized alkylidenetriphenylphosphoranes and chlorodifluoromethane has been found to be a useful alternative to the Wittig reaction for the synthesis of many difluoromethylene olefins. Both primary and secondary ylides which do not contain strongly electron-withdrawing substituents within the alkylidene portion of the ylide react with chlorodifluoromethane to give the corresponding difluoromethylene olefins in yields which are significantly better than those obtained by the Wittig reaction. The formation of triphenylphosphine oxide is avoided, and all phosphorus-containing moieties can be recovered and recycled. The reaction proceeds by initial dehydrochlorination of chlorodifluoromethane by the ylide to generate difluorocarbene. The intermediate difluorocarbene is then trapped by a second equivalent of the nucleophilic ylide. Mechanistic evidence indicates that either a zwitterionic intermediate or a three-membered cyclic phosphorane can account for the 1,1-difluoro-1-alkene products. The isolation of several 1-hydro-1-fluoro-1-alkene products such as FCH=CHPh, $FHC=CPh_2$, and FHC=CHCH=CHPh after steam distillation of the reaction mixtures, however, can only be accounted for via a three-membered cyclic phosphorane.

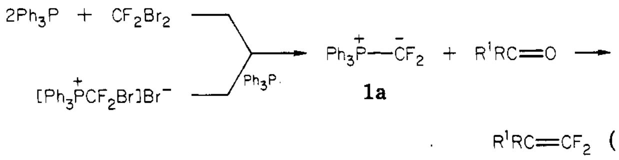
Within the past 2 decades the use of the Wittig reaction for the preparation of fluorinated olefins has been an area of great interest to many researchers. Great advances have been made during the last decade in the utilization of the Wittig reaction for the preparation of terminal *gem*-difluoromethylene olefins via difluoromethylene ylides.

The first synthetically useful preparation of a difluoromethylene ylide involved the reaction of triphenylphosphine and sodium chlorodifluoroacetate in the presence of aldehydes to yield the corresponding difluoromethylene olefins and triphenylphosphine oxide[2] (eq 1). This reaction was later extended to the use of polyfluorinated ketones.[3] While the use of nonactivated ketones was unsuccessful with triphenylphosphine, substitution of triphenylphosphine by tri-*n*-butylphosphine resulted in moderate to good yields of β-substituted difluoromethylene olefins from nonfluorinated ketones.[4]

$$Ph_3P + ClCF_2CO_2^-Na^+ + RCOR' \rightarrow RCR'{=}CF_2 + Ph_3PO \quad (1)$$

$$R = \text{alkyl, aryl};\ R' = H \text{ or } R_f$$

More recently, Naae and Burton[5] have reported that (difluoromethylene)triphenylphosphorane (**1a**) may be generated either in situ by reaction of 2 equiv of triphenylphosphine with 1 equiv of dibromodifluoromethane or by debromination of (bromodifluoromethyl)triphenylphosphonium bromide with triphenylphosphine (eq 2).



(2)

Ylide **1a** reacts with both aldehydes and fluorinated ketones to give difluoromethylene olefins in good to excellent yields. Substitution of tris(dimethylamino)phosphine for triphenylphosphine in the above scheme allowed this method to be extended to the use of nonfluorinated ketones.[5,6] Debromination of (bromodifluoromethyl)phosphonium bromides by group 2B metals in the presence of aldehydes and fluorinated ketones has been demonstrated to give good yields of difluoromethylene olefins.[6,7]

Use of the Wittig reaction for the preparation of terminal difluoromethylene olefins has certain inherent disadvantages. The major disadvantage of the Wittig reaction

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(1) (a) Taken in part from the Ph.D. Thesis of G.A.W., University of Iowa. (b) A preliminary report of this work has appeared: Wheaton, G. A.; Burton, D. J. *Tetrahedron Lett.* **1976**, 895. (c) For extensions of this work to organometallic derivatives see: Seyferth, D.; Wairsthon, K. R.; Linn, T. F. O.; Sepelak, D. J *J. Organomet. Chem.* **1981**, *205*, 301.

(2) Fugua, S. A.; Duncan, W. G.; Silverstein, R. M. *J. Org. Chem.* **1965**, *30*, 1027; *Tetrahedron Lett.* **1964**, 1461.

(3) See for example: (a) Burton, D. J.; Herkes, F. E. *J. Org. Chem.* **1967**, *32*, 1311. (b) Burton, D. J.; Herkes, F. E. *Tetrahedron Lett.* **1965**, 1883. (c) Barna, P. A. *Chem. Ind.* (*London*) **1966**, 2054.

(4) Fugua, S. A., Duncan, W. G.; Silverstein, R. M. *Tetrahedron Lett.* **1965**, 521; *J. Org. Chem.* **1965**, *30*, 2543.

(5) Naae, D. G.; Burton, D. J. *J. Fluorine Chem.* **1971**, *1*, 123; *Synth. Commun.* **1973**, *3*, 197.

(6) Naae, D. G. Ph.D. Thesis, University of Iowa.

(7) Kesling, H. S., Jr. Ph.D. Thesis, University of Iowa. Burton, D. J.; Kesling, H. S.; Naae, D. G. *J. Fluorine Chem.* **1981**, *18*, 293.

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for industrial or large-scale laboratory use of course is the consumption of the expensive tertiary phosphine via conversion to the phosphine oxide. Of more importance for small-scale laboratory olefin preparations, however, are side reactions involving the carbonyl substrates. Enolizable carbonyl compounds, especially ketones, are known to undergo condensation reactions in the presence of strongly basic ylides such as **1a** or **1b**, resulting in reduced yields of the desired olefins.[8] Generation of **1a** or its tris(dimethylamino) analogue (**1b**) by phosphine debromination of the (bromodifluoromethyl)phosphonium bromides results in the formation of dibromophosphoranes (**2**, eq 3).

$$[\mathrm{R_3\overset{+}{P}CF_2Br}]\mathrm{Br^-} + \mathrm{R_3P} \longrightarrow \underset{\substack{\mathbf{1a},\ \mathrm{R} = \\ \mathrm{Ph} \\ \mathrm{b},\ \mathrm{R} = \\ \mathrm{Me_2N}}}{\mathrm{R_3\overset{+}{P}\text{-}\overset{-}{C}F_2}} + \underset{\substack{\mathbf{2a},\ \mathrm{R} = \\ \mathrm{Ph} \\ \mathrm{b},\ \mathrm{R} = \\ \mathrm{Me_2N}}}{\mathrm{R_3PBr_2}} \qquad (3)$$

Some carbonyl compounds, especially aldehydes,[6,9] have been observed to react with dihalophosphoranes to yield the corresponding *gem*-dihaloalkanes and the corresponding tertiary phosphine oxide (eq 4). Maximum

$$\mathrm{R^1{}_3PX_2 + R^2CHO \rightarrow R^1{}_3PO + R^2CHX_2} \qquad (4)$$

$$\mathrm{X = Cl, Br;\ R = Ph, Me_2N}$$

utilization of the ylide may be realized by the use of an excess of the carbonyl compound; however, this often results in separation problems and is undesirable if the carbonyl compound is expensive or difficult to obtain. Generation of the ylides by metal debromination of the phosphonium bromides circumvents the problem of formation of **2** but results in a ylide species of reduced reactivity, which precludes reaction with all but the most activated carbonyl compounds such as fluorinated ketones.

Recently, reports of the formation of haloalkenes by the reaction of halocarbenes with nitrogen and phosphorus ylides have appeared in the literature. Reimlinger[10] obtained poor to good yields of halolalkenes from the reaction of halocarbenes with stable diazoalkanes, which may be considered one type of a nitrogen ylide. The applicability of this method, however, is very limited due to the inherent instability of most diazoalkanes. Oda and co-workers[11] have reported that halocarbenes are trapped by stabilized phosphonium ylides to yield the corresponding halo olefins and tertiary phosphines. While this method achieved only limited success insofar as olefin yields are concerned, it is significant that olefins were obtained without the formation of phosphine oxides.

It appeared that an approach of this type might solve the major limitation of the Wittig reaction for large-scale use if olefin yields could be improved and facile recovery of phosphine-containing materials could be attained. Both Reimlinger and Oda employed the haloform/base method for generation of the carbenes. This method produces additional side reactions and by products, complicating material recovery and requiring the use of large excesses of the haloform. We have investigated the possibility of using nonstabilized phosphonium ylides as bifunctional reagents in the reaction with chlorodifluoromethane, functioning first as a base to generate an intermediate difluorocarbene and second as a nucleophile to trap the intermediate difluorocarbene. We now report the results of our investigation.

Results and Discussion

We have found that nonstabilized alkylidene- and (arylalkylidene)triphenylphosphoranes, in which the negative charge on the ylidene carbon is not extensively delocalized by resonance or inductive effects, react readily with chlorodifluoromethane to give the corresponding 1,1-difluoro-1-alkenes according to eq 5. The yields of

$$\mathrm{2Ph_3P^+\text{-}^-CR^1R^2 + HCF_2Cl \rightarrow}$$
$$\mathrm{[Ph_3P^+CHR^1R^2]Cl^- + Ph_3P + F_2C{=}CR^1R^2} \qquad (5)$$

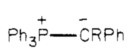
olefins obtained by this method range from modest to excellent, depending on the nature of the substituents R^1 and R^2. Both the coproducts, triphenylphosphine and the phosphonium salt, may be easily isolated in yields of ca. 90%.

In this investigation the ylides were pregenerated under a nitrogen atmosphere in aprotic solvents by treatment of a suspension of the corresponding triphenylphosphonium halide with an appropriate base. The chlorodifluoromethane was then condensed dropwise, via a dry ice coldfinger condenser, into the ylide solution, which was cooled in an ice-water bath with vigorous stirring. The reaction between the ylide and chlorodifluoromethane was characterized by discharge of the typical red or orange coloration associated with the ylide and by the appearance of a dense precipitate of the corresponding triphenylphosphonium halide. In most cases the reactions were complete within a few hours; however, the reaction mixtures were typically stirred at room temperature for 12–24 h prior to workup.

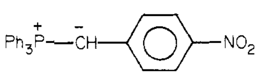
The phosphonium salts could be conveniently isolated by a simple filtration, and a single recrystallization gave material of sufficient purity for reuse. The product olefins were separated either by flash distillation or by steam distillation and were isolated by fractional distillation or preparative GLC. Depending on the solvent used, triphenylphosphine was recovered either by dilution of the reaction mixture, after flash distillation and filtration, with water followed by extraction or by recrystallization of the residue after flash distillation of the solvent. Steam distillation of the reaction mixture after filtration of the phosphonium salt resulted in precipitation of triphenylphosphine which was easily extracted. Again, a single recrystallization of the recovered phosphine resulted in material of sufficient purity to be recycled to the phosphonium salt with little or no loss of the phosphorus-containing material.

Scope and Limitations. In general, both primary and secondary phosphonium ylides react with chlorodifluoromethane equally well to give 1,1-difluoro-1-alkenes as shown in Table I. As is evident from Table I, ylides which possess only simple alkyl or aryl substituents on the ylidene carbon react with chlorodifluoromethane to give excellent yields of the corresponding olefins.

While steric effects of the substituents on the ylide carbon are of only minor importance insofar as olefin yields are concerned, the electronic effects of the substituents on the ylidene carbon were observed to be very important with respect to obtaining good olefin yields. Both benzylidenetriphenylphosphorane (**3a**) and



3a, R = H
b, R = Ph



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(8) Maerker, A. "Organic Reactions"; Adams, R., Ed.; Wiley: New York, 1965; Vol. 14, p 349.

(9) Rabinowitz, R.; Marcus, R. *J. Am. Chem. Soc.* **1962**, *54*, 1312.

(10) Reimlinger, H. *Angew. Chem.* **1962**, *74*, 153.

(11) (a) Oda, R.; Ito, Y.; Okano, M. *Tetrahedron Lett.* **1964**, 7. (b) Okano, M.; Ito, Y.; Oda, R. *Bull. Inst. Chem. Res., Kyoto Univ.* **1964**, *42*, 217. (c) Ito, Y.; Okano, M.; Oda, R. *Tetrahedron* **1966**, *22*, 2615.

Table I. Reactions of Nonstabilized Phosphonium Ylides with HCF_2Cl

$$2Ph_3\overset{+}{P}\text{-}\overset{-}{C}R^1R^2 + HCF_2Cl \longrightarrow [Ph_3\overset{+}{P}CHR^1R^2]X^- + Ph_3P + F_2C{=}CR^1R^2$$

R^1	R^2	solvent	% yield of olefin[a–c]
H	n-C_3H_7	triglyme	88 (58)[d]
H	n-C_6H_{13}	triglyme	93 (60)
H	n-$C_{11}H_{23}$	Et_2O	90 (68)
H	C_6H_5	triglyme	92 (60)[e]
H	$C_6H_4NO_2$-p	THF	trace
H	C_6F_5	triglyme	trace
H	$CH{=}CHC_6H_5$	triglyme	20 (15)[f]
H	$CH{=}CH_2$	triglyme	trace
CH_3	CH_3	triglyme	83 (70)
CH_3	C_2H_5	triglyme	81 (52)
CH_3	C_6H_5	triglyme	82 (60)
C_6H_5	C_6H_5	Et_2O	62 (57)[g]
c-C_5H_{10}		Et_2O	~100 (80)
c-C_4H_8		triglyme	90 (72)
H	OCH_3	triglyme	65[h] (40)
H	$OCH_2CH(CH_3)_2$	triglyme	35[h] (12)
H	p-$F_2C{=}CHC_6H_4$	THF	35 (12)

[a] GLC yield based on thermal conductivity corrections relative to an appropriate internal standard. [b] Product identity was confirmed by comparison of ^{19}F NMR, ^1H NMR, IR, and/or mass spectra with those of authentic samples prepared by alternate routes when possible. [c] Yield based on ylide according to the stoichiometry shown above. [d] Isolated yields are given in parentheses. [e] (Z)-FHC=CHPh was also isolated after steam distillation. [f] (Z)-FHC=CHCH=CHPh was also isolated after steam distillation. [g] FHC=CPh₂ was also isolated after steam distillation. [h] Fluorine-19 yield relative to internal $C_6H_5CF_3$ standard.

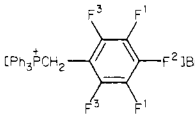
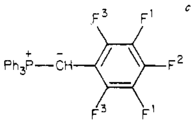
benzhydrylidenetriphenylphosphorane (**3b**), possessing electron-withdrawing phenyl substituents on the ylidene carbon, gave good yields of olefins upon reaction with chlorodifluoromethane. However, (p-nitrobenzylidene)triphenylphosphorane (**4**) reacted with chlorodifluoromethane only very slowly and gave only a trace of β,β-difluoro-p-nitrostyrene. Thus extensive electron delocalization of the negative charge density on the ylidene carbon into the aromatic ring greatly reduces the basicity of ylide **4** and greatly inhibits reaction of the ylide with chlorodifluoromethane. The reactivity of **3a** and **3b** toward chlorodifluoromethane suggests that the phenyl substituents in these ylides must withdraw electron density from the ylidene carbon primarily by induction.

The reaction between chlorodifluoromethane and [(F-phenyl)methylene]triphenylphosphorane (**5**) resulted in only traces of α-hydro-F-styrene (eq 6). The F-phenyl

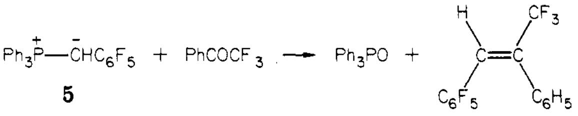
$$\underset{\mathbf{5}}{2Ph_3P^{+}\text{-}^{-}CHC_6F_5} + HCF_2Cl \rightarrow F_2C{=}CHC_6F_5 \quad (6)$$

substituent was not expected to significantly delocalize the electron density on the ylidene carbon by a resonance interaction, but the low reactivity of **5** toward chlorodifluoromethane and the ^{19}F NMR spectrum of **5** in THF indicate that extensive delocalization of electron density from the ylidene carbon into the aromatic ring does indeed occur in this ylide. The ^{19}F NMR spectra of **5** and its precursor [(F-phenyl)methyl]triphenylphosphonium bromide (**6**) are outlined in Table II. Upon addition of 1 equiv of n-butyllithium to a slurry of **6** in THF the ^{19}F NMR signals of the ortho, meta, and para fluorines of **5** are shifted upfield 15.4, 9.7, and 32.2 ppm, respectively. While the chemical shifts may be somewhat solvent dependent, the extremely large upfield shifts may be ascribed to extensive delocalization of the negative charge from the ylidene carbon into the aromatic ring. The larger upfield shifts observed for the ortho and para fluorines relative to the meta fluorines suggest that the delocalization of electron density is probably the result of a resonance interaction. Addition of 0.5 equiv of chlorodifluoromethane to this ylide solution resulted in no change in the spectrum after 16 h except for the appearance of a doublet at ϕ^* −72.6 [J(HCF) = 63.2 Hz] due to chlorodifluoromethane. Subsequent addition of 1 equiv of α,α,α-trifluoroacetophenone to this solution (eq 7) resulted in the complete disappearance from the ^{19}F NMR spectrum of the signals from **5**. The new signals which appeared were assigned to (E)-1-hydro-3-phenyl-1-(F-phenyl)propene (**7**). The formation of **7** in 70% yield indicates that the ^{19}F NMR signals observed prior to addition of trifluoroacetophenone were indeed due to the presence of ylide **5**.

Table II. ^{19}F NMR Spectra of $[Ph_3\overset{+}{P}CH_2C_6F_5]Br^-$ and $Ph_3\overset{+}{P}\text{-}\overset{-}{C}HC_6F_5$

structure	chemical shift,[a] ppm		
	F^3	F^2	F^1
 **6** [b]	−135.7 (m, 2 F)	−150.5 (m, 1 F)	−159.5 (m, 2 F)
 **5** [c]	−151.1 (m, 2 F)	−182.7 (m, 1 F)	−169.2 (m, 2 F)

[a] Chemical shifts reported relative to a $CFCl_3$ external (capillary) reference. [b] Spectrum recorded as a 10% solution in $DCCl_3$. [c] Spectrum recorded as a 10% solution in THF.



5 **7** (7)

Ylides such as allylidenetriphenylphosphorane (**8a**) and cinnamylidenetriphenylphosphorane (**8b**) reacted very slowly with chlorodifluoromethane (eq 8) to give only poor

$$Ph_3\overset{+}{P}\text{-}\overset{-}{C}H\text{-}CH{=}CHR + HCF_2Cl \longrightarrow F_2C{=}CHCH{=}CHR \quad (8)$$

8a, R = H; **b**, R = Ph — **9a**, R = H; **b**, R = Ph

yields of the expected olefins **9a** and **9b**. Allylic ylides such as **8a** and **8b** have been demonstrated to undergo reaction at either the α or γ carbon atoms,[12] indicating that the electron density is delocalized over the three-carbon system. Such delocalization of the electron density away from the ylidene carbon atom is responsible for the lowered reactivity of **9a** and **9b**. Stabilized, isolable ylides such as **10–13**, in which the negative charge on the ylidene carbon is extensively delocalized through conjugation, were found to be totally unreactive toward chlorodifluoromethane. Ylides such as these are only slightly basic and even require a strong acid such as HCl for protonation.

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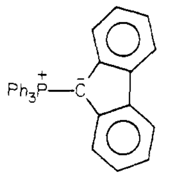
[12] Vedejs, E.; Barshas, J. P.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 3625.

$Ph_3\overset{+}{P}-\overset{-}{C}HCO_2Et$ **10** $\quad Ph_3\overset{+}{P}-\overset{-}{C}(CH_3)CO_2Et$ **11** $\quad Ph_3\overset{+}{P}-\overset{-}{C}HC{\equiv}N$ **12**



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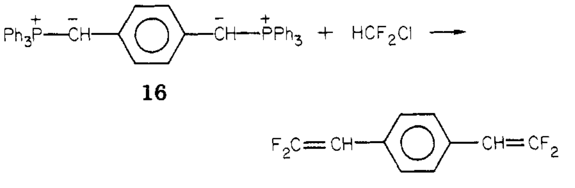
The preparation of 2,2-difluorovinyl ethers **15** by the reaction of (alkoxymethylene)triphenylphosphoranes **14** with chlorodifluoromethane (eq 9) resulted in only moderate success. (Isobutoxymethylene)triphenylphosphorane (**14b**) gave only 35% of vinyl ether **15b** while the more stable (methoxymethylene)triphenylphosphorane (**14a**) gave a 65% yield of vinyl ether **15a**. Both of these alkoxy-substituted ylides are extremely reactive but are also rather unstable. Ylide **14a** decomposes rapidly at room temperature while **14b** decomposes above −40 °C.[13] The low olefin yields probably reflect the instability of these ylides.

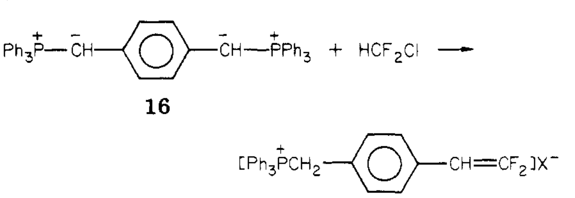
$$2Ph_3\overset{+}{P}\text{-}\overset{-}{C}HOR + HCF_2Cl \longrightarrow F_2C{=}CHOR \qquad (9)$$

14a, R = CH_3; **b**, R = $CH_2CH(CH_3)_2$ **15a**, R = CH_3; **b**, R = $CH_2CH(CH_3)_2$

The attempted reaction between the bis ylide *p*-xylylidenebis(triphenylphosphorane) (**16**) and chlorodifluoromethane (eq 10) resulted in a poor yield of β,β,β′,β′-tetrafluoro-*p*-divinylbenzene (**17**). The reason for the low olefin yield with this ylide is not understood. The low yield might be the result of two reactive ylide sites within the same molecule; one acting as the base and the other as a nucleophile with subsequent formation of a new phosphonium salt, **18** (eq 11). No evidence for the formation of **18** was observed by ^{19}F NMR or ^1H NMR, however. In any event, the significantly lower olefin yield obtained on using **16** may tend to preclude the use of bis ylides for this reaction.

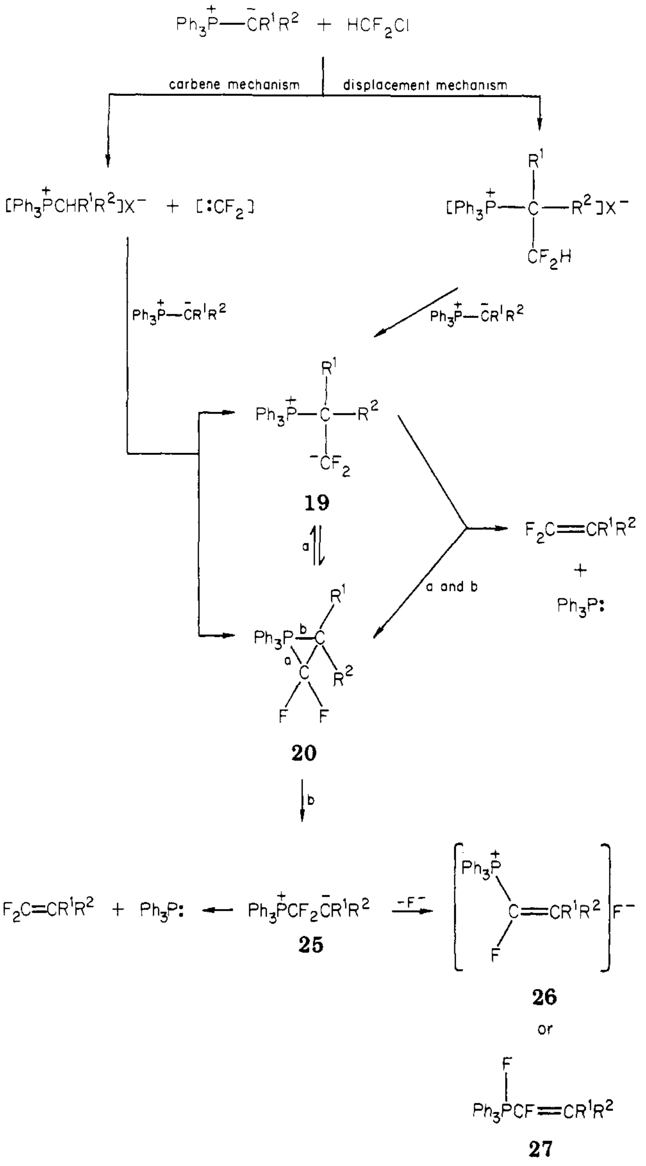


16 **17** (10)

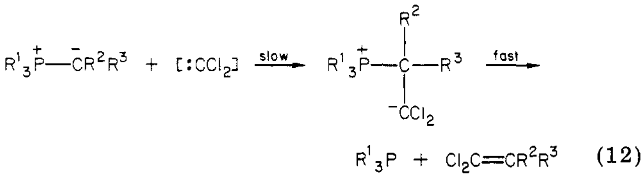


16 **18** (11)

Scheme I. Mechanisms for Reaction of Ylides with HCF_2Cl



19 **20** **25** **26** or **27**



$$R^1_3\overset{+}{P}-\overset{-}{C}R^2R^3 + [:CCl_2] \xrightarrow{slow} R^1_3\overset{+}{P}-\underset{\overset{|}{^-CCl_2}}{\overset{\overset{R^2}{|}}{C}}-R^3 \xrightarrow{fast} R^1_3P + Cl_2C{=}CR^2R^3 \qquad (12)$$

Mechanism. Oda and co-workers[14] reported that the reaction of dichlorocarbene with resonance-stabilized phosphorus ylides proceeds via rate-limiting attack of the electrophilic carbene upon the ylidene carbon atom. The intermediate thus formed, represented by Oda as a 1,3-dipolar species, collapses very rapidly with loss of phosphine to yield the observed olefins (eq 12). The reaction between nonstabilized ylides and chlorodifluoromethane, however, is somewhat more complicated. At least two mechanisms can account for both the products formed during the reaction and the observed stoichiometry. Intuitively, the most obvious mechanism for this reaction involves dehydrochlorination of chlorodifluoromethane by one molecule of ylide to generate difluorocarbene and the observed triphenylphosphonium halide as depicted in Scheme I. The carbene would then react rapidly with another molecule of ylide followed by rapid decomposition of the intermediate to olefin and triphenylphosphine as proposed by Oda. Difluorocarbene addition to an ylide may possibly occur to yield either a 1,3-dipolar species (**19**) or a highly strained three-membered cyclic phosphorane (**20**). A second mechanistic possibility, outlined in Scheme

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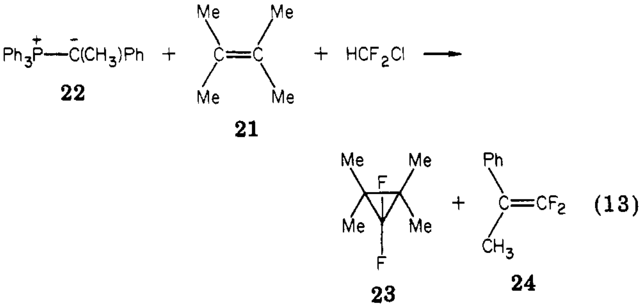
[13] Wittig, G.; Böll, W. *Chem. Ber.* **1962**, *95*, 2526.

[14] Ito, Y.; Okano, M.; Oda, R. *Tetrahadron* **1966**, *22*, 2615.

I, involves nucleophilic attack by the ylide upon chlorodifluoromethane with displacement of chloride ion to form an α-(difluoromethyl)triphenylphosphonium salt. A second molecule of ylide would then abstract the proton from the difluoromethyl group with subsequent loss of triphenylphosphine to yield the olefin. While both of these mechanisms account for the observed stoichiometry and the products obtained, little precedent exists in the literature for nucleophilic displacement reactions upon fluorinated methanes such as chlorodifluoromethane. Even strong nucleophiles such as alkali metal aryl sulfides are unreactive toward chlorodifluoromethane unless a strong base such as hydroxide or alkoxide is present, presumably to generate difluorocarbene which may then be trapped by the sulfide.[15] In none of the cases studied has any evidence of the formation of α-(difluoromethyl)triphenylphosphonium salts been observed.

The carbene mechanism shown in Scheme I is more consistent with both the observed inability of the resonance-stabilized ylides to react with chlorodifluoromethane and the observed order of relative reactivities, since the initial step in this sequence of reactions would require that the ylide be a strong base in order to dehydrochlorinate the chlorodifluoromethane. The apparent correlation of relative reactivity with ylide basicity suggests that the acid/base reaction resulting in difluorocarbene formation is the rate-limiting step of the reaction. This is consistent with the reactions of chlorodifluoromethane with other strong bases.

We have been able to successfully intercept difluorocarbene using 2,3-dimethyl-2-butene[21] in the reaction of (1-phenylethylidene)triphenylphosphorane (**22**) with chlorodifluoromethane (eq 13). When 2 equivalents of chlorodifluoromethane was added to a solution of 1 equiv of **22** and 4 equiv of **21** in triglyme at 0 °C, 1,1-difluoro-2,2,3,3-tetramethylcyclopropene (**23**) was formed in 21% yield in addition to a 59% yield of the expected olefin **24**. The formation of cyclopropane **23** indicates that difluorocarbene is indeed formed by reaction of ylides such as **22** and chlorodifluoromethane. The presence of olefin **21** decreased the yield of difluoromethylene olefin **24** to 59% from 82% in the absence of **21**, but the overall yield of fluorinated products (**23** and **24**) remained essentially unchanged from the 82% yield of **24** obtained in the absence of **21**.



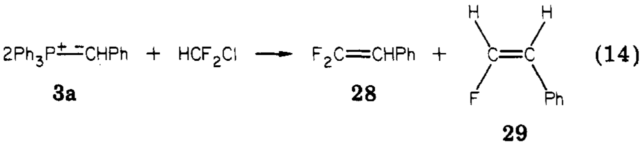
22 **21** **23** **24** (13)

The mechanism depicted in Scheme I involving nucleophilic displacement of chloride ion by ylide has not been disproved. However, the lack of precedents for such a chloride displacement, the many precedents for carbene formation upon reaction of chlorodifluoromethane with strong bases, and the ability to intercept difluorocarbene during the reaction between ylide **22** and chlorodifluoromethane and the subsequent reduction in the yield of olefin **24** strongly suggest that the difluorocarbene mechanism depicted in Scheme I is operative in the formation of 1,1-difluoro-1-alkenes by the reaction of nonstabilized ylides with chlorodifluoromethane.

The exact nature of the intermediate formed upon reaction between the ylide and difluorocarbene is open to speculation. The intermediate may be a 1,3-dipolar species (**19**, depicted in Scheme I) as proposed by Oda. Such an intermediate would be very short-lived due to the tendency of fluorine atoms to destabilize an adjacent negative charge. Elimination of triphenylphosphine from **19** would result in the formation of the product olefin. Cyclic phosphorane **20** would result from attack of the carbanionic center upon the positive phosphorus atom. Alternatively, phosphorane **20** could be formed directly by concerted addition of difluorocarbene across the ylidene-carbon–phosphorus bond. A similar cycloaddition mechanism has been proposed by Vedejs for the Wittig reaction between nonstabilized ylides and typical carbonyl compounds.[16]

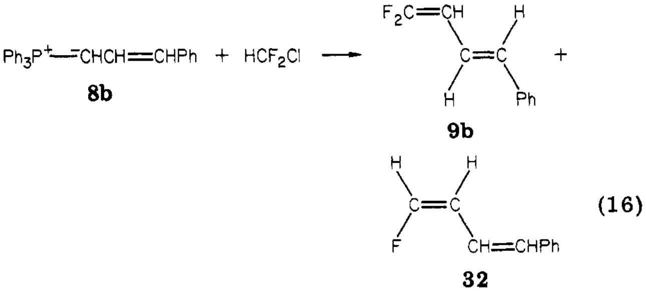
Phosphorane **20** could then undergo decomposition in a variety of ways as shown in Scheme I. Concerted loss of triphenylphosphine from **20** would yield the product 1,1-difluoro-1-alkene. Cleavage of carbon–phosphorus bond a would yield **19** which could either eliminate triphenylphosphine to yield the olefin or reform phosphorane **20**. Cleavage of carbon–phosphorus bond b would yield another 1,3-dipolar structure, **25**, which could also yield olefin by elimination of triphenylphosphine. Alternatively, **25** could collapse via elimination of fluoride ion to give a vinylphosphonium salt, **26**, or a vinylfluorophosphorane, **27**.

Steam distillation of reaction mixtures from the reactions of ylides possessing carbanion-stabilizing substituents on the ylidene carbon with chlorodifluoromethane resulted in isolation of *gem*-hydrofluoro olefins in addition to the expected *gem*-difluoro olefins. Ylide **3a**, upon reaction with chlorodifluoromethane followed by steam distillation, gave a 62% yield of a 92/8 mixture of β,β-difluorostyrene (**28**) and (*Z*)-β-fluorostyrene (**29**) (eq 14). The reaction with **3b** gave upon steam distillation a 70% yield of an 89/11 mixture of 1,1-difluoro-2,2-diphenylethylene (**30**) and 1-fluoro-2,2-diphenylethylene (**31**) (eq 15). Use of cinnamylidenetriphenylphosphorane (**8b**) in this reaction resulted in a 35% yield of a 57/43 mixture of diene **9b** and diene **32** (eq 16). ^{19}F NMR analysis of these three reaction



3a **28** **29** (14)

$$\underset{\mathbf{3b}}{2Ph_3P^{+}\text{-}{}^{-}CPh_2} + HCF_2Cl \rightarrow \underset{\mathbf{30}}{F_2C{=}CPh_2} + \underset{\mathbf{31}}{HFC{=}CPh_2} \qquad (15)$$



8b **9b** **32** (16)

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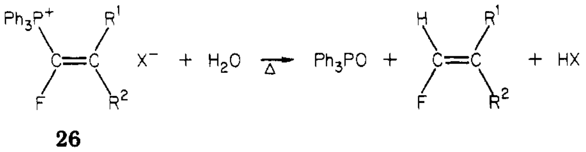
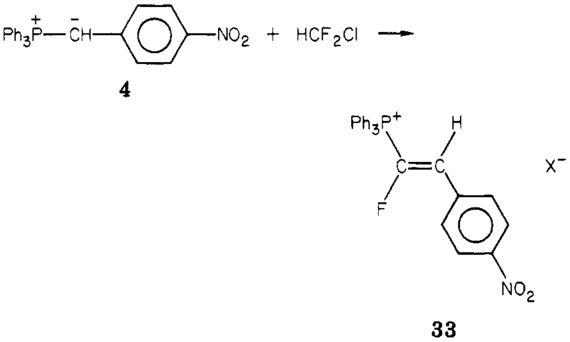
[15] (a) Miller, T. G.; Thanassi, J. W. *J. Org. Chem.* **1960**, *25*, 2009. (b) Van Pouche, R.; Pollet, R.; DeCat, A. *Tetrahedron Lett.* **1965**, 403.

[16] Vedejs, E.; Snoble, K. *J. Am. Chem. Soc.* **1973**, *95*, 5778.

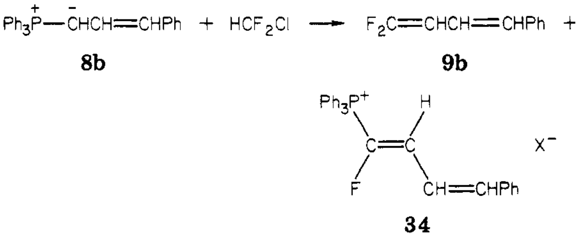
mixtures showed that the *gem*-hydrofluoro olefins were not present prior to steam distillation, indicating that they were formed during the distillation. Several routes by which these hydrofluoro olefins may have been formed were considered; however, the only route consistent with all the experimental observations is one involving hydrolysis of an (α-fluorovinyl)phosphonium salt such as **26** (eq 17) in Scheme I. Direct evidence for the possible intermediacy of such vinylphosphonium salts has been obtained by ^{19}F NMR analysis of the reaction mixture involving ylide **4** and CHF$_2$Cl (eq 18). After 24 h little consumption of chlorodifluoromethane had occurred; however, a signal did appear in the ^{19}F NMR spectrum which is consistent with vinylphosphonium salt **33**. This signal appeared as a doublet of doublets centered at ϕ* −142.8 [J(PCF) = 50.0 Hz, J(HC=CF-*trans*) = 48.0 Hz] which is consistent with structure **33** on the basis of the coupling constants and chemical shift.[17] Similarly, ^{19}F NMR analysis of the reaction between ylide **8b** and chlorodifluoromethane after 72 h showed signals for diene **9b** (eq 19) and a doublet of doublets, centered at ϕ* −143.2 [J(PCF) = 51.0 Hz, J(HC=CF-*trans*) = 48.5 Hz], which is consistent with phosphonium salt **34**. No signals from the hydrofluorodiene **32** were observed. Upon steam distillation a mixture of dienes **9b** and **32** was isolated. ^{19}F NMR analysis of the residue from the steam distillation showed that no fluorinated products remained, indicating that **34** had been totally hydrolyzed.



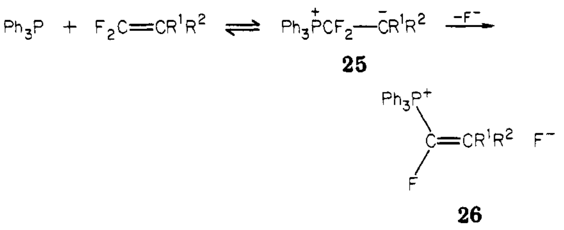
(17)



(18)



(19)

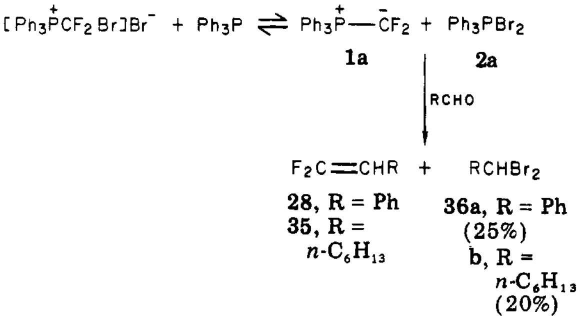


(20)

Formation of vinylphosphonium salts such as **26** may have occurred either by ring opening of a cyclic phosphorane intermediate as depicted in Scheme I or by nucleophilic addition–displacement reaction between triphenylphosphine and the corresponding 1,1-difluoro-1-alkene (eq 20). Previous investigations in this laboratory[18] have shown triphenylphosphine to be very unreactive toward such addition–elimination reactions with terminal difluoromethylene olefins. Even ylides have been observed to react only with highly fluorinated olefins of this type.[19] We, therefore, conclude that in at least these three cases difluoro olefin formation may proceed via a three-membered cyclic phosphorane such as **20**. Indeed, such cyclic phosphoranes may be intermediates in the reactions between all of the ylides investigated and chlorodifluoromethane; however, cleavage of the carbon–phosphorus bond b (Scheme I) which gives rise to the (α-fluorovinyl)phosphonium salts occurs only when the substituents on the ylidene carbon provide substantial stabilization for the developing negative charge in the transition state leading to carbanion **25**. In those cases in which the substituents on the ylidene carbon are unable to stabilize an adjacent negative charge, the concerted elimination of triphenylphosphine from the cyclic phosphorane may occur, or the cyclic phosphorane may decompose via the 1,3-dipolar species **19**. Alternatively, in the cases of those ylides possessing electron-releasing substituents on the ylidene carbon, a cyclic phosphorane may not be formed at all.

Advantages over the Witting Reaction. The preparation of 1,1-difluoro-1-alkenes by the reaction between nonstabilized triphenylphosphonium ylides and chlorodifluoromethane results in good yields of olefins without concurrent formation of triphenylphosphine oxide. The byproducts from this method of olefin preparation are triphenylphosphine and the corresponding alkyl- or (arylalkyl)triphenylphosphonium halide, both of which may be recycled. This method thus circumvents a major problem associated with the large-scale preparation of olefins by the Wittig route, the formation of triphenylphosphine oxide.

As previously mentioned, dibromotriphenylphosphorane (**2a**), formed during debromination of (bromodifluoromethyl)triphenylphosphonium bromide by triphenylphosphine (eq 21), may be expected to react with aldehydes to form 1,1-dibromoalkanes. Such has been observed to be the case in the preparation of olefin **28** or **35** by the Wittig reaction between ylide **1a** and benzaldehyde[6] or n-heptaldehyde respectively. A similar problem might be anticipated for preparation of other difluoromethylene α-olefins by the Wittig reaction between **1a** and aldehydes.



(21)

Enolizable ketones have a tendency to undergo base-initiated condensation reactions. Cyclopentanone, a readily enolizable ketone, has been observed to give rela-

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(17) Howells, R. D. Ph.D. Thesis, University of Iowa, pp 226–33.

(18) Howells, R. D. Ph.D. Thesis, University of Iowa, pp 273–85.

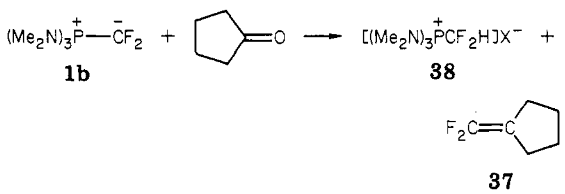
(19) Headley, J. A. Ph.D. Thesis, University of Iowa.

Table III. Comparison of Ylide-Carbene and Wittig Methods

$R^1R^2C{=}CF_2$		yield,[a] %	
R^1	R^2	ylide-carbene[b]	Wittig[c]
H	n-C_6H_{13}	93	72
H	C_6H_5	92	65[d]
H	$CH{=}CHC_6H_5$	20	56[e]
H	OCH_3	65	30
CH_3	CH_3	83	65
CH_3	C_2H_5	81	60
CH_3	C_6H_5	82	81[d]
C_6H_5	C_6H_5	62	19[d]
	c-C_5H_{10}	~100	71[d]
	c-C_4H_8	90	8

[a] GLC yields relative to an appropriate internal standard. [b] Yield based on a ylide/CHF_2Cl stoichiometry of 2/1. [c] Yield based on the carbonyl compound. [d] Taken from ref 6. [e] H. S. Kesling, private communication.

tively low olefin yields in reactions with strongly basic ylides. These low yields have been ascribed to the ease of enolization of cyclopentanone.[8,20] (Difluoromethylene)tris(dimethylamino)phosphorane (**1b**), being strongly basic, also might be expected to initiate self-condensation of enolizable ketones such as cyclopentanone. The reaction between **1b** and cyclopentanone (eq 22) resulted in only an 8% yield of (difluoromethylene)cyclopentane (**37**). Analysis of the reaction mixture by ^{19}F NMR indicated a 15% yield of the conjugate acid (**38**) of the ylide. GLC showed that 60% of the ketone remained unreacted. Similarly, the low yields of 1,1-difluoro-2-methyl-1-propene and 1,1-difluoro-2-methyl-1-butene from the reaction of **1b** with acetone and 2-butanone, respectively, may be due to competing condensation reactions since acetone has also been observed to yield mesityl oxide in reactions with strongly basic ylides.[21]



1b **38** **37** (22)

A comparison of the yields of a series of 1,1-difluoro-1-alkenes obtained by the ylide–chlorodifluoromethane reaction and by the Wittig reaction is presented in Table III. The yields of olefins which have only one substituent on the β-carbon (that is, those obtained from aldehydes by using the Wittig reaction) are much higher for the reactions between ylides and chlorodifluoromethane than those obtained by the Wittig reaction. The inferior yields obtained by using the Wittig reaction are most likely due to competition between the ylide and the dibromophosphorane for reaction with the aldehyde substrate, while no such side reactions occur in the reaction between ylides and chlorodifluoromethane. The yields of olefins possessing two substituents on the β-carbon (those obtained from ketones by using the Wittig reaction) compared much more favorably although the yields from the Wittig reaction are again somewhat lower. These lower yields obtained from the Wittig reaction suggest that the steric requirements of the Wittig reaction and the tendency of some ketones to undergo base-induced self-condensation reactions are again disadvantageous to the use of the Wittig reaction for the preparation of 1,1-difluoro-1-alkenes. The effects are suggested by the comparisons of the yield of 1,1-difluoro-2,2-diphenylethylene (**30**) and (difluoromethylene)cyclopentane (**37**) obtained by each of the two methods. While the Wittig reaction gave only an 8% yield of **37** the reaction of cyclopentylidenetriphenylphosphorane and chlorodifluoromethane gave a 90% yield of **37**. Similarly, the yield of **30** obtained from benzophenone via the Wittig reaction was only 19%[6] while the reaction between ylide **3b** and chlorodifluoromethane gave **30** in 62% yield.

Conclusions

The reactions of nonstabilized ylides with chlorodifluoromethane has proven to be a very viable alternative to the Wittig reaction as a route to 1,1-difluoro-1-alkenes. The ability to recover both the phosphonium salt and triphenylphosphine relatively easily circumvents the major problem inherent within the Wittig reaction: the conversion of the phosphine to phosphine oxide. The recovery of triphenylphosphine from the reaction of ylides with chlorodifluoromethane is much easier and less expensive than the conversion of phosphine oxides to the corresponding phosphines. The phosphine may then be recycled to phosphonium salt with little or no loss of the phosphorus-containing material, only the relatively inexpensive haloform chlorodifluoromethane being consumed in the reaction. The yields of recovered phosphonium salt and phosphine both approach 90%, and isolation and purification procedures are relatively simple.

The preparation of 1,1-difluoro-1-alkenes by this method results in excellent olefin yields in those cases in which the ylidene carbon atom does not possess strongly electron-withdrawing substituents. In all cases of this nature, the yields of olefins obtained by the ylide–chlorodifluoromethane reaction are significantly better than those obtained from the Wittig reaction of a difluoromethylene ylide with the corresponding carbonyl compound. For the preparation of 1,1-difluoro-1-alkenes which have only one alkyl substituent on the β-carbon, the ylide chlorodifluoromethane reaction results in excellent yields, and no nonproductive side reactions occur in this synthesis, unlike the Wittig reaction. Thus, the ylide–chlorodifluoromethane reaction makes use of both the phosphorus-containing material and the alkylidene moiety with maximum efficiency.

The reaction between alkylidenetriphenylphosphoranes and chlorodifluoromethane proceeds by initial dehydrochlorination by the ylide to generate difluorocarbene. The intermediate difluorocarbene is then trapped by the nucleophilic ylide. The evidence indicates that the reaction between the ylide and difluorocarbene may proceed by either or both of two pathways as detailed in Scheme I. Addition of difluorocarbene to the ylidene carbon results in a zwitterionic intermediate which either collapses rapidly to olefin and phosphine or may cyclize to a three-membered cyclic phosphorane. This phosphorane may then eliminate phosphine to yield olefin or ring-open to yield an (α-fluorovinyl)phosphonium salt which, upon hydrolysis, affords the observed hydrofluoro olefins (Scheme I). These two routes are indistinguishable for the formation of the difluoro olefins, but the formation of the (α-fluorovinyl)phosphonium salts can only be explained via the cyclic phosphorane.

Experimental Section

Melting points were obtained in capillary tubes by using a Thomas-Hoover Unimelt apparatus and are corrected. The boiling points were obtained during fractional distillation by means of

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[20] Wittig, G., Böll, W., and Krück, K. *Chem. Ber.* **1962**, 95, 2514.

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a partial immersion thermometer and are uncorrected. The boiling points of known compounds were in good agreement with reported values. The infrared spectra were recorded by using liquid films between sodium chloride plates, solids in KBr pellets, or ca. 10% (w/v) solutions in CCl$_4$ with matched liquid cells (0.1-mm path length) on a Beckman IR-20a spectrophotometer. ^{1}H NMR spectra were recorded by using ca. 10% (w/v) solutions in either CDCl$_3$ or CCl$_4$ on a Varian A-60 spectrometer. The chemical shifts are reported in parts per million downfield from a tetramethylsilane internal standard. ^{19}F NMR spectra were recorded by using either aliquots or reaction mixtures of ca. 10% (w/v) solutions and operating at 94.075 MHz in HR (nonlock) mode. All chemical shifts are reported in ϕ^* values upfield from the external (capillary) CFCl$_3$ standard. Product yields were determined from area ratios obtained by cutting out and weighing the peaks from a photocopy of the spectrum. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-66 mass spectrometer operating at 70 eV. Mass spectral samples were isolated from reaction or product mixtures by the analytical GLC capillary technique of Burson and Kenner. Analytical and preparative GLC were performed on a Hewlett-Packard F&M Model 720 dual-column gas chromatograph equipped with thermal-conductivity detectors and using helium as a carrier gas. Product yields were determined by comparing the relative areas under peaks vs. an appropriate internal standard, corrected for differences in detector responses. Column A was a 10 ft × 0.25 in. copper column packed with 15% (w/w) silicon gum rubber SE-30 on 80–100-mesh Chromosorb P. Column B was a 10 ft × 0.5 in. copper column packed with 20% (w/w) SE-30 on 80–100-mesh Chromosorb P. Column C was a 10 ft × 0.25 in. copper column packed with 15% (w/w) Carbowax 20M on 80–100-mesh Chromosorb P. Column D was a 10 ft × 0.5 in. copper column packed with 20% (w/w) Carbowax 20M on 80–100-mesh Chromosorb P.

Chloroform was washed with water, predried over calcium chloride, filtered, and stored over 4A molecular sieves in a dark bottle. Diethyl ether was predried over calcium chloride, filtered, and stored over fresh sodium wire. Ethanol (absolute and 95%) was used as received. Triglyme (Ansul Ether 161) and THF were distilled from sodium benzophenone ketyl and were stored over 4A molecular sieves in capped bottles under nitrogen. Triphenylphosphine (Cincinnati Milacron) was recrystallized from 95% ethanol and then dried at 50 °C in vacuo. Tris(dimethylamino)phosphine was prepared by the method listed in the literature[22] and was stored in a sealed bottle under nitrogen.

1,1-Difluoro-1-pentene. Methyllithium (1.90 M in ether, 44.8 mL, 0.085 mol) was added dropwise to a cooled (0 °C) vigorously stirred slurry of *n*-butyltriphenylphosphonium bromide (34.0 g, 0.085 mol) in triglyme (200 mL) under nitrogen. The reaction mixture was stirred for 1 h at room temperature, the ether and methane were distilled in vacuo, and then chlorodifluoromethane (3.72 g, 0.043 mol) was condensed into the reaction mixture with cooling. The mixture was stirred for 2 h at room temperature and then flash distilled to give a 58% (2.62 g, 0.025 mol) isolated yield of 96% pure 1,1-difluoro-1-pentene: mass spectrum, *m/e* (relative intensity) 106 (93), 78 (42), 77 (100), 59 (28), 51 (83), 45 (16), 42 (79), 41 (36), 39 (30), 32 (50), 31 (36), 29 (63); IR (gas, 25 mmHg) 2960 (s), 2880 (w), 1744 (s), 1456 (m), 1358 (w), 1315 (m), 1275 (w), 1248 (m), 1198 (s), 1122 (m), 1053 (w), 1002 (w), 912 (m), 846 (w), 793 (m), 716 (s), 678 (w); ^{1}H NMR (10% DCCl$_3$, Me$_4$Si) δ 4.14 (ddt, 1 H, vinyl H), 1.93 (m, 2 H, CH$_2$), 1.34 (m, 2 H, CH$_2$), 0.92 (t, 3 H, CH$_3$), *J*(FC=CH-*trans*) = 25.0 Hz, *J*(FC=CH-*cis*) = 3.7 Hz, *J*(vinyl H, CH$_2$) = 7.6 Hz, *J*(CH$_2$, CH$_3$) = 6.2 Hz, all other coupling remains unresolved; ^{19}F NMR (10% DCCl$_3$, CFCl$_3$ external) ϕ^* −90.3 (ddm, 1 F, vinyl F cis to H), −92.8 (ddm, 1 F, vinyl F trans to H), *J*(FC=CH-*trans*) = 24.8 Hz, *J*(FC=CH-*cis*) = 3.4 Hz, *J*(FCF) = 57.3 Hz, all other coupling remains unresolved.

Repetition of the reaction with *n*-hexane as an internal standard resulted in an 88% GLC yield of the olefin on column A.

1,1-Difluoro-1-octene (35). Methyllithium (2.0 M in ether, 50.0 mL, 0.100 mol) was added dropwise with cooling to a vigorously stirred slurry of *n*-heptyltriphenylphosphonium bromide (44.1 g, 0.100 mol) in triglyme (150 mL) under nitrogen. The reaction mixture was stirred for 1 h at room temperature, and then the ether and methane were distilled in vacuo, followed by the addition of chlorodifluoromethane (8.65 g, 0.100 mol) to the reaction mixture. The reaction mixture was then stirred for 12 h at room temperature. The reaction mixture was flash distilled, and the distillate was fractionally distilled through a 15-cm Vigreux column to give a 60% (4.62 g, 0.030 mole) isolated yield of 99% pure **35** identical with an authentic sample.

Repetition of the reaction with cyclohexane as an internal standard resulted in a 93% GLC yield of **35** on column A.

1,1-Difluoro-1-tridecene. Phenyllithium (2.0 M in 70:30 benzene–ether, 25.0 mL, 0.050 mol) was added dropwise to a stirred, cooled (0 °C) solution of *n*-dodecyltriphenylphosphonium bromide[25] (26.5 g, 0.050 mol) in THF (50 mL) under nitrogen. The reaction mixture was stirred for 1 h at room temperature, and then chlorodifluoromethane (4.35 g, 0.050 mol) was condensed into the reaction mixture. The mixture was stirred for 24 h at room temperature and then poured into brine (300 mL). The organic layer was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate, the ether and benzene were evaporated on a rotary evaporator, the residue was filtered, and the filtrate was distilled through a 15-cm Vigreux column to give a 68% (3.70 g, 0.017 mol) isolated yield of 98% pure 1,1-difluoro-1-tridecene: bp 100–102 °C (1 mmHg); mass spectrum, *m/e* (relative intensity) 218 (10), 154 (33), 77 (55), 70 (38), 69 (36), 57 (74), 56 (46), 55 (42), 45 (36), 43 (100), 41 (44); IR (neat) 2914 (s), 2867 (m), 1742 (s), 1460 (w), 1304 (w), 1224 (w), 1037 (w), 890 (w), 796 (w), 732 (w), 694 (w); ^{1}H NMR (10% DCCl$_3$, Me$_4$Si) δ 4.09 (dtd, 1 H, vinyl H), 1.96 (m, 2 H, CH$_2$), 1.28 (br s, 18 H, (CH$_2$)$_9$), 0.88 (t, 3 H, CH$_3$), *J*(FC=CH-*trans*) = 25.0 Hz, *J*(FC=CH-*cis*) = 3.5 Hz, *J*(vinyl H, CH$_2$) = 7.5 Hz, *J*(CH$_2$, CH$_3$) = 4.8 Hz, all other coupling remains unresolved; ^{19}F NMR (10% DCCl$_3$, CFCl$_3$ external) ϕ^* −89.7 (ddm, 1 F, vinyl F cis to H), −92.2 (ddm, 1 F, vinyl F trans to H), *J*(FC=CH-*trans*) = 25.2 Hz, *J*(FC=CH-*cis*) = 3.4 Hz, *J*(FCF) = 49.0 Hz.

Repetition of the reaction with toluene as an internal standard resulted in a 90% GLC yield of the olefin on column A.

***β,β*-Difluorostyrene (28).** Phenyllithium (2.0 M in 70:30 benzene–ether, 50.0 mL, 0.100 mol) was added dropwise to a cooled (0 °C) slurry of benzyltriphenylphosphonium chloride (38.9 g, 0.100 mol) in triglyme (150 mL) under nitrogen with vigorous stirring. The resulting deep-red solution was stirred at room temperature for 1 h, and then chlorodifluoromethane (4.33 g, 0.050 mol) was condensed into the reaction mixture. After being stirred for 12 h at room temperature, the reaction mixture was filtered. The solid which was collected was recrystallized from ethanol–ether to give 87% (16.9 g, 0.0435 mol) benzyltriphenylphosphonium chloride. The filtrate was flash distilled, and the distillate was washed with water (2 × 100 mL), dried, and fractionally distilled through a 15-cm Vigreux column to give a 60% (4.20 g, 0.030 mol) isolated yield of 98% pure **28** identical with an authentic sample. Dilution of the residue from the flash distillation with water (500 mL) followed by extraction with chloroform gave an 85% yield (11.2 g, 0.0425 mol) of triphenylphosphine after recrystallization from 95% ethanol.

Repetition of the reaction with toluene as an internal standard resulted in a 92% GLC yield of **28** on column A.

***β,β*-Difluoro-*p*-nitrostyrene.** Phenyllithium (1.49 M in 70:30 benzene–ether, 13.4 mL, 0.020 mol) was added dropwise to a cooled (0 °C) slurry of (*p*-nitrobenzyl)triphenylphosphonium bromide[27] (9.68 g, 0.020 mol) in THF (20 mL) under nitrogen. The reaction mixture was stirred for 0.5 h at room temperature, and chlorodifluoromethane (1.72 g, 0.020 mol) was condensed into the reaction mixture. After the mixture was stirred for 72 h at room temperature, GLC analysis on column A showed only traces of *β,β*-difluoro-*p*-nitrostyrene. ^{19}F NMR analysis of the reaction mixture showed the presence of unreacted chlorodifluoromethane [ϕ^* −72.3 (d), *J*(HCF) = 63.6 Hz] and a signal which was assigned

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to the vinylphosphonium salt **33**: ϕ^* −142.8 (dd), J(PCF) = 50.1 Hz, J(FC=CH-*trans*) = 48.5 Hz. No signals were observed for β,β-difluoro-*p*-nitrostyrene.

1-Hydro-*F*-styrene. Methyllithium (1.90 M in ether, 11.4 mL, 0.022 mol) was added dropwise to a cooled (0 °C) slurry of [(*F*-phenyl)methyl]triphenylphosphonium bromide[28] (11.4 g, 0.022 mol) in THF (30 mL) under nitrogen with vigorous stirring. The reaction mixture was stirred for 1.5 h at room temperature, and then chlorodifluoromethane (1.30 g, 0.015 mol) was condensed into the reaction mixture. After the mixture was stirred for 16 h, GLC analysis on column A showed only a trace of 1-hydro-*F*-styrene. ^{19}F NMR analysis of the reaction mixture showed the presence of unreacted chlorodifluoromethane and the ylide **5**: ϕ^* −151.1 (m, 2 F, *o*-F), −169.2 (m, 2 F, *m*-F), −182.7 (m, 1 F, *p*-F), the coupling remains unresolved. Addition of α,α,α-trifluoroacetophenone (3.48 g, 0.020 mol) to the reaction mixture resulted in a very exothermic reaction accompanied by discharge of the typical reddish color of the ylide. The reaction mixture was stirred for 12 h at room temperature and filtered, and then the filtrate was poured into water (200 mL). The organic layer was separated, the aqueous layer was extracted with ether (2 × 30 mL), the organic layer and ether extracts were combined and washed with water (2 × 100 mL), and the ether solution was dried over anhydrous magnesium sulfate. The ether was evaporated on a rotary evaporator, and the residue was taken up in pentane (20 mL) and filtered to remove the precipitated phosphine oxide. The pentane was evaporated from the filtrate, and the resulting reddish brown solid was recrystallized from pentane to give **7**: 4.73 g (0.015 mol, 70%); fluffy yellow needles; mp 61–63 °C; mass spectrum, *m/e* (relative intensity) 338 (93), 318 (100), 299 (36), 269 (84), 268 (37), 250 (45), 219 (64), 135 (34), 77 (24), 51 (21); IR ($HCCl_3$) 3058 (w), 1648 (w), 1513 (m), 1490 (s), 1372 (w), 1280 (s), 1255 (w), 1168 (s), 1120 (s), 1067 (w), 997 (m), 968 (m), 936 (w), 904 (w), 686 (m), 628 (m); ^{1}H NMR (10% $DCCl_3$, Me_4Si) δ 7.25 (s, 5 H, C_6H_5), 7.02 (q, 1 H, vinyl H), J(HC=CCF_3-*cis*) = 1.6 Hz; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ external) ϕ^* −65.9 (d, 3 F, vinyl CF_3), −137.7 (m, 2 F, *o*-F), −152.9 (m, 1 F, *p*-F), −161.6 (m, 2 F, *m*-F), J(HC=CCF_3-*cis*) = 1.8 Hz, all other coupling remains unresolved. Anal. Calcd for $C_{15}H_6F_8$: C, 53.27; H, 1.79. Found: C, 53.09; H, 2.00.

1,1-Difluoro-4-phenyl-1,3-butadiene (9b). Phenyllithium (1.49 M in 70:30 benzene–ether, 53.7 mL, 0.080 mol) was added dropwise with cooling (0 °C) to a vigorously stirred slurry of *trans*-cinnamyltriphenylphosphonium chloride (**27**; 33.3 g, 0.081 mol) in triglyme (100 mL) under nitrogen. The resulting deep red solution was stirred at room temperature for 1 h, and then chlorodifluoromethane (6.92 g, 0.080 mol) was condensed into the reaction mixture. After being stirred for 72 h at room temperature, the reaction mixture had become deep violet. The reaction mixture was flash distilled, and the distillate was washed with brine (3 × 100 mL) and dried over anhydrous magnesium sulfate. The volatile components were evaporated in vacuo, and **9b** (15%, 1.00 g, 0.006 mol) was isolated by preparative GLC on column D: mass spectrum, *m/e* (relative intensity) 166 (100), 165 (37), 164 (23), 151 (19), 147 (22), 146 (89), 145 (15), 116 (19), 115 (52), 77 (19), 51 (21), 32 (56); IR (neat) 3085 (w), 3062 (w), 3030 (w), 1715 (s), 1629 (w), 1595 (m), 1575 (w), 1495 (m), 1446 (w), 1350 (m), 1325 (w), 1291 (m), 1271 (m), 1180 (s), 1116 (w), 1066 (w), 955 (s), 928 (s), 928 (s), 848 (w), 826 (m), 744 (s), 688 (m); ^{1}H NMR (10% $DCCl_3$, Me_4Si) δ 7.32 (s, 5 H, C_6H_5), 6.76 (ddm, 1 H, CH=CPh), 6.44 (dm, 1 H, =CHPh), 5.17 (dddm, 1 H, F_2C=CH), J(FC=CH-*trans*) = 23.8 Hz, J(FC=CH-*cis*) = 0.9 Hz, J(=CHCH=) = 9.0 Hz, J(HC=CH-*trans*) = 16.5 Hz, all other coupling remains unresolved; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ external) ϕ^* −85.3 (dd, 1 F, vinyl F trans to H), −87.0 (dd, 1 F, vinyl F cis to H), J(FC=CH-*trans*) = 23.6 Hz, J(FC=CH-*cis*) = 0.9 Hz, J(FCF) = 26.6 Hz.

Repetition of the reaction with mesitylene as an internal standard resulted in a 20% GLC yield of **9b**.

1,1-Difluoro-1,3-butadiene (9a). Phenyllithium (1.49 M in 70:30 benzene–ether, 6.7 mL, 0.010 mol) was added dropwise to a cooled (0 °C) slurry of allyltriphenylphosphonium bromide[29] (3.83 g, 0.010 mol) in triglyme (10 mL). The reaction mixture was stirred for 0.5 h at room temperature, and then chlorodifluoromethane (0.43 g, 0.005 mol) was condensed into the flask. After the mixture was stirred at room temperature for 72 h, ^{19}F NMR analysis of the reaction mixture showed unreacted chlorodifluoromethane and a trace signal assigned to **9a**, ϕ^* −120.8 (m). Dilution of the reaction mixture with ether (50 mL) followed by filtration afforded only a black tarry material.

1,1-Difluoro-2-methyl-1-propene. Methyllithium (1.90 M in ether, 52.6 mL, 0.100 mol) was added dropwise to a cooled (0 °C) slurry of isopropyltriphenylphosphonium iodide[30] (43.2 g, 0.100 mol) in triglyme (150 mL). The reaction mixture was stirred for 1 h at room temperature and the ether and methane were distilled away in vacuo and collected in a dry ice–2-propanol trap. Chlorodifluoromethane (4.33 g, 0.050 mol) was then condensed dropwise into the reaction mixture while the flask was cooled in an ice–water bath. After being stirred for 4 h at room temperature, the reaction mixture was heated to 60 °C while dry nitrogen was bubbled through it. After 2 h a 70% (3.22 g, 0.035 mol) isolated yield of 98% pure 1,1-difluoro-2-methyl-1-propene was obtained: bp 11–13 °C (752 mmHg); mass spectrum, *m/e* (relative intensity) 92 (100), 91 (24), 77 (44), 65 (72), 64 (39), 51 (76), 41 (68), 39 (53), 28 (68); IR (gas, 20 mmHg) 2994 (m), 2941 (m), 2882 (m), 1773 (s), 1449 (m), 1227 (s), 1200 (s), 1156 (s), 1100 (s), 953 (m), 808 (w), 801 (s), 709 (w), 706 (m); ^{1}H NMR (10% $DCCl_3$, Me_4Si) δ 1.56 (t), J(FC=CCH_3) = 3.3 Hz; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ external ϕ^* −97.8 (heptet), J(FC=CCH_3) = 3.2 Hz.

The reaction mixture was suction filtered, and the solid which was collected was recrystallized from ethanol–ether to yield 90% (19.4 g, 0.045 mol) isopropyltriphenylphosphonium iodide, mp 196–198 °C (lit.[30] mp 197–198 °C). The filtrate was poured into 500 mL of cold water and extracted with chloroform (2 × 100 mL). The chloroform extracts were dried over anhydrous magnesium sulfate, the solvent was evaporated, and the solid residue was recrystallized from 95% ethanol to give an 87% (11.4 g, 0.044 mol) yield of triphenylphosphine (mp 79–80 °C).

Repetition of the reaction employing *n*-hexane as an internal GLC standard on column A gave an 83% glc yield of olefin.

1,1-Difluoro-2-methyl-1-butene. Methyllithium (1.90 M in ether, 21.0 mL, 0.040 mol) was added dropwise with vigorous stirring to a cooled (0 °C) slurry of *sec*-butyltriphenylphosphonium bromide[24] (16.0 g, 0.040 mol) in triglyme (80 mL). The reaction mixture was stirred for 1 h at room temperature, and then the ether and methane were distilled in vacuo, followed by the addition of chlorodifluoromethane (1.73 g, 0.020 mol). The mixture was stirred for 4 h at room temperature and then flashed distilled. The flash distillate was fractionally distilled through a 15-cm glass-helices-packed column to give a 52% (1.10 g, 0.0104 mol) isolated yield of 97% pure 1,1-difluoro-2-methyl-1-butene: bp 25.5–27 °C (752 mmHg); mass spectrum, *m/e* (relative intensity) 106 (25), 91 (64), 77 (100), 65 (54), 64 (17), 51 (75), 41 (37), 39 (25), 28 (92); IR (gas, 20 mmHg) 2985 (m), 2950 (m), 2890 (m), 1770 (s), 1466 (m), 1383 (w), 1340 (w), 1280 (s), 1215 (s), 1168 (s), 1075 (s), 1026 (w), 922 (m), 721 (w); ^{1}H NMR (10% $DCCl_3$; Me_4Si) δ 1.92 (m, 2 H, CH_2), 1.55 (t, 3 H, vinyl CH_3), 0.99 (t, 3 H, CH_3), J(FC=CCH_3-*trans*) = 3.2 Hz, J(FC=CCH_3-*cis*) = 3.2 Hz, J(CH_2, CH_3) = 7.8 Hz, all other coupling remains unresolved; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ external) ϕ^* −98.4 (complex m).

Repetition of the reaction with *n*-hexane as an internal GLC standard resulted in an 81% GLC yield of the olefin on column A.

1,1-Difluoro-2,2-diphenylethylene (30). Methyllithium (1.90 M in ether, 28.4 mL, 0.054 mol) was added dropwise under nitrogen with cooling (0 °C) to a vigorously stirred slurry of benzhydryltriphenylphosphonium bromide[31] (27.5 g, 0.054 mol) in THF (100 mL). The resulting deep red solution was stirred for 1 h at room temperature, and then chlorodifluoromethane (6.92 g, 0.080 mol) was condensed into the reaction solution. After being stirred for 72 h at room temperature, the reaction mixture was filtered, the solvent was evaporated from the filtrate, pentane was

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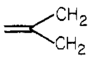
added, the mixture was filtered to remove precipitated triphenylphosphine, and the pentane was evaporated from the filtrate. Fractional distillation through a 15-cm Vigreux column gave a 57% (3.32 g, 0.016 mol) isolated yield of 96% pure **30** identical with an authentic sample.

Repetition of the reaction with 1,1-diphenylethylene as an internal GLC standard resulted in a 62% GLC yield on column A.

(Difluoromethylene)cyclohexane. Methyllithium (1.90 M in ether, 52.6 mL, 0.100 mol) was added dropwise to a slurry of cyclohexyltriphenylphosphonium bromide (**32**; 42.5 g, 0.100 mol) in ether (150 mL) under nitrogen with cooling (0 °C) in an ice–water bath. The resulting solution was stirred for 1 h at room temperature, and then CHF_2Cl (4.33 g, 0.050 mol) was condensed into the reaction mixture with vigorous stirring. After being stirred at room temperature for 4 h, the reaction mixture was filtered to give a 90% yield (19.9 g, 0.045 mol) of cyclohexyltriphenylphosphonium bromide. The filtrate was concentrated to ca. 25 mL by distillation of the ether and then was flash distilled. The residue from the flash distillation was recrystallized from 95% ethanol to give an 88% (11.5 g, 0.044 mol) yield of triphenylphosphine. The flash distillate was fractionally distilled through a 15-cm Vigreux column to give an 80% (5.29 g, 0.040 mol) yield of pure (difluoromethylene)cyclohexane identical with an authentic sample.

Repetition of the reaction with toluene as an internal standard resulted in an essentially quantitative GLC yield of the olefin on column A.

(Difluoromethylene)cyclopentane (37). Methyllithium (1.90 M in ether, 21.0 mL, 0.040 mol) was added dropwise to a cooled (0 °C) slurry of cyclopentyltriphenylphosphonium bromide (16.5 g, 0.040 mol) in triglyme (100 mL) under nitrogen. The reaction mixture was stirred for 1 h at room temperature, and then chlorodifluoromethane (3.46 g, 0.04 mol) was condensed into the reaction mixture. After being stirred for 12 h, the reaction mixture was filtered, and the filtrate was flash distilled. The flash distillate was fractionally distilled through a 15-cm glass-helices-packed column to give a 72% (1.70 g, 0.015 mol) isolated yield of 98% pure **37**: bp 73–75 °C (752 mmHg); mass spectrum (relative intensity) 118 (61), 104 (29), 90 (44), 77 (100), 67 (46), 64 (17), 54 (21), 39 (17); IR (neat) 2960 (m), 2875 (w), 1778 (s), 1450 (w), 1312 (w), 1251 (m), 1175 (m), 1053 (m), 999 (w), 947 (w); ^1H NMR (10% $DCCl_3$, Me_4Si) δ 2.23 (complex m, 4 H, I), 1.66 (complex m, 4 H, II); ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ external) ϕ^* −93.1 (complex m).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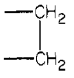
II

Repetition of the reaction with toluene as an internal GLC standard resulted in a 90% GLC yield of **37** on column A.

2,2-Difluorovinyl Methyl Ether (15a). Methyllithium (1.90 M in ether, 26.3 mL, 0.050 mol) was added dropwise with cooling (−4 to −5 °C) to a vigorously stirred suspension of (methoxymethyl)triphenylphosphonium chloride[34] (17.1 g, 0.050 mol) in triglyme (50 mL) under nitrogen. The reaction mixture was stirred at −5 °C for 1 h while the ether and methane were distilled in vacuo. The chlorodifluoromethane (2.16 g, 0.025 mol) was condensed into the reaction mixture, and after being stirred at room temperature for 4 h, the reaction mixture was flash distilled. Preparative GLC with column B resulted in a 40% (0.94 g, 0.010 mol) isolated yield of pure **15a**: mass spectrum, *m/e* (relative intensity) 94 (100), 79 (31), 65 (14), 64 (7), 63 (12), 62 (16), 51 (89), 50 (10), 32 (17), 31 (15), 29 (70), 28 (67), 27 (10), 15 (18); IR (10% CCl_4) 3045 (w), 3006 (w), 2937 (m), 2838 (m), 1776 (s), 1465 (m), 1451 (m), 1352 (m), 1248 (s), 1232 (s), 1144 (s), 996 (m), 962 (w), 931 (s), 812 (w), 723 (m); ^1H NMR (10% CCl_4, Me_4Si) δ 5.58 (dd, 1 H, vinyl H), 3.58 (s, 3 H, CH_3), $J(FC{=}CH\text{-}trans) = 16.0$ Hz, $J(FC{=}CH\text{-}cis) = 2.7$ Hz; ^{19}F NMR (10% CCl_4, $CFCl_3$ external) ϕ^* −102.2 (dd, 1 F, vinyl F trans to H), −121.2 (dd, 1 F, vinyl F cis to H), $J(FC{=}CH\text{-}trans) = 15.3$ Hz, $J(FC{=}CH\text{-}cis) = 2.6$ Hz, $J(FCF) = 77.6$ Hz.

Repetition of the reaction with α,α,α-trifluorotoluene as an internal standard resulted in a 65% NMR yield of **15a**.

2,2-Difluorovinyl Isobutyl Ether (15b). An ethereal solution of *n*-butyllithium (1.10 M, 54.6 mL, 0.060 mol) was added dropwise with vigorous stirring to a slurry of isobutoxymethyltriphenylphosphonium chloride (23.1 g, 0.060 mol) in triglyme (100 mL) cooled to −45 °C in dry ice–2-propanol. The reaction mixture was stirred at −45 °C for 0.5 h, and then chlorodifluoromethane (5.19 g, 0.060 mol) was slowly condensed into the reaction mixture, maintaining the temperature below −35 °C. The mixture was allowed to warm to room temperature and then stirred for an additional 2 h. The mixture was filtered, and the filtrate was poured into brine (500 mL). The organic layer was separated and dried over anhydrous calcium chloride. The ether was distilled through a 15-cm glass-helices-packed column, and the residue was flash distilled [60 °C (10 mmHg)]. Preparative GLC of the flash distillate on column D gave a 12% (0.82 g, 0.004 mol) isolated yield of 99% pure **15b**: mass spectrum, *m/e* (relative intensity) 136 (10), 80 (16), 57 (100), 56 (27), 55 (15), 51 (10); IR (CCl_4) 2960 (m), 2925 (w), 2875 (m), 1772 (s), 1472 (m), 1350 (s), 1243 (s), 1193 (m), 1147 (w), 1010 (m) 930 (m), 788 (m); ^1H NMR (10% CCl_4, Me_4Si) δ 5.53 (dd, 1 H, vinyl H), 3.40 (d, 2 H, OCH_2), 1.91 (m, 1 H, CH), 0.92 (d, 6 H, CH_3), $J(FC{=}CH\text{-}trans) = 16.0$ Hz, $J(FC{=}CH\text{-}cis) = 2.8$ Hz, $J(CH_2,CH) = 6.6$ Hz, $J(CH,CH_3) = 6.4$ Hz; ^{19}F NMR (10% CCl_4, $CFCl_3$ external) ϕ^* −103.4 (dd, 1 F, vinyl F trans to H), −124.3 (dd, 1 F, vinyl F cis to H), $J(FC{=}CH\text{-}trans) = 16.1$ Hz, $J(FC{=}CH\text{-}cis) = 2.6$ Hz, $J(FCF) = 82.9$ Hz.

Repetition of the reaction with α,α,α-trifluorotoluene as an internal ^{19}F NMR standard resulted in a 35% NMR yield of **15b**.

***β,β,β′,β′*-Tetrafluoro-*p*-divinylbenzene (17).** Phenyllithium (2.0 M in 70:30 benzene–ether, 100.0 mL, 0.200 mol) was added dropwise to a cooled (0 °C) slurry of *p*-xylylidenebis(triphenylphosphonium bromide) (78.8 g, 0.100 mol) in THF (150 mL) under nitrogen. The resulting solution was stirred at room temperature for 1 h, and then chlorodifluoromethane (8.65 g, 0.100 mol) was slowly condensed into the reaction mixture with cooling. The reaction mixture was stirred for 24 h at room temperature and then filtered. The filtrate was concentrated on a rotary evaporator, and the concentrate was flash distilled [70 °C (1 mmHg)]. Preparative GLC of the flash distillate on column B resulted in a 12% (1.21 g, 0.006 mol) isolated yield of 99% pure **17**: mass spectrum, *m/e* (relative intensity) 202 (6), 201 (48), 151 (27), 134 (18), 92 (46), 91 (100), 77 (11), 73 (12), 65 (16), 51 (16), 39 (16); IR (neat) 3115 (w), 3058 (w), 2778 (w), 1923 (w), 1739 (s), 1524 (w), 1433 (m), 1364 (s), 1295 (w), 1255 (s), 1177 (s), 948 (s), 858 (s), 703 (w); ^1H NMR (10% $DCCl_3$, Me_4Si) δ 7.15 (s, 4 H, C_6H_4), 5.09 (dd, 2 H, vinyl H), $J(FC{=}CH\text{-}trans) = 25.8$ Hz, $J(FC{=}CH\text{-}cis) = 4.2$ Hz; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ external) ϕ^* −82.0 (dd, 2 F, vinyl F trans to H), −84.0 (dd, 2 F, vinyl F cis to H), $J(FC{=}CH\text{-}trans) = 26.0$ Hz, $J(FC{=}CH\text{-}cis) = 4.4$ Hz, $J(FCF) = 31.5$ Hz.

Repetition of the reaction with toluene as an internal standard resulted in a 35% GLC yield of **17** on column A.

1,1-Difluoro-2-phenylpropene (24). A solution of *n*-butyllithium (2.0 M in hexane, 50.0 mL, 0.100 mol) was added dropwise with external cooling (0 °C) under nitrogen to a slurry of (1-phenylethyl)triphenylphosphonium bromide[24] (44.7 g, 0.100 mol) in triglyme (200 mL). The resulting solution was stirred for 1 h at room temperature, and then chlorodifluoromethane (8.65 g, 0.100 mol) was condensed into the reaction mixture with vigorous stirring. After being stirred for 24 h at room temperature, the reaction mixture was flash distilled, the distillate was washed with water and dried over anhydrous magnesium sulfate, and the hexane was distilled at atmospheric pressure. Fractional distillation of the residue through a 15-cm Vigreux column gave a 60% (4.63 g, 0.030 mol) isolated yield of 99% pure **24** identical with an authentic sample.

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(34) Methoxymethyltriphenylphosphonium chloride was prepared in this laboratory by D. A. Wiebe.

(35) Triphenylphosphine (131.2 g, 0.50 mol) and chloromethyl isobutyl ether (61.3 g, 0.50 mol) were refluxed in benzene (500 mL) for 15 h to yield 75% (142.2 g, 0.37 mol) of isobutoxymethyltriphenylphosphonium chloride: mp 197–200 °C dec.; ^1H NMR (10% $DCCl_3$, Me_4Si) δ 7.72 (m, 15 H, C_6H_5), 5.83 (d, 2 H, P–CH_2), 4.48 (d, 2 H, O–CH_2), 1.80 (m, 1 H, CH), 0.77 (d, 6 H, CH_3), $J(P, CH_2) = 3.9$ Hz, $J(CH_2, CH) = 6.2$ Hz, $J(CH, CH_3) = 6.4$ Hz.

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Repetition of the reaction with toluene as an internal standard resulted in an 82% GLC yield of **24** on column A.

Reaction of 22 with Chlorodifluoromethane and 2,3-Dimethyl-2-butene (21). Phenyllithium (1.49 M in 70:30 benzene–ether, 6.71 mL, 0.01 mol) was added dropwise to a cooled (0 °C) slurry of (1-phenylethyl)triphenylphosphonium bromide (4.47 g, 0.01 mol) in triglyme (20 mL) under nitrogen. The mixture was stirred for 0.5 h at room temperature and then was cooled to 0 °C in an ice–water bath. To this solution was added 2,3-dimethyl-2-butene (**21**) (3.50 g, 4.76 mL, 0.04 mol) followed by the addition of chlorodifluoromethane (1.72 g, 0.02 mol). The reaction mixture was allowed to warm to room temperature over 1 h and then was stirred at room temperature for 24 h. At this time GLC analysis on column A relative to toluene as an internal standard showed the presence of 59% **24** and 21% 1,1-difluoro-2,2,3,3-tetramethylcyclopropane (**23**).

Reaction of 3a and Chlorodifluoromethane and Steam Distillation. Phenyllithium (2.0 M in benzene–ether, 10.0 mL, 0.020 mol) was added dropwise to a cooled (0 °C) slurry of benzyltriphenylphosphonium chloride (7.78 g, 0.020 mol) in triglyme (20 mL) under nitrogen with vigorous stirring. After the mixture was stirred at room temperature for 1 h, chlorodifluoromethane (1.73 g, 0.020 mol) was condensed into the reaction mixture. After being stirred for 12 h, the reaction mixture was steam distilled to give a 62% yield of olefins by ^{19}F NMR analysis which was a 92:8 mixture of **28** [ϕ^* −83.9 (dd), −85.7 (dd), J(FC═CH-*trans*) = 26.5 Hz, J(FC═CH-*cis*) = 4.3 Hz, J(FCF) = 33.2 Hz] and **29**: ϕ^* −122.8 (dd), J(FC═CH-*trans*) = 44.7 Hz, J(HCF) = 82.0 Hz. **29** was identified by enhancement of its ^{19}F NMR signal with that of an authentic sample.[37]

Reaction of 3b and Chlorodifluoromethane and Steam Distillation. To **3b** (0.020 mol), generated by using phenyllithium, in THF (20 mL) was added chlorodifluoromethane (1.73 g, 0.020 mol). The reaction mixture was stirred for 72 h at room temperature and then filtered. Steam distillation of the filtrate resulted in a 65% yield of an 89:11 mixture of **30** [ϕ^* −88.1 (s)] and **31** [ϕ^* −127.1 (d), J(HCF) = 83.0 Hz] as determined by ^{19}F NMR analysis with $C_6H_5CF_3$ as an internal standard. **31** was identified by enhancement of its ^{19}F NMR signal with that of an authentic sample.[38]

Reaction of 8b and Chlorodifluoromethane and Steam Distillation. To a solution of **8b** (0.040 mol), generated by using phenyllithium, in triglyme (50 mL) was added chlorodifluoromethane (3.46 g, 0.040 mol), and the reaction mixture was stirred for 72 h. At this time ^{19}F NMR analysis showed the presence of **9b** [ϕ^* −85.3 (dd), −87.0 (dd), J(FC═CH-*trans*) = 23.6 Hz, J(FC═CH-*cis*) = 0.9 Hz, J(FCF) = 26.6 Hz] and **34**: ϕ^* −143.2 (dd), J(FC═CH-*trans*) = 48.5 Hz, J(PCF) = 51.0 Hz. The reaction mixture was steam distilled to give a mixture, 35% yield by ^{19}F NMR analysis, of a 57:43 mixture of **9b** and **32**: ϕ^* −127.2 (dd), J(FC═CH-*trans*) = 37.0 Hz, J(HCF) = 77.4 Hz. **32** was identified by enhancement of its ^{19}F NMR signal with that of an authentic sample.[39]

Reaction of 1b with Cyclopentanone. Tris(dimethylamino)phosphine (3.26 g, 0.020 mol) in triglyme (10 mL) was added dropwise to a cooled (0 °C) solution of dibromodifluoromethane (2.10 g, 0.010 mol) in triglyme (20 mL) with vigorous stirring, maintaining the temperature of the reaction mixture below 10 °C. The resulting slurry of white phosphonium salt was allowed to warm to room temperature and was stirred for 1 h. Cyclopentanone (1.26 g, 0.015 mol) was added, and the reaction mixture was heated to 70–80 °C and maintained at this temperature for 20 h. GLC analysis on column A with toluene as an internal standard resulted in an 8% yield of **37**. The reaction mixture was filtered, and ^{19}F NMR analysis of the filtrate relative to $C_6H_5CF_3$ as an internal standard showed a 9% yield of **37**. ^{19}F NMR analysis of the solid material collected by filtration revealed it to be an 85:15 mixture of $[(Me_2N)_3P^+CF_2Br]Br^-$ [ϕ^* −48.6 (d), J(PCF) = 83.0 Hz] and $[(Me_2N)_3P^+CF_2H]X^-$: ϕ^* −128.1 (dd), J(PCF) = 87.0 Hz, J(HCF) = 48.0 Hz.

Reaction of 1a with Methyl Formate. To a cooled solution of triphenylphosphine (26.2 g, 0.100 mol) in triglyme (100 mL) was added dibromodifluoromethane (21.0 g, 0.100 mol). The heavy white precipitate which formed immediately was stirred for 1 h at room temperature, and then cadmium metal (dust, 33.7 g, 300 mmol) was added via a solids addition tube followed by methyl formate (3.0 g, 0.050 mol). Following a short (ca. 5 min) induction period, a vigorous exothermic reaction occurred. After the mixture was stirred overnight at room temperature, GLC analysis on column C showed some formation of **15a**. ^{19}F NMR analysis of the reaction mixture relative to a $C_6H_5CF_3$ internal standard indicated a 30% yield of **15a** was achieved.

Acknowledgment. We thank the Army Research Office, the Air Force Office of Scientific Research, and the National Science Foundation for support of our work. Initial support of this project by the Petroleum Research Fund, administered by the American Chemical Society, is also gratefully acknowledged.

Registry No. **1a**, 33558-14-4; **1b**, 379-22-6; **3a**, 16721-45-2; **3b**, 4214-38-4; **4**, 6933-17-1; **5**, 37516-12-4; **6**, 13509-91-6; **7**, 84787-36-0; **8a**, 15935-94-1; **8b**, 56374-74-4; **9b**, 28321-12-2; **14a**, 20763-19-3; **14b**, 84787-32-6; **15a**, 2260-62-0; **15b**, 84787-34-8; **17**, 76841-60-6; **21**, 563-79-1; **22**, 58594-19-7; **23**, 823-25-6; **24**, 700-59-4; **28**, 405-42-5; **29**, 20405-78-1; **30**, 569-72-2; **31**, 390-75-0; **32**, 84787-35-9; **35**, 592-93-8; **37**, 694-75-7; HCF_2Cl, 75-45-6; $Ph_3P{=}CH(CH_2)_2CH_3$, 3728-50-5; $Ph_3P{=}CH(CH_2)_5CH_3$, 55367-56-1; $Ph_3P{=}CH(CH_2)_{10}CH_3$, 54208-04-7; $Ph_3P{=}C(CH_3)_2$, 16666-80-1; $Ph_3P{=}C(CH_3)C_2H_5$, 21481-98-1; $Ph_3P{=}CHC_6H_4CH{=}CF_2$-*p*, 84787-33-7; $F_2C{=}CH(CH_2)_2CH_3$, 4980-66-9; $F_2C{=}CH(CH_2)_{10}CH_3$, 60053-29-4; $F_2C{=}C(CH_3)_2$, 381-66-8; $F_2C{=}C(CH_3)C_2H_5$, 60053-30-7; cyclohexylidenetriphenylphosphorane, 16666-81-2; cyclopentylidenetriphenylphosphorane, 21482-00-8; (difluoromethylene)cyclohexane, 696-32-2; $[(Me_2N)_3PCF_2Br]Br$, 58310-30-8; *α,α,α*-trifluoroacetophenone, 434-45-7; cyclopentanone, 120-92-3; methyl formate, 107-31-3.

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[37] An authentic sample of **29** was prepared by the Wittig reaction between benzaldehyde and (fluoromethylene)triphenylphosphorane.

[38] An authentic sample of **31** was prepared by the Wittig reaction between benzophenone and (fluoromethylene)triphenylphosphorane.

[39] An authentic sample of **32** was prepared by the Wittig reaction between *trans*-cinnamaldehyde and (fluoromethylene)triphenylphosphorane.