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PRELIMINARY NOTE

The Reaction of Alkylidene Ylides With Fluoroolefins

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Fluoroolefins are well known to be highly electrophilic and to undergo nucleophilic substitution reactions with ease [1]. Our work in recent years with phosphonium ylides [2] (which can be viewed as stabilized nucleophiles) suggested that such ylides should react easily with fluoroolefins *via* an addition-elimination reaction to produce unsaturated phosphonium salts as outlined schematically below:

$$Ph_3\overset{+}{P}-\overset{-}{C}R^1R^2 \;+\; F_2C=CR^3R^4 \longrightarrow [Ph_3\overset{+}{P}-CR^1R^2-CF_2-\overset{-}{C}R^3R^4]$$

$$[Ph_3\overset{+}{P}-CR^1R^2-CF_2-\overset{-}{C}R^3R^4] \xrightarrow{\underline{-F^-}} [Ph_3\overset{+}{P}-CR^1R^2-CF=CR^3R^4]F^-$$

Hydrolysis of phosphonium salts usually ejects the most stable carbanion [3], which in the above outline generalized example would be expected to be the fluorine-containing group. Depending on the ease of protonation *vs*. elimination, the resultant carbanion could produce either olefinic or allenic

$$[Ph_3\overset{+}{P}-CR^1R^2-CF=CR^3R^4]F^- \xrightarrow{\underline{Hyd.}} R^1R^2\overset{-}{C}-CF=CR^3R^4 \leftrightarrow R^1R^2-C=CF-\overset{-}{C}R^3R^4$$

$$\downarrow$$

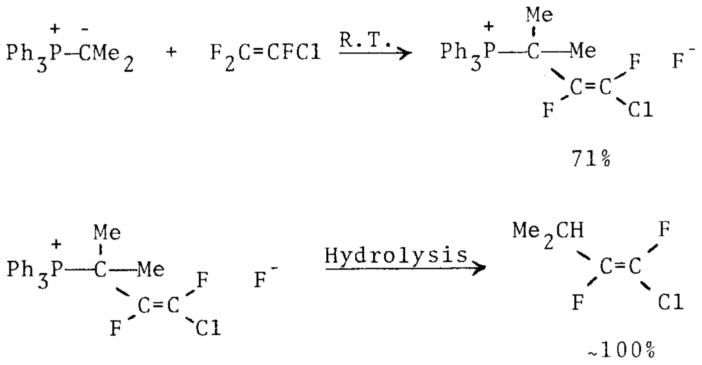
$$R^1R^2C=C=CR^3R^4 \text{ or } R^1R^2CHCF=CR^3R^4 \text{ or } R^1R^2C=CFCHR^3R^4$$

products and potentially afford a facile synthetic route to unsaturated organofluorine compounds not easily attainable by other currently available methods.

We have observed two general types of behavior in these reactions, and this communication outlines the results of our initial investigations.

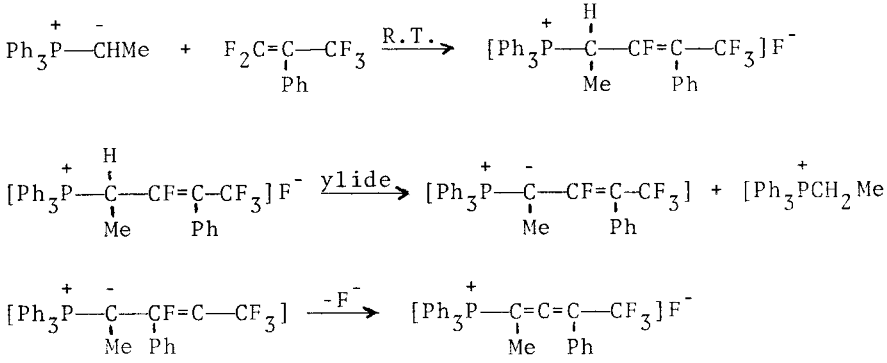
Type A: Ylides containing no *α*-hydrogen

With ylides of this type ($R^1,R^2 \neq H$) the reaction sequence proceeds precisely as outlined above for the generalized case. The stoichiometry is clearly 1:1, and simple vinylic fluorine substitution occurs to produce the allylic phosphonium salt [4]. A typical example is shown below:



Type B: Ylides containing an *α*-hydrogen

With ylides of this type the initially formed phosphonium salt reacts *via* a transylidation reaction with additional reactant ylide to produce a new fluorine-containing ylide - which undergoes *β*-elimination to ultimately form an allenic phosphonium salt. A typical illustration of this type of behavior is shown below:



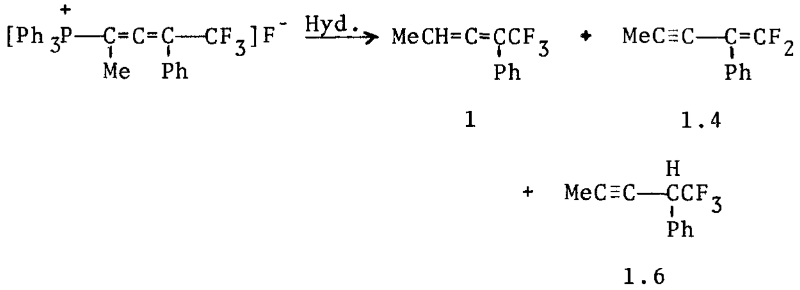
$$Ph_3\overset{+}{P}-\overset{-}{C}HMe + F_2C=\underset{Ph}{C}-CF_3 \xrightarrow{R.T.} [Ph_3\overset{+}{P}-\overset{H}{\underset{Me}{C}}-CF=\underset{Ph}{C}-CF_3]F^-$$

$$[Ph_3\overset{+}{P}-\overset{H}{\underset{Me}{C}}-CF=\underset{Ph}{C}-CF_3]F^- \xrightarrow{ylide} [Ph_3\overset{+}{P}-\overset{-}{\underset{Me}{C}}-CF=\underset{Ph}{C}-CF_3] + [Ph_3\overset{+}{P}CH_2Me$$

$$[Ph_3\overset{+}{P}-\overset{-}{\underset{Me}{C}}-\underset{Ph}{C}F=C-CF_3] \xrightarrow{-F^-} [Ph_3\overset{+}{P}-\underset{Me}{C}=C=\underset{Ph}{C}-CF_3]F^-$$

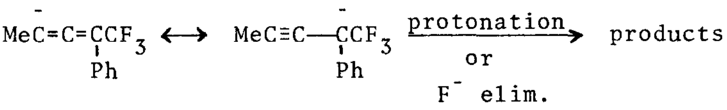
The stoichiometry of the reaction (ylide:olefin of 2:1) is in agreement with this type of behavior, and the hydrolysis products can only be accounted for via this type of reaction sequence. Subsequent to the completion of this work, Bestmann et. al. [5] have recently reported similar behavior with the simple methylene ylide in related systems, and their work is in complete agreement with our results.

Hydrolysis of the allenic phosphonium salt again produces a fluorine-containing anion, but product formation is not as clear-cut as in type A above. Three products are produced in



$$[\mathrm{Ph_3\overset{+}{P}{-}\underset{Me}{C}{=}C{=}\underset{Ph}{C}{-}CF_3}]F^- \xrightarrow{\text{Hyd.}} \underset{1}{\mathrm{MeCH{=}C{=}\underset{Ph}{C}CF_3}} + \underset{1.4}{\mathrm{MeC{\equiv}C{-}\underset{Ph}{C}{=}CF_2}} + \underset{1.6}{\mathrm{MeC{\equiv}C{-}\overset{H}{\underset{Ph}{C}}CF_3}}$$

an overall yield of 50% (based on starting olefin) in a ratio of 1:1.4:1.6 [6]. The products can easily be accounted for either by protonation or elimination reactions of the carbanion formed on hydrolysis.



$$\mathrm{Me\overset{-}{C}{=}C{=}\underset{Ph}{C}CF_3} \longleftrightarrow \mathrm{MeC{\equiv}C{-}\overset{-}{\underset{Ph}{C}}CF_3} \xrightarrow[\substack{\text{or} \\ \text{F}^-\text{ elim.}}]{\text{protonation}} \text{products}$$

The increased amounts of acetylenic type products produced most likely is a reflection of the charge density stabilization provided by the trifluoromethyl and phenyl groups.

In summary, the reaction of phosphonium ylides with fluoroolefins followed by hydrolysis of the resultant phosphonium salt does seem to offer a facile synthetic entry into some interesting unsaturated fluorinated systems. The type A behavior described is straightforward, and by the proper choice of ylide and olefin the substituents on the olefinic carbons can be easily varied. The type B behavior is obviously more complicated and the product distribution on hydrolysis may be dictated by the ability of the substituents to stablize the negative charge density in the intermediate carbanion. However, the method does potentially offer a facile one-step method to some interesting allenic or acetylenic organofluorine compounds.

Our work in this area continues to explore the scope of this reaction and will be reported in future publications.

1 R. D. Chambers and R. H. Mobbs, Advances in Fluorine Chemistry, Butterworth, 4 (1965), 50.

2 cf. D. J. Burton and P. E. Greenlimb, J. Org. Chem., 40 (1975), 2796.

3 M. Grayson and P. T. Keough, J. Amer. Chem. Soc., 82 (1960), 3919.

4 The stereochemistry shown for both the phosphonium salt and the olefin (from hydrolysis) is based on the magnitude of the J(F-F) coupling of 132-136 Hz respectively.

5 H. J. Bestmann and G. Schmid, Tetrahedron Letters (1975), 4025.

6 The ^{1}H and ^{19}F NMR, Ir, and mass spectra are consistent with the assignment of all the unsaturated hydrolysis products.