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PRELIMINARY NOTE

A Stereoselective Reduction of Polyfluorinated Olefins. A Facile Conversion of Difluoromethylene Olefins to Fluoromethylene Olefins *via* Vinyl Phosphoranes and Vinyl Phosphonium Salts

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Metallation of fluoromethylene olefins provides useful intermediates for further stereochemical synthetic sequences [1]. The requisite olefin precursors have been obtained either by chemical modification of fluorinated olefins [2-6] or Wittig type reactions [7]. These methods yield stereoselectively either the thermodynamically stable olefin or mixtures enriched in the more stable isomer. Here, we report a facile synthesis of the *thermodynamically less stable fluoromethylene olefin isomer* from the readily accessible vinyl phosphorane or vinyl phosphonium salt.

It has been established that the reaction of *F*-1-alkenes (**1**) with tertiary phosphine (**2**) stereoselectively yields vinyl phosphoranes (**3**) [8] or vinyl phosphonium salts [9]. Hydrolysis of (**3**) or (**4**) with water or dilute base stereospecifically gives the fluoromethylene olefin with *retention* of stereochemistry.

Table 1 summarizes the data for several representative olefins. Note that vinyl phosphorane formation occurs with formation of *only* the terminal phosphorane. No isomeric phosphoranes which could be formed by an S_N2' reaction were observed. Hydrolysis results in replacement of phosphorous with hydrogen (or deuterium). Since (**3**) or (**4**) are produced *insitu* [8], the overall net result is a one-pot stereoselective reduction of the difluoromethylene olefin to the fluoromethylene olefin.

This method gives *only* the (E)-isomer from *F*-propene. Earlier work has conclusively shown the (Z)-isomer to be the thermodynamically stable isomer of this pair [3]. In all cases, the stereoselective formation of the vinyl phosphorane with the R_F group *trans* to phosphorous is observed. Hydrolysis gives the olefin with the R_F group and hydrogen *trans*.

TABLE 1

Hydrolysis of vinylphosphorane (3) or vinyl phosphonium tetrafluoroborate (4) to fluoromethylene olefin (5)

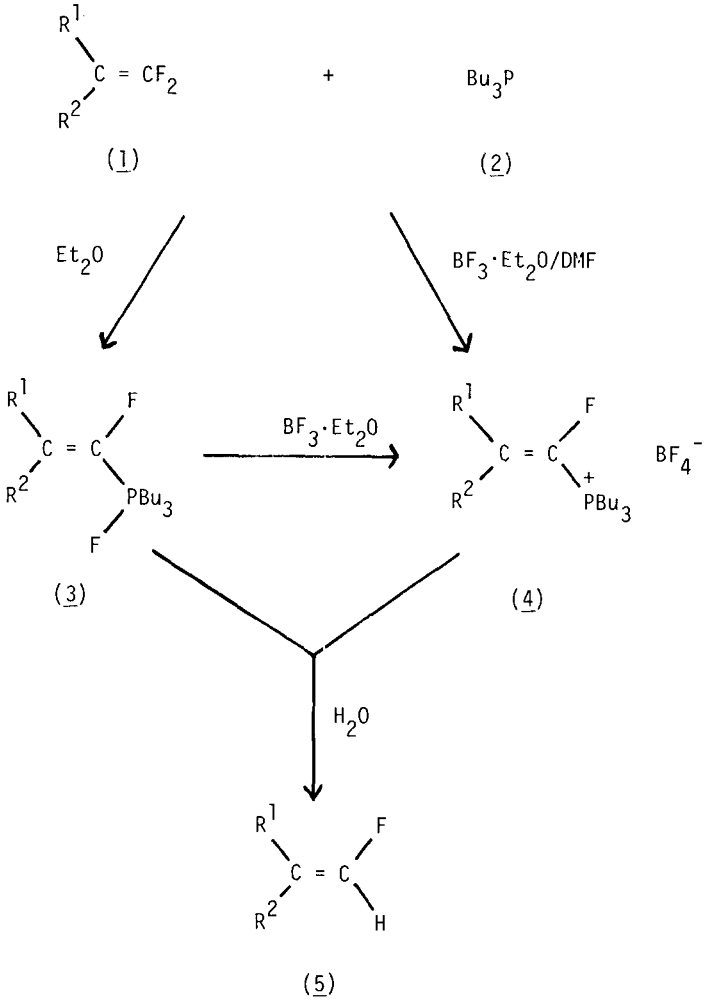
(3) or (4)	E/Z^c	%(5)^{a,b,d}	E/Z(5)^c
$CF_3CF = CFP(F)Bu_3$	0/100	97 (51)	100/0
$CF_3(CF_2)_2CF = CFP(F)Bu_3$	0/100	- (72)	100/0
$CF_3(CF_2)_4CF = CFP(F)Bu_3$	0/100	85	100/0
$PhC(CF_3) = CFP(F)Bu_3^{e}$	88/12	100 (61)	12/88
$PhC(CF_2CF_3) = CFP(F)Bu_3$	92/8	- (47)	0/100
$p\text{-}MeOC_6H_4C(CF_3) = CFP(F)Bu_3$	95/5	100 (52)	9/91
$[PhCH = CF\overset{+}{P}Bu_3]\ BF_4^{-f}$	100/0	- (87)	0/100

a) Determined by ^{19}F NMR vs. internal $C_6H_5CF_3$., b) Yield in parentheses is overall isolated yield from olefin (1)., c) E/Z ratio is determined from the coupling constant in the ^{19}F NMR spectrum., d) All products exhibited spectral data in accord with the assigned structure and gave satisfactory mass spectral or analytical data., e) hydrolysis with D_2O gave only the deuterated olefin, f) DMF used as solvent.

In cases where (3) is unstable or is formed slowly in ether, the reaction can be carried out in moist DMF to give (5) directly. However, stereochemical control is decreased under these conditions.

$$CF_3CCl = CF_2 + Bu_3P \xrightarrow{H_2O/DMF} CF_3CCl = CFH \quad 54\%(E/Z = 87/13)$$

$$PhCCl = CF_2 + Bu_3P \xrightarrow{H_2O/DMF} PhCCl = CFH \quad 73\%(71/29\ \text{mixture})$$



This remarkably simple, rapid, and clean reaction provides a ready synthetic entry to the isomeric olefins currently inaccessible by existing methods.

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REFERENCES

1 J.L. Hahnfeld and D.J. Burton, Tetrahedron Letters, (1975), 773.

2 D. Sianesi and R. Fontanelli, Ann. Chem. (Italy), 55 (1965), 850.

3 R.N. Haszeldine, J.R. McAllister, and A.E. Tipping, J.C.S. Perkin Trans I, (1975), 2015.

4 L.I. Zakharkin and V.N. Lebedev, J. Fluorine Chem., 3 (1973/1974), 237

5 S. Hayashi, T. Nakai, N. Ishikawa, D.J. Burton, D.G. Naae, and H.S. Kesling, Chemistry Letters, (1979), 983.

6 A.L. Anderson, R.T. Bogan, and D.J. Burton, J. Fluorine Chem., 1 (1971/1972), 121.

7 D.J. Burton and P.E. Greenlimb, J. Org. Chem., 40 (1975) 2796., J. Fluorine Chem., 3 (1973/1974), 447.

8 D.J. Burton, S. Shin-ya, and R.D. Howells, J. Amer. Chem. Soc., 101 (1979), 3689.

9 The vinyl phosphoranes (3) slowly react with DMF when this solvent is employed, (4) is the preferred intermediate.