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The Preparation of α-Fluorosulfoxides and Vinyl Fluorides

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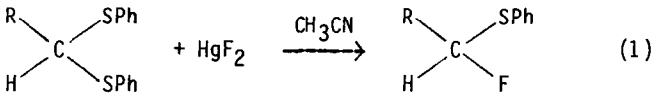
Summary: Treatment of thioacetals with HgF_2 in anhydrous acetonitrile, followed by oxidation with MCPBA results in the formation of α-fluorosulfoxides, which can be pyrolyzed to give vinyl fluorides.

Synthetic procedures for the preparation of organofluorine compounds are of current interest because these compounds can be used as a probe of various biochemical processes. A number of approaches to alkenyl fluorides has been developed, including the elimination of HF from difluoro compounds with alumina[1], treatment of vinyl lithium reagents with N-fluoro-N-alkylsulfonamides[2] and by the Wittig reaction of fluoromethylenetriphenylphosphorane[3]. In this letter, we present a complementary synthesis of terminal vinyl fluorides from the dithioacetals of various aldehydes.

Because of stabilization of carbocations by α-thio groups[3] and because of the affinity of mercury for sulfur, we speculated that thioacetals, readily available from aldehydes, would give α-fluorothioethers on treatment with HgF_2 in aprotic media. Precedent for this



1 **2** (1)

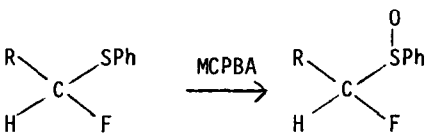
transformation is found in the conversion of thioacetals to acetals in anhydrous alcohol in the presence of $HgCl_2$[5]. In the first reaction, fluoride attacks the α-thiocarbocation intermediate, while in the second alcohol acts as the nucleophile.

Not unsurprisingly, the stabilization of α-thiocarbocations results in limited stability of α-fluorothioethers. In fact, the only α-fluorothioethers that have been characterized

contain either a p-methoxyphenylthio group[6], an α-carboalkoxy group[7], or an unsubstituted fluoromethyl group[8]. Groups that supress the formation of an α-thiocarbocation account for the stability of these compounds.

The α-fluorothioether is complexed with the mercuric ion when formed in reaction (1). Treatment of the complex with basic $NaBH_4$ liberates the free α-fluorothioether which can be characterized by ^1H and ^{19}F NMR. However, attempted purification by distillation or chromatography results in decomposition.

The crude α-fluorothioethers can be oxidized **in situ** by the method of McCarthy, Peet and coworkers[6] to give stable α-fluorosulfoxides. The procedure reported here complements the work of McCarthy, et al., who treated sulfoxides with DAST to form an α-fluorosulfide which was subsequently oxidized to the α-fluorosulfoxide. In reaction (1) the HgF_2 used to convert the thioacetal to the α-fluorothioether doesn't pose hazards that may be involved with the use of DAST[9]. The reactions shown in equations (1) and (2) also complement the method of Reutrakul and Rukachaisirikul[10] who studied the reaction of lithio fluoromethyl phenyl sulfoxide with alkyl halides.



2 **3** (2)

Table I lists the α-fluorosulfoxides prepared by eq. 1 and 2. A typical procedure follows. To a solution of the thioacetal of phenylacetaldehyde (3.22g, 0.01 mole, in 75mL dry acetonitrile) is added mercuric fluoride (2.38g, 0.01 mole Ozark-Mahonning) under nitrogen. After stirring 18h, the solution is added to 150mL 0.5M $NaBH_4$ (3M NaOH) and $HCCl_3$ (200mL) and stirred for 2h. The solution is filtered and the organic layer is evaporated to give the α-fluorosulfide (1.90g, 0.0082 mole). The crude sulfide is dissolved in 100mL $CHCl_3$ and m-CPBA (1.77g, 0.0082 mole) is added at -20° C. The solution is stirred 12h and then added to 100mL 10% NaOH. The organic layer is separated, dried and evaporated to give the α-fluorosulfoxide (1.93g, 78%). The α-fluorosulfoxide is purified by flash chromatography using petroleum ether and ethyl acetate.

Table I. Preparation of α-Fluorosulfoxides

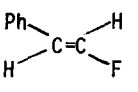
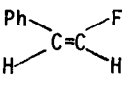
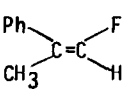
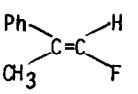
Thioacetal	Sulfoxide[a]	% Yield	mp(°C)	^{19}F NMR
$PhCH(CH_3)CH(SPh)_2$	$PhCH(CH_3)CHFSOPh$	48	68-70	188 ($^2J_{HF}$=54, $^3J_{HF}$=37 Hz)
$Et_2CHCH(SPh)_2$	$Et_2CHCHFSOPh$	68	49-52	189 ($^2J_{HF}$=54, $^3J_{HF}$=34 Hz)
$Ph_2CHCH(SPh)_2$	$Ph_2CHCHFSOPh$	59	128-130	185 ($^2J_{HF}$=54, $^3J_{HF}$=39 Hz)
$PhCH_2CH_2CH(SPh)_2$	$PhCH_2CH_2CHFSOPh$	86	oil	187 ($^2J_{HF}$=51, $^3J_{HF}$=30 Hz)
$PhCH_2CH(SPh)_2$	$PhCH_2CHFSOPh$	78	oil	187 ($^2J_{HF}$=54, $^3J_{HF}$=34 Hz)
$Me_3CCH(SPh)_2$	$Me_3CCHFSOPh$	60	80	189 ($^2J_{HF}$=50 Hz)

a. Satisfactory analyses obtained on all new compounds.

The α-fluorosulfoxides with a β-hydrogen can be pyrolyzed to terminal vinyl fluorides as shown in equation 3. Since the α-fluorosulfoxides are formed as mixtures of diastereomers both E- and Z-alkenes are formed on elimination as shown in Table II.

$$RCH_2\underset{F}{C}HSOPh \xrightarrow{\text{heat}} RCH{=}CHF \qquad (3)$$

Table II. Preparation of Vinyl Fluorides

Sulfoxide	Alkene	^{19}F NMR[a]	% Yield
$Ph_2CHCHFSOPh$	$Ph_2C{=}CHF$	129 ($^2J_{HF}$=83 Hz)	38
$PhCH_2CHFSOPh$		131 ($^2J_{HF}$=80 Hz)	62
		123 ($^2J_{HF}$=80 Hz)	
$PhCH(CH_3)CHFSOPh$		125 ($^2J_{HF}$=85 Hz)	80
		133 ($^2J_{HF}$=85 Hz)	

a. The chemical shifts and coupling constants are in accord with those observed in ref. 3.

Further experiments on the dithioacetals of ketones and functionalized aldehydes are planned so as to extend the scope of the reaction. Reduction of the intermediate α-fluorosulfides to give alkyl fluorides is also contemplated.

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