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A NEW SYNTHESIS OF ALKYL FLUORIDES

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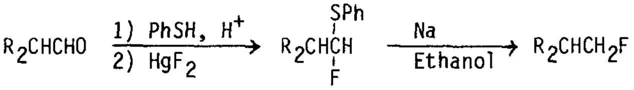
Summary: Reduction of α-fluorosulfides with sodium in alcohol results in the formation of fluoroalkanes.

We recently reported a novel synthesis for α-fluorosulfides from thioacetals and mercuric fluoride in acetonitrile at room temperature.[1] Purification of the unstable α-fluorosulfides proved impossible, thus they were oxidized to the more stable α-fluorosulfoxides. After purification and analysis they were pyrolyzed to vinyl fluorides. In an attempt to extend the use of these selectively fluorinated sulfides, a method to reductively desulfurize them to alkyl fluorides has been developed.

Alkali metals have been used to desulfurize allylic sulfides.[2,3] Lithium in liquid ammonia has been reported to reduce carbon sulfur bonds of thiols albeit in low yields.[4] Recently, Kodama reported the cleavage of alkyl sulfur bonds by sodium in tert-butyl alcohol.[5] We wish to report the use of sodium metal in ethanol to desulfurize α-fluorosulfides.



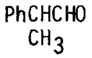
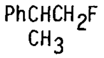
$$R_2CHCHO \xrightarrow[2)\ HgF_2]{1)\ PhSH,\ H^+} R_2CH\underset{F}{\overset{SPh}{C}}H \xrightarrow[Ethanol]{Na} R_2CHCH_2F$$

In a typical reduction, the α-fluorosulfide (0.1 mol) is stirred in a round bottom flask equipped with a water cooled condenser with 50 mL of absolute ethanol. Freshly cut slivers of sodium (0.5 mol) are dropped down the condenser into the flask. The solution is allowed to reflux while the sodium reacts and is then extracted with water and ether to give the alkyl fluorides in 63-91% yield from the α-fluorosulfide. The results, shown in the Table, give yields for the three step conversion from the aldehyde. For the two lower boiling fluoroalkanes methanol was used as solvent and decane (bp, 174°C) as the extractant from which the fluoroalkane was distilled. When higher boiling primary alcohols were used, elimination of HF to give a vinyl sulfide was a competing reaction. Substitution of lithium for sodium resulted in only 10% cleavage.

Thus, aldehydes, by way of their acetals, can conveniently be converted into alkyl fluorides.

TABLE

Preparation of Alkyl fluorides

Aldehyde	Alkyl fluoride	% Yield	bp,°C(Torr)	^{19}F(NMR)	Ref.
$(CH_3)_3CHO$ [a]	$(CH_3)_3CCH_2F$	32	40-41	-220 ($^2J_{HF}$=50.2Hz)	6
$(CH_3CH_2)_2CHCHO$ [a]	$(CH_3CH_2)_2CHCH_2F$	38	94-95	-227 ($^2J_{HF}$=51,$^3J_{HF}$=19.2Hz)	7
Ph_2CHCHO	Ph_2CHCH_2F	81	180(15)	-215 ($^2J_{HF}$=51,$^3J_{HF}$=19Hz)	8
$PhCH_2CHO$	$PhCH_2CH_2F$	44	63(15)	-215 ($^2J_{HF}$=48,$^3J_{HF}$=24Hz)	9
 $\underset{CH_3}{PhCH}CHO$	 $\underset{CH_3}{PhCH}CH_2F$	48	65(15)	-216 ($^2J_{HF}$=51,$^3J_{HF}$=19Hz)	b
$PhCH_2CH_2CHO$	$PhCH_2CH_2CH_2F$	62	70(15)	-220 ($^2J_{HF}$=51,$^3J_{HF}$=19Hz)	10

a. CH_3OH was used in place of CH_3CH_2OH. b. Anal. Calcd for $C_9H_{11}F$: C, 78.23; H, 8.02. Found: C, 78.34; H, 8.02.

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