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REACTION OF SF<sub>4</sub> WITH ALCOHOLS: PREPARATION OF  
2-(FLUOROMETHYL)FURAN AND 2-FLUORO-1-PHENYLETHANE

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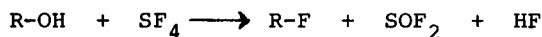
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SUMMARY

The fluorination of (2-furyl)methanol and 2-phenylethanol with sulfur tetrafluoride is described. The reactions were carried out in glass tubes at -50°C in the presence of triethylamine or pyridine in dichloromethane or cyclohexane solution. The products, (2-fluoromethyl)furan and 2-fluoro-1-phenylethane, were identified by <sup>1</sup>H and <sup>19</sup>F NMR and mass spectrometry.

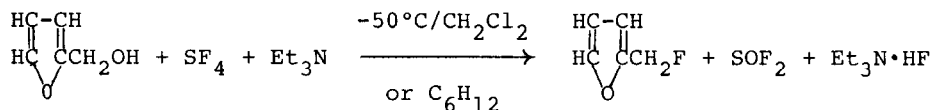
RESULTS AND DISCUSSION

Sulfur tetrafluoride is suitable for the conversion of alcohols to fluorides [1], provided that the chemical reagents and products do not decompose during the course of the reaction



[2]. With aliphatic alcohols in particular, decomposition is often a problem and consequently various alternative fluorinating agents have been introduced, including diethylaminosulfur trifluoride [3], SeF<sub>4</sub>·pyridine [4], and HF·amine reagents [5]. Previously, we found that fluorination of substituted benzyl alcohols with SF<sub>4</sub> occurred smoothly in glass apparatus in the presence of Et<sub>3</sub>N as HF scavenger [6]. To test this procedure on more sensitive alcohols, we studied the reactions of SF<sub>4</sub> with (2-furyl)methanol and 2-phenylethanol.

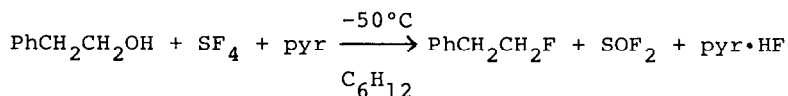
The reaction with (2-furyl)methanol took place in a sealed glass tube in dichloromethane or cyclohexane solution, on warming from  $-196$  to  $-50^{\circ}\text{C}$ . With cyclohexane as solvent, two



layers formed at  $-50^{\circ}\text{C}$ , and the evolution of gas bubbles (presumably  $\text{SOF}_2$ ) was observed from the bottom dark brown layer.

(2-Fluoromethyl)furan decomposed during distillation, but separation in 20% yield and purification without decomposition was accomplished by gas chromatography. The product was identified by  $^1\text{H}$  and  $^{19}\text{F}$  NMR and mass spectrometry.

The fluorination of  $\text{PhCH}_2\text{CH}_2\text{OH}$  was also studied. Although  $\text{PhCH}_2\text{CH}_2\text{F}$  can be prepared from  $\text{PhCH}_2\text{CH}_2\text{OH}$  [3,4], tosylates [7], or  $\text{PhCH}_2\text{CH}_2\text{COOH}$  [8], it has not, as far as we are aware, been prepared from  $\text{PhCH}_2\text{CH}_2\text{OH}$  and  $\text{SF}_4$ . The procedure was similar to that described for (2-furyl)methanol, except that pyridine was used as the HF scavenger.



Although HF is sometimes used as a catalyst or solvent in  $\text{SF}_4$ -alcohol reactions [9], its effect on sensitive alcohols must be considered if the fluorinating properties of  $\text{SF}_4$  are to be fully utilized. Analogous reactions of sulfur fluorides in the presence of base or alkali metal fluorides [10] are also consistent with the view that HF must be controlled in these systems. With more stable reagents and products, including acidic alcohols [1], such precautions are apparently unnecessary.

## EXPERIMENTAL

(2-Furyl)methanol and 2-phenylethanol were commercial samples which were re-distilled prior to use.  $\text{SF}_4$  was handled in a metal vacuum line. Glass reaction tubes were dried in an oven or treated with  $(\text{Me}_3\text{Si})_2\text{NH}$  and then evacuated.

$^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were recorded on Varian A-56/60A and HA100 spectrometers with the use of  $\text{Me}_4\text{Si}$  and  $\text{CFCl}_3$  as internal reference. Mass spectra were obtained on a Finnigan 1015 quadrupole mass spectrometer. Gas chromatographic separations were carried out on a Varian 1700 instrument and conditions were optimized using  $(2\text{-furyl})\text{CH}_2\text{OSiMe}_3$ .

$(2\text{-Furyl})\text{CH}_2\text{OSiMe}_3$  was prepared by gently refluxing  $(2\text{-furyl})\text{methanol}$  (3 g),  $\text{Me}_3\text{SiCl}$  (3.3 g) and  $\text{Et}_3\text{N}$  (3.8 g) for 30 min, followed by distillation of  $(2\text{-furyl})\text{CH}_2\text{OSiMe}_3$  at 124-128°C under house vacuum (58% yield). Mass spectrum:  $m/z(\text{ion})$  170( $\text{M}^+$ ), 155( $\text{M}^+-15$ ), 142( $\text{M}^+-28$ ).  $^1\text{H NMR}(\text{CCl}_4)$ :  $\delta$  0.1 ppm(s,9H), 4.5 ppm(s,2H), 6.2 ppm(m,2H), 7.3 ppm(m,1H).

#### Preparation of (2-fluoromethyl)furan

In dichloromethane:  $\text{SF}_4$  (31 mmol) was condensed from a metal vacuum line into a glass reaction tube containing  $(2\text{-furyl})\text{methanol}$  (3 g, 31 mmol),  $\text{Et}_3\text{N}$  (3.1 g, 31 mmol), and dichloromethane (5 mL) at -196°C and the tube was sealed. Reaction occurred on warming to -50°C within 5 min, yielding a homogeneous brown solution. Attempted distillation at 55-90°C at atmospheric pressure gave a black decomposed solid. However, separation and purification was achieved by gas chromatography, and the product (2-fluoromethyl)furan (20% yield) was identified by MS and NMR. Mass spectrum:  $m/z(\text{ion})$  100( $\text{M}^+$ ), 99( $\text{M}^+-\text{H}$ ), 84( $\text{M}^+-16$ ), 81( $\text{M}^+-19$ ), 69( $\text{M}^+-31$ ), 56( $\text{M}^+-44$ ).  $^1\text{H NMR}(\text{C}_6\text{H}_{12})$ :  $\delta$  4.9 ppm(d,2H  $^2\text{J}_{\text{HF}}=50$  Hz), 6.0-6.2 ppm(m,2H), 7.1 ppm(m,1H).  $^{19}\text{F NMR}(\text{C}_6\text{H}_{12})$ :  $\delta$  -238 ppm( $^2\text{J}_{\text{FH}}=50$  Hz).

In cyclohexane: The reaction was carried out as described above using  $(2\text{-furyl})\text{methanol}$  (3 g, 31 mmol),  $\text{Et}_3\text{N}$  (3.1 g, 31 mmol) and  $\text{SF}_4$  (31 mmol) in cyclohexane (5 mL). Two layers

formed at  $-50^{\circ}\text{C}$ , light brown on top and dark brown on bottom and continuous evolution of gas from lower layer (presumably  $\text{SO}_2$ ) was observed. (2-Fluoromethyl)furan was formed in 18% yield.

Without solvent: The reaction of (2-furyl)methanol (20 mmol) with  $\text{SF}_4$  (21 mmol) and  $\text{Et}_3\text{N}$  (21 mmol) was attempted without a solvent, but this resulted in an explosion.

### Preparation of 2-fluoro-1-phenylethane

The procedure described above was used for the reaction of  $\text{SF}_4$  and 2-phenylethanol, except that pyridine was added instead of  $\text{Et}_3\text{N}$ , in cyclohexane solution. The product  $\text{PhCH}_2\text{CH}_2\text{F}$  (35% yield) was identified by NMR [8].  $^1\text{H}$  NMR( $\text{C}_6\text{H}_{12}$ ):  $\delta$  2.8 ppm (d, t 2H,  $^3\text{J}_{\text{HH}}=6.8$  Hz,  $^3\text{J}_{\text{HF}}=24$  Hz), 4.4 ppm (d, t 2H,  $^2\text{J}_{\text{HF}}=47$  Hz,  $^3\text{J}_{\text{HH}}=6.8$  Hz), 6.9-7.1 ppm (m, 5H).  $^{19}\text{F}$  NMR( $\text{C}_6\text{H}_{12}$ ):  $\delta$  -215 ppm.

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