samples. The results of the experiments and a representative run are tabulated in Tables I and III.

TABLE III
REPRESENTATIVE RUN.
RAW KINETIC DATA FROM THE REACTION OF
2-(N,N-DIETHYLAMINO)-1-(2,4,6-TRIMETHYLPHENYL)ETHANOL
WITH 4 N HCl AT 100°

Time, min	Absorbance (at 267 nm)
0	0.547
19	0.432
37	0.346
58	0.282
79	0.225
98	0.184
118	0.152

Registry No.—ArCOCH$_3$ (Ar = C$_6$H$_5$), 98-86-2; ArCOCH$_3$ (Ar = p-CH$_3$C$_6$H$_4$), 122-00-9; ArCOCH$_3$ (Ar = 2,4-di-CH$_3$C$_6$H$_3$), 89-74-7; ArCOCH$_3$ (Ar = 2,4,6-tri-CH$_3$C$_6$H$_2$), 1667-01-2; ArCOCH$_2$Br (Ar = C$_6$H$_5$), 70-11-1; ArCOCH$_2$Br (Ar = p-CH$_3$C$_6$H$_4$), 619-41-0; ArCOCH$_2$Br (Ar = 2,4-di-CH$_3$C$_6$H$_3$), 26346-85-0; ArCOCH$_2$Br (Ar = 2,4,6-tri-CH$_3$C$_6$H$_2$), 4225-92-7; ArCOCH$_2$NEt$_2$ (Ar = C$_6$H$_5$), 4061-29-4; ArCOCH$_2$NEt$_2$ (Ar = p-CH$_3$C$_6$H$_4$), 39008-15-6; ArCOCH$_2$NEt$_2$ (Ar = 2,4-di-CH$_3$C$_6$H$_3$), 39008-16-7; ArCOCH$_2$NEt$_2$ (Ar = 2,4,6-tri-CH$_3$C$_6$H$_2$), 39008-17-8; Br$_2$, 7726-95-6; LiAlH$_4$, 16853-85-3; diethylamine, 109-89-7.

An Improved Synthesis of 2-Chloro-2-fluoropropane

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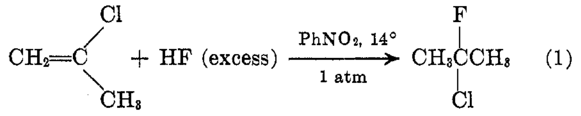
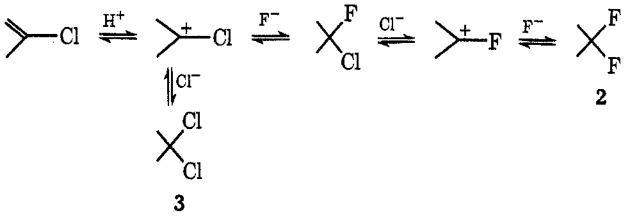
2-Chloro-2-fluoropropane (**1**) was first prepared in 10–15% yield by the action of antimony trifluoride containing 5% bromine on 2,2-dichloropropane in 1937 by Henne.[1] Small yields of **1** can also be prepared[2] by heating (CH$_3$)$_2$CClN(O)=NF to 60° and by the action of chlorine in the liquid or gas phase on 2-fluoropropene.[3-5] The free-radical chlorination of 2-fluoropropane gave 2-chloro-2-fluoropropane in 77% yield.[6] Henne[7] found that the reaction of 2-chloropropene with anhydrous fluoride (without solvent) yielded a mixture of 2,2-difluoropropane and 2,2-dichloropropane instead of the simple addition product **1**. However, Chapman[8] did obtain a 47% yield of **1** by the stannic chloride catalyzed addition of anhydrous hydrogen fluoride to 2-chloropropene.

We have found that the simple addition of hydrogen fluoride to 2-chloropropene to produce **1** can be achieved very smoothly and in high yield (75%) when the reaction is carried out in nitrobenzene at 14° for 10 min, as shown in eq 1. The use of nitrobenzene moderated the reactivity of hydrogen fluoride and permitted the clean addition of HF across the double bond without further reaction to produce 2,2-difluoropropane (Scheme I) or the formation of tars. Reaction times greater than 10 min led to a disproportionation, producing 2,2-difluoropropane (**2**) and 2,2-dichloropropane (**3**) as shown in Scheme I. The disproportionation products **2** and **3** were readily distinguished from **1** by their nmr spectrum. The methyl absorption of **2** was a triplet, of **3** was a singlet, and of **1** was a doublet.



$$CH_2{=}C(Cl)CH_3 + HF\ (excess) \xrightarrow[1\ atm]{PhNO_2,\ 14^\circ} CH_3CF(Cl)CH_3 \qquad (1)$$

SCHEME I



The yield (75%) was based on isolated material. However, an nmr spectrum of the crude reaction mixture showed no products other than **1** and indicates, if allowances are made for recovered starting material and for evaporation (bp 35°) of product during work-up, that the addition is highly efficient.

Experimental Section

To 80 ml of nitrobenzene (dried, reagent) in a 125-ml Teflon bottle containing a Teflon-coated magnetic stirring bar was added 10.0 g (0.130 mol) of 2-chloropropene. Anhydrous hydrogen fluoride gas was rapidly added to the cooled (14°) mixture until 22 g (1.1 mol) had been absorbed. The mixture was allowed to stir for 10 min, and then rapidly added to cold water. Carbon tetrachloride (300 ml) was added, the organic layer was washed three times with water and dried (Na$_2$SO$_4$), and the solution was distilled on a spinning band column to yield 10.7 g of liquid, bp $<50^\circ$ (mostly 35°). Integration of the pmr spectrum indicated that 13 mol % (11 wt %) of the isolated material was 2-chloropropene. Thus a yield of 75% and an efficiency of 89% were realized. The sample was redistilled on a spinning band column to obtain pure 2-chloro-2-fluoropropane: bp 33–35°; ir 824 and 604 cm^{-1}; pmr (CDCl$_3$) (60 MHz) δ 1.99 (d, J = 19.0 Hz); pmr (acetone-d_6) (100 MHz) δ 1.85 (d, J = 19.0 Hz); ^{19}F nmr (acetone-d_6) (100 MHz) δ 10.42 upfield from external CF$_3$CO$_2$H (septet, J = 19.0 Hz); mass spectrum (70 eV) m/e (rel intensity) 96 (0), 83 (7), 81 (20), 61 (100), 59 (11), 45 (13), 41 (36), 39 (15), 33 (7), 27 (6).

Registry No.—**1**, 420-44-0; 2-chloropropene, 557-98-2; hydrogen fluoride, 7664-39-3.

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