A NEW SYNTHESIS OF ALKYL FLUORIDES

THE PYROLYSIS OF 2-ALKYLPSEUDOURONIUM FLUORIDES AND FLUOROBORATES[1]

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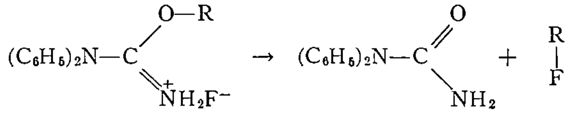
ABSTRACT

The pyrolysis of 2-alkylpseudouronium fluorides and fluoroborates at approximately 185° gave alkyl fluorides in yields of up to 77%. The method is most useful for the preparation of primary alkyl fluorides; attempts to prepare secondary fluorides, such as cyclohexyl fluoride, gave the corresponding alkenes.

In the general investigation of new methods of forming the C—F bond, we have examined the pyrolysis of 2-alkylpseudouronium fluorides and fluoroborates. The reaction is analogous to the decomposition of 2-alkylpseudouronium chlorides (1).



$$(C_6H_5)_2N{-}C(O{-}R){=}\overset{+}{N}H_2F^- \rightarrow (C_6H_5)_2N{-}C({=}O)NH_2 + R{-}F$$

The pseudouronium salts were most conveniently prepared from diphenylcyanamide and the appropriate alcohols in the presence of potassium *tert*-butoxide (1–3). The reaction is readily followed by infrared spectroscopy: the C≡N stretching band at 2 250 cm^{-1} gives way to the new C=N band at 1 640 cm^{-1}. Maximum yields are obtained when the alcohols are freshly distilled and when moisture is rigorously excluded. The fluoride salts were prepared by mixing a dried ethereal solution of the resultant free base with an ethereal solution of hydrogen fluoride; the fluoroborates were obtained with 48% aqueous fluoroboric acid. The fluorides usually had the approximate composition B·3HF whereas the fluoroborates had the expected stoichiometrical composition B·HBF$_4$. (These ratios were used in the calculation of yields.) Occasionally other methods of preparation were used (3), but were generally less satisfactory. Some yields of pseudouronium salts are shown in Table I.

TABLE I

2-Alkylpseudouronium fluorides and fluoroborates

	$(C_6H_5)_2NC(OR){=}\overset{+}{N}H_2F^-$		$(C_6H_5)_2NC(OR){=}\overset{+}{N}H_2BF_4^-$	
R	Yield (%)	Melting point (°C)	Yield (%)	Melting point (°C)
$CH_3(CH_2)_4$	92	124–125	72	97–98
$CH_3(CH_2)_5$	88	118–121	83	98–99
$CH_3(CH_2)_7$	88	127–128	76	97–98
$CH_3(CH_2)_9$	89	123–125	75	86–87
$CH_3(CH_2)_{11}$	88	128–130	—	—
$C_6H_5CH_2$	80	119–120	90	128–129
C_6H_{11}	85	180–185	—	—
$Cl(CH_2)_6$	93	115–120	—	—
$F(CH_2)_6$	83	118–120	—	—

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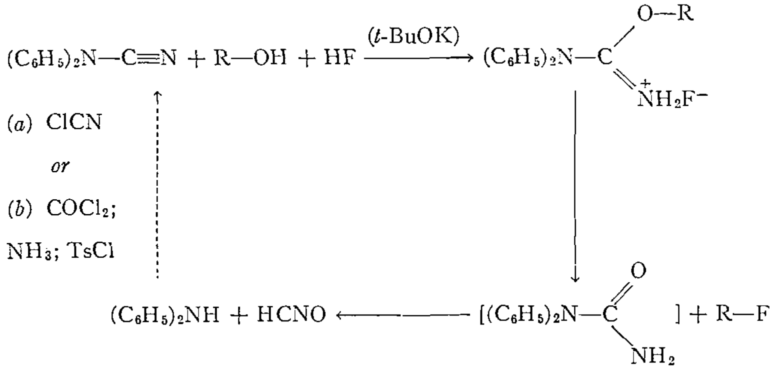
The best yields of alkyl fluorides were obtained when the pyrolysis of the salts was carried out at a temperature of about 185°. The residue contained diphenylamine (92% yield); this product is consistent with the well-known decomposition of 1,1-diphenylurea to diphenylamine and cyanic acid. The amine can readily be reconverted into diphenylcyanamide by common synthetic procedures in 90% yield or better. The overall reaction may thus be considered as the reaction of an alcohol with hydrogen fluoride to give an alkyl fluoride; the diphenylcyanamide is alternately consumed and reformed.



The pyrolysis may be carried out with or without solvents (Table II). The following high-boiling solvents were examined: mesitylene, octadecane, paraffin wax, diethylene glycol, and triethylene glycol, but in no case was the yield improved. The nonpolar solvents gave results comparable with those obtained by straight pyrolysis, whereas the

TABLE II
Some percentage yields of alkyl fluorides

R—F	Method of pyrolysis*	Via F^- salt	Via BF_4^- salt
$CH_3(CH_2)_4F$	Alone	42	—
	KHF_2;† no solvent	44	—
	KHF_2; octadecane	44	52
	KHF_2; mesitylene	44	57
$CH_3(CH_2)_5F$	KHF_2; no solvent	52	—
	KHF_2; octadecane	56	58
$CH_3(CH_2)_7F$	KHF_2; no solvent	70	47
	KHF_2; octadecane	76	55
	KHF_2; diethylene glycol	30	—
	KHF_2; triethylene glycol	23	—
$CH_3(CH_2)_9F$	Alone	53	0‡
	KHF_2; no solvent	77	53
	KHF_2; octadecane	69	55
$CH_3(CH_2)_{11}F$	KHF_2; no solvent	70	—
	KHF_2; wax	61	—
$C_6H_5CH_2F$	KHF_2; no solvent	34	0
	KHF_2; wax	21	—
$C_6H_{11}F$	KHF_2; wax	0§	—
$Cl(CH_2)_6F$	KHF_2; no solvent	48	—
$F(CH_2)_6F$	KHF_2; no solvent	51‖	—

*All pyrolyses were carried out by heating the reaction flask in an air bath.
†The molar ratio of KHF_2 to salt was usually 2 in the case of the fluorides and 4 in the case of the fluoroborates.
‡1-Decene (45% yield) was obtained.
§Cyclohexene (56% yield) was obtained.
‖From $F(CH_2)_6OH$.

polar solvents were usually less effective. Some yields were improved by adding potassium bifluoride to the pseudouronium salt before pyrolysis; this is necessary, in the case of the fluoroborates, to suppress alkene formation. Isolation and purification of the alkyl fluorides followed standard patterns.

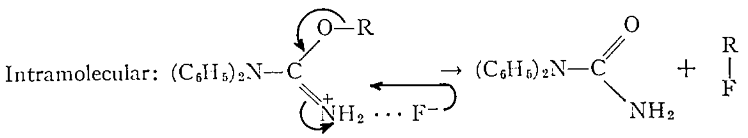
Some variations in the procedure were examined briefly. Free 2-alkylpseudourea bases, on pyrolysis with an excess of potassium bifluoride, gave no alkyl fluorides. 2-Alkylpseudouronium fluorides, on pyrolysis with an excess of ammonium chloride, gave a mixture of alkyl chlorides and alkyl fluorides (RCl:RF = 3:1). 2-Alkylpseudouronium chlorides, on pyrolysis with an excess of potassium bifluoride, gave only alkyl chlorides.

As the work proceeded, it became apparent that, for two reasons, the method is mainly of value in the preparation of *primary* alkyl fluorides. Firstly, primary alcohols form the pseudouronium salts far more readily than do secondary and tertiary alcohols. Secondly, secondary and tertiary alkyl groups, under the conditions of pyrolysis, tend to form the corresponding alkene rather than the alkyl fluoride; thus, 2-cyclohexyl-3,3-diphenylpseudouronium fluoride gave cyclohexene exclusively (56%).

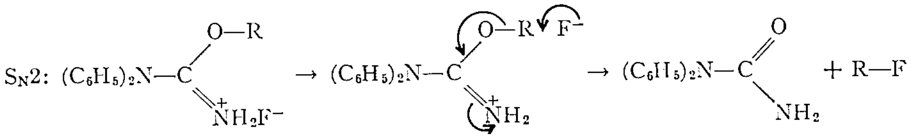
It was hoped that the method could be simplified by using imidate hydrofluorides or fluoroborates in place of the pseudouronium salts. So far, however, we have not been successful in forming the necessary salts, although we have examined a number of routes and techniques. Another alternative, involving the pyrolysis of a mixture of a carbamate and potassium bifluoride, was also unsuccessful.

It is probable that the mechanism of pyrolysis parallels that of the decomposition of imidate hydrochlorides. Kinetic results (4) in chloroform or *tert*-butyl alcohol at 60° (first-order disappearance of halide ion) were consistent with two routes, which, when applied to the pseudouronium fluorides, may be represented as follows:

[i]



[ii]



For compounds in which R is optically active, the first of these would be expected to result in retention of configuration (S_Ni), and the second in inversion (S_N2). The fact that Walden inversion, in the pyrolysis of crystalline *sec*-butyl acetimidate hydrochloride, has now been observed (5) and that the rates of decomposition of imidate salts are of the same order as those of other recognized S_N2 reactions (4) makes *ii* the mechanism of choice. It is uncertain (but likely) that this conclusion can be applied to the pyrolysis of pseudouronium salts in the solid phase; studies involving optically active pseudouronium salts derived from RCHDOH (6) would clarify this point.

EXPERIMENTAL

The preparations described below represent a typical example of each procedure; obvious variations for obtaining different members have not been included. Melting points (uncorrected) were determined on a Kofler hot stage, and infrared spectra with Beckman IR-7 and IR-5 infrared spectrophotometers. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York 77. Fractionations were carried out with a 23-plate platinum-plated spinning-band column.

2-Decyl-3,3-diphenylpseudouronium Fluoride

Freshly distilled 1-decanol (150 g), diphenylcyanamide (38.8 g, 0.2 mole), and potassium *tert*-butoxide (0.5 g) were heated under reflux overnight on a steam bath with mechanical stirring. The infrared spectrum of an aliquot in chloroform indicated the complete disappearance of the C≡N band at 2 250 cm^{-1} and the presence of a C═N band at 1 640 cm^{-1}. The unreacted excess of 1-decanol was recovered by distillation under reduced pressure (b.p. 73–74° at 0.4 mm) and the viscous residue was dissolved in anhydrous ether (250 ml). Anhydrous hydrogen fluoride (15 g) (NOTE: *Use rubber gloves*) in cold ether (100 ml) was then added to the ethereal solution of the pseudourea base, which was contained in a polythene beaker. The mixture was stirred and cooled to −50°. The resultant salt was filtered off, washed several times with cold ether, and dried in a desiccator over potassium hydroxide pellets; yield: 73.0 g, 89%. Recrystallization from chloroform – petroleum ether (35–60°) gave colorless needles, m.p. 123–125°.

Titrimetric analysis, using 0.01 *N* sodium hydroxide, indicated that the product usually contained the elements of 3HF, but some variation in fluorine content was observed. This is consistent with the well-known tendency of hydrogen fluoride to form double molecules, complexes, and hydrofluorides of crystallization (7); with weak bases, for example, the molar ratio of HF to base varies between 1 and 4. For purposes of calculation in this work, the composition was taken to be B·3HF.

Melting points of the fluoride salts are listed in Table I. Two analyses follow.

2-Pentyl-3,3-diphenylpseudouronium Fluoride

Anal. Calcd. for $C_{18}H_{25}F_3N_2O$: C, 63.16; H, 7.36; N, 8.18; F, 16.64. Found: C, 62.90; H, 7.25; N, 8.29; F, 16.85.

2-Octyl-3,3-diphenylpseudouronium Fluoride

Anal. Calcd. for $C_{21}H_{31}F_3N_2O$: C, 65.60; H, 8.13; N, 7.29; F, 14.83. Found: C, 65.97; H, 7.76; N, 7.30; F, 15.37.

2-Decyl-3,3-diphenylpseudouronium Fluoroborate

The free pseudourea base was prepared as in the above procedure, with diphenylcyanamide (29.1 g, 0.15 mole), freshly distilled 1-decanol (100 g), and potassium *tert*-butoxide (0.5 g). After recovery of the excess 1-decanol by distillation under reduced pressure, the residue was dissolved in ether (200 ml) and to it was added 48% aqueous fluoroboric acid (50 ml). The ether was allowed to evaporate overnight at room temperature. The oily residue was dissolved in chloroform (250 ml), and the resultant solution was washed with water, dried over anhydrous sodium sulfate, and concentrated to about 100 ml. On careful dilution with petroleum ether (35–60°), the fluoroborate salt crystallized as colorless needles (49.5 g, 75%), m.p. 86–87°. It may be recrystallized from chloroform – petroleum ether (35–60°) and should be stored in a desiccator over potassium hydroxide pellets.

Titrimetric analysis, using 0.01 *N* sodium hydroxide, indicated the composition $B \cdot HBF_4$. Two analyses follow.

2-Pentyl-3,3-diphenylpseudouronium Fluoroborate

Anal. Calcd. for $C_{18}H_{23}BF_4N_2O$: C, 58.41; H, 6.26; N, 7.57; F, 20.52. Found: C, 58.35; H, 6.44; N, 7.73; F, 20.37.

2-Octyl-3,3-diphenylpseudouronium Fluoroborate

Anal. Calcd. for $C_{21}H_{29}BF_4N_2O$: C, 61.18; H, 7.09; N, 6.79; F, 18.43. Found: C, 61.37; H, 7.24; N, 6.71; F, 18.60.

1-Fluorodecane (from Fluoride Salt)

A 500 ml round-bottomed flask, fitted with an 8 inch vertical air condenser carrying a Claisen-type distillation head leading to appropriate condensers and traps, was charged with a finely ground mixture of 2-decyl-3,3-diphenylpseudouronium fluoride (41.2 g, 0.1 mole) and potassium bifluoride (15.6 g, 0.2 mole). The flask was gradually heated in an air bath until decomposition started (ca. 185°). The temperature was then maintained at about 250° until distillation ceased; thereafter, the temperature was raised to about 300° and the pressure was reduced to ensure complete isolation of the product (15.3 g). The distillate was dissolved in ether (50 ml), and the ethereal solution was washed with 2% aqueous sodium bicarbonate and with water. After this solution was dried over anhydrous sodium sulfate and after removal of the ether, fractionation of the residue gave 1-fluorodecane (12.3 g, 77%), b.p. 187–190°, n_D^{25} 1.4087 (lit. (8) b.p. 74–75° at 13 mm, n_D^{25} 1.4080). The identity of the product was further confirmed by gas–liquid chromatographic analysis and infrared spectroscopy.

The residue, after pyrolysis, was treated with hot water (200 ml) and transferred to a beaker. The oily suspension solidified on the addition of aqueous sodium hydroxide, and cooling. The product was filtered, washed with water, dried in a desiccator, and recrystallized from aqueous methanol; yield: 15.6 g, 92%. It was proved to be identical with diphenylamine by the usual physical and chemical methods.

1-Fluorodecane (from Fluoroborate Salt)

The pyrolysis was carried out in the same equipment and by the same method as in the previous procedure, with 2-decyl-3,3-diphenylpseudouronium fluoroborate (44.0 g, 0.1 mole) and potassium bifluoride (31.2 g, 0.4 mole) in octadecane (100 g). The decomposition started at 225° and the temperature was maintained at

300° until distillation had ceased. The distillate (12 g) was washed, dried, and purified as before, yielding pure 1-fluorodecane (8.8 g, 55%), b.p. 184–187°, n_D^{25} 1.4084 (lit. (8) b.p. 74–75° at 13 mm, n_D^{25} 1.4080). The identity of the product was further confirmed by the usual methods.

1-Chloro-6-fluorohexane and *1,6-difluorohexane* were prepared by the above procedures (Table II); their identities were confirmed by reference to authentic samples (9).

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