⁂Fluorination of Fatty Alcohols with 1,1,2,3,3,3-Hexafluoropropyl Diethylamine

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ABSTRACT

Fluorination of fatty alcohols with 1,1,2,3,3,3-hexafluoropropyl diethylamine (PPDA) was investigated. A mixture of lauryl fluoride (yield 45%) and lauryl 2,3,3,3-tetrafluoropropionate (yield 22%) was obtained from the reaction of PPDA and lauryl alcohol. Similar results were obtained from other fatty alcohols.

INTRODUCTION

Fluorinated compounds have been widely utilized in biochemical investigations. However, fluorination of fatty alcohols and their application have not been well known. We now wish to report the convenient fluorination of fatty alcohols. 2-Chloro-1,1,2-trifluorotriethylamine, FAR, has been known as a useful fluorinating agent for alcohols (1). Recently, it was reported that 1,1,2,3,3,3-hexafluoropropyl diethylamine is useful as a fluorinating agent for alcohols and carboxylic acids (2). As this reagent is the adduct of perfluoropropene and diethylamine, it is abbreviated as PPDA in this paper. Fluorination of some standard alcohols using PPDA was carried out (2). However, the reaction of higher fatty alcohols with PPDA is not well known. On examination of this reaction, we found that mixtures of a fluoride and an ester are obtained in high yields from fatty alcohols and PPDA.

EXPERIMENTAL

Reaction of Lauryl Alcohol (I) with PPDA

A solution of PPDA (14.1 g, 63 mmol) in dry tetrahydrofuran (10 mL) was added dropwise into a solution of lauryl alcohol (I) (9.3 g, 50 mmol) in tetrahydrofuran (20 mL) at room temperature. After stirring for 2 hr at 40-50 C, the reaction mixture was left overnight. It was thrown into water and an oily product was extracted with diisopropyl ether. The ether extract was washed with water, dried over anhydrous sodium carbonate, filtered, and evaporated to remove the solvent. The residue was distilled to give the following fractions: (i) 75-85 C/17 mm Hg, 7.5 g; (ii) 80-150 C/17 mm Hg, 13.0 g.

The main component of fraction (i) was N,N-diethyl 2,3,3,3-tetrafluoropropionamide. Fraction (ii) was a mixture of the amide (10%), lauryl fluoride (**II**) (34%), lauryl 2,3,3,3-tetrafluoropropionate (**III**) (51%) and an unidentified product (5%). These compositions were determined by gas chromatography. [Shimadzu GC-3BF, column Silicone DC 200 (10%) on Celite 545 (3 m), temperature 150 C, carrier gas N_2, 40 mL min^{-1}]. Fraction (ii) was redistilled to give the following fractions: fraction (iia) 100-120 C/17 mm Hg, 4.5 g; fraction (iib) 120-140 C/17 mm Hg, 2.0 g; fraction (iic) 140-150 C/17 mm Hg, 4.0 g. Fraction (iia) (2.0 g) was chromatographed over a column of silica gel (50.0 g) and the elution was done with *n*-hexane. Elution gave 1.5 g of pure lauryl fluoride (**II**). IR(cm^{-1}): 1005, 1045; ^{1}H NMR (δ, ppm): 0.90 (3H, t, J=6 Hz, CH_3-), 1.1-1.7 (18H, m, $CH_3(CH_2)_9$-), 1.7-2.1 (2H, m, -CH_2CH_2F), 4.48 (2H, dt, J_{HF} = 48.3 Hz, J_{HH} = 6 Hz, -CH_2F); ^{19}F NMR (δ, ppm) ($CDCl_3$): signal of F was recognized at 137.8 ppm upfield from the external standard of CF_3COOH, (t, t, $J_{H(b)F}$ = 46.8 Hz, $J_{H(a)F}$ = 23.4 Hz).

$$CH_3(CH_2)_9\overset{a}{C}H_2\overset{b}{C}H_2F \qquad \textbf{(II)}$$

Fraction (iic) (3.0 g) was chromatographed over a column of silica gel (60.0 g) and the elution was done with *n*-hexane containing increasing amounts of acetone; each fraction of 10 mL was collected. Elution with *n*-hexane/acetone (95:5, v/v) gave 2.0 g of lauryl 2,3,3,3-tetrafluoropropionate (**III**) as an oil. IR (cm^{-1}): 1775, 1225, 1200, 1050; ^{1}H NMR (δ, ppm): 0.90 (3H, t, J=6 Hz, CH_3-), 1.2-1.6 (18 H, m, $CH_3(CH_2)_9$-), 1.6-1.9 (2H, m, -CH_2CH_2OCO), 4.37 (2H, t, J=6.3 Hz, -CH_2OCO), 5.16 (1H, d, t, $J_{HF(a)}$=46.2 Hz, $J_{HF(b)}$=6.3 Hz, CHF); ^{19}F NMR (δ, ppm) ($CDCl_3$): signal of F(b) was recognized at 16.0 downfield from the external standard of CF_3COOH (d, d, $J_{F(a)F(b)}$=12.0 Hz, $J_{HF(b)}$=6.4 Hz, CF_3). Signal of F(a) was recognized at 126.2 upfield from the external standard of CF_3COOH (d, q, $J_{HF(a)}$=45.5 Hz, $J_{F(a)F(b)}$=12.0 Hz, CHF(a)).

$$CH_3(CH_2)_{11}OC\overset{\overset{O}{\|}}{\underset{}{}}CH\overset{a}{F}\overset{b}{C}F_3 \qquad \textbf{(III)}$$

TABLE I

Fluorination of Fatty Alcohols
$RCH_2OH \rightarrow RCH_2F + RCH_2OCOCHFCF_3$

Alcohol	Fluoride (yield %)[a]	Ester (yield %)[a]
Decyl alcohol	bp 73-75 C/20 mm Hg[b] (53%)	bp 120-124 C/20 mm Hg[b] (15%)
Lauryl alcohol	bp 110-120 C/17 mm Hg (45%)	bp 130-140 C/17 mm Hg (22%)
Myristyl alcohol	bp 130-135 C/22 mm Hg (36%)	bp 135-140 C/22 mm Hg (27%)
Cetyl alcohol	bp 125-128 C/3-4 mm Hg (37%)	bp 130-140 C/3-4 mm Hg (12%)
Stearyl alcohol	mp 31-31.5 C (51%)	mp 51-53 C (16%)
Oleil alcohol	bp 145-150 C/3 mm Hg (79%)	bp 150-157 C/3 mm Hg (4%)

[a]The yield was calculated as isolated yield.
[b]The separation of fluoride and ester was done by spinning band fractionating column (Taika Industry Co. Ltd.).

Pure lauryl fluoride, 4.28 g (22.7 mmol), was obtained from fraction (iia) 3.37 g) and fraction (iib) (0.91 g). The yield of lauryl fluoride was 45%. Pure ester, 3.26 g (10.8 mmol) was obtained from fraction (iib) (0.60 g) and fraction (iic) (2.66 g). The yield of ester was 22%.

Other fatty alcohols were fluorinated in the same manner, and the results are listed in Table I.

RESULTS AND DISCUSSION

Convenient fluorination of standard alcohols with PPDA was reported recently (2). This paper concerns a fluorination of higher fatty alcohols using PPDA. We have found that a mixture of fluorinated hydrocarbon and 2,3,3,3-tetrafluoropropionate was obtained in high yield. For example, lauryl fluoride (**II**) and lauryl 2,3,3,3-tetrafluoropropionate (**III**) were obtained by the reaction of lauryl alcohol and PPDA as shown in the Experimental section.

$$\underset{\textbf{(I)}}{CH_3(CH_2)_{10}CH_2OH} \xrightarrow{\text{PPDA}} \underset{\textbf{(II)}}{CH_3(CH_2)_{10}CH_2F} + \underset{\textbf{(III)}}{CH_3(CH_2)_{10}CH_2OC(=O)CHFCF_3}$$

Other fluorides and esters were prepared in high yields and the results are listed in Table I. The foregoing observations indicate that reaction of PPDA with lower primary alcohols yields fluorides, and reaction with low secondary and tertiary alcohols yields fluorides and olefins (2), but the reaction of higher primary alcohols gives a mixture of fluorides and esters. Application of these fluorine compounds as insecticides and surfactants is now in progress at our laboratory.

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