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Technical

♣Fluorination of Methyl Ricinolate with N, N-Diethyl-1,1,2,3,3,3-hexafluoropropylamine

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ABSTRACT

Fluorination of methyl ricinolate (I) with N,N-diethyl-1,1,2,3,3,3-hexafluoropropylamine (PPDA) was attempted to give methyl 12-fluoro-9-octadecenoate (II) in 61% yield.

INTRODUCTION

Recently, we have reported that N,N-diethyl-1,1,2,3,3,3-hexafluoropropylamine (PPDA, Ishikawa reagent) is useful as a fluorinating agent for primary fatty alcohols (1) and diols (2). However, the reaction of methyl ricinolate (I) with PPDA has not been reported previously. On examination of this reaction, we found that the hydroxy group of secondary alcohol (I) can be fluorinated by PPDA.

EXPERIMENTAL

Reaction of Methyl Ricinolate (I) with PPDA

A solution of PPDA (10.0 g, 45 mmol) in dicholoromethane (20 ml) was added one drop at a time into a solution of methyl ricinolate (6.24 g, 20 mmol; $[\alpha]_D^{29}$ + 5.418, c = 2.18 in methanol) in dichloromethane (30 ml) at room temperature. After having been stirred for 6 hr at 30 C, the reaction mixture was left overnight. It was then added to water (100 ml), and the oily product was extracted with dichloromethane. The extract was washed with water, dried over anhydrous sodium carbonate, filtered and evaporated to remove the solvent. The residue was distilled with a small pot still to give the following fractions: (i) - 120 C/10^{-2} mmHg, 0.5 g; (ii) 120-122 C/10^{-2} mmg, 4.4 g. Redistillation of fraction (ii) with a pot still gave fluoride (II) boiling at 120 C/10^{-2} mmHg (3.8 g; yield 61%).

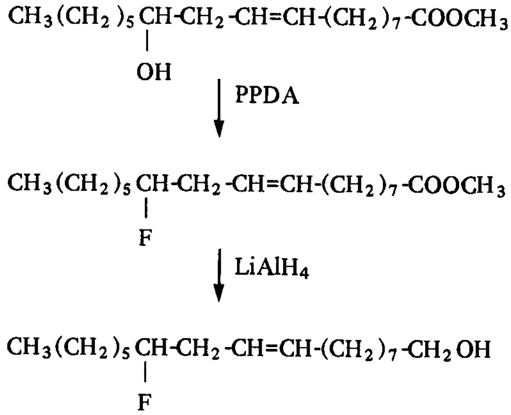
The purity of the fluoride (II) was ascertained by thin layer chromatography using silica gel with a mixture of n-hexane (95%) and ethyl acetate (5%) as a solvent. Only one spot was obtained (Rf=0.71). The physical properties were as follows. IR (cm^{-1}): 1738, 1642, 1200, 1170, 840, 720; ^1H NMR (δ, ppm): 0.89 (3H, t, J=5.0Hz, $C\underline{H}_3$-), 1.33 (18H, s, -CH_2-), 1.85-2.70 (8H, m, -$C\underline{H}_2$-CHF-$C\underline{H}_2$CO and -$C\underline{H}_2$-CH=CH-$C\underline{H}_2$-), 3.65 (3H, s, -$COOCH_3$), 4.50 (1H, dm, J_{HF}=48.0Hz, -CHF-), 5.44 (2H, m, -C$\underline{H}$=C$\underline{H}$); ^{19}F NMR (δ, ppm) ($CDCl_3$): signal of F (multiplet) was recognized at 98.5 upfield from the external standard of CF_3COOH; $[\alpha]_D^{29}$ + 1.74 (c=2.22 in methanol). Compound (II) exhibited ions at m/e 294 (M±HF) and m/e 262 (M±HF and CH_3OH) in its mass spectrum. Fluoride (II) (0.70 g) was hydrogenated over Pd-C catalyst in n-hexane and absorbed 50 cc of hydrogen (0 C, 760 mmHg). IR (cm^{-1}): 1740, 1170, 1198; ^1H NMR (δ, ppm): 0.89 (3H, t, J=5.0Hz, CH_3-), 1.28 (24H, s, -CH_2-), 1.68 (4H, m, -$C\underline{H}_2$-CHF-), 2.24 (2H, t, J=8.0Hz, -CH_2COOCH_3), 3.44 (3H, s, -$COOCH_3$), 4.52 (1H, dm, J=44.0Hz, -C$\underline{H}$F-); ^{19}F NMR (δ, ppm) ($CDCl_3$); signal of F (multiplet) was recognized at 99 upfield from the external standard of CF_3COOH. Compound (IV) showed ions at m/e 296 (M±HF) and m/e 264 (M±HF-CH_3OH) in its mass spectrum.

Reduction of Methyl 12-Fluoro-9-octadecenoate (II) with Lithium Aluminum Hydride

A solution of compound (II) (0.3 g) in dry diethyl ether (30 ml) was dropped into a suspension of lithium aluminum hydride (0.2 g) in dry diethyl ether (30 ml) at 0 C. After stirring for 5 hr, the reaction mixture was decomposed by adding 1% hydrochloric acid. It was extracted with diethylether. The ether extract was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated to remove the solvent. The residue was chromatographed with silica gel column using n-hexane containing ethyl acetate (1%) as a solvent. From the elution, 0.1 g of 12-fluoro-9-octadecenol (III) was obtained. It showed the following properties. Ir (cm^{-1}): 3200, 1640, 1058, 720; NMR (δ, ppm): 0.98 (3H, t, J=5.0Hz, CH_3-), 1.28 (20H, s, -CH_2-), 1.70-2.60 (8H, m, other -CH_2-), 3.50 (1H, s, -O$\underline{H}$), 4.43 (1H, dm, -CHF-), 5.35 (2H, m, -CH=CH-); ^{19}F NMR (δ, ppm) ($CDCl_3$): signal of F (multiplet) was recognized at 98.5 upfield from the external standard of CF_3COOH.

RESULTS AND DISCUSSION

We have reported that PPDA can be applied for fluorination of primary fatty alcohols and various glycerol derivatives (1,2). However, fluorination of standard secondary alcohols with PPDA gave a mixture of fluoride, a dehydration product and a dimeric ether. On trial, the fluorination of methyl ricinolate (I) with PPDA was examined. The use of an excess of dichloromethane as a solvent is the best condition for its preparation of the fluoride (II), which was obtained in 61% yield. II was purified by molecular distillation; in thin layer chromatography it showed a single spot. The structure of II was determined by the spectral data of IR, ^{1}H NMR, ^{19}F NMR and MS. Reduction of II with lithium aluminum hydride gave 12-fluoro-9-octadecenol (III). Biochemical investigation of these fluorides is now in progress at our laboratory.



(I)

$$CH_3(CH_2)_5\underset{\displaystyle OH}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOCH_3$$

$$\Big\downarrow \text{PPDA}$$

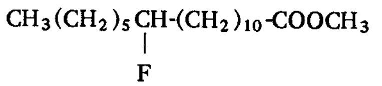
(II)

$$CH_3(CH_2)_5\underset{\displaystyle F}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOCH_3$$

$$\Big\downarrow \text{LiAlH}_4$$

(III)

$$CH_3(CH_2)_5\underset{\displaystyle F}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_2OH$$



(IV)

$$CH_3(CH_2)_5\underset{\displaystyle F}{CH}\text{-}(CH_2)_{10}\text{-}COOCH_3$$

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Catalytic Effect of Amines on the Ethoxylation of Dodecyl Alcohol

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ABSTRACT

The catalytic activity of several tertiary amines on the ethoxylation of dodecyl alcohol has been investigated. It has been established that the rate of the reaction is proportional to the concentration of the catalyst over the range of 10-25% and that the reaction rate has an extremum at 80 C.

The catalytic effect of trialkyl amines increases if two of the alkyl groups are methyl. The product distribution is that of the Weibull-Nycander-Gold type and is independent of the concentration of the catalyst and reaction temperature. Distribution constants calculated according to Natta-Mantica vary with the average degree of ethoxylation, i.e., the Weibull-Törnquist effect is observed. This can be explained if an interaction is assumed between the polyethylene glycol chain formed and the quaternary ammonium ion formed in the first step of ethoxylation.

INTRODUCTION

The ethoxylation of dodecyl alcohol has been reported previously (1). The reaction is catalyzed by alkali hydroxides at temperatures above 100 C, except in cases when special additives are used (2). These conditions cause some difficulties, since an increase in reaction temperature can result in the discoloration of the product. Thus, an attempt was made to catalyze the ethoxylation with amine catalyst, so as to allow the reaction to proceed at a lower reaction temperature.

The ethoxylation of fatty alcohols also can be carried out with an amine catalyst. In some cases primary or secondary amines are used (3), and the amine is also ethoxylated. However, tertiary amines generally are used as catalysts (4, 5, 6, 7).

Under amine catalysis the mechanism of the reaction is different from that of catalysis by alkali hydroxides.

Tertiary amine catalysis is a two-stage process (7): the first reaction, between the amine and ethylene oxide, leads to a quaternary ammonium zwitterion