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REACTION OF ALCOHOLS WITH N,N-DIETHYL-1,1,2,3,3,3-HEXAFLUORO-PROPYLAMINE IN THE PRESENCE OF DIISOPROPYLETHYLAMINE

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SUMMARY

The reaction of N,N-diethyl-1,1,2,3,3,3-hexafluoropropylamine (PPDA) with various alcohols in the presence of diisopropylethylamine gave their corresponding 2,3,3,3-tetrafluoropropionate esters. For example, geranyl 2,3,3,3-tetrafluoropropionate 2 was obtained from the reaction of PPDA with geraniol 1.

INTRODUCTION

Recently, we reported that N,N-diethyl-1,1,2,3,3,3-hexafluoropropylamine (PPDA) is useful as a fluorinating reagent for fatty alcohols [1], haloalcohols [2] and hydroxyesters [3]. In some cases [2], the 2,3,3,3-tetrafluoropropionate esters were formed also (ROH → RF + ROCOCHFCF$_3$). The reactions of alcohols with PPDA in the presence of a tertiary amine have not been studied in detail, and on examination of this reaction we have found that the corresponding 2,3,3,3-tetrafluoropropionate esters were obtained.

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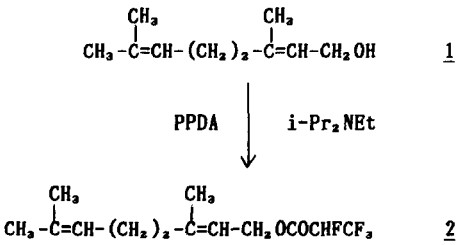
RESULTS AND DISCUSSION

The reactions of PPDA with α,β-unsaturated alcohols did not give their corresponding fluorides. Side reactions such as isomerization, cyclization and dehydration of alcohols are apt to occur. It is suspected that these isomerizations are caused by hydrogen fluoride produced during fluorination. To remove this hydrogen fluoride, the reaction was attempted in the presence of a tertiary amine.

We have found that the reactions of various α,β-unsaturated alcohols with PPDA in the presence of di-isopropylethylamine gave the corresponding 2,3,3,3-tetrafluoropropionate esters. For example, from the reaction of PPDA with geraniol 1, geranyl 2,3,3,3-tetrafluoropropionate 2 was obtained in 41 % yield.



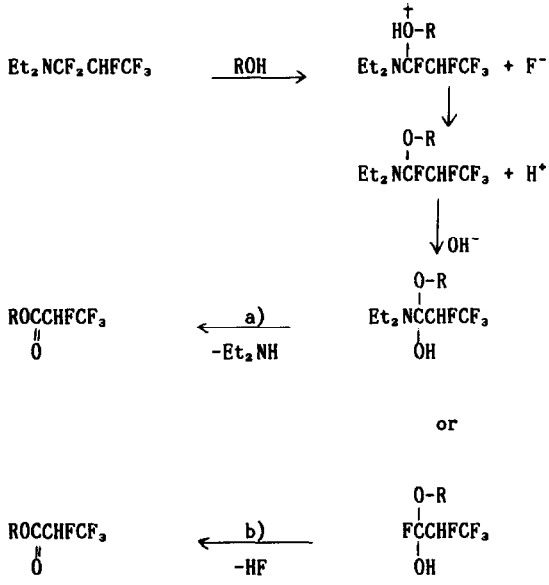
Similarly, 2,3,3,3-tetrafluoropropionate esters were obtained from the reaction of PPDA with other alcohols in the presence of di-isopropylethylamine. The examples studied are all given in Table 1.

The reaction of alcohols with PPDA under our conditions probably proceeds as indicated in the Scheme given on p. 19. We suggest that di-isopropylethylamine reacts with HF produced during fluorination.

EXPERIMENTAL

Reaction of geraniol 1 with PPDA

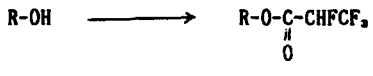
A solution of PPDA (9.20 g, 41.3 mmol) in CH_2Cl_2 (20 ml) was added dropwise into a solution of geraniol 1 (3.08 g, 20.0 mmol)(trans-isomer,



80 %; cis-isomer, 20 %) and diisopropylethylamine (5.16 g, 40.0 mmol) in CH_2Cl_2 (20 mℓ) at room temperature. After stirring for 5 hr, the reaction mixture was left overnight. It was poured into water and an oily product was extracted with diethylether. The 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) ~ 80 ℃/22 mmHg, 1.0 g; (ii) 80 ~ 118 ℃/22 mmHg, 4.0 g; (iii) 118 ~ 124 ℃/22 mmHg, 2.8 g; (iv) residue, 1.0 g. Fraction (i) changed to black color, and was a mixture of various components by gas chromatographic analysis. Fraction (ii) was a mixture of N,N-diethyl 1,1,2,3,3,3-hexafluoropropionamide (90 %) and other components (10 %). Fraction (iii) was a mixture of the amide (10 %) and 2 (90 %). These compositions were determined by gas chromatography. [Shimadzu GC-3BF; column, Silicone DC-200 (20 %) on Celite 545 (3 m); temperature 150 ℃; carrier gas, N_2, 40 ml min^{-1}]. Fraction (iii) (2.8 g) was chromatographed on a silica gel column (20.0 g) and eluted with n-hexane containing 2 % ethylacetate. Elution gave 2.3 g of pure geranyl 2,3,3,3-tetrafluoropropionate 2 (yield 41.1 %) (trans-isomer,

TABLE 1

Reaction of Alcohols with PPDA in the Presence of Diisopropylethylamine



(A) (B)

Compound (A)	Compound (B)[1] Boiling Point (℃/mmHg) (Yield %[2])	^{19}F NMR (relative to an external CF_3COOH standard at 56.44 MHz) -CHFCF$_3$ δ, ppm	J(HF)	J(FF)	-CHFCF$_3$ δ, ppm	J(FF)	J(FH)
α,β-Unsaturated Alcohols							
Geraniol	118 ~ 121/22 (41 %)	+124.5 (dq)	45.1	13.2	-1.8 (dd)	13.2	6.6
Cinnamic alcohol	160 ~ 163/18 (29 %)	+124.5 (dq)	45.1	15.2	-1.7 (dd)	15.2	6.0
Lavandulol	87 ~ 90/22 (30 %)	+121.8 (dq)	39.5	11.7	-4.7 (dd)	11.7	6.6
Farnesol	103 ~ 105/2 (33 %)	+124.0 (dq)	39.5	10.3	-2.1 (dd)	10.3	6.0

Phytol	90 ~ 100° /0.4 [3] (35 %)	+125.0 (dq)	46.1	11.3	-2.5 (dd)	11.3	6.6
Ethyl mandelate	130 ~ 132/22 (29 %)	+125.3 (dq)	40.0	10.9	-1.9 (dd)	10.9	5.6
Other Alcohols							
Oleyl alcohol	80 ~ 90/0.4 [3] (56 %)	+124.7 (dq)	39.9	10.9	-2.3 (dd)	10.9	5.6
Nopol	92 ~ 95/24 (30 %)	+120.0 (dq)	40.0	11.3	-2.0 (dd)	11.3	5.6
Diethyl DL-malate	120 ~ 123/24 (47 %)	+125.0 (dq) [4]	38.5	11.3	-2.5 (dd)	11.3	5.6
DL-Leucis acid ethyl ester	110 ~ 115° /25 (25 %)	+123.0 (dq) [4]	37.5	11.2	-2.4 (dd)	11.0	5.5

[1] These products are new compounds. The microanalyses were in satisfactory agreement with the calculated values: C ± 0.30 % H ± 0.04 %.

[2] The yield was calculated as isolated yield.

[3] This temperature was that of bath temperature of pot still in molecular distillation.

[4] Diastereomer ratio is 7 : 3.

80 %; cis-isomer, 20 %); IR (cm^{-1}): 1770 (-C=O), 815 (-C=CH-); ^1H NMR (δ, ppm): 4.9 ~ 5.7 (3H, m, -C=C<u>H</u> × 2, -C<u>H</u>FCF$_3$), 4.9 (2H, d, J=7.0 Hz, -C=C-C<u>H$_2$</u>-O), 2.05 (4H, m, -CH$_2$ × 2), 1.68 (6H, s, CH$_3$ × 2), 1.60 (3H, s, CH$_3$) [δ values (ppm) relative to a TMS internal standard at 56.44 MHz].

Other alcohols were treated with PPDA in the same manner, and the results are listed in Table 1.

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