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REACTIONS OF MONOESTERS OF ETHYLENE GLYCOL WITH N,N-DIETHYL-1,1,2,3,3,3-HEXAFLUOROPROPYLAMINE

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SUMMARY

By reaction with 1,1,2,3,3,3-hexafluoropropyldiethylamine (PPDA), various monoesters of ethylene glycol gave a mixture of the corresponding monofluorides and 2,3,3,3-tetrafluoropropionate esters. The antimicrobial properties of these fluorine compounds for a spent coolant were examined.

INTRODUCTION

Fluorinated compounds have been widely prepared and utilized in biochemical and industrial investigations [1]. Recently, we reported that 1,1,2,3,3,3-hexafluoropropyl diethylamine (PPDA) is a useful fluorinating agent for hydroxyesters [2] and halogeno alcohols [3]. We have now studied the reactions of various monoesters of ethylene glycol with PPDA and found that a mixture of the corresponding 2,3,3,3-tetrafluoropropionate and monofluoride was obtained, except in a few cases.

Diesters of ethylene glycol and diethylene glycol are used as antimicrobial reagents or plasticizers [4]. The antimicrobial property for water-soluble cutting fluids of fluorine compounds has not been reported in detail.

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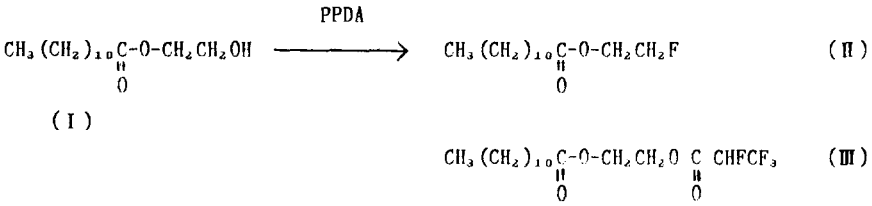
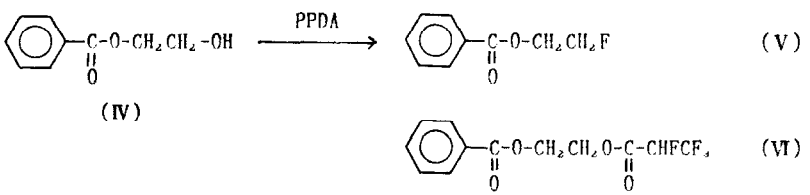
This paper also describes our evaluation of these new fluorine compounds for spent coolant of water-soluble cutting fluids.

RESULTS AND DISCUSSION

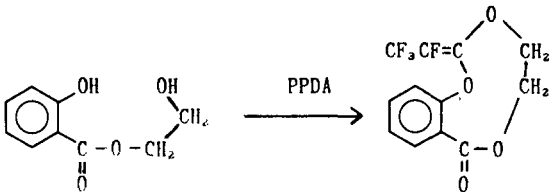
We have reported the reaction of PPDA with various alcohols. Fluorination of a fatty alcohol with PPDA gives a mixture of the fluoride and 2,3,3,3-tetrafluoropropionate [5]. The reaction of PPDA with a fatty acid monoester of ethylene glycol also gave a mixture of the corresponding fluoride and fluoroester. For example, from ethylene glycol monolaurate (I) and PPDA, a mixture of 2-fluoroethyl laurate (II) (3.0 %) and lauroyloxyethyl 2,3,3,3-



tetrafluoropropionate (III) (43.8 %) was obtained. In the case of fatty acid monoesters, lower monoesters such as those from octanoic or hexanoic acid give a mixture of fluorides and propionates. However, higher monoesters such as those from myristic or oleic acid give tetrafluoropropionates as their main products. From other acid monoesters of ethylene glycol, the corresponding tetrafluoropropionates were obtained as their main products (Table 1).



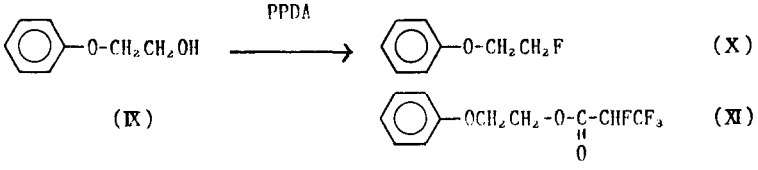
Reaction of PPDA with monoesters of aromatic carboxylic acids of ethylene glycol also gave mixtures of fluorides and propionates. For example, from ethylene glycol monobenzoate (Ⅳ), a mixture of benzoyloxyethyl fluoride (Ⅴ) (5 %) and benzoyloxyethyl 2,3,3,3-tetrafluoropropionate (Ⅵ) (60 %) was obtained. From other aromatic acids monoesters of diols, corresponding fluorides and propionates were obtained as shown in Table 1. In contrast, however, a cyclic compound, 1,2-benzo-3-oxo-8-tetrafluoroethylidene-4,7,9-trioxacyclononane (Ⅷ) was obtained from the reaction of PPDA with ethylene glycol monosalicylate (Ⅶ). This undesirable reaction of (Ⅶ) is



(Ⅶ) (Ⅷ)

interesting. However, other mono salicylates of diethylene glycol, triethylene glycol and propylene glycol did not show this abnormal reaction, but gave their corresponding tetrafluoro propionates.

Fluorination of monoethers of ethylene glycol was attempted and a mixture of fluoride and tetrafluoropropionate was obtained from the reaction of PPDA and an ethylene glycol monoalkyl or monoaryl ether. For example, fluorination of phenoxyethyl alcohol (Ⅸ) with PPDA gave a mixture of phenoxyethyl fluoride (Ⅹ) (65 %) and phenoxyethyl 2,3,3,3-tetrafluoro propionate (Ⅺ) (20 %).



(Ⅸ) (Ⅹ) (Ⅺ)

TABLE 1

Fluorination of Monoesters of Ethylene Glycol and Diethylene Glycol with PPDA (all compounds reported are new)

Alcohols $RCOOC_2H_4OH$	Product[a] Fluoride: $RCOOC_2H_4F$ Ester: $RCOOC_2H_4OCOCHFCF_3$	Boiling Point ℃/mmHg (yield %)[b]	^{19}F NMR δ, ppm (Hz) CHF	CF_3	CH_2F
Fatty Acid Esters					
Ethylene glycol monohexanoate	Fluoride	85 ~ 95/30 (24.7)			+146.7(t,t) (J_{HF}=48.0, J_{HF}=29.8)
	Ester	100 ~ 105/30 (18.1)	+123.3(d,q) (J_{HF}=43.2, J_{FF}=11.7)	-2.0(d,d) (J_{FF}=11.7, J_{HF}=6.0)	
Ethylene glycol monooctanoate	Fluoride	120 ~ 125/34 (40.0)			+143.0(t,t) (J_{HF}=47.9, J_{HF}=30.1)
	Ester	132 ~ 134/34 (30.4)	+124.5(d,q) (J_{HF}=41.2, J_{FF}=12.2)	-1.5(d,d) (J_{FF}=12.2, J_{HF}=5.6)	
Ethylene glycol monodecanoate	Fluoride	110/7 (30.2)			+143.0(t,t) (J_{HF}=42.8, J_{HF}=28.8)
	Ester	115 ~ 120/7 (30.3)	+125(d,q) (J_{HF}=44.4, J_{FF}=12.2)	-1.8(d,d) (J_{FF}=12.2, J_{HF}=5.6)	

Ethylene glycol monolaurate	Fluoride	115 ~ 120° /0.1 (3.0)			+143.0(t,t) (J_{HF}=48.3, J_{HF}=29.8)
	Ester	125 ~ 130° /0.1 (43.8)	+123.0(d,q) (J_{HF}=46.1, J_{FF}=11.5)	-2.75(d,d) (J_{HF}=6.6, J_{FF}=11.5)	
Ethylene glycol monomyristate	Ester	140 ~ 150/0.01 (50.0)	+122.5(d,q) (J_{HF}=45.1, J_{FF}=12.2)	-2.75(d,d) (J_{FF}=12.2, J_{HF}=6.6)	
Ethylene glycol monooleate	Ester	180 ~ 190/0.01 (60.0)	+124.0(d,q) (J_{HF}=45.1, J_{FF}=12.2)	-2.0(d,d) (J_{FF}=12.2, J_{HF}=6.6)	
Aromatic Acid Esters					
Ethylene glycol monobenzoate	Fluoride	90/50 (5.0)			+125.0(m)
	Ester	110/50 (60.0)	+129.0(d,q) (J_{HF}=46.0, J_{FF}=10.3)	-1.5(d,d) (J_{HF}=6.0, J_{FF}=10.3)	
1,2-Propylene glycol 2-benzoate	Fluoride	120/40 (50.0)			+110.5(t,d) (J_{HF}=41.4, J_{HF}=16.9)
	Ester	trace			

(continued)

TABLE 1 (cont.)

Alcohols $RCOOC_2H_4OH$	Product Fluoride: $RCOOC_2H_4F$ Ester: $RCOOC_2H_4OCOCHFCF_3$	Boiling Point ℃/mmHg (yield %)	^{19}F NMR δ, ppm (Hz) CHF	CF_3	CH_2F
1,2-Propylene glycol 1-benzoate	Fluoride	115/40 (70.0)	+74.5(m)		
	Ester	trace			
Ethylene glycol monosalicylate	c	149 ~ 155/27 (mp 73.5-74) (65.0)	[=CFCF$_3$] +108.0(q) (J_{FF}=7.5)	-5.0(d) (J_{FF}=7.5)	
1,2-Propylene glycol 1-salicylate	Fluoride	90 ~ 95/2 (30.0)	+100.0(m)		
	Ester	110/2 (20.0)	+105.9(d,q) (J_{HF}=51.7, J_{FF}=7.5)	-5.7(d,d) (J_{HF}=5.3, J_{FF}=7.5)	
Diethylene glycol monosalicylate	Fluoride	130 ~ 140/4 (20.0)			+140.1(t,t) (J_{HF}=28.2, J_{HF}=46.1)
	Ester	145 ~ 148/4 (30.0)	+123.3(d,q) (J_{HF}=45.0, J_{FF}=10.7)	-1.73(d,d) (J_{HF}=5.6, J_{FF}=10.7)	
Ethylene glycol monophenyl acetate	Fluoride	trace			
	Ester	130 ~ 140/33 (43.0)	+124.0(d,q) (J_{HF}=41.4, J_{FF}=11.3)	-1.7(d,d) (J_{FF}=11.3, J_{HF}=5.6)	

Other Esters

Ethylene glycol mono-2-bromovalerate	Ester	140 ~ 143/37 (55.9)	+124.0(d,q) (J_{HF}=45.0, J_{FF}=11.3)	-1.7(d,d) (J_{FF}=11.3, J_{HF}=6.4)
Ethylene glycol mono-ω-bromo-undecanoate	Ester	130 ~ 134/5 (61.1)	+124.0(d,q) (J_{HF}=44.4, J_{FF}=10.3)	-2.0(d,d) (J_{FF}=10.3, J_{HF}=5.6)
Ethylene glycol monocyclohexyl acetate	Ester	108 ~ 113/47 (57.3)	+123.6(d,q) (J_{HF}=44.2, J_{FF}=12.4)	-2.53(d,d) (J_{FF}=12.4, J_{HF}=6.0)
Ethylene glycol monocitronellate	Ester	150 ~ 151/3 (55.5)	+124.0(d,q) (J_{HF}=44.0, J_{FF}=10.3)	-1.5(d,d) (J_{FF}=10.3, J_{HF}=6.0)
Ethylene glycol monogeranate	Ester	82 ~ 84/4.5 (62.6)	+124.0(d,q) (J_{HF}=47.0, J_{FF}=10.9)	-1.6(d,d) (J_{FF}=10.9, J_{HF}=6.0)

(continued)

TABLE 1 (cont.)

Alcohols $RCOOC_2H_4OH$	Product Fluoride: $RCOOC_2H_4F$ Ester: $RCOOC_2H_4OCOCHFCF_3$	Boiling Point °C/mmHg (yield %)	^{19}F NMR δ, ppm (Hz) CHF	CF_3	CH_2F
Etheric Alcohols					
Propylene glycol monophenylether	Fluoride	77° /30 (14.3)	+99(m)		
	Ester	87 ~ 88/30 (28.6)	+123(d,q) (J_{HF}=44.2, J_{FF}=11.3)	-2.75(d,d) (J_{HF}=5.9, J_{FF}=11.3)	
Ethylene glycol monophenylether	Fluoride	60 ~ 67/5 (65.0)			+117(m)
	Ester	73 ~ 77/5 (20.5)	+123.5(d,q) (J_{HF}=46.1, J_{FF}=12.2)	-2.0(d,d) (J_{HF}=6.5, J_{FF}=12.2)	
Diethylene glycol mono-n-hexylether	Fluoride	70 ~ 75/30 (70.0)			+141(t,t) (J_{HF}=39.5, J_{HF}=24.4)
	Ester	85 ~ 95/30 (15.0)	+118(d,q) (J_{HF}=38.5, J_{FF}=10.3)	-1.9(d,d) (J_{FF}=10.3, J_{HF}=5.6)	

[a] The isolation of fluorides or esters was done by fractional distillation through a small Widmer column.
[b] The yield was calculated as isolated yield.
[c] See Experimental Section.

The foregoing observations indicate that reactions of PPDA with monoesters of fatty acids yields tetrafluoropropionates as their main products, reaction with monoesters of aromatic carboxylic acids yields mixtures of fluorides and tetrafluoropropionates, and only the reaction of ethylene glycol monosalicylate gives a cyclic fluorine compound. In all cases, N,N-diethyl-2,3,3,3-tetrafluoropropioamide was obtained. The mechanism of its formation is described in reference [3].

It has been reported that the diesters of ethylene glycol and diethylene glycol possess antimicrobial activity against a grampositive bacterium [4]. However, the industrial application of these diesters for water soluble cutting fluids has not been well examined. Many water-soluble cutting fluids are apt to be spoiled by various minute organisms after the long use. We examined the antimicrobial activities of the new diesters containing fluorine atoms. As contaminated liquid, a spent coolant (live fungi above 10^7/ml) was used from an industrial factory. A mixture of an aqueous or an emulsion solution of a sample, a cornstarch soup, a spent coolant and cast-iron chips (FC-20) was kept at 35 ℃, and generation of an unpleasant odour was checked. When this had not appeared after ten days, it was judged that antimicrobial activity was good. Interestingly, we have found that some aqueous emulsions of these diesters containing fluorine atoms showed a considerably antimicrobial property for water-soluble cutting fluids. For example the aqueous emulsions of benzoyloxyethyl 2,3,3,3-tetrafluoropropionate and 2-fluoropropyl benzoate showed considerable antimicrobial activity for spent coolant of water-soluble cutting fluids as shown in the Experimental Section. These new additives for water-based cutting fluids were not previously known. Other work on application of these fluorine compounds is now in progress at our laboratory.

EXPERIMENTAL

The reaction products were analyzed by GLC on a Shimadzu Model GC-3BF Chromatograph using a 3m × 3mm column of 15 % Silicone DC 200 on 60 ~ 80 mesh Celite 545. ^{1}H NMR and ^{19}F NMR spectra were obtained using $CDCl_3$ as a solvent on a Hitachi Model R-24 spectrometer. The chemical schift values are expressed in δ value (ppm) relative to a TMS internal standard (^{1}H NMR), and ppm values relative to an external CF_3COOH (^{19}F NMR) (positive values upfield). IR spectra were obtained on a JASCO Model IR-G infrared spectrophotometer.

Commercial samples of monoesters of ethylene glycol and diethylene glycol were used.

Reaction of Ethylene Glycol Monolaurate (I) with PPDA

To a solution of ethylene glycol monolaurate (I) (3.0g) in dichloromethane (30 ml), a solution of PPDA (5.0 g) in dichloromethane (20 ml) was added drop by drop at room temperature. After stirring for 3 hr, the reaction mixture was left overnight. To the mixture, 100 ml of water were added, and it was extracted with diisopropyl ether. The ether extracts were washed with water, dried over a mixture of anhydrous sodium sulfate and anhydrous sodium carbonate, and evaporated. The residue was distilled to give the following fractions: (i) ~ 90 ℃/27 mmHg, 4.5 g; (ii) ~ 120 ℃/10^{-1} mmHg, 0.3 g; (iii) 120 ~ 130 ℃/10^{-1} mmHg, 2.0 g. Analysis of fraction (i) indicated that it was N,N-diethyl-2,3,3,3-tetrafluoropropionamide. Fraction (ii) was a mixture of 2-fluoroethyl laurate (II) (50 %) and lauroyloxyethyl 2,3,3,3-tetrafluoropropionate (III) (50 %). Compound (II) (0.10 g) was isolated by preparative gas chromatography from fraction (ii) (yield 3.3 %). IR (cm^{-1}): 1720; ^1H NMR (δ, ppm): 1.00 (3H, t, J=5.0 Hz, CH_3), 1.35 (18H, m, $-(CH_2)_9-$), 2.37 (2H, t, J=7.0 Hz, $-C\underline{H}_2-CO$), 4.20 (2H, t, J=6.0 Hz, $-O-C\underline{H}_2-$), 4.48 (2H, dt, J_{HF}= 48.3 Hz, J_{HH} =6.0 Hz, $-CH_2F$). ^{19}F NMR: +143.0 ppm (tt, J_{HF} =48.3 Hz, J_{HF} =29.8 Hz). Fraction (iii) was pure (III) (yield 43.8 %). IR (cm^{-1}): 1738, 1780; NMR (δ, ppm): 0.89 (3H, t, J=5.0 Hz, CH_3-), 1.26 (18H, m, $-(CH_2)_9-$), 2.26 (2H, t, J=6.0 Hz, $-C\underline{H}_2-CO$), 3.65 (2H, t, J=5.0 Hz, $-O-C\underline{H}_2-$), 4.09 (2H, t, J=5.0 Hz, $-C\underline{H}_2-O-$), 5.09 (1H, dq, J_{HF} =46.0 Hz, J_{HF}=6.0 Hz, $-C\underline{H}FCF_3$); ^{19}F NMR: +123.0 ppm (dq, J_{HF}=46.0 Hz, J_{FF} =11.5 Hz, $-CH\underline{F}CF_3$), -2.75 ppm (dd, J_{HF}= 6.0 Hz, J_{FF} =11.5 Hz).

Reaction of Ethylene Glycol Monosalicylate (VII) with PPDA

A mixture of PPDA (21.0 g, 0.094 mol) in CH_2CL_2 (20 ml) was added dropwise into a solution of (VII) (8.0 g, 0.044 mol) in CH_2CL_2 (30 ml) at room temperature. After stirring for 3 hr, the reaction mixture was left overnight. It was treated in the usual way, and the ether extracts were evaporated to remove the solvent. The residue was distilled to give the following fractions: (i) ~ 90 ℃/27 mmHg, 15.0 g; (ii) 90 ~ 149 ℃/27 mmHg, 0.5 g; (iii) 149 ~ 155 ℃/27 mmHg, 5.6 g. Analysis of fraction (i) indicated that it was N,N-diethyl-2,3,3,3-tetrafluoropropionamide. Fraction (ii) was a

mixture of the amide (50 %) and 1,2-benzo-3-oxo-8-tetrafluoroethylidene-4,7,9-trioxacyclononane (Ⅷ) (50 %). Fraction (iii) was pure (Ⅷ) (yield 65 %). It was solidified and recrystallized from a mixture of n-hexane containing dichloromethane (5 %). Mp 73.5 ~ 74.0 ℃; IR (cm^{-1}): 1785, 1592, 1200, 1050, 760, 623; ^1H NMR (δ, ppm): 4.28 (4H, m, $-C\underline{H}_2-$), 7.25 (4H, m, aromatic protons); ^{19}F NMR: +108.0 ppm (q, J_{FF}=7.5 Hz, -CF-), -5.0 ppm (d, J_{FF}= 7.5 Hz, CF_3-); MS (m/e): M^+ 292.0372 (measured value) (theoretical for $C_{12}H_8O_4F_4$, 292.0358).

Reaction of Phenoxyethyl Alcohol (Ⅸ) with PPDA

A mixture of PPDA (9.0 g, 0.0405 mol) in CH_2Cl_2 (20 ml) was added dropwise into a solution of (Ⅸ) (4.0 g, 0.029 mol) in CH_2Cl_2 (30 ml) at room temperature. After stirring for 3 hr, the reaction mixture was left overnight. It was treated as usual, and the ether extracts were evaporated to remove the solvent. The residue was distilled to give the following fractions: (i) ~ 60 ℃/5 mmHg, 4.5 g; (ii) 60 ~ 67 ℃/ 5 mmHg, 3.6 g; (iii) 67 ~ 73 ℃/ 5 mmHg, 0.1 g; (iv) 73 ~ 77 ℃/5 mmHg, 1.7 g. Analysis of fraction (i) was N,N-diethyl-2,3,3,3-tetrafluoropropionamide. Fraction (ii) was a mixture of the amide (20 %) and the fluoro ether (X) (80 %). Fraction (iv) was tetrafluoro ester (Ⅺ) (97 %) and other compounds (3 %). These compositions were determined by gas chromatography [Shimadzu GC-3BF, column Silicone DC-200 (15 %) on Celite 545 (3 m), temperature 180 ℃, carrier gas N_2, 40 ml/min]. Fraction (ii) (3.5 g) was chromatographed on a silica gel column (25.0 g) and eluted with n-hexane containing 1 % ethylacetate. Elution gave 2.62 g (yield 65 %) of pure 2-fluoroethyl phenyl ether (X). IR(cm^{-1}): 1600, 1250, 760, 698; ^1H NMR (δ, ppm): 4.25 (2H, m, Ph-O-$C\underline{H}_2-$), 4.43 (2H, dt, J_{HF}=66.0Hz, J_{HH}=4.8Hz, $-C\underline{H}_2F$), 7.0 (5H, m, C_6H_5-); ^{19}F NMR: +117 (m). Phenoxyethyl 2,3,3,3-tetrafluoropropionate (Ⅺ) was isolated from fraction (iii) by gas-chromatographic trapping. IR (cm^{-1}): 1680, 1220, 1124, 760, 598; ^1H NMR (δ, ppm): 4.10 (2H, t, J_{HH}=6.0 Hz, $-OC\underline{H}_2-$), 4.57, (2H, t, J_{HH}=6.0 Hz, $-C\underline{H}_2OCO-$), 5.00 (1H, dq, J_{HF}=6.5 Hz, J_{HF}=46.1 Hz, $-C\underline{H}FCF_3$), 7.00 (5H, m, C_6H_5-); ^{19}F NMR: +123.5 (dq, J_{HF}=46.1 Hz, J_{FF}=12.2 Hz), -2.0 (dd, J_{HF}=6.5 HZ, J_{FF}= 12.2 HZ). Other ether alcohols were fluorinated in the same manner, and the results are listed in Table 1.

Antimicrobial Tests of Fluorine Derivatives of Glycols

A mixture of 2.0 g of a sample, 110 g of water, 0.5 g of emulgene (emulsifier), 0.5 g of FA-30 and 0.5 g of triethanolamine was vigorously agitated. To this emulsion solution, 5 g of cast-iron chips (FC-20), 5 g of YCC Broth (Eiken Chem. Co. Ltd.) and 1.0 g of a spent coolant were added. The solution was kept at 35 ℃. The number of days until an unpleasant odour had appeared was checked. All compounds listed in Table 1 were subjected to antimicrobial tests. With benzoyloxyethyl 2,3,3,3-tetrafluoropropionate and 2-fluoropropyl benzoate, unpleasant odour was not observed during ten days. Other compounds delayed its appearance for less than five days.

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