♣A Convenient Method for Preparation of Monofluorocarboxylic Acids

S. Watanabe[a,*], T. Fujita[a], M. Sakamoto[a], H. Endo[a] and T. Kitazume[b]

[a]Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 260, and [b]Department of Bioengineering, Tokyo Institute of Technology, Tokyo, Japan

Monofluoro esters were prepared by the reaction of hydroxy esters with N,N-diethyl-1,1,2,3,3,3-hexafluoro propylamine (PPDA). Saponification of these monofluoroesters with enzyme (lipase MY) was attempted to give their corresponding monofluorocarboxylic acids in moderate yields.

A convenient preparative method for monofluorocarboxylic acids has not been known. 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 fatty alcohols (1) and hydroxyesters (2). Defluorinative reactions are apt to occur upon saponification of fluorocompounds with potassium hydroxide or sodium hydroxide. On examination of this reaction, we found that the use of enzyme (lipase MY) was effective for hydrolysis of monofluoroesters. We have reported that some α-substituted fatty acids had excellent properties for water soluble cutting fluids (3). We examined anti-rust properties of these monofluorocarboxylic acids.

EXPERIMENTAL

Fluorination of hydroxyesters. Monofluoroesters were prepared from hydroxyesters by the action of PPDA as reported previously (2).

Saponification of ethyl ω-fluoroundecanoate (I) with lipase MY. A mixture of ethyl ω-fluoroundecanoate (I) (2.5 g, 0.0108 mol), lipase MY (*Candida cylindracea*, Meito Sangyo Co. Ltd.) (10 g) and water (100 cc) was agitated for 6 hr at 38 C. The mixture was extracted with diisopropyl ether. The ether extract was washed with water several times, dried over anhydrous sodium sulfate, filtered and evaporated to remove the solvent. The residue was solidified and recrystallized from a mixture of n-hexane (80%) and ethyl acetate (20%) to give the acid (II) (1.2 g, yield 48%) (mp 31-32 C). ^{1}H NMR (δ, ppm): 9.3 (1H, s, COOH), 4.30 (2H, dt, J_{HF} = 47.6 Hz, J_{HH} = 6.0 Hz, $-C\underline{H}_2F$), 2.27 (2H, t, J = 6.0 Hz, $-C\underline{H}_2COOH$), 1.32 (16H, s, $-(CH_2)_8$-); IR (cm^{-1}): 3500 (−COOH), 1720 (−C=O); ^{19}F NMR (δ, ppm) ($CHCl_3$): signal of F (multiplet) was recognized at 137.2 upfield from the external standard of CF_3COOH.

Hydrolysis of ethyl ω-fluoroundecanoate (I) with sodium bicarbonate. A mixture of ethyl ω-fluoroundecanoate (I) (1.6 g, 0.0069 mol), sodium bicarbonate (2.5 g, 3.0×10^{-2} mol), isopropanol (50 ml) and water (50 ml) was treated as reported elsewhere (4) to give ω-fluoroundecanoic acid (II) in yield of 25%.

Test method. Aqueous solutions (1.0%) of triethanolamine salts of the acids listed in Table 1 were used. Distilled and deionized water was used for corrosion tests. When city water was used in Tokyo and Chiba, Japan, the same results were obtained in the corrosion and lubricity tests.

Method A (corrosion test with cast iron chips), Method B (corrosion test with steel panels), the surface tensions (dyne/cm) and friction coefficient were measured as reported previously (3).

RESULTS AND DISCUSSION

We have reported that PPDA can be applied for fluorination of hydroxyesters (2). However, saponification of these monofluoroesters with potassium hydroxide or sodium hydroxide did not give their corresponding monofluorocarboxylic acids owing to defluorinative reaction. On trial, the saponification of monofluoroesters with enzyme (lipase MY) was examined. The use of an excess of water as a solvent at 38-40 C was the best condition for its preparation of the monofluorocarboxylic acid, which was obtained in 50-70% yield. For example, ω-fluoroundecanoic acid (II) was obtained in 48% yield from ethyl ω-fluoroundecanoate (I) by the

TABLE 1

Preparation of Monofluorocarboxylic Acids

Carboxylic acid	Yield (%) $NaHCO_3$	 Lipase MY	M.P. (°C/32 mm Hg)[a]	^{19}F NMR (ppm) -CHF- or $-CH_2F$
3-Fluoro-5-methylhexanoic acid	20	30	140-142[a]	+ 100.0 (m)
ω-Fluoroundecanoic acid	25	48	31-32	+ 137.2 (m)
ω-Fluorododecanoic acid	30	75	83-84	+ 136.0 (m)
12-Fluoro oleic acid	26	75	30-32	+ 98.7 (m)
α-Fluorophenyl acetic acid	15	40	72-73.5	+ 97.5 (d, J_{HF} = 47.6 Hz)
β-Fluoro-β-phenyl propionic acid	15	30	47-48	+ 91.75 (m)

[a]Boiling point.

---

[*]To whom correspondence should be addressed.

TABLE 2

Cutting Fluid Characteristics of Monofluorocarboxylic Acids

Fluorocarboxylic acids	Anti-rust test[a] Method A[b]	Anti-rust test[a] Method B	Friction coefficient	Surface tension (dyn/cm)
3-Fluoro-5-methylhexanoic acid	6	6	—	—
ω-Fluoroundecanoic acid	10	10	0.09	43
ω-Fluorododecanoic acid	8	8	0.10	38
12-Fluoro oleic acid	8	8	0.08	34
12-Fluoro-9,10-epoxy stearic acid	10	10	0.10	39
2-Fluoro-2-phenylacetic acid	6	7	0.267	55
3-Fluoro-3-phenylpropionic acid	8	9	0.163	40

[a] Aqueous solutions (1.0%) of triethanolamine salts were used.

[b] Method A is corrosion test with cast-iron chips; method B is corrosion test with steel panels.

Values of 10 show no rust and values 8 show a small amount of rust.

action of enzyme (lipase MY). These results are shown in Table 1.

$$\mathrm{CH_2F\,(CH_2)_9COOH_2H_5} \rightarrow \mathrm{CH_2F\,(CH_2)_9COOH}$$

(I) (II)

Saponification of fluoroesters by using sodium bicarbonate solution is known (4). However, the yields of fluorocarboxylic acids with the known method (4) are low, 20-30%.

Bioactive investigation of fluorine compounds has been widely known. However, application for water-soluble cutting fluids additives has not been investigated. We examined the anti-rust properties of these various monofluorocarboxylic acids. We have found that aqueous solution (1.0%) of triethanolamine salt with ω-fluoroundecanoic acid (II) showed excellent properties in corrosion test with cast-iron chips (method A) and steel panels (method B). Aqueous solutions of triethanolamine salts with other fluorocarboxylic acids did not show good antirust properties. These results are shown in Table 2.

ACKNOWLEDGMENT

N. Ishikawa of the Tokyo Institute of Technology guided us in this work.

REFERENCES

1. Watanabe, S., T. Fujita, K. Suga and I. Nasuno, *J. Am. Oil Chem. Soc. 60*:1678 (1983).
2. Watanabe, S., T. Fujita, Y. Usui and T. Kitazume, *J. Fluorine Chem. 31*:247 (1986).
3. Watanabe, S., T. Fujita, K. Suga and K. Sugahara, *J. Am. Oil Chem. Soc. 60*:40 (1983).
4. Tsuchima, T., K. Kawada, J. Nishikawa, T. Sato, K. Tori and T. Tsuji, *J. Org. Chem. 49*:1163 (1984).

[Received June 16, 1986]