Journal of Fluorine Chemistry, 48 (1990) 77–84

Received: August 1, 1989; accepted December 13, 1989

SYNTHETIC UTILITY OF 3-(PERFLUORO-1,1-DIMETHYLBUTYL)-1-PROPENE. PART III. SYNTHESIS AND PROPERTIES OF (PERFLUORO-1,1-DIMETHYLBUTYL) ACETIC AND PROPIONIC ACIDS AND THEIR SALTS

W.DMOWSKI, H.PLENKIEWICZ and K.PIASECKA-MACIEJEWSKA

Institute of Organic Chemistry, Polish Academy of Sciences,
01-224 Warsaw (Poland)

D.PRESCHER, J.SCHULZE and I.ENDLER

Central Institute of Organic Chemistry, Academy of Sciences of the G.D.R., 1199 Berlin (G.D.R.)

SUMMARY

The new highly fluorinated acids, $CF_3CF_2CF_2C(CF_3)_2CH_2COOH$ and $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2COOH$, were synthesised by oxidation of the title alkene, $CF_3CF_2CF_2C(CF_3)_2CH_2CH=CH_2$, and of its alcohol derivative, $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2CH_2OH$, respectively. Sodium salts of the new fluorinated acids were prepared and some of their properties as surfactants have been determined and compared with those of totally fluorinated sodium alkanoates with the same number of carbon atoms.

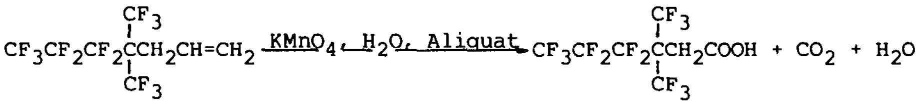
INTRODUCTION

Per- and polyfluoroalkanoic acids are the most widely used intermediates for the synthesis of fluorosurfactants. Totally fluorinated acids are manufactured by an electrofluorination process or by functionalisation of the tetrafluoroethylene telomer iodides [1]. Also, partially fluorinated acids are usually prepared from perfluoroalkyl iodides via free-radical addition of these iodides to terminally unsaturated acids to provide a homologous series of perfluoroalkyl-terminated alkanoic acids [2]. As a continuation of the studies on functionalisation of the readily available 3-(perfluoro-1,1-dimethylbutyl)-1-propene [3,4], we report another approach to perfluoroalkyl alkanoic acids by oxidation of this alkene and its alcohol derivative, 3-(perfluoro-1,1-dimethylbutyl)propan-1-ol. Surface activities of sodium salts of the new acids are reported.

RESULTS AND DISCUSSION

The double bond in 3-(perfluoro-1,1-dimethylbutyl)-1-propene (1) is rather resistant to common oxidising agents; it failed to react with 30% aqueous hydrogen peroxide or with sodium hypochlorite in an acetonitrile-water system. However, alkene 1 has been successfuly converted to the corresponding 1,2-epoxypropane by oxidation with peracids, although the reaction proceeds very slowly to give only moderate yields [3].

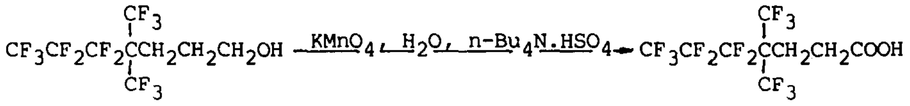
The oxidation of alkene 1 with aqueous potassium permanganate is also sluggish, but we have found that the reaction is efficiently accelerated by addition of a phase transfer catalyst; methyltricaprylammonium chloride (Aliquat 336) has been found to be an excellent catalyst. The reaction temperature is a critical factor and the best results were achieved within a rather narrow range of 50 - 60°C. Under these conditions, the oxidation proceeded exothermally such that the required temperature was maintained by dropwise addition of the alkene to the vigorously stirred water suspension of potassium permanganate containing a catalytic amount of Aliquat. A 50% isolated yield of (perfluoro-1,1-dimethylbutyl)acetic acid (2) was obtained by careful control of the reaction temperature, but even a slight increase in temperature resulted in evolution of carbon dioxide with a considerable drop in yield of the acid 2. The oxidation proceeds quantitatively but acid 2 was isolated in a considerably lower yield because a significant amount was lost during distillation. The poor efficiency of the distillation is due to a white, unidentified solid which co-distills with the first fraction of the acid. Nevertheless, careful fractionation allowed acid 2 of ca. 98% purity to be obtained.



$$CF_3CF_2CF_2\overset{CF_3}{\underset{CF_3}{C}}CH_2CH{=}CH_2 \xrightarrow{KMnO_4,\ H_2O,\ Aliquat} CF_3CF_2CF_2\overset{CF_3}{\underset{CF_3}{C}}CH_2COOH + CO_2 + H_2O$$

1 2

The potassium permanganate oxidation of 3-(perfluoro-1,1-dimethylbutyl)propan-1-ol (3) gave 3-(perfluoro-1,1-dimethylbutyl)propionic acid (4) having one carbon atom more than the acid obtained by oxidation of alkene 1. The oxidation without a catalyst also proceeds very slowly; at 70°C less then 50% conversion was achieved. In this case, addition of Aliquat gave no expected catalytic effect but, in the presence of tetrabutylammonium hydrosulphate the reaction was completed in 24 hours to give acid 4 in a 74% isolated yield and of ca. 98% purity.



$$CF_3CF_2CF_2\overset{CF_3}{\underset{CF_3}{C}}CH_2CH_2CH_2OH \xrightarrow{KMnO_4,\ H_2O,\ n\text{-}Bu_4N.HSO_4} CF_3CF_2CF_2\overset{CF_3}{\underset{CF_3}{C}}CH_2CH_2COOH$$

3 4

Acids 2 and 4 are not sufficiently soluble in water to examine their properties as surfactants. These acids, especially 4, are also barely miscible with aqueous sodium hydroxide thus making it difficult to prepare their sodium salts by this way. The salts, $CF_3CF_2CF_2C(CF_3)_2CH_2COONa$ (5) and $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2COONa$ (6), were successfully prepared in methanolic solutions by neutralising the acids with sodium methoxylate. Salts 5 and 6 were characterised by determining surface tensions and interfacial tensions of their aqueous solutions as functions of the concentration (Figures 1 and 2) and by contact angles at droplets on paraffin and polytetrafluoroethylene (PTFE) at concentrations greater than c.m.c.(critical micelle con-

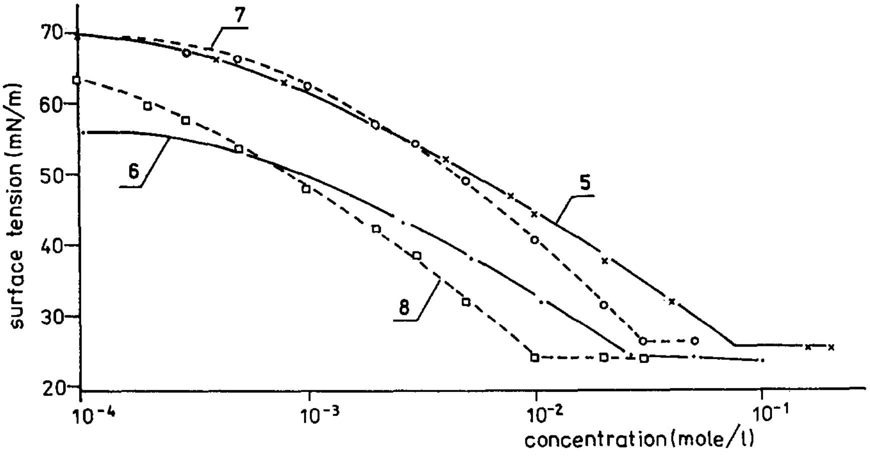


Fig.1. Surface tensions (at 25°C) of aqueous solutions of fluoroalkanoates: $CF_3CF_2CF_2C(CF_3)_2CH_2COONa$ (5), $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2COONa$ (6), $CF_3(CF_2)_6COONa$ (7), $CF_3(CF_2)_7COONa$ (8).

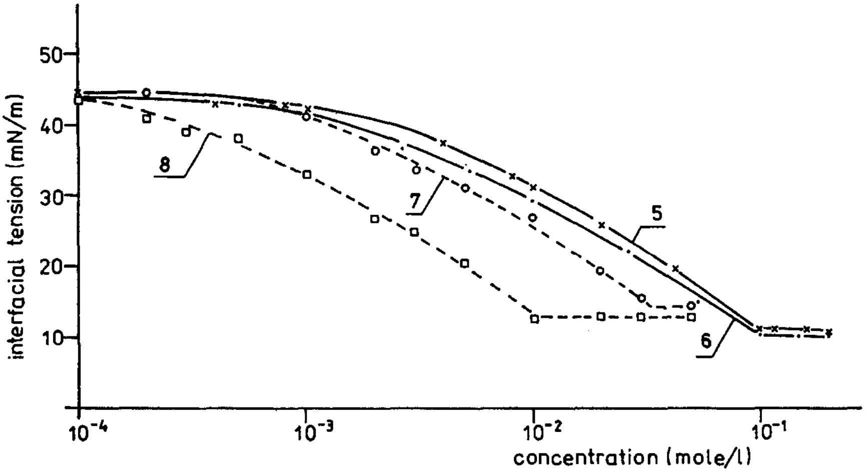


Fig.2. Interfacial tensions (at 25°C) in a water/n-heptane system containing fluoroalkanoates: $CF_3CF_2CF_2C(CF_3)_2CH_2COONa$ (5), $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2COONa$ (6), $CF_3(CF_2)_6COONa$ (7), $CF_3(CF_2)_7COONa$ (8).

centration) (Table 1). The results have been compared with values obtained for commercial sodium perfluorooctanoate (7) and sodium perfluorononanoate (8) containing the same number of carbon atoms.

TABLE 1

Wettabilities of paraffin and PTFE by aqueous solutions of sodium fluoroalkanoates 5 - 8 (at concentrations greater than c.m.c) and by water.

Sublayer	Contact angle (degree) for:				
	5	6	7	8	water
Paraffin	60	50	49	59	107
PTFE	39	13	57	55	128

Salts 5 and 6 have shown remarkable surface activity. They reduce the surface tension of water solutions to a level comparable to totally fluorinated compounds 7 and 8, although at somewhat higher concentrations. The critical micelle concentration (c.m.c.) is *ca.* 0.04 mole/l higher for compounds 5 and 6 than for the fully fluorinated salts 7 and 8, possibly due to the lower hydrophobicity of the former compounds. Interfacial tensions, measured in a water/n-heptane system, are similar for both salts 5 and 6. In this system, the interfacial tensions at c.m.c have shown lower values for surfactants 5 and 6 as compared to 7 and 8. This behaviour could be explained as a result of the interaction of the CH_2 groups in the former compounds with the organic phase. Contact angles, measured at droplets of aqueous solutions of 5 and 6 on paraffin or PTFE, demonstrate good wettabilities. Particularly small values, smaller than those for perfluorinated surfactants 7 and 8, were obtained on PTFE. The new fluorosurfactants do not show enough foam ability to be measured.

EXPERIMENTAL

Boiling and melting points are uncorrected. The NMR spectra were recorded with a Brucker 500 MHz instrument and the IR spectra with a Beckmann Acculab TM-1 and a Specord 75 IR (VEB Carl Zeiss, Jena) spectrometers. Purity of the acids were determined by GLC using a 3.5 m x 4 mm column packed with Chromosorb G coated with 3% Silicon Oil SE-52.

The measurements of surface and interfacial tensions were carried out following the Du Noüy ring-method. Contact angles were determined at droplets on paraffin and PTFE by optical projection.

Syntheses of 3-(perfluoro-1,1-dimethylbutyl)-1-propene (1) [5] and 3-(perfluoro-1,1-dimethylbutyl)propan-2-ol (3) [3] have been described previously.

(Perfluoro-1,1-dimethylbutyl)acetic acid (2)

The reaction was carried out in a 250 ml three-necked flask equipped with a strong mechanical stirrer, a reflux condenser, a thermometer, and a dropping funnel.

Finely powdered potassium permanganate (35 g, 220 mmoles), water (25 ml), and Aliquat 336 (1 g, 2.5 mmoles) were placed in the reaction vessel and warmed to 50°C. The heat source was removed after which 3-(perfluoro-1,1-dimethylbutyl)-1-propene (18 g, 50 mmoles) was added dropwise, while vigorously stirring, in such a rate to keep the reaction temperature within the range 50 - 60°C (exothermic effect). After completion of the addition (ca. 30 min), the stirring was continued for an additional one hour while keeping the temperature at 60°C by means of external heating and, finally, the reaction mixture was decolourised by adding a small amount of methanol. Then, water (50 ml) was added, the reaction mixture was warmed up to 90°C and, filtered while hot through a Büchner funnel under slight vacuum after which the precipitate of manganese dioxide was washed with boiling water (30 ml). The combined eluents were extracted once with diethyl ether (30 ml), the ether layer was thoroughly separated and the water solution was strongly acidified with concentrated sulphuric acid (10 ml); the bottom layer of (perfluoro-1,1-dimethylbutyl)acetic acid was formed. This layer was separated, the water layer was extracted with ether (3 x 30 ml) and the extracts were combined with the main portion of the acid and dried over anhydrous magnesium sulphate. The residue obtained after removal of the solvent was vacuum distilled* to give (perfluoro-1,1-dimethylbutyl)acetic acid (12 g, 63.6%) of ca. 98% purity (GLC estimate). A colourless viscous liquid; b.p. 108°C/18 Torr, 64°C/0.2 Torr; m.p. 16 - 18°C. Found: C, 25.6; H, 0.7; F, 65.3%. $C_8H_3F_{13}O_2$ requires: C, 25.4; H, 0.8; F, 65.3%. ^1H NMR ($CDCl_3$, TMS): 3.20 ppm (2H, s), 8.60 ppm (1H, broad). ^{19}F NMR ($CDCl_3$, CCl_3F): 64.3 ppm (6F), 80.6 ppm (3F), 108.2 ppm (2F), 123.6 ppm (2F). IR (neat): ν (C=O) = 1755 cm^{-1} (vs).

3-(Perfluoro-1,1-dimethylbutyl)propionic acid (4)

Finely powdered potassium permanganate (19 g, 120 mmoles), water (120 ml), 3-(perfluoro-1,1-dimethylbutyl)propan-1-ol (30 g, 79 mmoles), and tetrabutylammonium hydrosulphate (1 g, 3 mmoles) were placed together in a 250 ml three-necked flask and vigorously stirred at 65 - 70°C for 24 hours, then worked up as described above. Vacuum distillation gave 3-(perfluoro-1,1-dimethylbutyl)propionic acid (23 g, 74%) of ca. 98% purity (GLC estimate). A white crystalline solid; b.p. 96°C/1.2 Torr, 84°C/0.6 Torr; m.p. 42 - 43°C. Found: C, 27.5; H, 1.2; F, 63.0%. $C_9H_5F_{13}O_2$ requires: C, 27.6; H, 1.3; F, 63.0%. ^1H NMR ($CDCl_3$, TMS): 2.58 ppm (2H), 2.76 ppm (2H), 11.63 ppm (1H, broad). ^{19}F NMR ($CDCl_3$, CCl_3F): 64.4 ppm (6F), 80.6 ppm (3F), 108.05 ppm (2F), 123.6 ppm (2F). IR (CCl_4): ν (C=O) = 1720 cm^{-1} (vs).

Sodium (perfluoro-1,1-dimethylbutyl)acetate (5)

The sodium salt was prepared by adding at ambient temperature equimolar amounts of methanolic sodium methoxylate to a stirred methanolic solution of acid 2 and evaporating of the solvent. The salt was purified by recrystallisation from dioxane. Found: C, 24,2; H, 0,8; F, 61.7; Na, 5.9 %. $C_8H_2F_{13}O_2Na$ requires: C, 24.0; H, 0.5; F, 61.8; Na, 5.8 %. IR (KBr): ν (COO^-) = 1590 cm^{-1} (s).

---

* At the beginning a white unidentified substance distills and solidifies in the condenser.

Sodium 3-(perfluoro-1,1-dimethylbutyl)propionate (6)

The salt was prepared from acid 4 as described above and recrystallised from acetonitrile. Found: C, 25.9; H, 1,3; F, 59.7; Na, 5.7 %. $C_9H_4F_{13}O_2Na$ requires: C, 26.1; H, 1.0; F, 59.7; Na, 5.6 %. IR (KBr): ν (COO^-) = 1560 cm^{-1} (s).

ACKNOWLEDGMENTS

This work has been supported by the Polish Academy of Sciences within the project C.P.B.P.-01.13.1.21 and by the Academy of Sciences of the G.D.R..

REFERENCES

1 R.E.Banks, 'Organofluorine Chemicals and Their Industrial Application', Ellis Horwood, Chichester (1979), chapter 11.

2 N.O.Brace, J.Org.Chem., 27 (1962) 4491.

3 W.Dmowski, H.Plenkiewicz and J.Porwisiak, J.Fluorine Chem., 41 (1988) 191.

4 H.Plenkiewicz and W.Dmowski, J.Fluorine Chem., 45 (1989) 389.

5 W.Dmowski and R.Wozniacki, Pol.Pat., 145018 (1985); W.Dmowski and J.Porwisiak, Pol.Pat.Appl. P-265914 (1987).