An Improved Synthesis of Perfluorocarboxylic Acids

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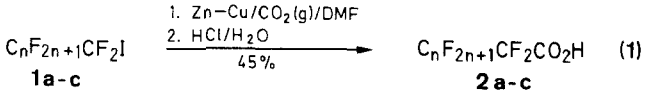
Perfluoroalkyl iodides $C_nF_{2n+1}CF_2I$ ($3 < n < 7$) were converted to perfluoroalkanecarboxylic acids $C_nF_{2n+1}CF_2CO_2H$ in 91% yield, by reaction with zinc–copper couple in the presence of solid carbon dioxide in trimethyl phosphate as the solvent.

Perfluorocarboxylic acids $C_nF_{2n+1}CO_2H$ ($4 < n < 12$) are of considerable industrial interest as precursors of surfactants. We have searched for a new synthetic method for these acids, since none of the reactions described in the literature are totally satisfactory. For example, in some cases the loss of two fluorine atoms[3,5,7] is not economically viable, in others the yields of the acids are not sufficiently high.[1,2,4,8–11] Furthermore the reactions are not amenable to an industrial scale because either mercury is used[6] or the use of pressure is required, and moreover there were difficulties in isolating the acids obtained[12] (formation of complex with dimethylformamide).

We were therefore drawn to consider the optimization of a reaction previously investigated in our laboratory (eq. 1)



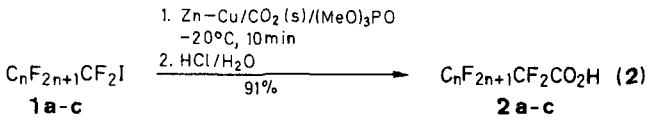
(1)

1,2	a	b	c
n	3	5	7

This reaction involves the formation of intermediary perfluoroalkylzinc iodide which becomes adsorbed on the metal surface and is very reactive. This remarkable reactivity is shown in the dipolar aprotic solvents dimethyl sulfoxide and dimethylformamide[9,13] with a number of substrates, e.g. sulfur dioxide, which leads to the formation in good yields of the corresponding perfluorosulphonic acid chlorides. Similar reactions take place with alkyl carbonates[11] and alkyl phosphates,[14] as solvents.

These observations led us to modify the reaction conditions as follows. Firstly, the use of solid rather than gaseous carbon dioxide for the carbonatation, since carbon dioxide is only slightly soluble in the solvent used. Secondly, the use of trimethyl phosphate as the solvent since its melting point (−46 °C) is much lower than that of dimethylformamide, and it has the further advantage it is stable to perfluoroorganozinc compounds below 60 °C.[13] And finally, carbon dioxide has a greater solubility in trimethyl phosphate than in dimethylformamide or dimethyl sulfoxide.

The addition of perfluoroalkyl iodide to zinc–copper couple in the presence of solid carbon dioxide in trimethyl phosphate as the solvent gives, after hydrolysis, the corresponding perfluoroalkanecarboxylic acid in 91% yield.



(2)

It is envisaged that the reaction follows the mechanism outlined above via a perfluoroalkylzinc iodide.

This reaction thus constitutes a general method for the preparation of perfluorocarboxylic acids from the corresponding perfluoroalkyl iodides in good yield, and also has the possibility of repeatedly using the solvent.

All reagents were of commercial quality from freshly opened containers. Reagents quality solvents were used without further purification. Starting materials come from Atochem Company. All reactions were carried out under atmospheric pressure. Yields refer to isolated compounds. Obtained products were compared to authentic samples. Melting points were taken using a Tottoli apparatus and are uncorrected. Microanalyses were obtained using a Dionex 2001 element analyser. Mass spectra were recorded on a Jeol JMS D100 spectrometer. All reactions were monitored by NMR studies. ^{1}H- and ^{19}F-NMR spectra were obtained using a VARIAN EM390 (90 MHz) spectrometer.

Perfluoropentanoic Acid (2a); Typical Procedure:

The Zn–Cu couple is prepared by the addition of Zn powder (5.6 g, 0.1 mol) in small portions to a vigorously stirred solution of $(AcO)_2Cu$ (0.2 g, 0.001 mol) in hot AcOH. After a rapid exothermic reaction the mixture is cooled, the AcOH evaporated *in vacuo*. The freshly prepared couple is dispersed in trimethyl phosphate (30 mL) saturated with CO_2 (22 g, 0.5 mol) by addition of solid CO_2. The mixture is kept at −20 °C and the perfluorobutyl iodide (**1a**; 34.6 g, 0.1 mol) is rapidly added over 10 min with stirring. The mixture is instantaneously hydrolyzed with 30% HCl, the organic layer separated, dried ($MgSO_4$) and distilled to give **2a**, identical to an authentic sample; yield: 24 g (91%); bp 127 °C (Lit.[15] bp 120 °C).

$C_5HF_9O_2$ (263.9) calc. C 22.75 F 64.75
found 22.81 64.70

^{1}H-NMR (acetone-d_6/TMS): δ = 12.3 (s, 1 H).

^{19}F-NMR (acetone-d_6/$CFCl_3$): δ = 81.7 (t, 3F, CF_3), 118.6 (t, 2F, CF_2CO_2H).

MS (70 eV): *m/z* (%) = 264 (M^+), 219 (100), 200 (70).

Perfluoroheptanoic Acid (2b)

Perfluorohexyl iodide (**1b**; 44.6 g, 0.1 mol) is converted, according to the previous procedure, into pure perfluoroheptanoic acid (**2b**), identical to an authentic sample; yield: 33.1 g (91%) bp 105 °C/40 Torr (Lit.[9,10,15] bp 105 °C/40 Torr). After recrystallization from CCl_4, compound **2b** is obtained as white crystals; mp 54 °C.

$C_7HF_{13}O_2$ (363.9) calc. C 23.10 F 67.84
found 23.28 67.79

^{1}H-NMR (acetone-d_6/TMS): δ = 12.3 (s, 1 H).

^{19}F-NMR (acetone-d_6/$CFCl_3$): δ = 81.6 (t, 3F, CF_3), 119.2 (t, 2F, CF_2CO_2H).

MS (70 eV): *m/z* (%) = 364 (M^+), 319 (100), 300 (65).

Perfluorononanoic Acid (2c):

Perfluorooctyl iodide (**1c**; 54.6 g, 0.1 mol) treated as above, leads, after recrystallization from CCl_4, to the formation of perfluoro-

nonanoic acid (**2c**) as white crystals, identical to an authentic sample; yield: 42.2 g (91%); mp 65°C (Lit.[9,10] mp 69–71°C).

$C_9HF_{17}O_2$ (463.9) calc. C 23.30 F 69.59
found 23.38 69.61

^{1}H-NMR (acetone-d_6/TMS): δ = 12.3 (s, 1H).

^{19}F-NMR (acetone-d_6/$CFCl_3$): δ = 81.2 (t, 3F, CF_3), 119.8 (t, 2F, CF_2CO_2H).

MS (70 eV): m/z (%) = 464 (M^+), 419 (80), 400 (100).

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