Preparation of Perfluoroalkane Carboxylic and Sulphonic Acid Derivatives by the Action of Metallic Couples on Perfluoroalkyl Iodides in Dimethyl Sulphoxide

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Summary Perfluoroalkyl iodides react with carbon dioxide and sulphur dioxide, in the presence of zinc–copper type metallic couples in dimethyl sulphoxide, to give the corresponding carboxylic and sulphonic acids derivatives in 40–80% yields.

Industrially important perfluoroalkane carboxylic and sulphonic acids have been prepared mainly by electrochemical fluorination.[1] Unfortunately in this process the yields decrease as the length of the hydrocarbon chain increases. However, recent results have shown that it was possible to obtain perfluoroalkanesulphonic acids, R_FSO_3H, or their derivatives, from the corresponding perfluoroalkyl iodides (obtained industrially by telomerization of tetrafluoroethylene with CF_3I or C_2F_5I, from the Produits Chimiques Ugine Kuhlmann Company) by a chemical method in good yields.[2,3] The intermediates in these syntheses were either the methyl perfluoroalkyl sulphides, R_FSMe,[2] or the perfluorinated Grignard reagents, R_FMgBr.[3] We have shown recently[4] that metallic couples, such as Zn–Cu, could increase the reactivity of perfluoroalkyl iodides in many reactions with Me_2SO as solvent.

Table 1. Preparation of R_FCO_2H according to equation (1).

			R_FCO_2H		
R_FI	Amount R_FI/mmol	Conditions[a]	B.p./°C (mmHg) [m.p./°C]	% Yield[b]	% R_FI consumed
C_4F_9I	50	(A)	70 (40)	40	90
	80	(B)		42	
$C_6F_{13}I$	50	(A)	105 (50)	45	95
	400	(C)		63	
$C_8F_{17}I$	50	(A)	[71]	47	80

[a] Molar ratio couple:R_FI 1·5:1 throughout. (A) 100 ml Me_2SO solvent, CO_2 (40 ml/min) bubbled through R_FI–couple–Me_2SO suspension for 3 h at 25 °C; (B) 40 ml Me_2SO, CO_2 bubbled for 1·5 h at 30 °C; (C) 600 ml Me_2SO, CO_2 bubbled for 1·5 h at 30 °C. [b] Based on R_FI consumed.

We now report the first use of these metallic couples in a new and convenient synthesis of perfluoroalkanecarboxylic acids, R_FCO_2H, and perfluoroalkanesulphonyl chlorides, R_FSO_2Cl.

Perfluoroalkyl iodides react at room temperature, in a dispersion of Zn–Cu couple in Me_2SO, with CO_2 according to equation (1), and with SO_2 according to equation (2).

$$R_FI + \text{Zn–Cu} + CO_2 \xrightarrow[\text{ii, aq. HCl}]{\text{i, } Me_2SO} R_FCO_2H \qquad (1)$$

$$R_FI + \text{Zn–Cu} + SO_2 \xrightarrow[\text{ii, } Cl_2\text{,MeOH}]{\text{i, } Me_2SO} R_FSO_2Cl \qquad (2)$$

The Zn–Cu couple was obtained from zinc powder and copper acetate [molar ratio Zn:$(AcO)_2Cu$ 100:1] in anhydrous Me_2SO, under nitrogen, and was used freshly prepared. Other couples, for example Pb–Zn, Cd–Zn, or Hg–Zn led to the same results.

Reaction (1) was carried out by adding the perfluoroalkyl iodide in a stirred suspension of the couple in Me_2SO, and simultaneously bubbling carbon dioxide. After hydrolysis (aq. HCl), the acids R_FCO_2H were isolated and purified by vacuum distillation and/or recrystallisation.

Table 2. Preparation of R_FSO_2Cl according to equation (2).

			R_FSO_2Cl		
R_FI	Amount R_FI/mmol	Conditions[a]	B.p./°C (mmHg) [m.p./°C]	% Yield[b]	% R_FI consumed
C_4F_9I	50	(A)	103 (760)	40	90
	30	(B)		55	
$C_6F_{13}I$	50	(A)	55 (20)	40	95
	800	(C)		80	
$C_8F_{17}I$	50	(A)	98 (20) [37]	52	80
	200	(D)		75	

[a] Molar ratio couple : R_FI 1·5 : 1 throughout. (A) R_FI added to suspension of couple in Me_2SO (100 ml) saturated with SO_2; reaction time 3 h, temp. 25 °C; (B) 120 ml of Me_2SO; SO_2 bubbled (120 ml/min) through R_FI–couple–Me_2SO suspension for 2 h at 30 °C; (C) 400 ml Me_2SO; SO_2 bubbled as before for 4 h at 45 °C; (D) 200 ml Me_2SO; SO_2 bubbled for 2 h at 45 °C. The reaction was strongly exothermic and external cooling was required in all cases. [b] Based on R_FI consumed.

Reaction (2) was carried out by adding the iodide R_FI in a suspension of the couple in Me_2SO previously saturated with SO_2, or by bubbling SO_2 in the suspension after addition of the R_FI. In both cases, the intermediate isolated was treated with chlorine in a methanolic or aqueous medium; the chlorides R_FSO_2Cl were purified, after decantation, by vacuum distillation.

All the products were characterised by their ^{19}F n.m.r. and mass spectra. The pure sulphonyl chlorides and the *S*-benzylthiouronium salts of the carboxylic acids gave satisfactory elemental analyses.

Results are shown in Tables 1 and 2.

It is reasonable to assume that these reactions involve the formation of zinc salts as intermediates, arising from the insertion of CO_2 and SO_2 into a perfluoro-organometallic compound of the type R_FZnI, the reactivity of which should be increased on the metallic surface of the finely divided couple. It is clear that the solvent and the couple play an important role and allow the reaction to occur (CO_2 is without effect on C_3F_7ZnI under normal conditions[5]).

The present results show that metallic couples increase the reactivity of perfluoroalkyl iodides,[4] and also lead to the synthesis of industrially important perfluoro-compounds.

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