

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

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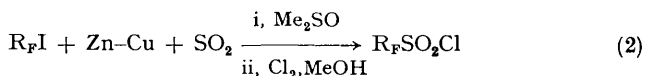
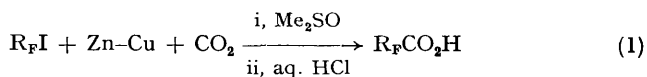
**Summary** Perfluoroalkyl iodides react with carbon dioxide and sulphur dioxide, in the presence of zinc-copper type metallic couples in dimethyl sulphoxide, to give the corresponding carboxylic and sulphonic acids derivatives in 40–80% yields.

INDUSTRIALLY important perfluoroalkane carboxylic and sulphonic acids have been prepared mainly by electrochemical fluorination.<sup>1</sup> 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.<sup>2,3</sup> The intermediates in these syntheses were either the methyl perfluoroalkyl sulphides,  $R_FSM_e$ ,<sup>2</sup> or the perfluorinated Grignard reagents,  $R_FMgBr$ .<sup>3</sup> We have shown recently<sup>4</sup> that metallic couples, such as Zn–Cu, could increase the reactivity of perfluoroalkyl iodides in many reactions with  $Me_2SO$  as solvent.

merization of tetrafluoroethylene with  $CF_3I$  or  $C_2F_5I$ , from the Produits Chimiques Ugine Kuhlmann Company) by a chemical method in good yields.<sup>2,3</sup> The intermediates in these syntheses were either the methyl perfluoroalkyl sulphides,  $R_FSM_e$ ,<sup>2</sup> or the perfluorinated Grignard reagents,  $R_FMgBr$ .<sup>3</sup> We have shown recently<sup>4</sup> that metallic couples, such as Zn–Cu, could increase the reactivity of perfluoroalkyl iodides in many reactions with  $Me_2SO$  as solvent.

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).



The Zn–Cu couple was obtained from zinc powder and copper acetate [molar ratio Zn : (AcO)<sub>2</sub>Cu 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  $Me_2SO$ ,

R <sub>F</sub> I	Amount R <sub>F</sub> I/mmol	Conditions <sup>a</sup>	R <sub>F</sub> CO <sub>2</sub> H		% R <sub>F</sub> I consumed
			B.p./°C (mmHg) [m.p./°C]	% Yield <sup>b</sup>	
C <sub>4</sub> F <sub>9</sub> I	50	(A)	70 (40)	40	90
	80	(B)		42	
C <sub>6</sub> F <sub>13</sub> I	50	(A)	105 (50)	45	95
	400	(C)		63	
C <sub>8</sub> F <sub>17</sub> I	50	(A)	[71]	47	80

<sup>a</sup> Molar ratio couple:R<sub>F</sub>I 1.5:1 throughout. (A) 100 ml  $Me_2SO$  solvent,  $CO_2$  (40 ml/min) bubbled through R<sub>F</sub>I-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. <sup>b</sup> Based on R<sub>F</sub>I consumed.

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).

$R_FI$	Amount $R_FI$ /mmol	Conditions <sup>a</sup>	$R_FSO_2Cl$		
			B.p./°C (mmHg) [m.p./°C]	% Yield <sup>b</sup>	% $R_FI$ 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	

<sup>a</sup> 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. <sup>b</sup> 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-benzylthiuronium 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<sup>5</sup>).

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

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<sup>1</sup> R. N. Haszeldine, *J. Chem. Soc.*, 1956, 173; T. J. Price and P. N. Trott, U.S.P. 1956, 273,298.

<sup>2</sup> B. Haley, R. N. Haszeldine, B. Hewitson, and A. E. Tipping, *J.C.S. Perkin I*, 1976, 525 and references therein.

<sup>3</sup> P. Moreau, G. Dalverny, and A. Commeyras, *J. Fluorine Chem.*, 1975, 5, 265.

<sup>4</sup> H. Blancou, P. Moreau, and A. Commeyras, to be published.

<sup>5</sup> W. T. Miller Jr., E. Bergmann, and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, 79, 4159.