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PRELIMINARY NOTE

ULTRASOUND-PROMOTED DIRECT CARBOXYLATION OF PERFLUOROALKYL IODIDES

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SUMMARY

Perfluoroalkyl iodides were directly carboxylated with Zn and CO_2 under ultrasonic irradiation affording the corresponding perfluoroalkanoic acids.

INTRODUCTION

Among the various methods available for the preparation of long chain perfluoroalkanoic acids, the direct carboxylation of perfluoroalkyl iodides with carbon dioxide seems to be the most attractive. Commeyras et al. have reported this reaction, in which perfluoroalkyl iodides were metallized with a zinc-copper couple and were then treated with carbon dioxide [1].

In our continuous study of ultrasound-promoted reactions [2], we have found that ultrasound is also extremely effective in promoting the carboxylation of perfluoroalkyl iodides via a zinc complex.

EXPERIMENTAL

In small scale reactions ($R_fI \sim 10$ mmol), the reaction vessel was placed in the water bath of a laboratory ultrasonic cleaner (100 W, 45 KHz). Typically a mixture of R_fI (10 mmol), zinc powder (0.02 g-atom) and a

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[+] On leave from Toyo Soda Mfg. Co.

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solvent (20 ml) was placed in a flask (50 ml) and CO_2 gas was bubbled in until saturation was achieved. Ultrasonic irradiation was applied for 1 h with the continued bubbling of CO_2, and the reaction mixture was after-treated as will be mentioned below.

Commercially available zinc powder could be used without any activation, and the solvent, dried over molecular sieve (4A), was used without further purification. The choice of solvent used is very important and we have found that dimethylformamide is the most suitable for this purpose.

The results are shown in Table 1.

TABLE 1

Carboxylation of R_fI (R_fI 10 mmol scale)

R_f	R_fCO_2	
	BP [MP] $^oC/mm^{a)}$	Yield %
n-C_8F_{17}	[69-71] ([71])	72
n-C_6F_{13}	105/40 (105/50)	77
n-C_4F_9	70/40 (70/40)	61
i-C_3F_7	65/47	48

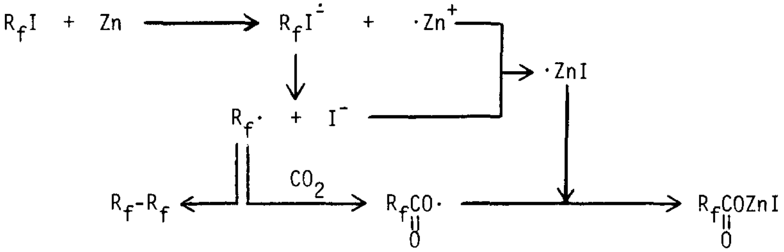
a) The values in parentheses give those in lit. 1.

In large scale reactions ($R_fI \sim 0.1$ mol), a more powerful ultrasonic cleaner was used. For example, a mixture of $C_8F_{15}I$ (54.6 g), zinc powder (13 g) and dimethyl formamide (200 ml) were placed in a flask supported in the bath of an ultrasonic cleaner (500 W, 40-90 KHz) which is normally used for the cleaning of electronics instruments. Carbon dioxide was introduced through a $CaCl_2$ dry tube until the mixture was saturated with tha gas. Ultrasonic irradiation was applied with the continuous bubbling of CO_2, the temperature rising to 50-60 ^oC. After 2 h of irradiation dilute hydrochloric acid was added to dissolve the excess Zn and to free the carboxylic acid. The perfluorononanoic acid was extracted with ether and after evaporation of the solvent the residue was dissolved in a dilute aqueous alkali. Acidification of the solution gave the crude perfluorononanoic acid (81%), which was recrystallized from CCl_4, yielding a pure product (33.4 g, 72%), mp 69-71 ^oC.

RESULTS AND DISCUSSION

When dimethyl sulfoxide was used as the solvent, the yield of the carboxylic acid reduced to 57%. Other aprotic solvents such as tetrahydrofuran or acetonitrile afforded no carboxylic acids but gave the homocoupled product, $C_{16}F_{34}$, mp 129 ^oC, in 36 and 24% yield respectively. This is presumably caused by the low solubilities of CO_2 in these solvents.

The reaction mechanism may be written as shown below.



Thus a single electron was transfered from Zn to R_fI giving a radical anion $R_fI^{\dot{-}}$, which should collapse instantly providing the $R_f\cdot$ radical. When CO_2 is present close to the perfluoroalkyl radical, the latter may be trapped by the former affording the perfluoroalkanecarboxylate radical, $R_f\underset{\overset{\|}{O}}{C}O\cdot$, while in the absense of nearby CO_2, the homocoupling of the latter is likely to occur.

The cavitation in the solvent caused by the ultrasound should give a site for the reaction by collecting the reactants, i.e., R_fI, Zn and CO_2. The high pressure and temperature caused by the subsequent decavitation should enable the reaction to proceed.

Further investigation is underway.

REFERENCES

1 H. Blancou, P. Moreau and A. Commeyras, J. Chem. Soc. Chem. Commun., 1976, 885.

2 T. Kitazume and N. Ishikawa, Chem. Lett., 1981, 1679; 1982, 137, 1453.