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ULTRASOUND-PROMOTED HYDROPERFLUOROALKYLATION OF ALKYNES WITH PERFLUOROALKYLZINC IODIDE AND COPPER(I) IODIDE

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The reaction of perfluoroalkyl iodides with terminal alkynes and ultrasonically dispersed zinc in the presence of copper(I) iodide proceeded smoothly to give the corresponding vinyl perfluoroalkylides in good yields.

Although the utility of organometallic reagents has been generally recognized to be useful in organic synthesis,$^{1)}$ very little synthetic applications of perfluoroalkylmetallic reagents have been studied, due to their low reactivity and stability.$^{2)}$ Therefore, in the field of fluorine chemistry, it is sometimes required to use a new type of technical method to introduce perfluoroalkyl groups on organic molecules. Ultrasound provides a key solution of this problem$^{3)}$ and our recent communications$^{4,5)}$ indicated its considerable potentiality in the synthesis of perfluoroalkylzinc iodides.

In our continuing studies on the synthetic applications of perfluoroalkylmetal compounds with ultrasound, it has become possible to hydroperfluoroalkylate carbon-carbon triple bonds with perfluoroalkylzinc iodide in the presence of copper(I) iodide under ultrasonic irradiation.

$$R_fI + Zn \xrightarrow[\text{THF}]{\text{u.s.}} [R_fZnI] \xrightarrow[\text{THF}]{\text{CuI/u.s.}} [(R_f)_2CuZnI] \xrightarrow{\text{CH}\equiv\text{CR}} \xrightarrow{H^+} R_fCH{=}CHR$$

Although the light- or thermo-induced free radical addition of perfluoroalkyl iodides to alkynes has been reported by several groups,$^{6-12)}$ none of hydroperfluoroalkylation of alkynes has been reported. Ultrasound-promoted hydroperfluoroalkylation of alkynes with perfluoroalkylcuprates, which was formed in situ from perfluoroalkyl iodides and zinc in the presence of copper(I) iodide in tetrahydrofuran, smoothly proceeded as shown in Table 1. Various copper compounds, such as CuI, CuCl, $CuCl_2$, CuBr, and CuF_2, were examined as a copper metal source in this system. As a result, copper(I) iodide was found to be the most effective for this purpose. In this system, copper metal produced from the reduction of copper(I) iodide with ultrasonically dispersed zinc powder seemed to enhance the perfluoroalkylation. The reaction did not proceed at all without the aid of ultrasonic irradiation.

Typical procedures for the present reactions are as follows. A flask containing commercially available zinc powder (1.30 g, 0.02 g-atom), copper (I) iodide (0.72 g), trifluoromethyl iodide (2.15 g, 11 mmol), phenylacetylene (1.02 g, 10 mmol) and tetrahydrofuran (30 ml) was irradiated for 2 h in a water bath of ultrasound laboratory cleaner (35 W, 35 KHz). Then, the mixture was poured into a 2% HCl solution and an oily material was extracted with diethyl ether. After drying over magnesium sulfate, the solvent was removed. Distillation gave β-trifluoromethylstyrene in a yield of 65% (1.11 g), bp 71 - 73 °C/25 mmHg.

Table 1 Perfluoroalkylation of alkynes

R_f	Substrate	Product[a]	Yield (%)	Bp (°C/mmHg)[b]	E/Z ratio[c]
CF_3	$CH\equiv CPh$	$CF_3CH{=}CHPh$[d]	65	71-73/25 (64/18)	28/72
CF_3	$CH\equiv CBu$	$CF_3CH{=}CHBu$[e]	71	78-81/56	24/76
CF_3	$CH\equiv CCH_2OH$	$CF_3CH{=}CHCH_2OH$[f]	61	126-129 (128)	32/68
i-C_3F_7	$CH\equiv CPh$	i-$C_3F_7CH{=}CHPh$[e]	52	75-78/12	31/69
i-C_3F_7	$CH\equiv CCH_2OH$	i-$C_3F_7CH{=}CHCH_2OH$[e]	65	54-55/34	33/67
n-C_3F_7	$CH\equiv CCH_2OH$	n-$C_3F_7CH{=}CHCH_2OH$[e]	66	65-67/58	30/70
n-C_4F_9	$CH\equiv CCH_2OH$	n-$C_4F_9CH{=}CHCH_2OH$[e]	74	59-62/32	27/73
n-C_6F_{13}	$CH\equiv CCH_2OH$	n-$C_6F_{13}CH{=}CHCH_2OH$[e]	55	71-73/29	25/75

a. Structures were determined by means of IR, NMR and Mass spectral data. *b*. 1 mmHg = 133.3 Pa. *c*. Stereochemistry was determined from the relative intensities of ^{19}F nmr signals. *d*. T. Fuchikami, M. Yatabe and I. Ojima, *Synthesis*, 1981, 365. *e*. New compounds : The microanalysis was in satisfactory agreement with the calculated value (C, H, N : ± o.4). *f*. E. T. McBee, O. R. Pierce and D. D. Smith, *J. Am. Chem. Soc.*, 76, 3725 (1954).

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