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Copper salt-catalysed reaction of perfluoroalkyl halides with olefins

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Perfluoroalkyl halides react with olefins in the presence of copper acetate and hydrazine to give 1,2-addition products.

The adducts of perfluoroalkyl halides and unsaturated compounds have considerable commercial importance.[1] They have been used in the synthesis of fluorinated alcohols,[2] unsaturated compounds,[3] sulfonates, thiols *etc*.[4]

Free radical chain additions of perfluoroalkyl iodides to unsaturated compounds have been widely applied in the synthesis of perfluoroalkyl-substituted compounds.[1] Initiation of such reactions can be induced by UV radiation or heating above 200 °C.[5,6] Initiation has also been carried out using peroxides,[7] azonitriles,[7(*g*),8] or redox systems.[9] The addition mechanism has been described by Harash *et al.*[10] However, initiation by UV radiation or heating generally leads to low yields of products,[5,6] whereas the use of azo initiators can give rise to highly toxic decomposition products.[11] The use of peroxides can result in uncontrolled process with rapid decomposition of materials.[7(*b*)]

Thus, a more satisfactory redox initiating system involving the use of copper acetate/hydrazine hydrate was developed previously.[12] This system initiates the free radical chain addition of perfluoroalkyl iodides to unsaturated compounds under mild conditions (at 20–30 °C) with good yields of adducts.

Here, we present the application of this initiator to the synthesis of a large number of perfluoroalkylated compounds. As shown in Scheme 1,[†] the reaction of perfluoroalkyl halides **1a**–**g** with ethylene was carried out in an autoclave at 30 °C; addition products **2a**–**g** were formed in 40–80% yields.

$$\underset{\mathbf{1a\text{–}g}}{R_fX} + CH_2{=}CH_2 \longrightarrow \underset{\mathbf{2a\text{–}g}}{R_fCH_2CH_2X}$$

a $R_f = C_2F_5$, X = I
b $R_f = C_3F_7$, X = I
c $R_f = BrCF_2CF_2$, X = Br
d $R_f = BrCF_2CFCl$, X = Br
e $R_f = BrCF_2$, X = Br
f $R_f = CF_3CF_2CF(CF_3)$, X = I
g $R_f = CF_3(CF_2)_7$, X = I

Scheme 1 Reaction of perfluoroalkyl halides with ethylene.

$$R_fX + CH_2{=}CHY \longrightarrow R_fCH_2CHXY$$

1d,**h**,**i** **3a**–**c** **4a**–**e**

1d $R_f = BrCF_2CFCl$, X = Br **3a** Y = Bu
1h $R_f = ClCF_2CFCl$, X = Br **3b** $Y = Me(CH_2)_5$
1i $R_f = BrCF_2CF_2$, X = I **3c** $Y = CH_2OH$

4a $R_f = BrCF_2CFCl$, X = Br, Y = Bu
4b $R_f = BrCF_2CFCl$, X = Br, $Y = Me(CH_2)_5$
4c $R_f = BrCF_2CFCl$, X = Br, $Y = CH_2OH$
4d $R_f = ClCF_2CFCl$, X = Br, $Y = CH_2OH$
4e $R_f = BrCF_2CF_2$, X = I, $Y = CH_2OH$

Scheme 2 Reactions of perfluoroalkyl halides with olefins.

Reactions of perfluoroalkyl halides **1d**,**h**,**i** with hex-1-ene, oct-1-ene, and allyl alcohol were carried out at atmospheric pressure (Scheme 2);[‡] adducts **4** were obtained in good yields. All products were characterised by ^{1}H and ^{19}F NMR spectroscopy, and the purity was confirmed by GLC analysis.

Thus, a simple and highly effective procedure was developed for the reaction of perfluoroalkyl halides and olefins to form perfluoroalkyl-substituted haloalkanes.

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[†] *General procedure for the preparation of products* **2a**–**g**. A stirred steel autoclave with a needle valve was charged with isopropanol, perfluoroalkyl halides **1a**–**g**, copper acetate hydrate and hydrazine hydrate, and the autoclave was closed. After cooling with liquid nitrogen, the autoclave was charged with ethylene to an appropriate pressure, and the reaction mixture was stirred for 4–6 h at 30 °C. Residual gas from the autoclave was trapped into a trap cooled to –70 °C, and the liquid products were poured into an equal volume of cold aqueous 5% HCl. The lower layer was isolated, washed with water, dried with $MgSO_4$ and distilled. The products, reaction conditions (quantity of perfluoroalkyl halides, copper acetate, hydrazine hydrate; volume of isopropanol, ethylene pressure, autoclave volume and reaction time); yield of the product, conversion and bp of the products are given below.

2a: (4.47 mol, 0.63 mol, 4.48 mol, 600 ml, 30 atm, 2 dm^3, 4 h), 69%, 100%, 100 °C.

2b: (0.51 mol, 0.07 mol, 0.51 mol, 75 ml, 15 atm, 0.5 dm^3, 6 h), 70%, 60%, 118 °C.

2c: (1.15 mol, 0.16 mol, 1.16 mol, 25 atm, 1 dm^3, 6 h), 70%, 50%, 145 °C.

2d: (2.9 mol, 0.41 mol, 2.9 mol, 400 ml, 30 atm, 2 dm^3, 4 h), 39%, 100%, 163–165 °C.

2e: (1.43 mol, 0.19 mol, 1.44 mol, 150 ml, 30 atm, 1 dm^3, 6 h), 70%, 40%, 122–123 °C.

2f: (0.43 mol, 0.06 mol, 0.44 mol, 35 atm, 0.5 dm^3, 6 h), 81%, 100%, 130 °C.

2g: (2.2 mol, 0.33 mol, 2.2 mol, 35 atm, 2 dm^3, 6 h), 80%, 100%, 97 °C (14 Torr).

[‡] *General procedure for the preparation of* **4a**–**e**. A flask equipped with a stirrer, a thermometer, a dropping funnel and a reflux condenser was charged with isopropanol and a perfluoroalkyl halide (**1d**,**h**,**i**). Olefin (**3a**–**c**) and copper acetate monohydrate were added and hydrazine was carefully added with heat evolved. Then the mixture was stirred for 3–8 h at 20 °C and kept overnight. The reaction mixture was then poured into aqueous HCl; the lower layer was isolated, washed with water, dried with $MgSO_4$ and distilled. The products, reaction conditions (flask volume, volume of isopropanol, quantity of perfluoroalkyl halide, olefins, copper acetate monohydrate and hydrazine hydrate), yield of the product, conversion and bp are given below.

4a: (4 dm^3, 1.5 dm^3, 5.43 mol, 5 mol, 0.8 mol, 5.39 mol), 82%, 100%, 130–132 °C (20 Torr).

4b: (4 dm^3, 675 ml, 2.44 mol, 2.23 mol, 0.38 mol, 2.65 mol), 75%, 100%, 125–130 °C (12 Torr).

4c: (2 dm^3, 1.45 mole, 1.52 mol, 0.18 mol, 1.46 mol), 73%, 53%, 135–138 °C (17 Torr).

4d: (2 dm^3, 800 ml, 2.41 mol, 3.01 mol, 0.37 mol, 2.88 mol), 69%, 100%, 132–135 °C (12 Torr).

4e: (2 dm^3, 700 ml, 2.2 mol, 2.9 mol, 0.3 mol, 2.3 mol), 68%, 100%, 123 °C (18 Torr).