Journal of Fluorine Chemistry, *31* (1986) 237–240

Received: November 29, 1985; accepted: January 7, 1986

PRELIMINARY NOTE

Reaction of Hexafluoroisobutene with Hydrogen Peroxide/Ferrous Sulfate/Methanol

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SUMMARY

Hexafluoroisobutene was reacted in methanol with cyclohexanone peroxide (formed *in situ* from cyclohexanone and hydrogen peroxide) in the presence of ferrous ion to give the methyl ester of 8-trifluoromethyl-9,9,9-trifluorononanoic acid in fairly good yield.

Hexafluoroisobutene is a useful monomer for the synthesis of fluoropolymers [1].
We have already reported a synthetic route [2] and some reactions of intermediates which were obtained during the process of making the monomer[3].

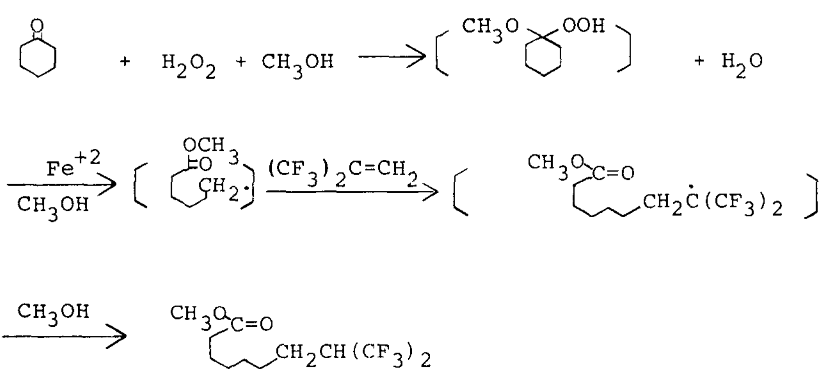
0022-1139/86/$3.50

In order to find further applications of the monomer, we reacted it in methanol with cyclohexanone peroxide in the presence of ferrous ion. The product methyl 8-trifluoromethyl-9,9,9-trifluorononanoate was obtained for the first time in fairly good yield.

The reaction of cyclohexanone peroxide (formed in situ from cyclohexanone and hydrogen peroxide) with ferrous ion in the presence of butadiene to give dimethyl 8,12-eicosadiene-1, 20-dioate has been reported [4].

Some fluoromonomers such as $CF_3CF{=}CF_2$ and $CF_2{=}CFCl$ were found to react with cyclohexanone peroxide in the same manner, the major products being methyl esters of monobasic acids [5].

The reaction between hexafluoroisobutene, cyclohexanone, hydrogen peroxide, methanol and ferrous ion proceeded smoothly and gave methyl 8-trifluoromethyl-9,9,9-trifluorononanoate as a main product.
Small amounts of a mixture of $H[C(CF_3)_2CH_2]_n(CH_2)_5COOCH_3$, (n=2,3), $(CF_3)_2C{=}CH[C(CF_3)_2CH_2]_n(CH_2)_5COOCH_3$, (n=1,2,3) and $CH_3OOC(CH_2)_5{-}[C(CF_3)_2CH_2]_n{-}(CH_2)_5COOCH_3$, (n=1,2) were detected by MS spectra as the by-products.
From the fact that $CH_3(CH_2)_4COOCH_3$ and $CH_3OOC(CH_2)_{10}COOCH_3$ were detected by MS spectra and VPC, the main reaction proceeded as suggested previously by M. S. Kharasch *et al.* [4].



Methyl 8-trifluoromethyl-9,9,9-trifluorononanoate

To a solution of 3.0 g of conc. H_2SO_4 in 600 ml of methanol was added 120 g (1.22 mole) of cyclohexanone, at 0-5 °C. 120 g of 35 % hydrogen peroxide was added to the mixture at this temperature and stirred for sixty minutes. The cyclohexanone peroxide solution thus prepared was added dropwise with stirring at -10 °C over a period of two hours to a mixture of 340 g (1.83 mole) of ferrous sulfate heptahydrate, 600 ml of methanol, and 300 g (1.83 mole) of hexafluoroisobutene. After completion of the addition, stirring was continued for another two hours and the mixture was warmed up to room temperature. Methanol was distilled off and the upper organic layer was washed with acid, water and dried over magnesium sulfate. The crude product, a light yellow oil (410 g) was fractionally distilled to give $(CF_3)_2CH(CH_2)_6COOCH_3$, BP. 102 °C/15 mm Hg, 96.3 g (26.8 %, yield based on cyclohexanone).

MS, m/e = 294 (M^+), 264 (M^+-OCH_3), 74 ($CH_2\overset{OH^+}{\overset{\|}{C}}OCH_3$), 69 ($CF_3$), 59 ($COOCH_3$), 50 ($CF_2$), ^1H NMR ($CDCl_3$) δ 1.2-2.0 ppm (10H, m, CH_2), 2.30 (2H, t, J = 7.3 Hz, CH_3CO), 2.86 (1H, α-sep, J = 6.0, 8.4 Hz, CH), 3.65(3H, s, OCH_3), ^{19}F NMR ($CDCl_3$, ext TFA) δ 100.2 ppm (6F, d, J = 8.9 Hz, CF_2).

To extend the procedure to other fluoroolefins, we attempted the reaction by the previously described procedure with $C_8F_{17}CH=CH_2$ but the yield of the expected ester $C_8F_{17}CH_2(CH_2)_6COOCH_3$ [MS, m/e = 576 (M^+), 545 (M^+-OCH_3), 74 (CH_2-$\underset{OH^+}{\underset{\|}{C}}OCH_3$)] was low.

We would like to express our appreciation to the members of the Research Department and the Technical Department for their help. We would also like to thank Professor N. Sonoda (Osaka University) for his advice.

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