Journal of Fluorine Chemistry 131 (2010) 17–20

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis of perfluoro-*t*-butyl trifluorovinyl ether and its copolymerization with TFE

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ARTICLE INFO

Article history:
Received 15 July 2009
Received in revised form 14 September 2009
Accepted 18 September 2009
Available online 28 September 2009

Keywords:
Hypofluorite
Trifluorovinyl ether
Fluoromonomer
Synthesis
Copolymerization

ABSTRACT

Perfluoro-*t*-butyl trifluorovinyl ether $(CF_3)_3COCF{=}CF_2$ was prepared by the addition of perfluoro-*t*-butyl hypofluorite $(CF_3)_3COF$ to 1,2-dichloro-1,2-difluoroethylene followed by dechlorination. The obtained trifluorovinyl ether monomer readily copolymerizes with TFE in the presence of a radical initiator.

1. Introduction

Fluorinated vinyl ethers were initially obtained by the addition of alcohols to fluoroolefins, followed by the elimination of hydrogen fluoride under alkali conditions [1–6]. Later on, fluorinated vinyl ethers were directly synthesized by the reaction of alcohol-free sodium alcoholates with fluoroolefins [7]. When tetrafluoroethylene (TFE) was used as the fluoroolefin, the resulting products were trifluorovinyl ethers $ROCF{=}CF_2$ [8,9]. R could be a variety of alkyl groups, such as methyl, ethyl (including trifluoroethyl), isopropyl, *tert*-butyl, etc. The apparent reactivity of the alcoholates toward tetrafluoroethylene increased in the following order: methyl, ethyl < isopropyl, *tert*-butyl [9]. However, *tert*-butyl trifluorovinyl ether was very unstable and decomposed, upon standing, to the acyl fluoride and isobutene.

It has been established that completely fluorinated primary alcohols are inherently unstable and cannot be isolated [10]. Hence, it is apparent that the above techniques for the preparation of trifluorovinyl ethers are not suitable for the preparation of perfluorinated vinyl ethers and vinyl ethers wherein the ether oxygen is attached to a CF_2 group. Therefore, different synthetic routes were developed to produce perfluorinated vinyl ethers. For example, perfluorinated vinyl ethers were made by the reaction of the corresponding acyl fluorides with hexafluoropropylene epoxide (HFPO), followed by pyrolysis of the extended acyl fluoride products over sodium carbonate [11,12]. Another process to produce perfluorinated vinyl ethers involves the addition of hypofluorites R_fOF to halogenated olefin $FClC{=}CClF$ followed by dechlorination [13–15]. The versatility of perfluorinated vinyl ethers prepared by the latter process depends on the hypofluorites R_fOF. A variety of fluoroxy compounds including perfluoro-*tert*-butyl hypofluorite have been synthesized [16–22] since trifluoromethyl hypofluorite CF_3OF was first prepared in 1948 [23].

Perfluoroalkyl trifluorovinyl ethers [24–26] and perfluoroalkoxyalkyl trifluorovinyl ethers [27–34] have been synthesized and used as monomers in a variety of copolymerizations with TFE and/or VDF (vinylidene fluoride). To increase the amorphism of fluoropolymers, the bulk of side chain of trifluorovinyl ether is important. To improve the optical properties and thermal stability of fluoropolymers, high fluorine content of side chains is desired. Among all perfluoroalkyl trifluorovinyl ethers, perfluoro-*t*-butyl trifluorovinyl ether has not been explored. The synthesis of perfluoro-*t*-butyl trifluorovinyl ether monomer has not been reported, though its hydrocarbon counterpart, *t*-butyl trifluorovinyl ether, was reported a long time ago [9]. Herein, we describe the synthesis of perfluoro-*t*-butyl trifluorovinyl ether and its copolymerization with TFE.

2. Results and discussion

Perfluoro-*t*-butyl trifluorovinyl ether could be synthesized either by reacting perfluoro-*t*-butoxide with TFE or by adding perfluoro-*t*-butyl hypofluorite to 1,2-dichloro-1,2-difluoroethylene followed by dechlorination. Considering the weak nucleo-

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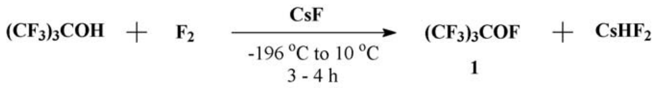
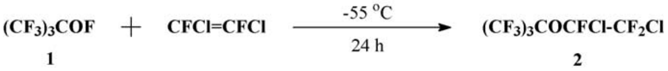
doi:10.1016/j.jfluchem.2009.09.012



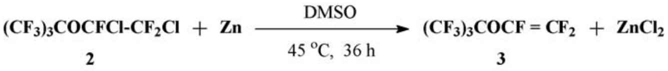
$$(CF_3)_3COH + F_2 \xrightarrow[\substack{\text{-196 °C to 10 °C} \\ \text{3 - 4 h}}]{CsF} \underset{1}{(CF_3)_3COF} + CsHF_2$$

Scheme 1. Fluorination of perfluoro-*t*-butyl alcohol.



$$\underset{1}{(CF_3)_3COF} + CFCl{=}CFCl \xrightarrow[\text{24 h}]{\text{-55 °C}} \underset{2}{(CF_3)_3COCFCl\text{-}CF_2Cl}$$

Scheme 2. Addition of perfluoro-*t*-butyl hypofluorite to 1,2-dichloro-1,2-difluoroethylene.



$$\underset{2}{(CF_3)_3COCFCl\text{-}CF_2Cl} + Zn \xrightarrow[\text{45 °C, 36 h}]{\text{DMSO}} \underset{3}{(CF_3)_3COCF = CF_2} + ZnCl_2$$

Scheme 3. Dechlorination of addition intermediate by zinc.

philicity and bulkiness of perfluoro-*t*-butoxide, the hypofluorite method was used in this research.

Perfluoro-*t*-butyl hypofluorite (**1**) was obtained by the direct fluorination of the corresponding alcohol in the presence of CsF, as shown in Scheme 1. The reaction condition used here is slightly different from that of literature where a large excess of fluorine (32 equiv.) was used without CsF as a catalyst [16].

The obtained perfluoro-*t*-butyl hypofluorite (**1**) can be handled in a glass vacuum line under low pressure (less than 200 Torr) over a short period of time without decomposition and explosion.

Hypofluorite (**1**) was combined with 1,2-dichloro-1,2-difluoroethylene to give addition intermediate (**2**), as shown in Scheme 2.

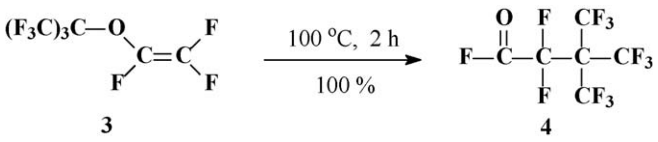
The intermediate (**2**) was dechlorinated by zinc in DMSO to provide the desired perfluoro-*t*-butyl trifluorovinyl ether monomer (**3**), as shown in Scheme 3.

When dechlorination was carried out at higher temperatures (>70 °C), the reaction mixture became viscous and the yield of the desired trifluorovinyl ether monomer decreased. This could be due to the reaction between the rearrangement intermediate of the trifluorovinyl ether product (see below) and the solvent DMSO.

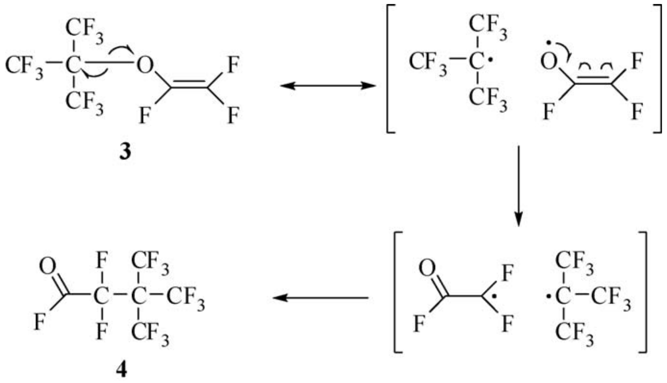
The instability of secondary and tertiary perfluorinated vinyl ethers was known and used to purify the corresponding primary isomers by selective pyrolysis [35]. The perfluoro-*t*-butyl trifluorovinyl ether (**3**) could be unstable at elevated temperatures. Therefore, compound (**3**) was tested for thermal stability, as shown in Scheme 4.

The trifluorovinyl ether (**3**) was converted into acyl fluoride (**4**) quantitatively upon heating at 100 °C for 2 h. This indicated an intramolecular rearrangement process for the conversion shown in Scheme 5.

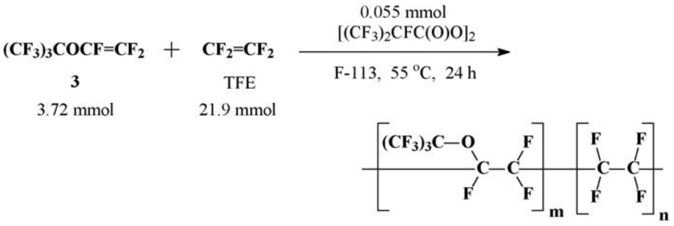
In the selective pyrolysis of secondary and tertiary perfluorinated vinyl ethers, it was believed that the perfluoro(isopropyl vinyl) ether rearranged to perfluoro-3-methylbutyryl fluoride at high temperatures (250–350 °C) [35]. A similar process was proposed for the thermal rearrangement of pentafluorosulfanyl trifluorovinyl ether to difluoro(pentafluorosulfanyl)acetyl fluoride, which was supported by EPR measurements [36]. These processes appear to occur by similar mechanisms.



Scheme 4. Thermal rearrangement of trifluorovinyl ether to acyl fluoride.



Scheme 5. Radical mechanism for the rearrangement of compound (**3**).



Scheme 6. Copolymerization between perfluoro-*t*-butyl trifluorovinyl ether (**3**) and TFE.

Perfluoro-*t*-butyl trifluorovinyl ether $(CF_3)_3COCF{=}CF_2$ does not homopolymerize in the presence of a radical initiator $[(CF_3)_2CFC(O)O]_2$ which was synthesized according to the literature [37,38]. This lack of homopolymerization character is also implied in the proposed thermal rearrangement process in Scheme 5. The radical intermediates initially generated by homolytic cleavage of trifluorovinyl ether (**3**) combined to give acyl fluoride (**4**) quantitatively instead of initiating the homopolymerization of trifluorovinyl ether (**3**). However, trifluorovinyl ether (**3**) readily copolymerizes with TFE in the presence of the radical initiator $[(CF_3)_2CFC(O)O]_2$, as shown in Scheme 6.

After the solvent F-113 (1,1,2-trifluorotrichloroethane) was evaporated and the residue was heated at 100 °C under vacuum overnight, the copolymer between perfluoro-*t*-butyl trifluorovinyl ether (**3**) and TFE was obtained as a white powder which was insoluble in the following solvents: F113, $CHCl_3$, $(CH_3)_2C{=}O$, CH_3OH, C_2H_5OH, DMF, and DMSO. The assumption that the copolymer would be very amorphous was not supported by the observed lack of solubility. No further efforts were made to optimize the copolymerization conditions. The primary goal of this study was to demonstrate the ability of $(CF_3)_3COCF{=}CF_2$ (**3**) to undergo copolymerization with TFE.

TGA of the copolymer between perfluoro-*t*-butyl trifluorovinyl ether (**3**) and TFE is shown in Fig. 1. The decomposition temperature of the copolymer synthesized under the above condition was lower than that of Teflon® (525 °C) [39] and Teflon® PFA (ca. 480 °C) [40], which provided good evidence for the copolymerization.

DSC of the copolymer between perfluoro-*t*-butyl trifluorovinyl ether (**3**) and TFE is shown in Fig. 2. There were two exotherm processes with small one at 215 °C and large one at 293 °C, which could be attributed to the decomposition process of the side chain of perfluoro-*t*-butyl trifluorovinyl ether units in the copolymer. The melting (308 °C) and recrystallization (274 °C) processes of the TFE blocks in the copolymer occurred at lower temperatures than that of PTFE (327 and 313 °C, respectively [41]).

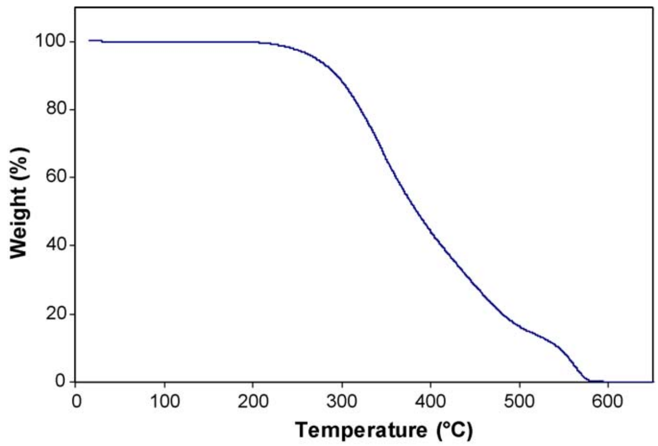


Fig. 1. TGA (N_2, 10 °C/min) of copolymer between perfluoro-*t*-butyl trifluorovinyl ether (**3**) and TFE.

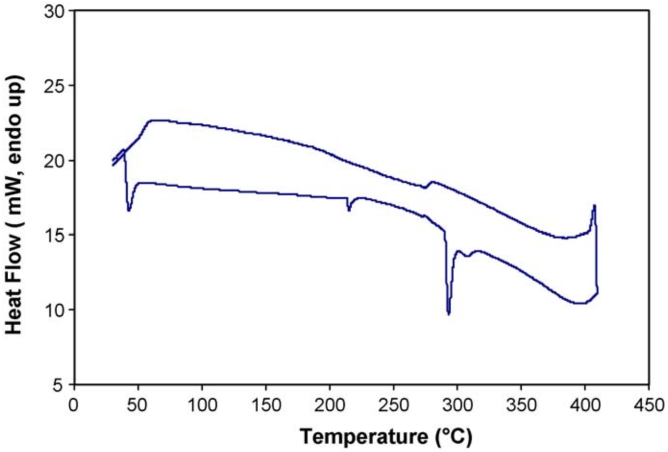


Fig. 2. DSC (10 °C/min) of copolymer between perfluoro-*t*-butyl trifluorovinyl ether (**3**) and TFE (heating–cooling process proceeded counterclockwise).

In summary, perfluoro-*t*-butyl trifluorovinyl ether has been synthesized by the addition of perfluoro-*t*-butyl hypofluorite to 1,2-dichloro-1,2-difluoroethylene followed by dechlorination with zinc in DMSO. At elevated temperatures, perfluoro-*t*-butyl trifluorovinyl ether is converted into acyl fluoride $FC(O)CF_2C(CF_3)_3$, possibly through an intramolecular rearrangement process.

Perfluoro-*t*-butyl trifluorovinyl ether does not homopolymerize. However, it readily copolymerizes with TFE in the presence of a radical initiator.

3. Experimental procedures

3.1. Instruments

^{19}F NMR spectra were obtained on a JEOL ECX 300 NMR at 282.78 MHz. $CFCl_3$ was used as the reference. Infrared spectra were recorded on a PerkinElmer 2000 FTIR. IR for a single compound was measured in gas phase at 5 Torr in a 10 cm glass cell with AgCl windows. IR for polymer was measured in a mixture with KBr.

3.2. Preparation of perfluoro-t-butyl hypofluorite $(CF_3)_3COF$ (1)

Dry CsF (25 g, which can be used three times) was added into a 150 mL Monel reactor inside a dry box under nitrogen protection. The nitrogen inside the reactor was then pumped off slowly through a vacuum line. Perfluoro-*t*-butanol $(CF_3)_3COH$ (0.989 g, 4.19 mmol) was transferred through the vacuum line into the reactor cooled with liq. N_2. The reactor was allowed to warm up with tap water. Fluorine (F_2, 8.00 mmol) was transferred into the metal reactor with liq. N_2 cooling. After removing liq. N_2, the metal reactor was left in the cold Dewar for 3–4 h. The temperature of the metal reactor rose to ca. 10 °C.

The metal reactor was cooled with liq. N_2 and the excess F_2 was removed by passing through soda lime column. The metal reactor was allowed to warm up slowly. By trap-to-trap distillation at −55 °C, −110 °C and −196 °C, the desired product $(CF_3)_3COF$ (**1**) was obtained in −110 °C trap (1.06 g, 4.19 mol, 100%) (*caution*: this reaction can be explosive, and a small scale reaction and careful control of the temperature are important). ^{19}F NMR (282.78 MHz, CCl_4): δ (ppm) 149.3 (tenfold, $^4J = 16.4$ Hz, 1F), −69.7 (d, $^4J = 16.4$ Hz, 9F). IR (gas phase, 5 Torr): ν (cm^{-1}) 1291(s), 1108(m), 1014(m), 984(m), 887(w, ν_{O-F}), 741(m), 735(m), 730(m), 539(w).

3.3. Addition of hypofluorite $(CF_3)_3COF$ (1) to halogenated olefin CFCl=CFCl

$(CF_3)_3COF$ (**1**) (1.04 g, 4.10 mmol) was transferred into a 150 mL Monel reactor with liq. N_2 cooling. CFCl=CFCl (0.520 g, 3.91 mmol) was then condensed through vacuum line into the reactor. The reactor was kept at −55 °C for 24 h. Trap-to-trap distillation at −45 °C, −100 °C and −196 °C was then carried out. In −45 °C trap, the desired addition product $(CF_3)_3COCFCl–CF_2Cl$ (**2**) was obtained (1.38 g, 3.56 mmol, 91.0%). ^{19}F NMR (282.78 MHz, $CDCl_3$): δ (ppm) −69.4 (d, $^5J = 9.76$ Hz, 9F), −70.4 (s(b), 2F), −76.3 (m, $^5J = 9.76$ Hz, 1F). IR (gas phase, 5 Torr): ν (cm^{-1}) 1281(s), 1230(w), 1186(s), 1153(s), 1077(m), 1017(s), 994(s), 978(s), 905(m), 837(m), 731(m), 541(w).

3.4. Dechlorination of $(CF_3)_3COCFCl–CF_2Cl$ by Zn in DMSO

In a dry box, Zn (1.50 g, 22.9 mmol) was added into a 250 mL of Ace thread reactor. Under N_2 protection, 30 mL of dry DMSO was injected into the reactor. The reactor was cooled with liq. N_2 and evacuated through a vacuum line. $(CF_3)_3COCFCl–CF_2Cl$ (**2**) (1.20 g, 3.10 mmol) was then transferred into the reactor. The reactor was allowed to warm up to room temperature slowly. The reaction mixture was then stirred and heated at 45 °C for 36 h.

A trap-to-trap distillation was conducted at −25 °C, −75 °C, −120 °C, and −196 °C. In −75 °C trap, the desired product $(CF_3)_3COCF{=}CF_2$ (**3**) (0.935 g, 2.96 mmol, 95.5%) was obtained as a colorless liquid. The b.p. of $(CF_3)_3COCF{=}CF_2$ was determined as 63–65 °C using a inverted bell capillary tube inserted into the liquid sample. During the cooling process, when the temperature decreased to the b.p. of the sample, the liquid sample started to rise into the inverted Bell capillary tube. ^{19}F NMR (282.78 MHz, $CDCl_3$): δ (ppm) −71.1 (s, 9F), −114.9 (dd, $^3J = 82.2$ Hz, $^3J = 65.7$ Hz, 1F), −120.1 (dd, $^2J = 110.1$ Hz, $^3J = 82.2$ Hz, 1F), −131.9 (dd, $^2J = 110.1$ Hz, $^3J = 65.7$ Hz, 1F). IR (gas phase, 5 Torr): ν (cm^{-1}) 1834(w, $\nu_{C=C}$), 1341(m), 1292(s), 1253(w), 1198(w), 1171(m), 1087(w), 1010(m), 984(m), 735(m), 541(w).

3.5. Thermal rearrangement of $(CF_3)_3COCF{=}CF_2$ (3) into $FC(O)CF_2C(CF_3)_3$ (4)

$(CF_3)_3COCF{=}CF_2$ (**3**) (0.158 g, 0.500 mmol) was sealed in a NMR tube under vacuum. The tube was heated at 100 °C for 2 h. ^{19}F NMR indicated the quantitative rearrangement of the starting vinyl ether into acyl fluoride $FC(O)CF_2C(CF_3)_3$ (**4**), a colorless liquid with m.p. 21 – 23 °C. ^{19}F NMR (282.78 MHz, $CDCl_3$): δ (ppm) 23.9 (m, 1F), −63.2 (td, ^4J = 9.87 Hz, ^5J = 6.56 Hz, 9F), −103.8 (m, 2F). IR (gas phase, 5 Torr): ν (cm^{-1}) 1886(s, $\nu_{C=O}$), 1294(s), 1203(s), 1074(w), 991(s), 910(m), 735(m), 670(m).

3.6. Copolymerization of $(CF_3)_3COCF{=}CF_2$ (**3**) with $CF_2{=}CF_2$ (TFE)

Into a 50 mL stainless steel reactor containing glass beads for stirring, 1,1,2-trifluorotrichloroethane F-113 (23 mL) and perfluorinated initiator $[(CF_3)_2CFC(O)O]_2$ (0.055 mmol in 0.27 mL of F-113, 0.21% in molar ratio of the total monomers) were added. The reactor was cooled at −196 °C and the air inside the reactor was evacuated. The reactor was warmed up to room temperature and then cooled at −196 °C. The evacuation of air inside the reactor was repeated. Two monomers, $(CF_3)_3COCF{=}CF_2$ (**3**) (1.18 g, 3.72 mmol) and $CF_2{=}CF_2$ (TFE) (2.19 g, 21.9 mmol), were introduced into the reactor through the vacuum line respectively. The reactor was then allowed to warm up to room temperature slowly, shaken and heated with a heating belt at 55 °C for 24 h.

The copolymerization mixture (a translucent viscous liquid) was poured into a flask, and the solvent was evaporated. The residue was heated at 100 °C under vacuum overnight to yield a white copolymer powder (2.60 g, 77.2%). IR (KBr mixture): ν (cm^{-1}) 1278(s), 1212(s), 1155(s), 990(m), 736(w), 639(m), 555(m), 508(s).

The copolymer was subjected to TGA and DSC characterization. TGA (N_2, 10 °C/min): −10% at 294 °C, −90% at 544 °C; DSC (10 °C/min): small exotherm at 215 °C, large exotherm at 293 °C. The copolymer was insoluble in F113 ($C_2F_3Cl_3$), $CHCl_3$, $(CH_3)_2C{=}O$, CH_3OH, C_2H_5OH, DMF, and DMSO from room temperature to the boiling points of the solvents, respectively.

Acknowledgements

We gratefully acknowledge the financial support of this research by Solvay Solexis and helpful discussions with Vito Tortelli.

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