Journal of Fluorine Chemistry 130 (2009) 830–835

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Synthesis of trifluoromethyl fluoroformate from trifluoromethyl hypofluorite and carbon monoxide: Thermal and catalyzed reaction

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ARTICLE INFO

Article history:
Received 4 May 2009
Received in revised form 30 June 2009
Accepted 6 July 2009
Available online 14 July 2009

Keywords:
Trifluoromethyl fluoroformate
Synthesis
Halogenated olefin
Radical chain reaction
Perfluoroalkyl hypofluorite
Carbon monoxide
Perfluorovinyl ether

ABSTRACT

New and improved routes to trifluoromethyl fluoroformate were developed. Sterically hindered halogenated olefins initiated the reaction of CF_3OF and CO under mild conditions, giving yields of up to 80%. The thermal reaction of CF_3OF and CO in a flow system was highly dependent on temperature and the type of tubular reactor material. A PTFE reactor gave moderate conversion and high selectivity for the formate at 120 °C.

1. Introduction

Trifluoromethyl fluoroformate, $CF_3OC(O)F$ **4**, was first reported by reaction of CF_3OF **1** and CO **2** photochemically or thermally [1], and then through a dimerization of COF_2 in presence of catalysts [2]. Its formation by other reactions as a minor or a side product was also reported later [3–9]. Another two homologs in this series, $CF_3CF_2OC(O)F$ and $(CF_3)_2CFOC(O)F$, were prepared in low yield through an oxidation of $CF_3CF{=}CFCF_3$ in presence of CF_3OF [10] and a reaction between $(CF_3)_2CFO^-Cs^+$ and COF_2 [11,12]. These fluoroformates along with others, as a general formula of $R_fOC(O)F$, were probably among the products of the preparation of some PFPE fluids through photochemical oxidation of hexafluoropropene and/or tetrafluoroethylene [3,4,13,14]. However, the products were mixtures of multiple homologs and the preparation of a single fluoroformate through these reactions was unlikely. The direct synthesis of the individual homolog in this series, $CF_3(CF_2)_nOC(O)F$ ($n \geq 2$), has not been demonstrated. Trifluoromethyl fluoroformate **4** is currently being used as the key intermediate to the vinyl ether, $CF_3OCF_2OCF{=}CF_2$, whose copolymers have been used to formulate a series of novel fluoroelastomers [15–20]. This vinyl ether, owing to the presence of the $-OCF_2O-$ group adjacent to the vinyl group, is very effective in lowering the glass transition temperatures of the corresponding polymers [20], essential for selected low temperature applications [21]. Higher homologs of this vinyl ether with general formula $CF_3O(CF_2O)_nCF_2OCF{=}CF_2$ ($n \geq 1$) are also of interest [22]. An efficient route to **4** is an enabler for the commercialization of these novel fluoroelastomers [23]. Recently, we have reported an alternative synthesis of **4** at 22 °C through a radical reaction between CF_3OF and CO initiated by elemental fluorine [24]. However, the single-cycle conversion in this reaction was low and further improvements would be strongly dependent on a sophisticated reaction system [24].

In this paper, we report a revised version of the thermal route to **4** [1] in a flow system together with a novel synthesis of **4** from the radical reaction between **1** and **2** initiated by some sterically hindered olefins (**3**), at low temperatures. Higher yields, up to over 80%, were obtained in proper experimental conditions with both routes.

The thermal reaction was revised trying to transform it from a kinetic case [24] to a useful synthetic method: the previous batch kinetic experiments became a flow reaction depending critically upon reactor materials and temperatures but giving high selectivity at reasonable conversion.

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doi:10.1016/j.jfluchem.2009.07.004

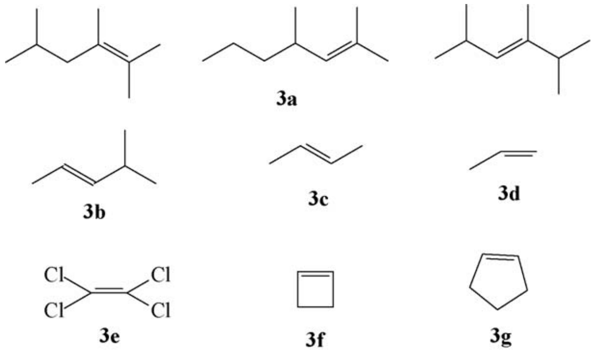


Fig. 1. Sterically hindered perhalogenated olefins used in the reaction.

Table 1
Reactions between **1** and **2** initiated by **3b**.

Run	**1** (mmol)	**2** (mmol)	**3b** (mmol)	Temp. (°C)	Time (d)	Yield (%)	Recovered **1** (mmol)
1	2.3	2.7	2.9	22	1	56.5	0
2	4.5	4.6	0.6	22	2	55.6	1.8
3	4.9	5.1	0.5	22	7	77.6	1.1
4	5.2	5.6	1.0	22	5	86.5	0.9
5	5.4	5.5	0.5	40	1	74.1	1.4
6	5.4	5.5	0.5	40	2	85.7	0.7
7	5.8	5.9	0.7	51	2	91.4	–

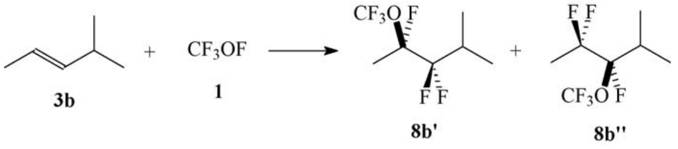
All the reactions were run in a 150 ml one-piece glass reactor.

2. Results and discussion

2.1. Synthesis of trifluoromethyl fluoroformate in presence of sterically hindered halogenated olefins

A mixture (**3a**) of three hexafluoropropene (HFP) trimers (see Fig. 1 for their structures) was attempted first. Another two HFP trimers, F-2,4-dimethyl-3-ethyl-2-pentene and F-3-isopropyl-4-methyl-2-pentene, have been used previously to make a persistent radical by reacting with undiluted elemental fluorine [26]. The resulting radical was stable to a number of strong oxidizers and only reacted with elemental fluorine slowly forming the corresponding perfluoroalkane. The mixture of the HFP trimers used in this study (**3a**), though not the same isomers, formed the same persistent radical after reacting with fluorine gas as confirmed by EPR spectrum (supplementary materials). We initially expected that **1**, having similar reactivity as elemental fluorine, would react with **3a** slowly to form the persistent alkyl radical and the resulting CF_3O radical **5**. Radical **5** is too bulky to react further with the alkyl radical so that **5** can probably initiate a radical chain reaction with CO to form **4**. However, the reaction did not proceed as we expected at room temperature. At higher temperature (47 °C), the reaction was completed with a 95.7% yield after 4 days. According to ^{19}F NMR, we did not see evidence of the formation of the persistent radical, so it appears to us that this reaction was only a thermal version between **1** and **2** [1].

The unsaturated bond of the HFP dimer (**3b**) is less sterically hindered than those of **3a** (see Fig. 1), therefore it was expected to be more accessible to the attack by **1**. The neat reaction of two HFP isomers (including **3b**) with **1** was reported to be sluggish at room temperature and elevated temperatures were necessary for the completion of the reaction [27]. The addition reaction between **1** and **3b** carried out in this study gave approximately 80% conversion at room temperature after 5 days, and then completed by reacting at 45 °C for 1 day. The regioselectivity of the reaction was excellent as reported [27]. However, the ratio between the two isomers (**8b**′/**8b**″) was 13/1 according to ^{19}F NMR spectra rather than the reported 24/1 at 45 °C. The stereochemistry of the reaction and the absolute chirality of the products were not determined (Scheme 1).



Scheme 1. Reaction between **3b** and **1**.

When **2** was added into the reaction, the desired fluoroformate **4** was generated at 22 °C with a 56.5% yield calculated based on the amount of **1** fed into the system (Run 1, Table 1). Apparently, the reaction was initiated by **3b** because neat thermal reaction between **1** and **2** could not occur at 22 °C (Ref. [1] reports a minimum reaction temperature of 90 °C but we had reaction at 82 °C. At 35 °C reaction was negligible). The reaction was completed within 1 day as confirmed by the disappearance of **1**. The adducts of **1** to **3b** were recovered as the major side products, meaning that the addition reaction between **1** and **3b** was responsible for the relatively low yield. In the subsequent reactions, the ratio of **3b** to **1** was reduced to suppress this addition reaction. However, the reaction rate for forming **4** seemed to be suppressed too (Runs 2 and 3, Table 1). Especially in Run 3, approximately 1/5 of **1** was still left intact after 7 days. The reaction was apparently incomplete since a trace amount of **3b** was also untouched according to the analysis of the products. After doubling the ratio of **3b** (Run 4, Table 1), the reaction proceeded somewhat faster with a higher conversion to **4**, but the reaction was still incomplete after 5 days. At the higher temperatures (Runs 5–7, Table 1), the reaction rate was faster and completed with a yield over 90% in 2 days.

All the reactions were run in a 150 ml one-piece glass reactor; the main side products collected in some of the Runs are listed in Table 2 (see Scheme 2). Silicon tetrafluoride should be generated from the slow etching of the glass wall by **1**. Its quantity may well be related to the residence time of **1** in the reactor. The generation of $CF_3(O)_nCF_3$ ($n = 2, 3$) **9**, due to the presence of traces of O_2, and $CF_3OC(O)OCF_3$ **10** as side products in this reaction indicates the generation of $CF_3O^\bullet$ **5** and $CF_3OC(O)^\bullet$ **6** radicals as the main intermediates during the reaction. The formation of $CF_3OCR_1R_2CR_3R_4F$ **8** comes from the fluorine transfer from **1** to $CF_3OCR_1R_2CR_3R_4$ radical **7**. The absolute quantities of **8** in the reaction were not high in most cases compared with the amounts of the dimer **3b** fed initially as well as of the desired product **4**. The majority of **3b** was still left intact after the reaction. Surprisingly, higher temperatures did not result in higher yields of **8b** (Table 2), suggesting that the quantity of **8b** was determined by a competition between the desired reaction forming **4** and the side reaction forming **8b**. This suggests that the reaction rate can be increased while not sacrificing the yield to **4** using elevated temperatures.

The slow reaction using **3b** appears to be the result of steric effects. In order to further accelerate the reaction, some less sterically hindered halogenated olefins were tested as listed in

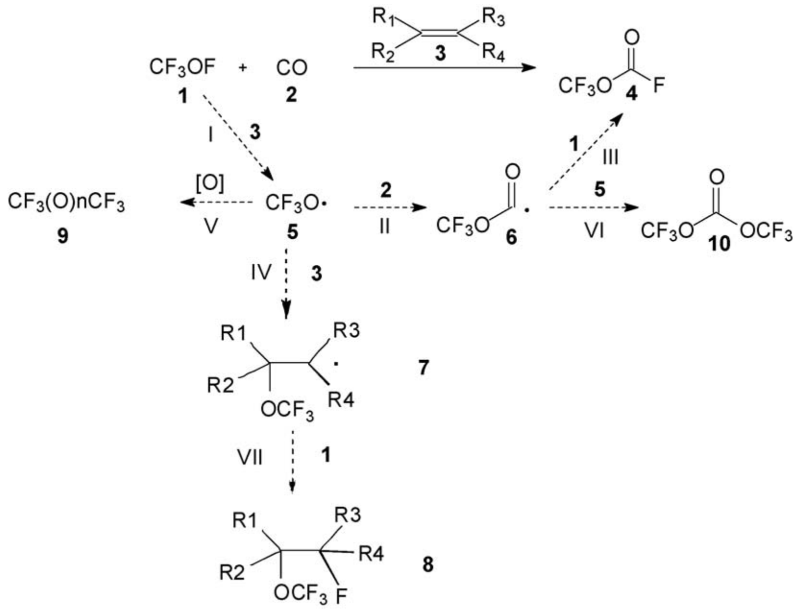
Table 2
Side products in the reaction between **1** and **2** initiated by **3b**.

Run[a]	$CF_3(O)_nCF_3$ (mmol)	SiF_4 (mmol)	**8b** (mmol)	Yield of **8b**[b] (%)	$CF_3OC(O)OCF_3$ (mmol)
3	0.08	0.19	0.11	22.4	–
6	0.04	0.1	0.07	13.2	–
7	0.16	0.06	0.07	12.1	0.16

All the data were based on ^{19}F NMR spectra.

[a] As in Table 1.

[b] Based on the amount of **3b** used.



Scheme 2. Possible reaction paths for the formation of **4** and side products.

Table 3
Reactions between **1** and **2** initiated by other olefins.

Olefin	**3** (mmol)	**1** (mmol)	**2** (mmol)	Time (days)	**4** (mmol)	Yield (%)	Recovered **1** (mmol)
3c	0.5	5.2	5.4	5	4.2	82.7	0.5
3d	0.6	4.9	5.3	4	3.5	72.2	0.7
3e	0.7	6.3	6.4	1	1.7	27.0	4.1[a]
3f	1.0	5.0	5.4	1	0	0	4.9
3g	1.0	5.1	5.6	3	0	0	2.2

All the reactions were run in a 150 ml one-piece glass reactor at room temperature.

[a] Contaminated with **4**.

Table 3. A perfluorinated 2-butene (**3c**) was first used. It has a trifluoromethyl group, CF_3–, in place of the isopropyl group of **3b**, so a faster reaction rate was expected [28]. Indeed, a higher yield was obtained in a shorter reaction time using **3c** (Run 1, Table 3) compared with that using **3b** (Run 3, Table 1), indicating the reaction rate was faster. However, the absolute reaction rate appeared to be still slow as approximately 10% of **1** remained after reaction. Analysis of the final reaction mixture (see Table 4), showed the majority of **3c** was unreacted after 5 days.

With the even less hindered double bond of hexafluoropropene (HFP, **3d**) the reaction was completed within 4 days with a yield of 72.2% (Run 2, Table 3). Unreacted **1** left after the reaction was apparently due to the complete consumption of **3d** before **1** was consumed (see Table 4). Using $CCl_2{=}CCl_2$ **3e**, the reaction proceeded even faster and was complete in 1 day. However, the yield was further lowered, due to the main side reaction of the addition **1** to **3e**. The fast reaction also resulted in lower ratios of some side products (see Table 4). Two cyclic perfluorinated olefins (**3f** and **3g**, Fig. 1), were explored but these did not result in the formation of **4**. Olefin **3f** was unreactive and **3g** led to unidentified products and loss of **1**.

Table 4
Side products in the reactions.

Olefin	$CF_3(O)_nCF_3$ (mmol)	SiF_4 (mmol)	**8** (mmol)	Yield of **8**[a] (%)
3c	0.06	0.04	0.18	34.0
3d	0.05	0.01	0.6	100
3e	–	–	0.7	100

All the data were based on ^{19}F NMR spectra.

[a] Based on the amount of olefin used.

Other hypofluorites in the series $F(CF_2)_nOF$ ($n = 2$, 3), $(CF_3)_2CFOF$, SF_5OF and $CF_2(OF)_2$, were tested to see whether the corresponding fluoroformates could be prepared. The fluoroformate, $SF_5OC(O)F$, was reported to form in the photochemical reaction of SF_5OF and **2** [29]. However, the thermal version of the reaction generated only trace amount of $SF_5C(O)F$ along with other products [30]. The compound $(CF_3)_2CFOC(O)F$ was also prepared earlier [10–12]. Compared with **1**, these hypofluorites are all of lower thermal stability and decomposition and other reactions were anticipated. We attempted to react the above hypofluorites with **2** in presence of **3c** or **3d**. However, only a trace amount of $CF_3CF_2OC(O)F$ was observed in the reaction of CF_3CF_2OF and **2** by NMR spectroscopy. In all the other cases, the adducts of the hypofluorites with the olefins were identified as minor products along with a mixture of COF_2, CF_4 and the expected decomposition products of the hypofluorite.

The side products generated in the reactions of **1** (Tables 2 and 4) suggest that the reaction path involves **5** as a key intermediate (see Scheme 2). In the neat reaction between **1** and **3b** [27] the radical **7b** has been detected using EPR spectroscopy, suggesting the reaction path of Step I and IV shown in Scheme 2. In the case of **3b**, it appears that the slow reaction between **5** and **3** allows **5** to react with **2** forming **4**. Radical **6** may also be present as an intermediate in the reaction, as evidenced by the formation of a side product **10** in some runs (Run 7 in Tables 1 and 2).

The proposed reaction path in Scheme 2 may indicate a way to improve both the reaction rate and yield. Step II and III appear to be

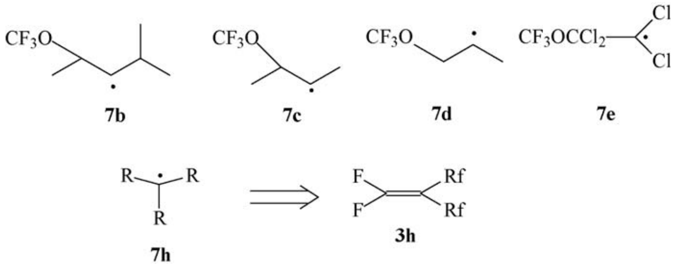


Fig. 2. Possible radicals of the olefins generated in the reactions of **1**.

Table 5
Reaction between 1.5 N l/h of **1**, 2.0 N l/h of **2** and 3.0 N l/h of He at 170 °C.

Reactor	Conversion CF_3OF	Selectivity CF_3OCOF	Selectivity COF_2
0.25 l nickel	45%	1%	99%
0.25 l, copper	41%	7%	93%
0.14 l, AISI316	23%	30%	70%
0.14 l, not passivated AISI316	23%	94%	6%
0.16 l, PTFE	33%	97%	3%
0.08 l, glass	18%	96%	4%

independent of the olefin, so the effect of olefin on reaction rate should occur mainly in Step I. We have shown that the less sterically hindered olefin was usually associated with a faster reaction (see Table 3), but with a lower yield of **4** (Step IV was faster). An olefin like **3h** (Fig. 2) could be more reactive than **3b** and **c** with CF_3O radical, its corresponding tertiary radical (**7h**), being more sterically hindered than **7b** and **c**. This could result in a slower abstraction of fluorine from CF_3OF (Step VII). Therefore, both a fast reaction (as in the case of **3d** and **e**) and a high yield (as with **3b** and **c**) may be possible if an olefin of this type is used.

2.2. Thermal synthesis of trifluoromethyl fluoroformate

According to the literature [1,25], no significant attempts to obtain **4** by thermal reaction between **1** and **2** at $T > 110\,^{\circ}C$ have ever been tried. The technical difficulties involved in managing strong oxidizers like hypofluorites in the presence of a reducer like **2**, at high temperatures, probably discouraged such experiments.

Leveraging on our experience in the proper and safe use and reaction of perfluoroalkyl hypofluorites [31] this thermal reaction was carried out in a continuous flow system with monitoring.

The reaction path proceeds through the typical steps of a radical reaction:

Initiation:

$$CF_3OF + CO \rightarrow CF_3O^{\bullet} + FCO^{\bullet}$$

$$FCO^{\bullet} + CF_3OF \rightarrow COF_2 + CF_3O^{\bullet}$$

Propagation:

$$CF_3O^{\bullet} + CO \rightarrow CF_3OCO^{\bullet}$$

$$CF_3OCO^{\bullet} + CF_3OF \rightarrow CF_3OCOF + CF_3O^{\bullet}$$

Termination:

$$2CF_3O^{\bullet} \rightarrow CF_3OOCF_3$$

$$2CF_3OCO^{\bullet} \rightarrow CF_3OC(O)C(O)OCF_3$$

$$CF_3OCO^{\bullet} + CF_3O^{\bullet} \rightarrow CF_3OC(O)OCF_3$$

$$CF_3O^{\bullet} + FCO^{\bullet} \rightarrow CF_3OCOF$$

$$2FCO^{\bullet} \rightarrow FC(O)C(O)F$$

$$CF_3OCO^{\bullet} + FCO^{\bullet} \rightarrow CF_3OC(O)C(O)F$$

The on-line GC analysis of the gaseous compounds exiting the thermal reactor showed the presence of starting reagents **1** and **2**, product **4** and COF_2 as main byproduct. Other byproducts CF_3OOCF_3, CF_4 and CO_2 were detected only in trace amounts.

In a typical run, carbon monoxide and trifluoromethyl hypofluorite **1** were fed continuously to the reactor maintained at the desired temperature. The exit gases, after GC analysis, were quenched in a cold solution containing 1,2-dichloro 1,2-difluoroethylene to consume the residual hypofluorite and forming $CF_3OCFClCF_2Cl$ [31].

In Table 5 the influence of the reactor material on conversion and selectivity is shown.

The conversion of **1**, having fixed the ratio of reagents, their concentration and the reaction temperature, depends on the volume of the reactor and hence is a function of the residence time. The selectivity of **4** strictly depends on the reactor material and on the “history” of the reactor: different materials give different selectivity. Metal reactors (Stainless Steel 316, Copper, Nickel, etc.) used for reaction with fluorine or hypofluorites have to be passivated before use to prevent highly exothermic side reactions or even explosions promoted by the metal surface. The internal walls have to be previously treated gradually with the diluted oxidant to form a protective layer of metal fluoride. Due to the presence of this fluoride layer, the selectivity of the fluoroformate decreases significantly along time with simultaneous formation of COF_2 due to the known fluoride induced decomposition of fluoroformate [2]. The equilibrium between **4** and COF_2 in the presence of metal fluorides allows the synthesis of **4** starting from COF_2 at very low temperature [2] but causes the irreversible decomposition of **4** at high temperature, even in gas phase. Nonetheless it is possible to get **4** in decent yield and good selectivity, even in metal reactors, playing on residence time, temperature and concentration. The effect of reaction temperature and dilution of the reactants are shown in Tables 6 and 7, respectively.

As expected, an increase in temperature increased the conversion of **1** and the decomposition of **4** due to the enhanced catalytic effect of the reactor internal surface (Table 6). More concentrated reagents, i.e. no dilution with inert gas, favour conversion to **4** and conversely cause greater decomposition of **4** to carbonyl difluoride (Table 7).

At $T > 220\,^{\circ}C$ we observed some micro-explosions during the reaction: to see what happens at higher temperature a reactor having only 1 ml volume was used to minimize the risks. In these conditions the conversion of the reagents was very low (<5%) up to

Table 6
Reaction between 1.5 N l/h of **1**, 1.5 N l/h of **2** and 4.5 N l/h of He in a 0.20 l SS 316 reactor.

Temperature	Conversion CF_3OF	Selectivity CF_3OCOF	Selectivity COF_2
160 °C	18%	86%	14%
180 °C	29%	85%	15%
200 °C	42%	84%	16%
220 °C	49%	80%	20%

Table 7
Reaction between 1.5 N l/h of **1**, 1.5 N l/h of **2** in a 0.20 l 316 SS reactor.

Temperature	Conversion CF_3OF	Selectivity CF_3OCOF	Selectivity COF_2
180 °C	75%	76%	24%
200 °C	81%	68%	32%
220 °C	83%	62%	38%

240 °C while the selectivity of **4** was very high (>95%); at $T > 250$ °C total conversion of the reagents was achieved with quantitative selectivity to COF_2. During the reaction if the temperature was decreased below 230 °C, decomposition stopped and reaction ceased. This phenomena cannot be explained by a total conversion of the reagents to **4** and its subsequent decomposition to COF_2, because a more gradual change would have been expected. The observed discontinuity may be tentatively related to a different mechanism. It is known [32] that hypofluorite **1** may decompose to COF_2 and fluorine at high temperature; in the presence of **2** a possible mechanism explaining the selective formation of COF_2 may be the following:

Initiation:

$$CF_3OF + CO \rightarrow CF_3O^{\bullet} + FCO^{\bullet}$$

Propagation:

$$CF_3O^{\bullet} \rightarrow COF_3 + F^{\bullet}$$

$$F^{\bullet} + CO \rightarrow FCO^{\bullet}$$

$$FCO^{\bullet} + CF_3OF \rightarrow COF_2 + CF_3O^{\bullet}$$

Termination:

$$F^{\bullet} + FCO^{\bullet} \rightarrow COF_2$$

This mechanism is supported by the measurement of the temperature at the point were the two reagents meet with a thermocouple inserted just inside the small metal reactor. When the decomposition to COF_2 started, a sudden increase of temperature was observed (370–400 °C, $\Delta T > 120$ °C).

Decomposition of **4** to COF_2 may become a serious problem when it is stored (pure or diluted) in a cylinder: **4** has a vapor pressure of about 6 bar at room temperature, while COF_2 exhibits a critical temperature of 22.8 °C and a vapor pressure of 55.4 bar at 21 °C [33]. Hence, the uncontrolled decomposition of **4** would lead to a dangerous increase in pressure inside the cylinder. Some tests were carried out storing **4** in a cylinder containing a powder constituted of metal fluorides (about 160 mg of powder per 1000 mg of **4**) deriving from a fluorine passivated SS 316 reactor (mainly nickel, chromium and iron fluorides) and monitoring the pressure continuously. After 90 h at room temperature a 47% decomposition was achieved. For comparison, a similar test using KF or KHF_2 (respectively 95 and 150 mg per 1000 mg of **4**) showed a 100% decomposition in 40 min.

No problems were experienced in storing small amounts of **4** even in the liquid phase, for several days, in clean, new (not passivated) SS 316 cylinders.

As in the olefin promoted reaction, attempts to carry out thermal carbonylation of higher perfluoroalkyl hypofluorites and particularly perfluoroethyl hypofluorite were unsuccessful.

$$CF_2CF_2OF + CO \not\rightarrow CF_2CF_2OCOF$$

Perfluoroethylhypofluorite is less stable than **1** and it is more stable conversely than higher homologues [34]. No trace of the desired perfluoroethyl fluoroformate was detected and only CF_4 and COF_2 (Table 8) were observed.

In the presence of **2** the only reaction occurring is the decomposition of CF_3CF_2OF: the reaction was initiated by **2**, then the oxyradical so formed decomposes rather then adding to carbon monoxide.

Initiation:

$$CF_3CF_2OF + CO \rightarrow CF_3CF_2O^{\bullet} + FCO^{\bullet}$$

$$CF_3CF_2OF + FCO^{\bullet} \rightarrow CF_3CF_2O^{\bullet} + COF_2$$

Propagation:

$$CF_3CF_2O^{\bullet} \rightarrow COF_2 + CF_3^{\bullet}$$

$$CF_3^{\bullet} + CF_3CF_2OF \rightarrow CF_4 + CF_3CF_2O^{\bullet}$$

Termination:

$$2CF_3^{\bullet} \rightarrow CF_3CF_3$$

Table 8

Reaction between 1.0 N l/h of CF_3CF_2OF, 1.0 N l/h of **2** and 8.0 N l/h of He in ❶ a 0.16 l PTFE reactor or ❷ a 0.85 l glass reactor.

Reactor	Temperature	Conversion CF_3CF_2OF
❶	100 °C	6%
❷	100 °C	60%
❶	120 °C	24%
❶	140 °C	48%
❶	160 °C	70%
❷	160 °C	7%[a]

[a] In absence on CO.

The role of carbon monoxide to initiate the reaction is outlined by the low decomposition of CF_3CF_2OF in the absence of CO at 160 °C (7%) compared to the 60% decomposition at 100 °C in the presence of CO (Table 8).

Summarizing, we have developed two convenient synthetic routes to trifluoromethyl fluoroformate by reacting trifluoromethyl hypofluorite with carbon monoxide: at or near room temperature, initiated by sterically hindered olefins and at higher temperatures ($T > 150$ °C) in a proper tubular reactor. Both syntheses allow the preparation of reasonable amounts of trifluoromethyl fluoroformate on a laboratory scale.

3. General experimental procedures

3.1. Instruments

^{19}F NMR spectrum was recorded on a Joel 300 MHz or a Varian 200 MHz FT/NMR.

The samples were sealed in a 4 mm glass tube with CCl_4 as solvent and $CFCl_3$ as reference. The tube was inserted into a regular 5 mm NMR tube during the measurement. Deuterated oxide, D_2O, was added in the outer tube for locking the signal. Infrared spectra are recorded on a PerkinElmer Spectrum 2000 series FTIR. The sample was analyzed in a 10 cm path length glass gas cell fitted with a Kontes–Teflon valve using AgCl window attached with Halocarbon 1500 wax. Gas chromatograms were recorded on a GC 8000 Top Carlo Erba gas chromatograph employing either a capillary 0.54 mm, 25 m silicone column (no hypofluorites present in the samples) and a 8 m PTFE column filled with Kel-F (20%) on PTFE microspheres for on-line analysis. Mass spectra were recorded on a Finnigan MAT SSQ700 chromatograph using a 50 m methyl silicone CPSIL (Varian-Chrompack) column.

3.2. Apparatus and reagents

The glassware used for olefin-initiated reaction was dried at 100 °C in an oven followed by an overnight (about 12 h) evacuation on a standard glass vacuum line. The chemical transformation and fractional separation were all performed on a glass vacuum line containing 4 U-traps [23]. Trifluoromethyl hypofluorite as well as the other hypofluorites, $F(CF_2)_nOF$ ($n = 2, 3$), $(CF_3)_2CFOF$, SF_5OF and $CF_2(OF)_2$, were prepared according to literature procedures [35–38]. The olefins and CO were all purchased from commercial sources and used as received.

The tubular reactors of different materials and appropriate volume, as reported in the text, were pretreated with diluted fluorine gas to remove any impurity and, for metal reactors, to passivate it. They were thermostated to the desired temperature by electric resistance heating. The flow of gaseous reagents was measured by thermal mass flowmeters. The flow coming out of the reactor was condensed in a trap maintained at −110 °C and containing 15 g of CFCl=CFCl to remove the residual hypofluorite as $CF_3OCFClCF_2Cl$, then distilled to separate **4**.

3.3. Reactions of 1

3.3.1. A typical procedure is described for the reactions of 1

3.3.1.1. Thermal reaction between 1 and 3b. A pre-dried 150 ml one-piece Pyrex reactor equipped with a Kontes glass-Teflon valve was used. First, the olefin **3b** (1.0 mmol) was added, followed by **1** (1.1 mmol). The reactor was warmed up slowly from −196 °C in a cold dewar and remained at room temperature for 5 days. The separation was done through trap-to-trap distillation using −100 and −196 °C traps. Unreacted **1** (0.3 mmol) was collected in −196 °C trap, while addition product **8b** contaminated with intact **3b** (1.0 mmol) were collected in −100 °C trap. Further separation using −80 and −196 °C traps collected **8b** (0.8 mmol, 80%) in −80 °C trap and **3b** (0.2 mmol) in −196 °C trap. The characteristic properties and spectral values of **8b** match with those described in earlier report [28].

3.3.1.2. Reaction between 1 and 2 initiated by 3b. A pre-dried 150 ml one-piece Pyrex reactor equipped with a Kontes glass-Teflon valve was used. The hypofluorite **1** (5.2 mmol) was condensed under vacuum on the bottom of the flask followed by **3b** (1.0 mmol) on the upper glass wall. Gaseous **2** (5.6 mmol) was then added. The reactor was warmed up slowly from −196 °C in a cold dewar and remained at room temperature for 4 h. The separation was done through trap-to-trap distillation using three traps with the temperatures set at −196, −130 and −100 °C. Unreacted **1** contaminated with a little **4** and SiF_4 (4.9 mmol) was collected in the −196 °C trap. The desired product, **4** (0.4 mmol) was collected in −130 °C trap. Unreacted **3b** (1.0 mmol) was collected in −100 °C trap. All the trapped chemicals were then returned to the reactor at −196 °C and more **2** (5.6 mmol) was added. The reactor was allowed to warm to 22 °C in the air and let stand for 5 days. The separation was repeated as above. Pure **4** (4.3 mmol, 82.7%) was collected in −135 °C trap. A mixture (1.2 mmol) was collected in −196 °C trap which contained **1** (0.9 mmol), **4** (0.2 mmol), and CF_3OOCF_3 and CF_3OOOCF_3 (0.1 mmol) based on ^{19}F NMR spectra. A mixture of **3b** and **8b** (0.9 mmol) was collected in −100 °C trap. The overall yield of **4** was 86.5%. The characteristic properties and spectral values of **4** match with those described in the earlier reports [1,8].

3.3.1.3. Thermal reaction between 1 and 2. As an example the reaction in a PTFE reactor is described.

A gaseous flow of 1.5 N l/h of **1**, 2.0 N l/h of **2** and 3.0 N l/h of He was fed into a tubular PTFE reactor, having an internal diameter of 4 mm and length of 13.2 m, maintained at 170 °C by an electric furnace. The flow was maintained for 4 h. The gas coming out of the reactor was condensed in a cold trap (−110 °C) containing 15 g of CFCl=CFCl. After fractional distillation of the resulting mixture 11.3 g of 99.8% pure **4** were collected (conversion CF_3OF: 33%; selectivity CF_3OCOF: 97%).

Acknowledgement

L. Du and D.D.D. gratefully acknowledge the financial support of Solvay Solexis.

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