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Ali Alaaeddine, Lolwa Haydar, Vincent Ladmiral, Wassim El Malti, Sylvain Caillol, et al.. Synthesis and Characterization of Original Fluorinated Cyclic Carbonates and Xanthates from Fluorinated Epoxides. *Comptes Rendus. Chimie*, 2023, 10.5802/crchim.216 . hal-03989242v1

HAL Id: hal-03989242

<https://hal.science/hal-03989242v1>

Submitted on 14 Feb 2023 (v1), last revised 14 Feb 2023 (v2)

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1 Type of the Paper (Article)

2 Synthesis and Characterization of Original Fluorinated Cyclic 3 Carbonates and Xanthates from Fluorinated Epoxides

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8 **Abstract:** The development of efficient methods for the cycloaddition of CX₂ (carbon dioxide (X=O)
9 or carbon disulfide (X=S)) with fluorinated epoxides to produce five-membered cyclic carbonates
10 (CCs) or xanthates (XAs) is a very attractive topic. In this work, the cycloaddition of CX₂ with
11 hexafluoropropene oxide (HFPO), 2-(trifluoromethyl)oxirane (TFEO), and
12 1,4-bis(2',3'-epoxypropyl) perfluorobutane (BEPFB) catalyzed by lithium bromide (LiBr) is de-
13 scribed. The listed reactions were optimized in terms of temperature, solvent, pressure, and reac-
14 tion time to lead to a series of original fluorinated five-membered CCs and XAs in high yields
15 (81–93%). The resulting compounds were characterized by FTIR, ¹H, ¹⁹F, and ¹³C NMR spectroscopy.
16

17 **Keywords:** carbon dioxide (CO₂); carbon disulfide (CS₂); cycloaddition; cyclic carbonates; renewa-
18 ble carbon source; xanthates.
19

20 1. Introduction

21 Regarded as a greenhouse gas, carbon dioxide (CO₂) is often considered as a useless
22 and detrimental waste. Its increasing concentration in the atmosphere is partly responsi-
23 ble for climate change. Nonetheless, CO₂ can also be regarded as a cheap, abundant, and
24 renewed carbon source. In addition, it is non-toxic (even though it is asphyxiant) and is
25 especially useful as a phosgene substitute [1]. Many interesting organic compounds,
26 including dimethyl carbonate [2], cyclic carbonates (CCs) [3], and urethanes [4] can be
27 synthesized using CO₂ as a building block [5,6].

28 Although the synthesis of CCs was first reported in the 1930s, the synthesis of
29 five-membered (or more) CCs is gaining increased attention. They are used to synthesize
30 polycarbonates [7–9], as aprotic polar solvents for organic reactions [10], electrolytes [11]
31 or solvents for lithium-ion batteries [12,13], and as intermediates in the manufacture of
32 fine chemicals [14–16]. CCs are highly implemented in polymer science ring-opening
33 polymerizations and reactions with amines, alcohols, thiols, and carboxylic acids [17].
34 For example, difunctional CCs can advantageously be reacted with diamines to produce
35 polyhydroxyurethanes, promising substitutes to polyurethanes, without using highly
36 toxic and carcinogenic isocyanates [14,18–22].

37 Several approaches can be used to synthesize five-membered CCs [23–25]. The most
38 efficient method is the insertion of CO₂ into epoxide rings. This reaction requires a cata-
39 lyst such as an alkali metal salts [26–28], metal oxides [29], Schiff base [30], ion-exchange
40 resins [31], polymers such as modified polystyrene [32], ionic liquids [33], SiO₂ modified
41 by quaternary ammonium or phosphonium salts [34], gold nanoparticles supported on
42 resins [35], or CO₂ adducts of N-heterocyclic carbenes [36]. Endo *et al.* reported that alkali
43 metal salts could be used as catalysts to synthesize CCs involving crown ethers as
44 co-catalysts [27]. Huang and Shi found that alkali metal salts could efficiently catalyze
45 cycloaddition of CO₂ with epoxides in the presence of PPh₃ and phenol [28]. Cellulose

24 **Citation:** Lastname, F.; Lastname, F.;
25 Lastname, F. Title. *Molecules* **2022**,
26 27, x. <https://doi.org/10.3390/xxxxx>

28 Academic Editor: Firstname
29 Lastname

30 Received: date

31 Accepted: date

32 Published: date

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could also improve the coupling reaction of CO₂ and epoxides catalyzed by KI [37].

Cyclic xanthates (XAs) constitute another family of interesting five-membered cyclic reactive species. They are highly reactive and can be easily prepared from epoxides and carbon disulfide (CS₂) at low temperatures (20–25°C) [38,39]. This reaction is usually carried out in organic solvent or water in the presence of a catalyst, such as amines, alkali metal salts, quaternary ammonium salts, potassium alcoholates, and transition metal complexes [40–44]. Petrov *et al.* demonstrated that fluorinated epoxides react with CS₂ selectively, leading to the corresponding cyclic XAs [45].

Although research on the synthesis and use of CCs- and to a lesser degree on cyclic XAs-based compounds is extensive, a few fluorinated derivatives bearing such functional groups have been reported [45]. Fluorinated materials usually exhibit outstanding properties [46–48] such as chemical resistance, thermal stability, hydrophobic and oleophobic properties, low dielectric constants and dissipation factors, excellent weathering, and interesting surface properties fulfilling the requirements for various high added-value applications. Therefore, the synthesis of compounds that carry both a fluorinated segment and cyclic carbonates or xanthates moiety would be highly interesting as reactive fluorinated intermediates.

This present study reports the cycloaddition of CX₂ [carbon dioxide (X=O) or carbon disulfide (X=S)] with three fluorinated epoxides: hexafluoropropylene oxide (HFPO), 2-(trifluoromethyl)oxirane (TFEO), and 1,4-bis(2',3'-epoxypropyl)perfluorobutane (BEPFB) (Figure 1) [13]. In the presence of lithium bromide (LiBr) as a catalyst, the cycloaddition produced six new five-membered CCs (HFPO-CC1, TFEO-CC3, BEPFB-CC5) and XAs (HFPO-CS2, TFEO-CS4, BEPFB-CS6).

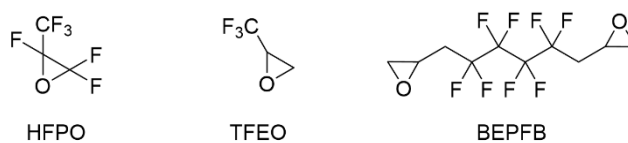
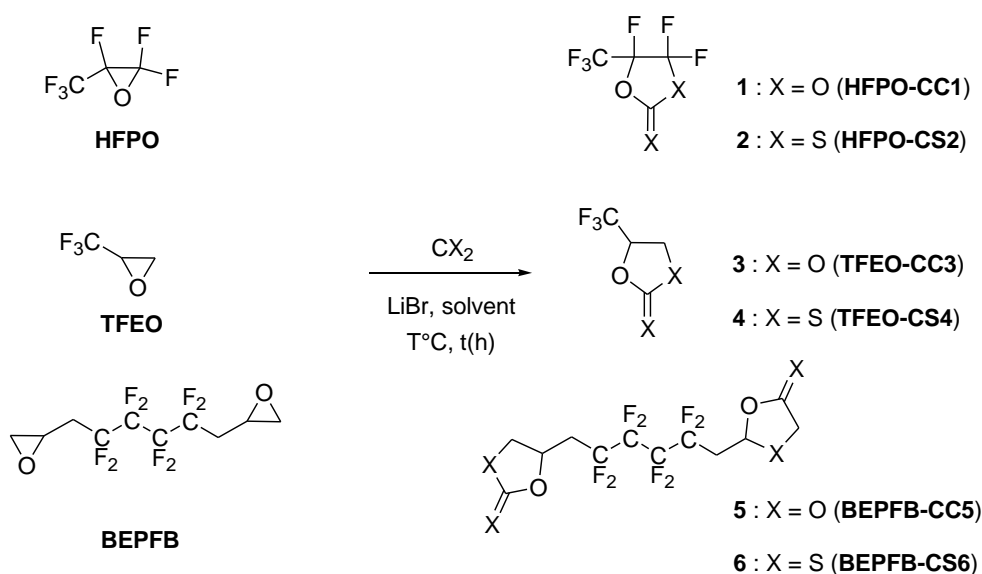


Figure 1. Structures of hexafluoropropylene oxide (HFPO), 2-(trifluoromethyl)oxirane (TFEO), and 1,4-bis(2',3'-epoxypropyl)perfluorobutane (BEPFB) used in this work

2. Results and Discussion

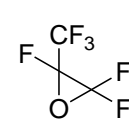
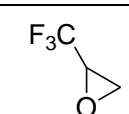

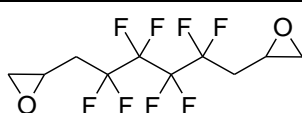

CCs can be prepared through the coupling reaction of CO₂ and strained heterocycles using a suitable catalyst [16,24]. This approach benefits from eliminating phosgene as a reagent and is 100% atom economical, making it a highly desirable transformation.

The insertion of CO₂ and CS₂ into HFPO, TFEO, and BEPFB was examined (Scheme 1), and various experimental conditions (choice of solvent, reaction duration, and temperature) have been investigated to improve the carbonation reaction. The results are summarized in Table 1.



Scheme 1. Synthesis of original five-membered fluorinated cyclic carbonates, CCs (HFPO-CC1, TFEO-CC3, BEPFB-CC5) and cyclic xanthates, XAs (HFPO-CS2, TFEO-CS4, BEPFB-CS6)

Table 1. Reactions of HFPO, TFEO, and BEPFB with CO₂ or CS₂^a

Run #	Epoxide	X in CX ₂	Solvent	T (°C)	t (h)	Yield ^b (%)
1		O	DMF	25	24	25
2		O	DMF	50	24	45
3		O	1,4-Dioxane	50	24	63
4		O	THF	50	24	56
5		O	1,4-Dioxane	70	24	72
6 ^c		O	neat	80	24	0
7		O	Acetone	65	24	85
8		O	Acetone	65	14	81
9 ^d		S	Acetone	65	14	83
10		O	DMF	80	24	93
11 ^d		S	Acetone	65	14	91
12 ^e		O	Acetone	65	24	33
13 ^e		O	Acetone	65	96	85

80

81

82

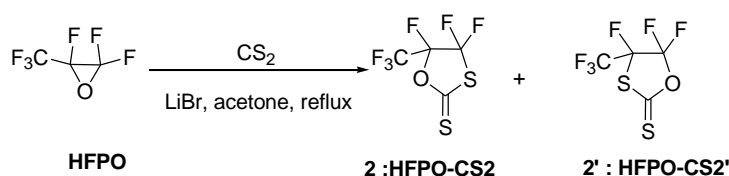
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14 ^e	S	Acetone	65	96	87
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^a Experimental conditions: The carbonation reactions were performed in pressure reactors under 4 bar of CO₂ and in the presence of 5 mol % of LiBr, or with 3 eq. of CS₂, T (°C), t(h). ^b Yields obtained after purification. ^c Reaction conducted without solvent in the presence of KBr/Lecithin as catalyst [49]. ^d This reaction was performed with 16 mol % of LiBr. ^e These reactions were performed with 10 mol % of LiBr.

First, the synthesis of HFPO-CC1 carried out with CO₂ in DMF at 25 °C or 50 °C proceeded with relatively modest yields (Table 1, runs 1 & 2). Subsequently, using 1,4-dioxane or THF as solvent (Table 1, runs 3 & 4) and increasing the temperature to 70 °C did prove beneficial, but the yields reached 72% at best (Table 1, run 5). The KBr/lecithin catalytic system, known to afford good results, was also tried in the carbonation of HFPO (Table 1, run 6). Surprisingly, this reaction did not yield any CC under the implemented conditions without any solvent. On the other hand, the carbonation in acetone at 65 °C gave the best yields (Table 1, runs 7 and 8), reaching 81% in 14 hours and 85 % in 24 hours.

The analog HFPO-based cyclic XA HFPO-CS2 was successfully synthesized in high yields (83%) using the same conditions by refluxing acetone in excess of CS₂ for 14 hours (Table 1, run 9). However, this reaction led to the formation of a minor by-product, HFPO-CS2' (Scheme 2). Earlier attempts to react oxiranes and CS₂ resulted in complex mixtures [7], and the formation of these regioisomers, HFPO-CS2 and HFPO-CS2', depends on the catalyst and the reaction conditions [50]. Selective formation of XAs (5-substituted 1,3-oxathiolane-2-thiones) was attained catalyzed by LiBr in appropriate solvents [44]. Thus, the non-catalyzed reactions conducted in this work were not expected to lead to the regioselective formation of cyclic XA [51]. A previous work has shown that triethylamine as a catalyst led to mixtures of products under high pressure [50]. On the other hand, lithium bromide [44], hydrotalcite [52], sodium methoxide [53], tributylphosphine, tetradentate Schiff-base aluminum complexes [41], and lithium perchlorate [54] selectively produced 1,3-oxathiolane-2-thiones.



Scheme 2. The reaction of HFPO with CS₂ catalyzed by LiBr

Trifluoromethyloxirane (TFEO) was nearly totally (93% yield) transformed into the corresponding CC, TFEO-CC3, by reaction with CO₂ in DMF in the presence of LiBr at 80°C (Table 1, run 10). Similar to the HFPO-CS2 case, the XA counterpart (TFEO-CS4) was easily obtained as a mixture of regioisomers in 91% yield using similar conditions as for HFPO (Table 1, run 11).

The reactions of CX₂ (X = O or S) with BEPFB proved to be slower than those performed with HFPO and TFEO (Table 1, runs 8-14). This could be ascribed to the strong electro-attractive effect of the fluorine atoms and the trifluoromethyl groups present on the epoxy rings of HFPO and TFEO. These strong electron-withdrawing groups induce a partial polarization of the carbon-carbon bond of the epoxide, which in turn enhances the electrophilic character of the carbon atom bearing the fluorine or trifluoromethyl group and its reactivity towards the bromide anion of the catalyst. The ring-opening of the epoxide by the bromide anion is believed to be the rate-determining step of the reaction of CO₂ and CS₂ onto epoxides. HFPO with a fully fluorinated backbone reacts with CO₂ or CS₂ quantitatively in 14 h (yield of 81% and 83%, respectively). In comparison, the re-

action with BEPFB needs 96 h to lead to carbonate BEPFB-CC5 or xanthate BEPFB-CS6 in high yields.

The FTIR spectrum of BEPFB-CC5 (Figure S8 in SI) confirmed the formation of the CC with the characteristic bands of the carbonate function: C=O bond stretching vibration at 1776 cm^{-1} , and other vibrations corresponding to C-C and C-O bonds appear at 1047 cm^{-1} and 1106 cm^{-1} , respectively. Similar observations are noted on the FTIR spectrum of BEPFB-CS6 (Figure S11 in SI) with the characteristic bands of the XA function: C=S bond stretching vibration at 1777 cm^{-1} .

The following section describes the NMR spectra of these novel fluorinated cyclic-carbonate BEPFB-CC5 and xanthate BEPFB-CS6, which possess the most complex chemical structures (Figure 2-4). The other products synthesized in this study have been characterized by ^1H , ^{19}F , and ^{13}C NMR spectroscopy and the corresponding spectra are shown in the SI (Figures S1-7 and S9-10).

Figure 2 displays the ^1H NMR spectra of cyclic-carbonate 5 (BEPFB-CC5) and xanthate 6 (BEPFB-CS6). These spectra clearly evidence the vanishing of the signals of the diepoxide at 2.6, 2.8, and 3.2 ppm replaced by AB systems (located at 4.6 and 4.2 ppm for 5; 3.9 and 3.7 ppm for 6), corresponding to the non-equivalent hydrogen atoms $\text{CH}_\text{A}\text{H}_\text{B}$ of the carbonate groups. The same observation can be made for the CH group of the carbonate ring with the chemical shift at 5.2 ppm for 5 and 5.6 ppm for 5 and 6, respectively, low field-shifted by the presence of the carbonyl group compared to the epoxide (3.2 ppm). Both hydrogens in CH_2CF_2 groups appear as one complex system centered at 2.9 ppm due to fluorine coupling in α and β positions.

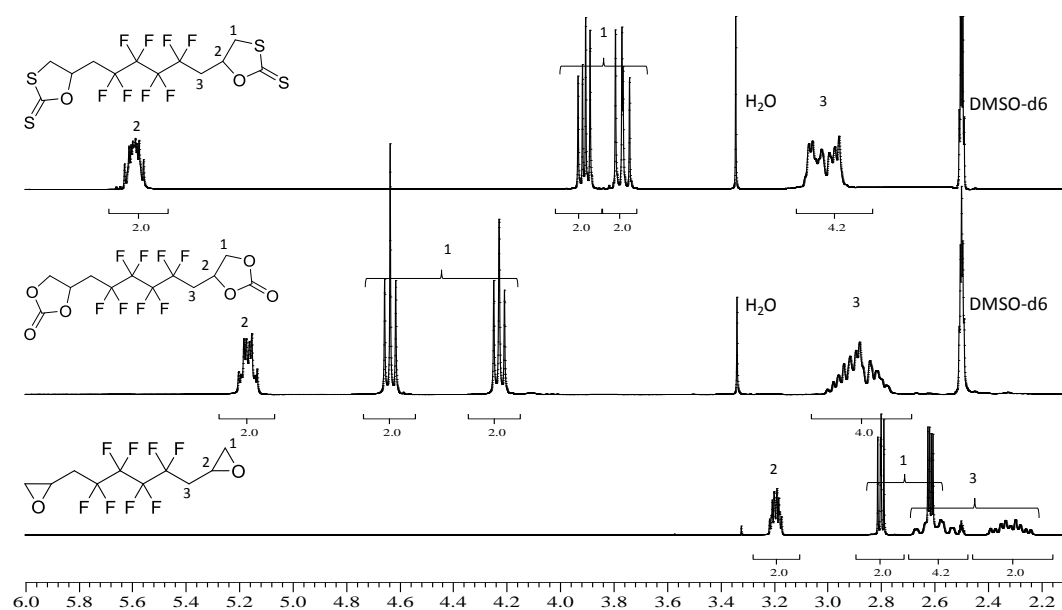
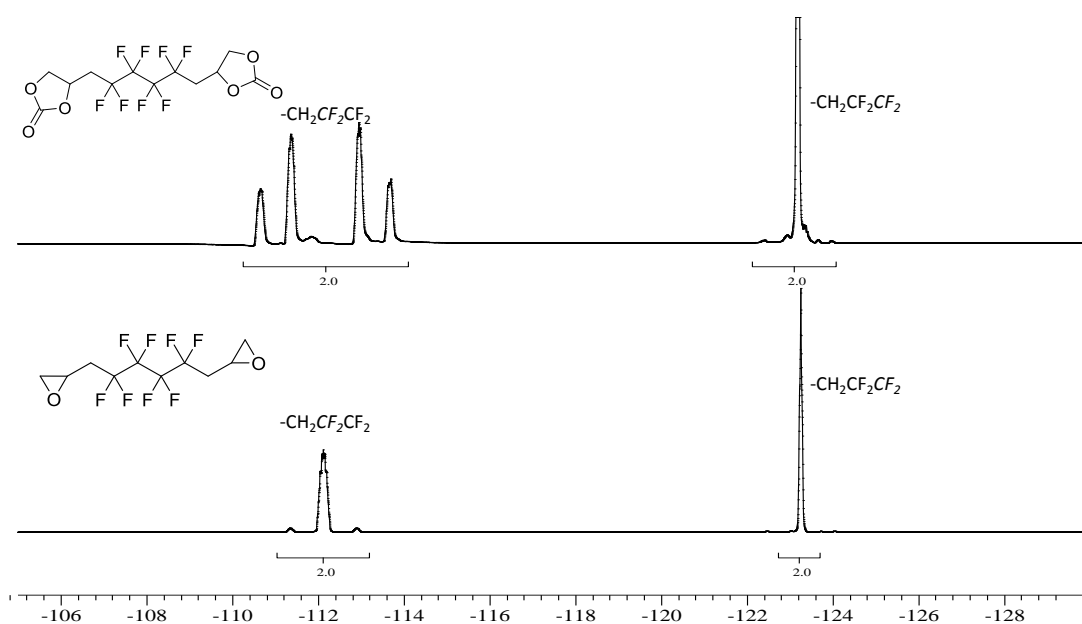


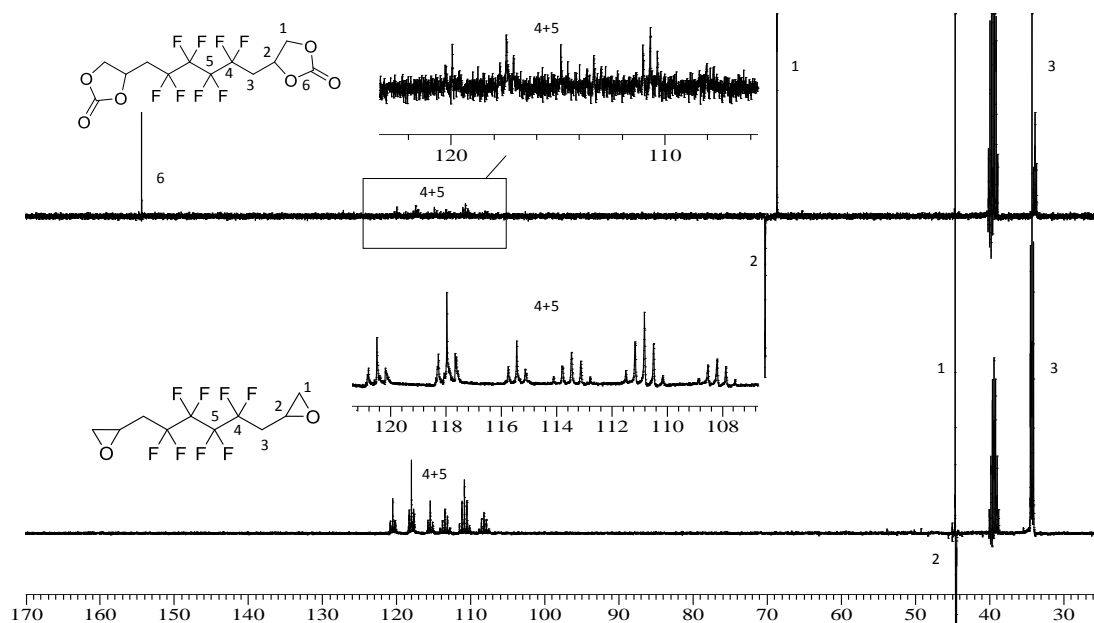
Figure 2. ^1H NMR spectra of BEPFB-CS6 (top spectrum), BEPFB-CC5 (middle spectrum), and BEPFB (bottom spectrum) (DMSO- d_6 , 20 $^\circ\text{C}$, 400 MHz)

The ^{19}F NMR spectrum of BEPFB-CC5 (Figure 3) displays an AB system at -112 ppm assigned to the $\text{CH}_2\text{CF}_\text{A}\text{F}_\text{B}\text{CF}_2$ groups of A and B diastereoisomers. Indeed, the chemical shifts are different because the product is a mixture of two diastereoisomers due to the presence of an asymmetric carbon on the cyclic carbonate. The signals at -123 ppm are assigned to the central difluoromethylene groups ($\text{CH}_2\text{CF}_2\text{CF}_2$). Similar observations were noted on the ^{19}F NMR spectrum of BEPFB-CS6 (Figure S9 in the SI).



160
161
162 **Figure 3.** ^{19}F NMR spectrum of BEPFB-CC5 (upper spectrum) and BEPFB (bottom spectrum) (DMSO- d_6 , 20 °C, 235.2 MHz)

163 BEPFB-CC5 was also characterized by ^{13}C NMR spectroscopy (Figure 4). The result-
164 ing spectrum exhibits the signal of the carbonyl groups of the CC at 154 ppm. As ex-
165 pected, the four CF_2 peaks appear between 106 and 120 ppm. Due to the presence of the
166 carbonyl group, the signal corresponding to the CH groups of the cyclocarbonate is low
167 field shifted to 70 ppm compared to that of the CH in the epoxide that is noted at 44 ppm.
168 Similar results were observed in the ^{13}C NMR spectrum of BEPFB-CS6 (Figure S10 in the
169 SI) except for the resonance of the XA moiety, highlighted at 212 ppm.



170
171
172 **Figure 4.** ^{13}C NMR spectrum of BEPFB-CC5 (upper spectrum) and BEPFB (bottom spectrum) (DMSO, 20 °C, 100.6 MHz)

173

174

3. Materials and Methods

Materials

1,4-bis(2',3'-epoxypropyl)perfluorobutane (BEPFB) was provided by TOSOH Finechemicals Corporation (Shunan, Japan). 2-(trifluoromethyl)oxirane (TFEO) provided by SynQuest (Alachua, Fa, USA). Hexafluoropropene oxide (HFPO), carbon disulfide (CS₂), lithium bromide (LiBr), sodium sulfate (Na₂SO₄), acetone (analytical grade), dichloromethane (DCM, analytical grade), methanol (analytical grade), N,N-dimethylformamide (DMF), 1,4-dioxane and tetrahydrofuran (THF, analytical grade) were purchased from Sigma-Aldrich. The deuterated solvents used in NMR spectroscopy were purchased from Euroiso-top (purity>99.8%).

Characterization

Nuclear Magnetic Resonance (NMR)

The NMR spectra were recorded on a Bruker AC 400 instrument, using deuterated chloroform (CDCl₃), deuterated dimethylsulfoxide (DMSO-d₆), or deuterated acetone (acetone-d₆) as the solvents. Tetramethylsilane (TMS) or trichloromonofluoromethane (CFCl₃) were used as references for ¹H (or ¹⁹F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording ¹H, ¹³C, (or ¹⁹F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 512), and a pulse width of 5 μs for ¹⁹F NMR.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were recorded on a Nicolet 210 FTIR spectrometer. The characteristic absorptions mentioned in the text were strong bands reported in cm⁻¹.

Autoclave operations

The carbonation reactions were performed in Hastelloy Parr autoclave systems (HC 276, 100 mL) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet, and outlet valves. An electronic device regulated and controlled both the stirring and heating of the autoclave. Before reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then conditioned for the reaction with a vacuum of 10⁻² mbar for 40 minutes to remove any trace of oxygen. The liquid and dissolved solid phases were introduced via a funnel. Then, the gases were introduced by double weighing (i.e., the weight difference before and after filling the autoclave with the gas).

Synthetic procedures

Synthesis of 4,4,5-trifluoro-5-(trifluoromethyl)-1,3-dioxolan-2-one (HFPO-CC1)

In a round-bottom flask (100 mL), LiBr (209 mg, 2.4 mmol) was dissolved in acetone (30 mL). The solution was transferred into a reactor via a funnel. The reactor was cooled to -30 °C, and Hexafluoropropene oxide HFPO (8 g, 4.8 mmol) was introduced by double weighing and then CO₂ (4 bar). The reaction was carried out at 50 °C for 15 hrs. Then, a pressure drop (30 bar) was noticed, probably due to the consumption of the HFPO and CO₂. At 35 °C, a rapid increase in temperature to 56 °C is observed, which shows that the reaction is exothermic. During the hour that followed this exothermic event, the pressure decreased from 30 to 12 bar for a temperature maintained at 50 °C. After the reaction, the autoclave was degassed (releasing unreacted HFPO and CO₂), and acetone was evaporated under a vacuum. The remaining crude was dispersed in deionized water (50 mL). The aqueous mixture was extracted three times with dichloromethane (200 mL). The organic phase was dried with Na₂SO₄, filtered, and the dichloromethane evaporated. The final product is a yellow liquid obtained in 81% yield (¹⁹F NMR spectrum, Figure S1 in the SI).

¹⁹F NMR (235.2 MHz, CDCl₃, δ): -135.1, -132.8, -129.8, -122.5 (CF), -87.2, -83.6, -78.2 (CF₂), -81.8 (CF₃).

Synthesis of 4,4,5-trifluoro-5-(trifluoromethyl)-1,3-oxathiolane-2-thione (HFPO-CS2)

In a round-bottom flask (100 mL), LiBr (209 mg, 2.4 mmol) and carbon disulfide (CS₂, 11.00 g, 144 mmol) were dissolved in acetone (30 mL). The solution was transferred into a reactor via a funnel. The reactor was cooled to -30 °C, and HFPO (8 g, 481 mmol) was introduced by double weighing. The reaction was carried out at 50 °C for 15 hrs. The purification was similar to that used for HFPO-CC1. The product was obtained as a colorless oil with 83% yield (¹⁹F and ¹³C NMR spectra, Figures S2 and S3 in the SI).

¹⁹F NMR (235.2 MHz, CDCl₃, δ): -132.8, -130.1, -122.8 (CF), -89.0, -87.4, -83.9, -78.5 (CF), -82.1 (CF₃).

¹³C NMR (100.6 MHz, CDCl₃, δ): 101.9- 108.9 (C-F), -113.6-125.5 (CF₂ and CF₂), 159.1 and 162.5 (C=S).

Synthesis of 4-(trifluoromethyl)-1,3-dioxolan-2-one (TFEO-CC3).

Trifluoroethyleneoxide (15.01 g, 153 mmol) and LiBr (644 mg, 7.7 mmol) were dissolved in DMF (40 mL). The solution was transferred into a reactor, and the atmosphere was replaced with CO₂ (8 bar). The reaction was carried out at 80 °C for 24 hrs. The reactor is degassed after reaction and cooling to release the unreacted CO₂. The crude reaction product was then distilled with a Kugelrohr distillation apparatus. After purification, the product was obtained as a colorless liquid (¹H, and ¹⁹F NMR spectra, Figures S4 and S5 in the SI).

¹H NMR (400.1 MHz, CDCl₃, δ): 4.53 (m, 1H, H_{3a}), 4.68 (m, 1H, H_{3b}), 5.03 (1H, H₂).

¹³C NMR (100.6 MHz, CDCl₃, δ): 31.1 (s, CF₃), 36.2 (s, C_{3a}), 36.3 (s, C_{3b}), 162.4 (s, C₁).

¹⁹F NMR (235.2 MHz, CDCl₃, δ): -80.2 (s, CF₃).

Synthesis of 5-(trifluoromethyl)-1,3-oxathiolane-2-thione (TFEO-CS4)

In a two-neck round-bottom flask (100 mL), trifluoroethyleneoxide (10.2 g, 104.1 mmol) and carbon disulfide (9.0 mL, 104.1 mmol, 1 eq) were introduced at 0 °C with a catalytic amount of LiBr (1.48 g, 17.2 mmol, 16.5 %mol) in THF (50 mL). After 20 min, the reaction was allowed to proceed at room temperature for 12 h. The mixture was then poured into ethyl acetate and washed twice with water. The organic phase was dried over magnesium sulfate before evaporating the solvent under a vacuum to obtain the pure product as a yellowish liquid (¹H and ¹⁹F NMR spectra, Figures S6 and S7 in the SI).

¹H NMR (400.1 MHz, CDCl₃, δ): 3.84 (m, 2H, H₃), 5.34 (1H, H₂).

¹³C NMR (100.6 MHz, CDCl₃, δ): 31.1 (s, CF₃), 36.2 (s, C_{3a}), 36.3 (s, C_{3b}), 162.4 (s, C₁).

¹⁹F NMR (235.2 MHz, CDCl₃, δ): -77.6 (s, CF₃).

Synthesis

4-[2,2,3,3,4,4,5,5-octafluoro-6-(2-oxo-1,3-dioxolan-4-yl)hexyl]-1,3-dioxolan-2-one (BEPFB-CC5)

The procedure was similar as that of the synthesis of HFPO-CC1. 1,4-bis(2',3'-epoxypropyl)perfluorobutane (10.02 g, 31.8 mmol) and LiBr (276 mg, 3.18 mmol) were dissolved in acetone (30 mL). The solution was transferred into a reactor, and the atmosphere was replaced with CO₂ (4 bar). The reaction was carried out at 65 °C for 96 hrs. During the reaction, an increase in the pressure inside the reactor was observed (up to 12 Bar) followed by a decreased pressure from 12 bar to 6 bar for a temperature maintained at 65 °C. After reaction and cooling, the reactor is degassed. The crude product was washed with acetone (100 mL), filtered and evaporated under a vacuum, and led to the desired product. The product was obtained as a white powder (¹H, ¹⁹F, ¹³C NMR spectra, and FTIR spectrum, Figures 2, 3, and 4 and Figure S8 in the SI)

¹H NMR (400.1 MHz, CDCl₃, δ): 2.90 (m, CH₂CF₂, 4H), 4.63 and 4.22 (m, OCH₂, 4H), 5.20 (m, CH, 1H).

¹⁹F NMR (235.2 MHz, CDCl₃, δ): -112.3 (AB system, CH₂CF_AF_BCF₂), -123.2 (s, CH₂CF₂CF₂).

¹³C NMR (100.6 MHz, CDCl₃, δ): 154.4 (C=O), 106.6-120.72 (CF₂), 70.2 (CH), 60.2 (OCH₂), 39.3 (CH₂CF₂).

Synthesis of
4-[2,2,3,3,4,4,5,5-octafluoro-6-(2-thioxo-1,3-oxathiolan-4-yl)hexyl]-1,3-oxathiolane-2-thione (BEPFB-CS6)

A similar procedure as that of the synthesis of HFPO-CS2. LiBr (276 mg, 1.59 mmol), carbon disulfide (7.00 g, 10 mmol) and 1,4-bis(2',3'-epoxypropyl)perfluorobutane (5.03 g, 15 mmol) were dissolved in acetone (30 mL). The solution was introduced into a reactor via a tight funnel. The reaction was carried out at 65 °C for 96 hrs. After opening the reactor, the crude reaction product was washed with dichloromethane (100 mL), filtered, and dried under a vacuum to lead to the desired product. The pure product was obtained quantitatively as a white powder (¹H, ¹⁹F, ¹³C NMR spectra and FTIR spectrum, Figure 2 and Figure S9-S11 in the SI).

¹H NMR (400.1 MHz, CDCl₃, δ): 3.02 (m, CH₂CF₂, 4H), 3.92 and 3.77 (m, OCH₂, 4H), 5.60 (m, CH, 1H).

¹⁹F NMR (235.2 MHz, CDCl₃, δ): -111.9 (AB system, CH₂CF_AF_BCF₂), -124.0 (s, CH₂CF₂CF₂).

¹³C NMR (100.6 MHz, CDCl₃, δ): 212.8 (C=S), 107.5-120.2 (CF₂), 84.6 (CH); 62.0 (OCH₂), 39.1 (CH₂CF₂).

4. Conclusions

In this study, a series of fluorinated epoxides were efficiently carbonated or modified into xanthate in mild conditions. These reactions efficiently led to the desired cyclic carbonates and cyclic xanthates in high yields (81-93 %) at 65 °C catalyzed by LiBr. Such novel carbonates and xanthates (**1-6**) were characterized by ¹H, ¹⁹F, ¹³C NMR, and FTIR spectroscopies. These synthesized carbonates and xanthates may find interesting applications. The bis(cyclocarbonate)s can produce novel fluorinated polyhydroxyurethanes (under progress) or polycarbonates. The cycloxanthates are potential solvents for liquid electrolytes in Lithium-ion batteries [13] and efficient chain transfer agents in controlled radical (co)polymerization of fluorinated monomers [55]. They can be used as precursors for poly(thio)urethane materials *via* ring-opening reaction using primary or secondary amines. These polymers possess thiols analogous to the hydroxyl groups of polyhydroxyurethanes. In addition, this functionality provides an exciting opportunity to prepare functional polymers *via* thiol-ene, thiol-yne or thia-Michael addition.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: ^{19}F NMR spectrum of HFPO-CC1 (1) recorded in CDCl_3 (20 °C, 235.3 MHz); Figure S2: ^{19}F NMR spectrum of HFPO-CS2 (2) and HFPO-CS2' (2') recorded in CDCl_3 (20 °C, 235.3 MHz); Figure S3: ^{13}C NMR spectrum of HFPO-CS2 (2) and HFPO-CS2' (2') recorded in CDCl_3 (20 °C, 100.6 MHz); Figure S4: ^1H NMR spectrum of TFEO-CC3 (3) recorded in CDCl_3 (20 °C, 400.1 MHz); Figure S5: ^{19}F NMR spectrum of TFEO-CC3 (3) recorded in CDCl_3 (20 °C, 235.3 MHz); Figure S6: ^1H NMR spectrum of TFEO-CS4 (4) recorded in CDCl_3 (20 °C, 400 MHz); Figure S7: ^{19}F NMR spectrum of TFEO-CS4 (4) recorded in CDCl_3 (20 °C, 235.3 MHz); Figure S8: FTIR spectrum of BEPFB-CC5 (5); Figure S9: ^{19}F NMR spectrum of BEPFB-CS6 (6) (upper spectrum) and BEPFB (lower spectrum) recorded in DMSO-d_6 , (20 °C, 235.3 MHz); Figure S10: ^{13}C NMR spectrum of BEPFB-CS6 (6) (upper spectrum) and BEPFB (lower spectrum) recorded in DMSO-d_6 (20 °C, 100.66 MHz); Figure S11: FTIR spectrum of BEPFB-CS6 (6).

Author Contributions: Conceptualization, B.A. and A.A.; methodology, A.A. and B.A.; validation, formal analysis, data curation, visualization, and supervision, B.A., A.A., V.L., S.C., and W.M.; investigation, L.H., B.A., A.A., V.L., S.C., and W.M.; resources, B.A., V.L., and S.C.; writing—original draft preparation, A.A., L.H., and W.M.; writing—review and editing, B.A., A.A., V.L., S.C. and W.M.; project administration, A.A. and B.A.. All authors have read and agreed to the published version of the manuscript.

Funding:

The authors thank CEA for financial support.

Data Availability Statement: Not applicable.

Acknowledgments: The authors are grateful to the Institut de Chimie of the CNRS and Arkema (Colombes and Pierre-Benite, France) for financial support by supplying us with free materials, TOSOH Finechemicals (Shiba, Japan), and SynQuest (Alachua, Fa, USA) that made this research possible. The authors thank Ecole Nationale Supérieure de chimie de Montpellier (ENSCM) and the Université Libanaise (UL) as well as Prof. B. Boutevin (ENSCM), Dr. V. Besse (ENSCM) and Dr. D. Naoufal (UL).

Conflicts of Interest: The authors declare no conflict of interest.

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