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Synthesis of Fluorinated Dialkyl Carbonates from Carbon Dioxide as a Carbonyl Source

Masafumi Sugiyama,^[a] Midori Akiyama,^[a] Kohei Nishiyama,^[b] Takashi Okazoe,^{*[a,c]} and Kyoko Nozaki^{*[a]}

[a] M. Sugiyama, Dr. M. Akiyama, Dr. T. Okazoe, Prof. Dr. K. Nozaki
Department of Chemistry and Biotechnology,
Graduate School of Engineering, The University of Tokyo
7-3-1 Hongo Bunkyo-ku, 113-8656, Tokyo(Japan)
E-mail: nozaki@chembio.t.u-tokyo.ac.jp
t-okazoe@chembio.t.u-tokyo.ac.jp

[b] K. Nishiyama
Department of Chemistry and Biotechnology,
Faculty of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, 113-8656, Tokyo(Japan)

[c] Dr. T. Okazoe
Materials Integration Laboratories,
AGC Inc.
1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-8755 (Japan)

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Abstract: Fluorinated dialkyl carbonates (DACs), which serve as environmentally benign phosgene substitutes, were successfully produced from carbon dioxide either directly or indirectly. Nucleophilic addition of 2,2,2-trifluoroethanol to carbon dioxide and subsequent reaction with 2,2,2-trifluoroethyltriflate (**3a**) afforded bis(2,2,2-trifluoroethyl) carbonate (**1**) in up to 79%. Additionally, carbonate **1** was obtained by the stoichiometric reaction of **3a** and cesium carbonate. Although bis(1,1,1,3,3,3-hexafluoro-2-propyl) carbonate (**4**) was difficult to be obtained by either of the above two methods, it could be synthesized by the transesterification of carbonate **1**.

Introduction

Electrophilic carbonyl sources which are composed of a carbonyl moiety with two leaving groups are essential reactants in organic chemistry (Figure 1a).^[1] They can be converted to various functional motifs like carbonate, carbamate, and urea, which are valuable in material science and medicinal chemistry. They also serve as a monomer for production of Polycarbonate (PC) by their reaction with bisphenol-A. Phosgene is the most commonly and widely-used electrophilic carbonyl source in industry. In laboratory synthesis, triphosgene, diphosgene, and carbodiimidazole (CDI) are also used as substitutes for highly-toxic phosgene.^[2] Usually, phosgene and its derivatives are so reactive that the desired carbonyl compounds are obtained with extremely high efficiency. For example, the PC obtained from phosgene exhibits very high molecular weight (Mw).^[3] However, there are some drawbacks: the carcinogenic and toxic nature

of phosgene requires great cautions to handle. Triphosgene and CDI are derived from highly toxic reagents such as chlorine or phosgene.^[4]

In this context, organic carbonates would be environmentally benign carbonyl sources because they are less toxic and produced without using harmful compounds. The reactivity of each carbonate depends on the pK_a value of the corresponding alcohol.^[5] Two representative examples are dimethyl carbonate (DMC) and diphenyl carbonate (DPC) (Figure 1b). DMC represents moderate reactivity due to the low acidity of methanol, which allows its usage as a carbonyl source for precise synthesis of small molecules,^[6] while its reactivity is not enough for polymerization with bisphenol-A to produce PC. On the other hand, DPC shows much higher reactivity than DMC owing to the higher acidity of phenol than methanol. Although DPC is too reactive to be used as a carbonyl source for fine chemicals, it is suitable for the synthesis of PC. A part of PC is industrially produced in the Asahi Kasei process, which utilized melt polymerization of bisphenol-A and DPC is carried out.^[7] It is noteworthy that, in this process, DPC is prepared *via* several steps from carbon dioxide (CO₂). Nevertheless, there is a significant disadvantage associated with utilizing DPC as a monomer: Phenol, eliminated along with polymerization of bisphenol-A and DPC, can hardly be removed from the reaction system due to its high boiling point, to shift the equilibrium between the monomers and PC.^[7e] Therefore, the molecular weight of the obtained

polymer is lower than that produced from phosgene. As the molecular weight decreases, melt and solution viscosities of the polymer decrease. Since shock resistance of PC depends on its viscosities, the polymer obtained from DPC is short of shock resistance, which is one of the most important properties of PC.^[8]

Hence, fluorinated carbonates are gathering great attention as environmentally benign alternative carbonyl sources.^[9] Owing to the high electron negativity of fluorine atom, the corresponding fluorinated alcohols show low pK_a values compared to those of non-fluorinated alcohols. In particular, bis(2,2,2-trifluoroethyl) carbonate (**1**) shows the middle reactivity between DPC and DMC, as the order of pK_a of the eliminating alcohols.^[5] It has been known that **1** is able to be converted to carbamate and isocyanate.^[10] Furthermore, Bogolubsky *et al.* and other group reported that **1** was a convenient condensation reagent for the selective synthesis of unsymmetrical ureas,^[5,11] which requires no special care to prevent formation of side products. It is also possible to employ **1** as a monomer for production of polycarbonate because of its high reactivity.^[12] In addition, the boiling point of the 2,2,2-trifluoroethanol is low enough to be removed from the reaction system, which promotes the condensation of bisphenol-A and **1**. Thus, the molecular weight of the obtained PC reaches as high as that of phosgene-derived PC (Figure 1b).

In spite of this potential, most of the reported methods to synthesize **1** still employ phosgene, either directly or generated *in situ*.^[13] Namely, we could not say that **1** is an actual phosgene-free carbonyl source. Recently, several patents on synthesis of **1** from hexachloroacetone^[14] or chloroform^[15] were published. Although these two are promising synthetic methods, we considered that it would be better if **1** is synthesized from carbon dioxide in order to develop a further environmentally friendly synthetic method (Figure 1c).

Carbon dioxide can be also considered as an electrophilic carbonyl source. Since carbon dioxide is low in toxicity, abundant, and inexpensive, the reactions employing carbon dioxide as a raw material have been well developed, and they are excellent synthetic methods from the viewpoint of green chemistry.^[16] For example, synthesis of polycarbonates from carbon dioxide was reported by the alternating copolymerization with epoxides^[17] or condensation polymerization with diols,^[18] although the products are limited to aliphatic ones. As for small molecules, dialkyl carbonates (DACs),^[19] diaryl carbonates,^[20] and aromatic carbamates^[21] can be synthesized directly from carbon dioxide. Here in this

work, we envisaged to synthesize fluorinated DACs directly from carbon dioxide.

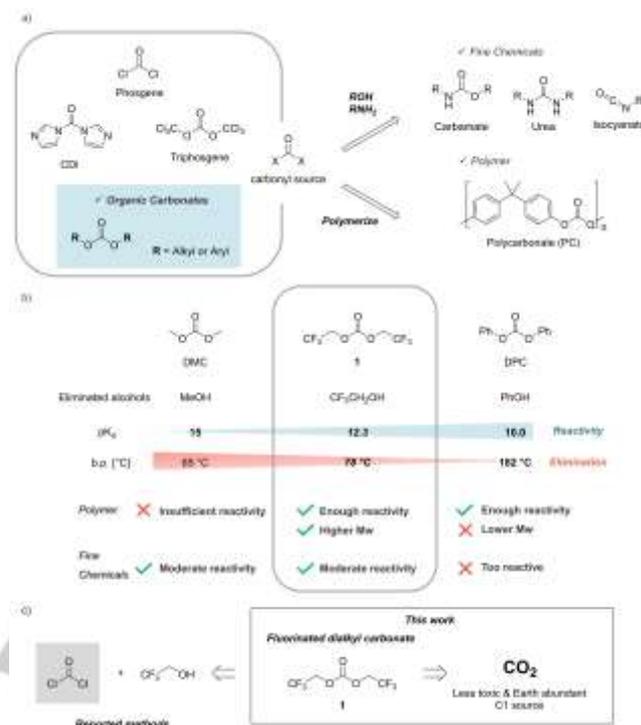


Figure 1. Introduction of fluorinated DACs. a) General usage of carbonyl sources. b) Advantages of fluorinated DACs compared to conventional organic carbonates. c) Previously reported synthetic methods and this work.

Strategy

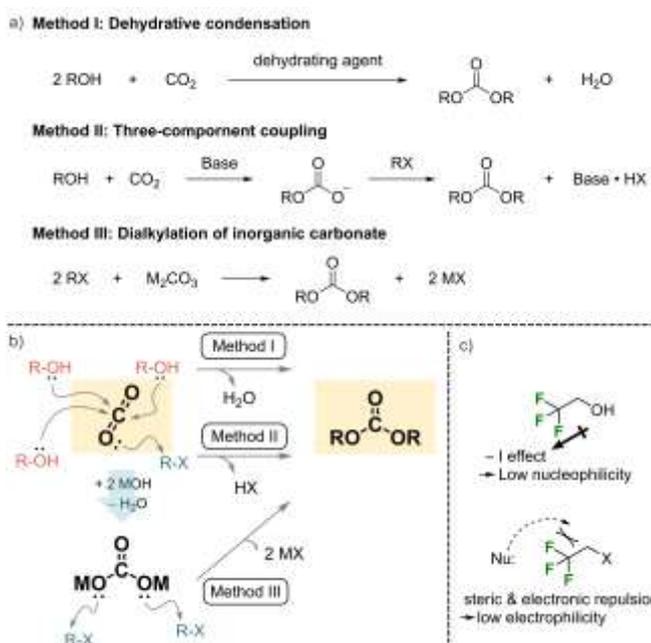
Aiming at the synthesis of fluorinated DAC **1**, we examined three methods I–III referring to the previously reported methods for the synthesis of DACs from CO_2 as shown in Scheme 1a.^[17a,19]

- I) Dehydrative condensation of CO_2 and two molecules of alcohol.^[22]
- II) Three-component coupling of alcohol, CO_2 , and electrophile.^[23]
- III) Dialkylation of inorganic carbonate by electrophile.^[24]

Above three methods are classified by the method for introduction of the two alkyl groups into the target molecules (Scheme 1b). In method I, DACs are obtained by nucleophilic addition of two alcohols to CO_2 and dehydration. Method II is a nucleophilic addition of one alcohol to CO_2 followed by trap of the oxygen anion by one electrophilic alkylating reagent. In method III, both two alkyl groups are introduced through alkylation of the two oxygen anions of an inorganic carbonate. DACs synthesized by method III is also regarded as CO_2 -derived, because inorganic carbonates (M_2CO_3) generate

through the reaction of metal hydroxide (MOH) or metal oxide (M₂O) and CO₂.

Comparing to the previously reported synthesis of non-fluorinated DACs, synthesis of **1** is rather challenging (Scheme 1c): the lower nucleophilicity of 2,2,2-trifluoroethanol (TFEA) due to the high electron negativity of fluorine atom would be problematic in methods I and II. Furthermore, alkylation by nucleophilic substitution at an alpha position of the trifluoromethyl group may be also problematic in methods II and III due to the steric and electronic repulsion between nucleophile and fluorine.^[25] In this study, we found that **1** could be synthesized from CO₂ in a high yield by each of method II and III when using 2,2,2-trifluoroethyl triflate, which is a strong electrophile.



Scheme 1. Strategy for the synthesis of bis(2,2,2-trifluoroethyl) carbonate (**1**) from carbon dioxide as a carbonyl source. a) Reported methods to synthesize non-fluorinated DAC from carbon dioxide. b) Relationships among three methods. c) Difficulties to introduce a fluorinated alkyl group.

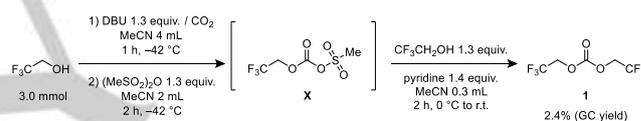
Results and Discussion

Synthesis of Bis(2,2,2-trifluoroethyl) Carbonate (**1**)

Method I: Dehydration condensation

First of all, synthesis of bis(2,2,2-trifluoroethyl) carbonate (**1**) was attempted by dehydration condensation (method I). Various dehydrating agents have been reported to be applicable to the synthesis of DACs from CO₂ and alcohols,^[22] thus we employed two of them for dehydration condensation of 2,2,2-trifluoroethanol (TFEA) and CO₂. When using 2-

cyanopyridine^[22c,d] as a dehydrating agent, the desired reaction hardly proceeded (see Supporting Information). This was probably due to the lower nucleophilicity of TFEA comparing to that of non-fluorinated alkyl alcohol. Another trial of the reaction of TFEA and CO₂ in the presence of methanesulfonic anhydride as a dehydrating agent afforded a trace amount of **1**. According to the known procedure for synthesis of phenyl 1-propyl carbonate from phenol and propan-1-ol,^[26] we mixed TFEA, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), CO₂, and methanesulfonyl anhydride in acetonitrile at -42 °C. For the reaction of propan-1-ol with methanesulfonyl anhydride under CO₂ pressure, formation of sulfonyl carbonate of propan-1-ol was confirmed by ¹H NMR analysis. Analogously, we assume sulfonyl carbonate intermediate **X** likely existed at this stage. Further addition of TFEA and pyridine to the mixture gave compound **1**, detected by GC in 2.4% yield from total TFEA (scheme 2). We concluded that it was difficult to obtain **1** in a sufficient yield by dehydration condensation even with a strong dehydrating reagent like methanesulfonyl anhydride.



Scheme 2. Dehydrative condensation (Method I)

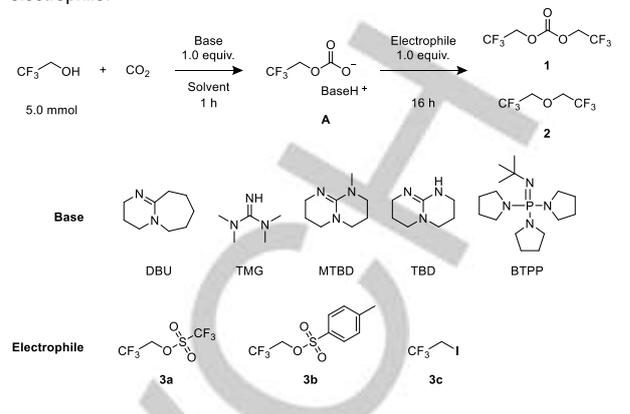
Method II: Three-component coupling reaction

Secondly, three-component coupling reaction of TFEA, CO₂ and electrophile was investigated (method II). Equimolar amount of TFEA and DBU were mixed in a 20 mL Schlenk flask, and then atmospheric pressure of CO₂ was introduced into the vessel. The reaction mixture was homogeneous ionic liquid. Under a similar reaction condition, Liu *et al.* confirmed the formation of TFEA-CO₂ adduct **A** is plausible.^[27] After stirring the mixture at 0 °C for 1 h, 2,2,2-trifluoroethyl triflate (**3a**) was added to the mixture and the mixture was stirred for further 16 h at 0 °C to provide the desired compound **1** in 51% (Table 1, entry 1). The yield of **1** was estimated by ¹⁹F NMR analysis. When the reaction was conducted at higher temperature, the yield of **1** decreased and that of bis(2,2,2-trifluoroethyl) ether (**2**) increased (entry 2). When the pressure of CO₂ was increased to 4.5 MPa, the generation of side products was suppressed (entry 3, see Supporting Information). Next, a suitable base for this reaction was surveyed (entry 4–9). With 1,1,3,3-tetramethylguanidine (TMG), both the yield of **1** and the conversion of **3a** were lower than those with DBU (entry 4). When 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) was

used, the yield of **1** was almost the same as that with DBU (entry 5). Moreover, the side product possibly resulted from the reaction of the base and the electrophile hardly generated (see Supporting information). With 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or phosphazene base P₁-*t*-Bu-tris(tetramethylene) (BTTP), the yield of **1** decreased, which was probably because they did not mix with TFEA (entry 6,7). When inorganic base was employed in the absence of solvent, the base was insoluble in TFEA and the desired compound was not obtained (entry 8,9). The use of DMF as a solvent solved the solubility problem so that Cs₂CO₃ gave the highest yield (79%) among the bases examined in this study (entry 10). Electrophiles were also investigated, but no reaction occurred with either 2,2,2-trifluoroethyl tosylate (**3b**) or 1,1,1-trifluoro-2-iodoethane (**3c**) (entry 11,12). Although alkyl iodides and alkyl tosylates are generally used as good electrophilic alkylating reagents, their electrophilicities were not sufficient in this case.^[28] Nucleophilic substitution at alpha position of the trifluoromethyl group is known to be difficult due to the steric and electronic repulsion between lone pairs of fluorine atoms and nucleophiles, and thus, a strong electrophile like **3a** was required for this reaction.^[25a] Finally, the large scale synthesis and isolation of compound **1** was accomplished in 27% yield (entry 13). Although the yield of **1** was not so high, solvent-free procedures (Entry 3,13) were better than the others in the viewpoint of greenness and sustainability.

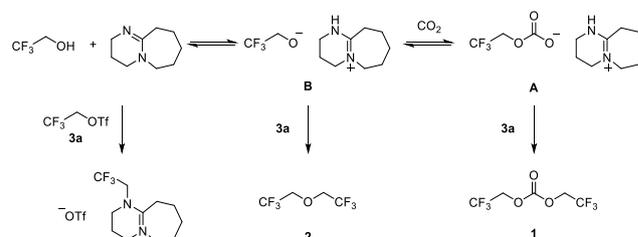
A plausible reaction mechanism is shown in **Scheme 3**. First, deprotonation of TFEA proceeds and the ion pair **B** generates. This equilibrium is considered to shift toward ion pair **B** with stronger organic bases. This nicely explains why **1** was obtained in higher yield with DBU ($pK_{BH} = 24.2$ in MeCN) or MTBD ($pK_{BH} = 25.5$ in MeCN) than with TMG ($pK_{BH} = 20.8$ in MeCN).^[29] Afterward, TFEA-CO₂ adduct **A** generates by nucleophilic addition of **B** to CO₂ (confirmed by *in situ* IR).^[27] In the last step, **A** reacts with **3a** to afford **1**. On the other hand, ether **2** is formed if **B** reacts with **3a**.^[30] Liu *et al.* reported that the reaction between **A** and **B** is reversible: Compound **A** was converted back to **B** either under N₂ bubbling or by heating.^[27] This result is in good agreement with our results that desired compound **1** was selectively obtained over **2** under higher CO₂ pressure at lower temperature.

Table 1. Optimization of the reaction condition for the synthesis of bis(2,2,2-trifluoroethyl) carbonate (**1**) from TFEA, carbon dioxide and electrophile.



Entry	Base	Electrophile	Solv.	Conv. (%) ^[a]	Yield (%) ^[d]	
					1	2
1 ^[a,e]	DBU	CF ₃ CH ₂ OTf	None	63	51	1.0
2 ^[b,e]	DBU	CF ₃ CH ₂ OTf	None	100	11	40
3 ^[c]	DBU	CF ₃ CH ₂ OTf	None	48	44	1.8
4 ^[c]	TMG	CF ₃ CH ₂ OTf	None	13	10	0
5 ^[c]	MTBD	CF ₃ CH ₂ OTf	None	69	52	0
6 ^[c]	TBD	CF ₃ CH ₂ OTf	None	32	1.1	0
7 ^[c,e]	BTTP	CF ₃ CH ₂ OTf	None	69	30	0
8 ^[c]	NaH	CF ₃ CH ₂ OTf	None	0	0	0
9 ^[c]	Cs ₂ CO ₃	CF ₃ CH ₂ OTf	None	0	0	0
10 ^[c]	Cs ₂ CO ₃	CF ₃ CH ₂ OTf	DMF	86	79	0
11 ^[c]	Cs ₂ CO ₃	CF ₃ CH ₂ I	DMF	0	0	0
12 ^[c]	Cs ₂ CO ₃	CF ₃ CH ₂ OTs	DMF	0	0	0
13 ^[f]	DBU	CF ₃ CH ₂ OTf	None	n.d.	27 ^[g]	n.d.

[a] 0 °C, 0.1 MPa [b] 50 °C, 0.1 MPa [c] 0 °C, 4.5 MPa [d] Based on electrophile, determined by ¹H and ¹⁹F NMR, except for entry 13. [e] 1.0 mmol of TFEA, DBU, and **3a** was used. [f] 43.1 mmol of TFEA, DBU, and **3a** was used. [g] isolated yield.



Scheme 3. Plausible reaction mechanism of three-component coupling with DBU as a base.

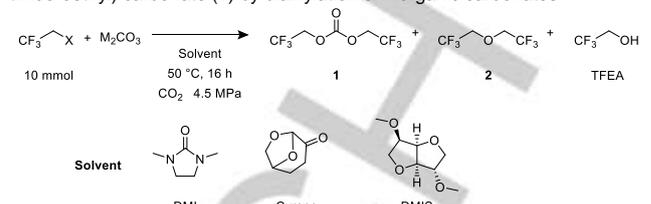
Method III: Dialkylation of inorganic carbonate

Subsequently to the three-component coupling (method II, Scheme 1a) described above, another method to synthesize **1**

was investigated: dialkylation of inorganic carbonate. First, 10 mmol of 2,2,2-trifluoroethyl triflate (**3a**) and Cs₂CO₃ (0.5 equiv.) were mixed under 4.5 MPa of CO₂ pressure in various solvents (Table 2, entry 1–3). After stirred for 16 h at 50 °C, the reaction mixture was analyzed by ¹H and ¹⁹F NMR spectroscopy. When the reaction was conducted in *N,N*-dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO), which are commonly used aprotic polar solvents, the desired compound **1** was observed together with side products **2** and TFEA (entry 1,2).^[24a] With 1,3-dimethyl-2-imidazolidinone (DMI), **1** was observed in a moderate yield (54%) and good selectivity of **1** (entry 3). In addition to the typical polar solvents above-mentioned, biodegradable sugar-derived polar solvents like Cyrene™ and dimethyl isosorbide (DMIS) were investigated (entry 4,5). Unfortunately, **1** was not obtained with either two solvents due to the low solubility of Cs₂CO₃.

Next, alkylating agents were examined (entry 6,7). Same as the result mentioned in Table 1, no reaction took place with 1,1,1-trifluoro-2-iodoethane (**3c**) or 2,2,2-trifluoroethyl tosylate (**3b**) (entry 6,7). By increasing the amount of Cs₂CO₃ (1.0 equiv.), the yield of **1** increased (entry 8). Inorganic carbonates with different metals were also investigated (entry 9,10). Even when using less expensive alkaline metal carbonates compared to Cs₂CO₃, **1** was observed although the yield and the selectivity decreased. In the previous studies on the synthesis of non-fluorinated DACs, the higher yield with Cs₂CO₃ than with Na₂CO₃ or K₂CO₃ was also reported and it was explained by the order of nucleophilicity of each metal carbonate,^[24b] which is known to increase as the radius of its counter cation becomes larger. From these observations, the reaction in the presence of 1 eq. of 18-crown-6 ether was also attempted, however the yield of **1** decreased and significant amount of TFEA generated (entry 11).

Table 2. Optimization of the reaction condition for the synthesis of bis(2,2,2-trifluoroethyl) carbonate (**1**) by dialkylation of inorganic carbonates.



Entry	M ₂ CO ₃ (equiv.)	X	Solv.	Conv. (%) ^[a]	Yield (%) ^[a]		
					1	2	TFEA
1	Cs ₂ CO ₃ (0.5)	OTf	DMF	72	36	Trace	11
2	Cs ₂ CO ₃ (0.5)	OTf	DMSO	100	14	3.5	68
3	Cs ₂ CO ₃ (0.5)	OTf	DMI	58	54	2.5	0.6
4	Cs ₂ CO ₃ (0.5)	OTf	Cyrene™	47	0	Trace	1.3
5	Cs ₂ CO ₃ (0.5)	OTf	DMIS	10	0	0	Trace
6	Cs ₂ CO ₃ (0.5)	I	DMI	0	0	0	0
7	Cs ₂ CO ₃ (0.5)	OTs	DMI	0	0	0	0
8	Cs ₂ CO ₃ (1.0)	OTf	DMI	81	77	0	0.9
9	K ₂ CO ₃ (1.0)	OTf	DMI	44	34	0	0.8
10	Na ₂ CO ₃ (1.0)	OTf	DMI	29	11	0	9.5
11 ^[b]	Cs ₂ CO ₃ (1.0)	OTf	DMI	100	43	0	40

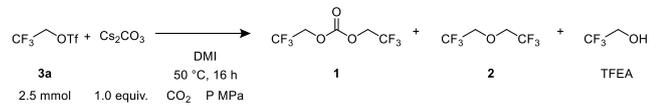
[a] Based on electrophile, determined by ¹H and ¹⁹F NMR. [b] 1.0 equiv. of 18-crown-6 ether was added.

The effect of CO₂ pressure was examined (Table 3). In the absence of CO₂, no desired compound was observed and instead, ether **2** and TFEA generated (Table 3, entry 1). When the reaction was conducted under 0.1 MPa pressure of CO₂, **1** was obtained in 55% (entry 2). By increasing the pressure of CO₂, the selectivity of carbonate **1** was improved at the expense of the conversion (entry 2–4).

A plausible reaction mechanism is shown in scheme 4. First, the reaction of one molecule of inorganic carbonate and trifluoroethyl triflate **3a** affords TFEA–CO₂ adduct **A'**, which then reacts with **3a** to give **1**. Meanwhile, if **A'** and **B'** are under equilibrium, alkoxide **B'** resulting from decarboxylation of **A'**

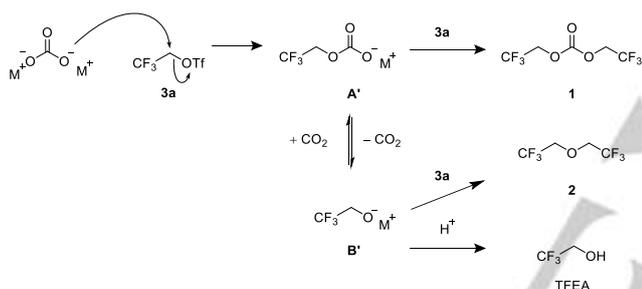
reacts with **3a** to give ether **2**. Protonation of **B'** by acidic work-up affords TFEA. Under the higher CO₂ pressure, the equilibrium shifts from **B'** to **A'** to cause the higher selectivity.

Table 3. Investigation of the effect of temperature and CO₂ pressure with cesium carbonate.



Entry	P (MPa)	Conv. (%) ^[a]	Yield (%) ^[a]		
			1	2	TFEA
1 ^[b]	0	100	Trace	34	40
2 ^[c]	0.1	100	55	1.8	26
3	1.0	95	69	0	18
4	3.0	74	66	0	11

[a] Based on electrophile, determined by ¹H and ¹⁹F NMR. [b] 7 h [c] 6 h



Scheme 4. Plausible reaction mechanism of dialkylation of inorganic carbonate (Method III)

Synthesis of Bis(1,1,1,3,3,3-hexafluoro-2-propyl) Carbonate (**4**)

Method II and III, by those **1** was successfully provided, were next applied to synthesizing bis(1,1,1,3,3,3-hexafluoro-2-propyl) carbonate (**4**). It was reported that Polycarbonate (PC) with much higher molecular weight was obtained from **4**^[31] and bisphenol-A when compared to other less toxic phosgene substitutes such as **1**^[12] or diphenyl carbonate (DPC)^[7] (Figure 2). This is because the eliminating 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) possesses higher acidity than TFEA and lower boiling point than phenol. Thus, we aimed at synthesis of **4** from CO₂.^[32] It is notable that the introduction of a hexafluoro-2-propyl moiety is considered to be far more challenging than that of a trifluoroethyl group due to the low nucleophilicity of HFIP and bulkiness of the hexafluoro-2-propyl group.

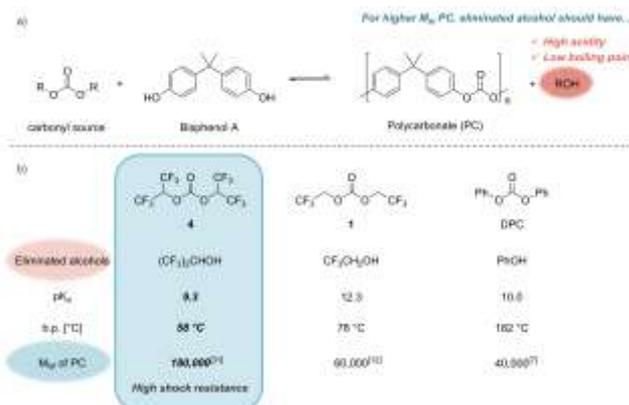
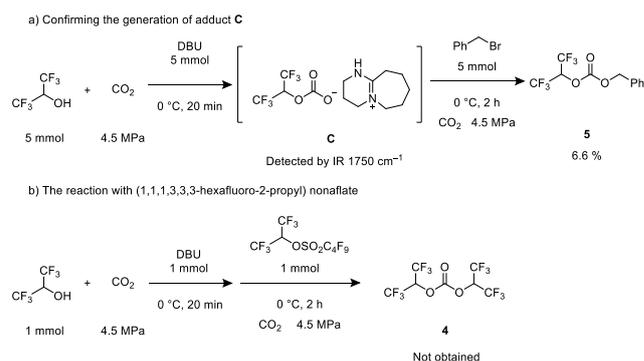


Figure 2. Advantage of bis(1,1,1,3,3,3-hexafluoro-2-propyl) carbonate (**4**) for polymerization. a) The general method to synthesize Polycarbonate (PC). b) Advantages of carbonate **4** compared to other organic carbonates.

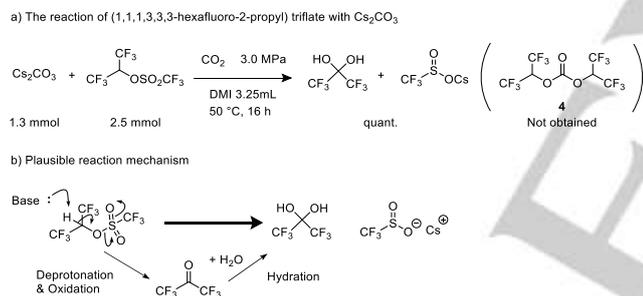
Method II and III

At first, method II was investigated (Scheme 5). Equimolar amount of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and DBU were mixed in a 50 mL autoclave. CO₂ gas was introduced into the vessel at 4.5 MPa and stirred at 0 °C for 20 min. Monitoring this reaction by *in situ* IR, a new peak at 1750 cm⁻¹ was observed after introduction of CO₂, which is assignable to the C=O stretching of HFIP-CO₂ adduct **C** (see Supporting Information). Thus, the mixture was treated with benzyl bromide in order to convert **C** to an isolable form. As expected, the reaction afforded carbonate **5**, which strongly indicates the generation of **C** (Scheme 5a). Notably, HFIP is one of the most acidic alcohols ($pK_a = 9.3$ in water)^[33a] due to the negative induction effect of the six fluorine atoms, and addition of HFIP to CO₂ has never been reported so far. Despite the formation of **C**, the desired compound **4** was not obtained by adding 1,1,1,3,3,3-hexafluoro-2-propyl nonaflate as an alkylating reagent to the reaction mixture (Scheme 5b). The lower reactivity of 1,1,1,3,3,3-hexafluoro-2-propyl nonaflate can be attributed to the steric and electronic repulsion between the hexafluoro-2-propyl moiety and the nucleophile. Actually, nucleophilic substitution with electrophiles bearing a hexafluoro-2-propyl group are limited to a few examples.^[34]



Scheme 5. Three-component coupling (Method II)

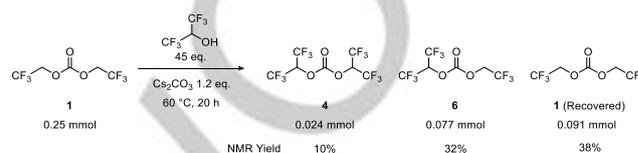
In order to accelerate the difficult nucleophilic substitution step, that is the reaction of **C** with the electrophile bearing a hexafluoro-2-propyl moiety, we thought of elevating the reaction temperature. For this purpose, method III is more favorable since the reaction could be conducted at higher temperature than method II in the synthesis of **1** (*vide supra*). Thus, Cs₂CO₃ (1.3 mmol) and 1,1,1,3,3,3-hexafluoro-2-propyl triflate (2.5 mmol) were mixed under 3.0 MPa of CO₂ pressure in DMI. After stirred for 16 h at 50 °C, the reaction mixture was analyzed by ¹H and ¹⁹F NMR spectroscopy. As a result, instead of the desired compound **4**, hydrated hexafluoroacetone and cesium trifluoromethane sulfinate were obtained quantitatively (Scheme 6a). This result can be explained by the mechanism shown in Scheme 6b. The proton of 1,1,1,3,3,3-hexafluoro-2-propyl triflate is predicted to be highly acidic because it is next to three electron withdrawing groups: two trifluoromethyl groups and a triflate moiety. This acidic proton can be abstracted by Cs₂CO₃ to cause reduction of the sulfur atom affording hydrated hexafluoroacetone and cesium trifluoromethane sulfinate.

**Scheme 6.** Dialkylation of inorganic carbonate (Method III)**Method IV**

Because it was difficult to obtain carbonate **4** either by method II or III, we tried another method to synthesize **4**: transesterification of organic carbonate synthesized from carbon dioxide. This transesterification strategy has been employed in the industrial production of diphenyl carbonate from DAC with phenol (pKa 10.0^[35]) as a nucleophile. We envisioned that even HFIP (pKa 9.3) could be introduced into carbonate by this method. As mentioned above, fluorinated carbonate **1** was successfully synthesized using CO₂ as a carbonyl source. Accordingly, conversion of **1** to **4** can be considered as an indirect synthesis of **4** from CO₂ as a carbonyl source.

In the reaction of **1** and HFIP (45 equiv.) in the presence of Cs₂CO₃ (1.2 equiv.), existence of **4** (10% yield), **6** (32% yield), and remaining **1** (38%) were confirmed by ¹⁹F NMR analysis of

the mixture (Scheme 7). Because there are sufficient temperature differences between boiling points of each carbonate (**4** : 97 °C,^[36] **1** : 118 °C^[37]), it is theoretically possible to isolate **4**. Actually, distillation of the resulting mixture afforded fractions with different composition ratio. Although it was difficult to isolate **4** from the crude mixture by simple distillation in a laboratory scale, **4** is assumed to be isolated by multistage distillation (see Supporting Information for the details, such as time course plot, fractional distillation, and control experiments).

**Scheme 7.** Transesterification (Method IV)**Conclusion**

In summary, we achieved the synthesis of fluorinated DACs **1** and **4** from CO₂ either directly or indirectly. Among all of the methods we reported in this literature, three-component coupling reaction using DBU (Table 1 entry 1–3, 13) was considered to be the best procedure in the viewpoint of green and sustainable chemistry. This is because the procedure is solvent-free and scalable, moreover isolation of **1** has been accomplished. However there still exists several issues to be resolved.

- 1) For environmentally benign synthesis, it is more desirable to use a non-chlorine derived compound. In our procedure, 2,2,2-trifluoroethyl triflate (**3a**) was prepared from trifluoromethanesulfonyl chloride. In order to prevent using chlorine-derived chemicals, **3a** should be produced from chlorine-free trifluoromethanesulfonic anhydride instead.^[38a] Actually, we also confirmed that **3a** could be synthesized by using trifluoromethanesulfonic anhydride. Commercially available HFIP is produced from hexachloroacetone, thus a chlorine-free production method is more preferable, which has already been reported.^[33b,c] (See Supporting Information, Scheme S3 for further discussion on the greenness and sustainability of the whole process).
- 2) The wastes generated through the process are also problematic. Particularly, if the triflate salt of DBU could be separated and reused, our method would be much better in terms of atom-economy.

Although these issues should be resolved for future improvement, the reported synthesis of fluorinated DACs from

CO₂ potentially lead to green and sustainable process for production of PC and fine chemicals.

Experimental Section

General

All manipulations were carried out using standard Schlenk techniques under N₂ purified by passing through a dry column (DC-L4, NIKKA SEIKO CO., LTD.) and a gas clean column (GC-RX, NIKKA SEIKO CO., LTD.).

Instrumentation

NMR spectra were recorded on JEOL JNM-ECZ400 (¹H: 400 MHz, ¹³C: 101 MHz, ¹⁹F: 376 MHz). ¹H NMR analyses were performed in chloroform-*d* with the number of FID's collected per sample of 8–128. Chemical shift values for protons are referenced to the residual proton resonance of chloroform-*d* (δ 7.26). ¹³C NMR analyses were performed in chloroform-*d* with the number of FID's collected per sample of 1024–2048. Chemical shift values for carbons are referenced to the carbon resonance of chloroform-*d* (δ 77.16). ¹⁹F NMR analyses were performed with the number of FID's collected per sample of 16–60. Chemical shift values for fluorine are referenced to the carbon resonance of α,α-trifluorotoluene (δ –63.20). High-resolution mass (HRMS) spectra were taken on a JEOL JMS-T100LP mass spectrometer with the electron spray ionization time-of-flight (ESI-TOF) method. GC analysis was performed by Agilent Technologies 7890B equipped with DB-1301 capillary column (0.250 ID, 1.00 μm df, 60 m). GC-TOFMS analysis was performed by Agilent Technologies 7890A equipped with DB-5 capillary column (30 m) and JEOL JMS-T100GC mass spectrometer with electron ionization time-of-flight (EI-TOF) or chemical ionization time-of-flight (CI-TOF) methods. *In situ* IR measurement was performed by using Mettler Toledo ReactIR 45 and analyzed by icIR. Preparative HPLC separation was carried out with a JAI NEXT (Japan Analytical Industry Co. Ltd.) equipped with a GPC column (Japan Analytical Industry Co. Ltd.; JAIGEL-2HR) by eluting with chloroform at room temperature.

Materials

2,2,2-Trifluoroethyl triflate,^[38] 1,1,1,3,3,3-hexafluoro nonaflate^[39] were synthesized following the literature procedures. The authentic sample of bis(1,1,1,3,3,3-hexafluoro-2-propyl) carbonate (**4**) was received from AGC Inc. Carbon dioxide (>99.5 vol%) was purchased from Suzuki Shokan Co., Ltd. and used as received. Cerium Oxide was purchased from Daiichi Kigenso Kagaku Kogyo Co., Ltd. Cyrene™ and DMIS were dried over CaH₂. All other materials were purchased from Kanto Chemical, FUJIFILM Wako Chemical, TCI, Aldrich and used as received.

Procedure for the synthesis of 2,2,2 trifluoroethyl trifluoromethane sulfonate (**3a**)^[38b]

To the solution of 2,2,2-trifluoroethanol (11.7 ml, 163 mmol) and triethylamine (22.8 mL, 163 mmol) in water (150 mL), trifluoromethanesulfonyl chloride (25.0 g, 148 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 8 h, and the lower organic layer was separated. The layer was washed with 1N HCl aq. 3 times and dried over Na₂SO₄ to give the product in 63% (21.7 g, 93.5 mmol). The product **3a** is a known compound and the ¹H and ¹⁹F NMR shifts in CDCl₃ are identical to those given in the following literature. **3a**^[42] ¹H-NMR (400 MHz, CDCl₃) δ 4.71 (q, *J* = 7.3 Hz, 2H); ¹⁹F-NMR (376 MHz, CDCl₃) δ –74.69 (t, *J* = 7.2 Hz, 3F), –74.48 (s, 3F).

Representative procedure for the three-component coupling (Table 1)

Table 1, Entry 3

1,8-Diazabicyclo[5.4.0]undec-7-ene (5.0 mmol) and 2,2,2-trifluoroethanol (5.0 mmol) were added to a 50 mL stainless autoclave filled with nitrogen gas. The vessel was pressurized by CO₂ (4.5 MPa) and stirred at 0 °C for 1 hour. Afterwards, 2,2,2-trifluoroethyl triflate (5.0 mmol) was charged into the mixture and stirred under CO₂ pressure (4.5 MPa) at 0 °C for 16 hours. After CO₂ pressure was leaked, the yield of **1** and **2** and the conversion of **3a** was determined by ¹H and ¹⁹F NMR using benzotrifluoride as internal standard. Bis(2,2,2-trifluoroethyl) carbonate (**1**) was obtained in 44% yield (determined by ¹H and ¹⁹F NMR). Optimization of the reaction condition was carried out by varying the reaction temperature, time, and base (**Entry 1–8**). **1**^[40] ¹H-NMR (400 MHz, CDCl₃) δ 4.58 (q, *J* = 8.0 Hz, 4H); ¹⁹F-NMR (376 MHz, CDCl₃) δ –74.69 (t, *J* = 7.9 Hz, 6F). **2**^[41] ¹H-NMR (400 MHz, CDCl₃) δ 4.00 (q, *J* = 8.0 Hz, 4H); ¹⁹F-NMR (376 MHz, CDCl₃) δ –75.13 (t, *J* = 8.3 Hz, 6F). **3a**^[42] ¹H-NMR (400 MHz, CDCl₃) δ 4.71 (q, *J* = 7.4 Hz, 4H); ¹⁹F-NMR (376 MHz, CDCl₃) δ –74.70 (t, *J* = 7.2 Hz, 3F), –74.48 (s, 3F)

Entry 10

Cesium carbonate (5 mmol), dehydrated *N,N*-dimethylformamide (13 mL), and trifluoroethanol (5 mmol) were added to a 50mL stainless autoclave filled with nitrogen gas. The vessel was pressurized by CO₂ (4.5 MPa) and stirred at 0 °C for 1 hour. Afterwards, 2,2,2-trifluoroethyl triflate (5 mmol) was charged into the mixture and stirred under CO₂ pressure (4.5 MPa) at 0 °C for 16 hours. After CO₂ pressure was leaked, crude mixture was submitted to NMR analysis directly. The yield of **1** and **2** and the conversion of **3a** was determined by ¹⁹F NMR using benzotrifluoride as internal standard. Bis(2,2,2-trifluoroethyl) carbonate (**1**) was obtained in 79% yield (determined by ¹H and ¹⁹F NMR). Optimization of the reaction conditions was carried out by using 1,1,1-trifluoro-2-iodoethane or 2,2,2-trifluoroethyl tosylate instead of 2,2,2-trifluoroethyl triflate (**Entry 11–12**). **1**^[40] ¹⁹F-NMR (376 MHz, DMF) δ –75.10 (t, *J* = 8.6 Hz, 6F). **2**^[41] ¹⁹F-NMR (376 MHz, DMF) δ –75.71 (t, *J* = 9.0 Hz, 6F). **3a**^[42] ¹⁹F-NMR (376 MHz, DMF) δ –75.32 (t, *J* = 8.3 Hz, 3F), –75.94 (s, 3F)

Table 1, Entry 13

1,8-Diazabicyclo[5.4.0]undec-7-ene (43.1 mmol) and 2,2,2-trifluoroethanol (43.1 mmol) were added to a 50 mL stainless autoclave filled with nitrogen gas. The vessel was pressurized by CO₂ (4.5 MPa) and stirred at 0 °C for 1 hour. Afterwards, 2,2,2-trifluoroethyl triflate (43.1 mmol) was charged into the mixture and stirred under CO₂ pressure (4.5 MPa) at 0 °C for 16 hours. After CO₂ pressure was leaked, obtained crude mixture was distilled to separate DBU and its salt. After distillate was decompressed under 40 torr at 20 °C for 5 h to remove low boiling point impurities, bis(2,2,2-trifluoroethyl) carbonate (**1**) was isolated in 27% yield (2.62 g, 11.6 mmol). The product **1** is a known compound and the ¹H and ¹⁹F NMR shifts in CDCl₃ are identical to those given in the following literature. **1**^[40] ¹H-NMR (400 MHz, CDCl₃) δ 4.58 (q, *J* = 8.1 Hz, 4H); ¹⁹F-NMR (376 MHz, CDCl₃) δ -74.68 (t, *J* = 7.9 Hz, 6F).

Representative procedure for dialkylation of inorganic carbonates (Table 2, 3)**Table 2 Entry 3**

Cesium carbonate (5 mmol), 2,2,2-trifluoroethyl triflate (10 mmol) and dehydrated 1,3-dimethyl-2-imidazolidinone (13 mL) were added to a 50mL stainless autoclave filled with nitrogen gas. The vessel was pressurized by CO₂ (4.5 MPa) and stirred at 50 °C for 16 hours. Bis(2,2,2-trifluoroethyl) carbonate (**1**) was obtained in 54% yield (determined by ¹H and ¹⁹F NMR). Optimization of the reaction conditions was carried out by varying the reaction temperature, time, solvent, electrophile, an additive, and inorganic carbonate (**Entry 1–11, Table 3**). **1**^[40] ¹⁹F-NMR (376 MHz, DMI) δ -75.08 (t, *J* = 8.6 Hz, 6F). **2**^[41] ¹⁹F-NMR (376 MHz, DMI) δ -75.72 (t, *J* = 9.0 Hz, 6F). **3a**^[42] ¹⁹F-NMR (376 MHz, DMI) δ -75.32 (t, *J* = 8.3 Hz, 3F), -76.04 (s, 3F)

Procedure for transesterification (Scheme 7.)

A 15 mL glass vial was charged with cesium carbonate (0.25 mmol) and 2,2-bis(4-methylphenyl) hexafluoropropane (0.25 mmol, internal standard). 1,1,1,3,3,3-Hexafluoro-2-propanol (1.17 mL, 45 equiv.), bis(2,2,2-trifluoroethyl) carbonate (**1**) was added to the vial *via* syringe. The reaction mixture was heated at 60 °C (thermostat bath temperature). The resulting crude mixture was submitted to ¹⁹F NMR analysis to determine the yield with an internal standard.

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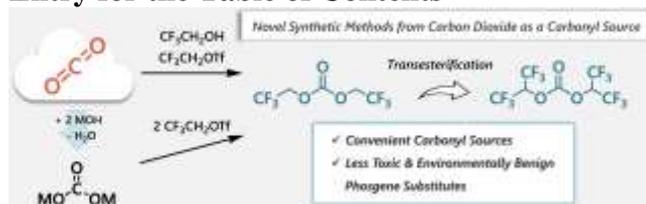
Keywords: Carbon dioxide fixation • Sustainable Chemistry • Phosgene free • Fluorinated carbonate • Polycarbonate

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Entry for the Table of Contents



Fluorinated dialkyl carbonates were successfully produced from carbon dioxide either directly or indirectly. They serve as environmentally benign, less toxic and convenient phosgene substitutes.

Institute and/or researcher Twitter usernames: ((optional))