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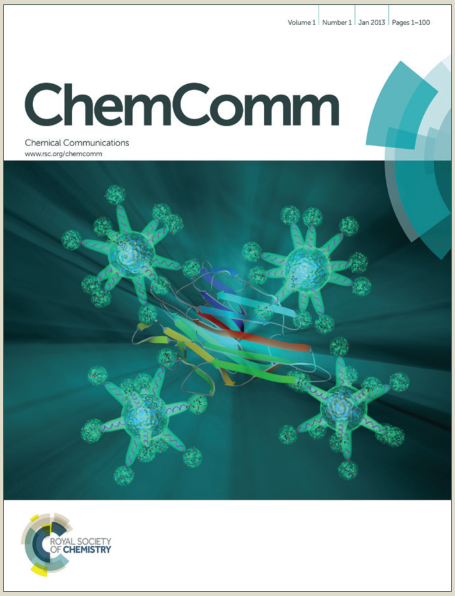

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Reactivity of Carbon Dioxide in Hydrofluoroethers: Facile Access to Cyclic Carbonates

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Marius Mamone, Thierry Milcent, Benoit Crousse*

The high solubility of CO_2 in hydrofluoroethers led to various cyclic carbonates with excellent selectivities and yields. The fluorinated phase increased the amount of CO_2 in contact with the reagents. Reactions could be realized in mild conditions at 80°C under atmospheric pressure or under 5 bar.

Carbon dioxide (CO_2), as the major greenhouse gas, accumulates in the atmosphere at an alarming pace and is suspected to cause global warming over the past several decades.[1] The transformation of CO_2 is limited because of its inherent thermodynamic stability, thus resulting in low reactivity.[2] In this context, the key issue to convert CO_2 into useful chemicals under mild reaction conditions will inevitably rely on its activation. Therefore, there is still a need to search for new types of reactions that are capable of efficiently converting CO_2 under very mild conditions. A reaction which is the most operated, is the synthesis of cyclic carbonates[3] which served as electrolytes in secondary batteries, aprotic polar solvents, monomers of polycarbonates and polyurethanes and raw materials in various chemical reactions.[2,3] Generally these cycloaddition reactions are either carried out under solvent-free conditions, or either under ionic liquid as both solvent and catalyst.[3] The use of classical solvents is not always effective for the reaction between CO_2 and epoxides due to the low solubility of CO_2 in these solvents.[4] However, some solvents reported in the literature by Rabai and Horvath in 1994,[5] are known having the distinction of dissolving a large quantity of gases : the perfluorinated solvents. These solvents which formed a third phase called the “Fluorous Phase” have been largely exploited in organic synthesis due to their specific properties, and in particular to their capacity to solubilise oxygen.[5, 6] However the environmental persistence of perfluocarbons (PFCs) such as perfluorohexane, perfluorocyclohexane, FC-75 for example, detracts from their use on large scale in different reactions. Conversely another family of perfluorinated solvents, less expensive than the PFCs, the hydrofluoroethers (HFEs) bearing both perfluorinated and hydrocarbon segments appeared as excellent substitute of PFCs. The HFEs display a combination of physical properties such as low surface tension, low flammability, and low toxicity. In addition they have a good environmental profile because they are considerably less persistent and have low global warming potential.[7]

While the fluorinated solvents are known to dissolve high quantity of CO_2,[5,8] surprisingly at our knowledge the fluorous phase has never been exploited in the reactivity of carbon dioxide. By against the very high solubility of compounds bearing perfluorinated chains in supercritical CO_2 is well known and reported.[9] Faced with this lack we report here our study on the synthesis of cyclic carbonates from CO_2 gas and epoxides with hydrofluoroethers, HFE-7200 and HFE-7500 (Fig. 1).

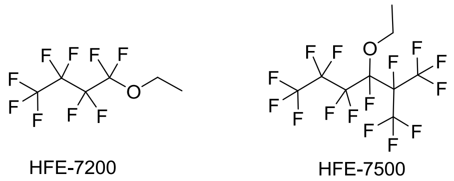

Fig. 1 Formulas of Hydrofluoroethers 7200 and 7500.

First in order to show the efficiency of these perfluorinated solvents and in comparison with other solvents, the cyclic carbonate reaction was performed at room temperature and at 80°C, and under 1 or 5 bar CO_2 in the presence of tetrabutylammonium iodide (TBAI) as catalyst, and the epoxide **1a**. Reactions were performed with vigorous stirring. Results are reported in the Table 1.

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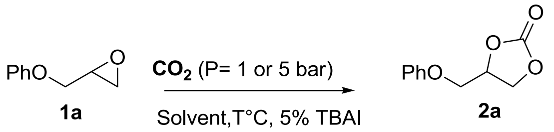
[a] *Univ Paris-Sud, BioCIS, CNRS, Faculté de Pharmacie, LabEx LERMIT, 5 rue J-B. Clément, 92290 Châtenay-Malabry, FRANCE*
E-mail: benoit.crousse@u-psud.fr

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table 1. Cyclic carbonate reaction in HFEs and in organic phase at 1 or 5 bar.



Entry	Solvent	P (bar)	T°C	Time (h)	1a/ 2a[a]
1	HFE-7200	1	rt	24	79/21
2	HFE-7200	5	rt	24	77/23
3	HFE-7200	5	80	5	0/100
4	HFE-7500	1	rt	24	64/36
5	HFE-7500	1	80	24	8/92
6	HFE-7500	5	rt	24	55/45
7	HFE-7500	5	80	3	0/100
8	$CF_3C_6H_5$	1	rt	24	92/8[b]
9	$CF_3C_6H_5$	5	rt	24	91/9[b]
10	$CF_3C_6H_5$	5	80	15	0/100
11	CF_3-C_6H_{11}	1	rt	24	95/5
12	C_6H_{12}	1	rt	24	98/2
13	AcOEt	1	rt	24	98/2
14	Acetone	1	rt	24	98/2
15	MEK	1	rt	24	93/7
16	MEK	5	80	10	0/100
17	HFE-7500/MEK	1	rt	24	90/10
18	neat	1	rt	24	96/4

a. Ratio determined by ^{1}H NMR. b. Presence of side products.

Conventional organic solvents showed a very low efficiency. In benzotrifluoride, partially fluorinated solvent, a very small conversion (8-9%) was observed at room temperature under 1 or 5 bar (entries 8, 9). The conversion is complete when reaction was performed at 80°C under 5 bar after 15h (entry 10). In the CF_3-cyclohexane, only 5% of conversion was observed (entry 11). In classical solvents such as cyclohexane, ethyl acetate, acetone, the conversions after 24h were only of 2% (entries 12-14). In Methyl Ethyl Keton (MEK) which is generally the solvent used for reactions involving carbon dioxide gas[10] led only 7% of cyclic carbonate (rt, 1 bar, entry 15), but the conversion was complete at 80°C under 5 bar after 10h (entry 16). However without exception, all fluorinated solvents shown a better efficiency in the cyclic carbonate reaction with higher conversions after 24h. HFE-7200 and HFE-7500 led to a conversion of 21% and 36% respectively at room temperature at 1 bar (entries 1 and 4). The higher pressure did not improve considerably the conversion (23% for HFE-7200, entry 2 and 45% for HFE-7500, entry 6). The conversion and the reaction time could be upgraded at 80°C (entry 5). The best conditions are obtained under 5 bar at 80°C. Reactions are faster : 5h for HFE-7200 (entry 3), and only 3h for the HFE-7500 (entry 7). No degradation or formation of polymers are observed. The cyclic carbonate **2a** was obtained with an excellent selectivity. From this study, the mixture HFE-7500/MEK (1/1) is not at all effective (entry 17). The contribution of the HFE-7500 properties is lost. In addition, when reaction was performed neat, the conversion was only 4% (entry 18). Furthermore It should be noted that at higher pressure (10, 20, 50 bar), there was no improvement at all.

Recognizing that the epoxide and the catalyst are slightly soluble in the perfluorinated solvents, the reactions were heterogeneous. In this case, the hydrofluoroethers rich in CO_2, could facilitate the delivery of the CO_2 towards the reagents. Furthermore, the heating had to increase the exchange between the reagents and the CO_2 dissolved in the perfluorinated solvent. We can assume that the reaction took place at the interface of the fluorous phase and the medium comprising the epoxide and the TBAI (Fig. 2).

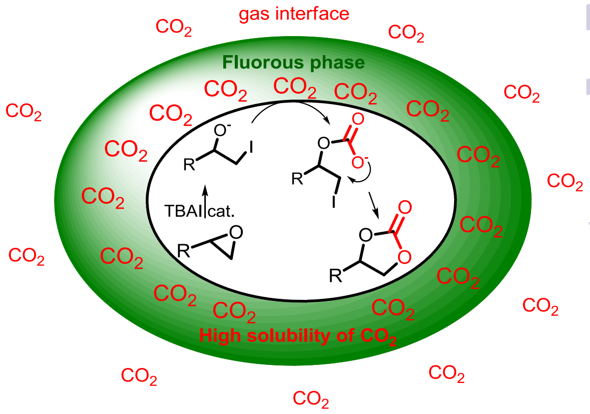
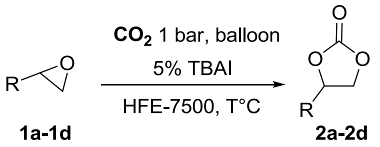


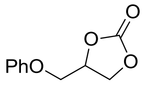
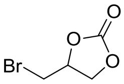
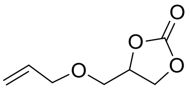
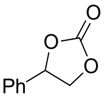
Fig. 2. Reaction at the interface.

We tried to improve the conditions by testing other different catalysts such as tetrabutylammonium bromide (TBAB), KBr, NaI, KI… Only the TBAB is efficient and led to the same result that the TBAI. The other catalysts did not show improvement. In particular with the counterion such as Na and K, a precipitate was observed and the reaction did not occur.

Knowing that very mild conditions (temperature close to room temperature and low pressure) are always required, we first oriented our studies on the previous very mild conditions (table 1, entries 4 and 5 : CO_2 1 bar, rt or 80°C, 5% TBAI, HFE-7500). Results are summarized in the Table 2.

Table2. Cyclic carbonate reaction in HFE-7500.



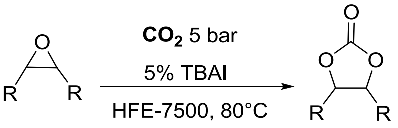
Entry	Carbonate **2**	T°C	Time	**2** select. (yield)[b] %
1	 **2a**	rt	55h	95 (91)
2	**2a**	80	26h	>99 (90)
3	 **2b**	rt	48h	>99 (89)
4	**2b**	80	24h	>99 (91)
5	 **2c**	rt	49h	>99 (92)
6	**2c**	80	21h	>99 (90)
7	 **2d**	rt	24h	20[a]
8	**2d**	80	16h	50[a]

a. % of conversion determined by ^{1}H NMR. b. Isolated yields.

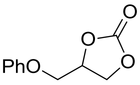
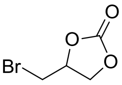
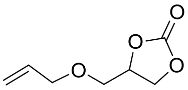
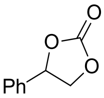
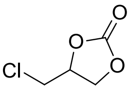
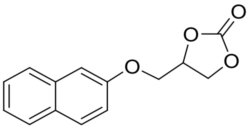
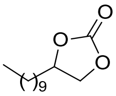
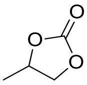
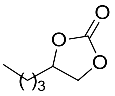
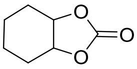
From epoxides **1a**, **1b**, **1c** reasonable to complete conversions are observed into cyclic carbonates at room temperature (entries 1, 3, 5). Reactions required more or less 48-55 h with a complete selectivity. Always under 1 bar but at 80°C, reaction times are shorter (21-26 h, entries 2, 4, 6). Reactions were clean and with a complete conversion and selectivity to carbonates without side products. However for the less reactive epoxide **1d**, conversion are very low at room temperature and at 80°C, 20 and 50% respectively (entries 7, 8). It should be noted that at 80°C the medium is still heterogeneous. Thus the heating must surely increase the exchange between the CO_2 dissolved in the perfluorinated solvent and the reagents.

Furthermore as previously observed (Table 1, entry 7), the reaction time was extremely reduced when reaction was performed at 80°C under 5 bar. This result encouraged us to use these conditions (HFE-7500 / 5 bar / 80°C) for other less reactive epoxides. The different results are reported in the Table 3.

Table 3. Cyclic carbonate reaction under 5 bar at 80°C.



1a-1j **2a-2j**

Entry	Carbonate **2**	Time	**2** select. (yield)[a] %
1	 **2a**	3h	>99 (96)
2	 **2b**	3h	>99 (92)
3	 **2c**	4h	>99 (98)
4	 **2d**	6h	>99 (91)
5	 **2e**	3.5h	>99 (90)
6	 **2f**	5h	>99 (89)
7	 **2g**	5h	>99 (98)
8	 **2h**	6h	>99 (80)
9	 **2i**	7h	>99 (85)
10	 **2j**	10h	9%[b]

a. Isolated yield. b. % conversion determined by ^{1}H NMR.

For epoxides, conversion is complete and the selectivity into cyclic carbonates is superior to 99%. No degradation or formation of polymers are observed. It was demonstrated that terminal epoxides with both electron-donating (entries 1, 3, 4, 6-9) and electron-withdrawing groups (entries 2, 5) could be transformed to the corresponding cyclic carbonates with excellent yields. We then also investigated the use of more challenging internal epoxides. Unfortunately, the cyclic epoxide **1j** was only converted to a low conversion into carbonates (entry 10).

At the end of the reaction, the cyclic carbonates and the HFE-7500 could be easily separated after addition of non miscible solvent such as MeOH for example. In the case of **2a**, **2d** and **2i** which are solid, a simple filtration is required. The cyclic carbonates could be obtained pure after flash chromatography. The HFE-7500 could be recovered and recycled for further reactions.

Conclusions

In summary we demonstrated that the hydrofluoroethers allowed the delivery of the CO_2 towards the reagents and favoured the reaction, in comparison to classical organic solvents. For example these solvents and in particular the HFE-7500 were excellent for the synthesis of cyclic carbonates from epoxides and CO_2. The conditions are very mild for reactive epoxides (1 atm of CO_2/80°C and 5 bar/80°C), and did not required supplementary co-catalyst. The combination Fluorous Phase/Carbon Dioxide in other reactions is under investigation in our laboratory.

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