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Phosgene-free synthesis of symmetric bis(polyfluoroalkyl) carbonates

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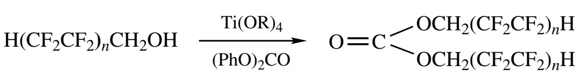
A phosgene-free synthesis of symmetric bis(polyfluoroalkyl) carbonates involves the transesterification of diphenyl carbonate with polyfluoroalkanols promoted by stoichiometric amounts of titanium(IV) alkoxides.



$$H(CF_2CF_2)_nCH_2OH \xrightarrow[(PhO)_2CO]{Ti(OR)_4} O{=}C\begin{matrix}OCH_2(CF_2CF_2)_nH\\OCH_2(CF_2CF_2)_nH\end{matrix}$$

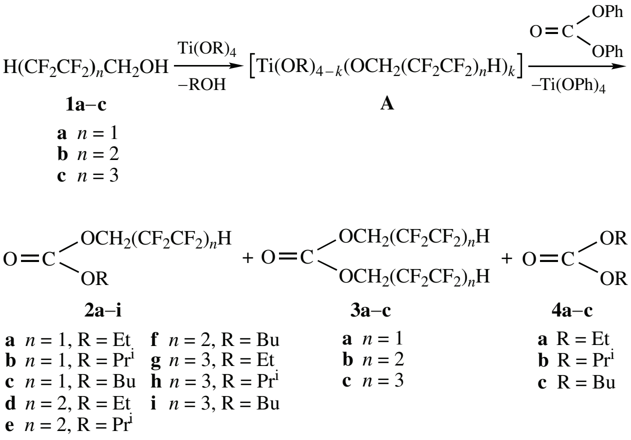
Keywords: transesterification, titanium alkoxides, polyfluoalkanols, dialkyl carbonates, organofluorine compounds.

Incorporation of fluorine atoms or fluorinated functional groups into hydrocarbon-based compounds makes it possible to obtain derivatives with unique physical, biological and chemical properties.[1–3] Fluorine-containing esters of carbonic acid may serve as an example. They are successfully used in modern nanotechnology, chemical industry, power engineering, electronics,[4] in electrolyte components of chemical current sources[5–8] and as starting compounds in the syntheses of polyfluorinated carbamates.[9]

The traditional method for synthesizing dialkyl carbonates, including fluorine-containing ones, is based on the reaction of alcohols with phosgene.[10] The synthesis of polyfluorinated carbonates by the reaction of 2,2,3,3-tetrafluoropropan-1-ol with CCl_4 in the presence of $AlCl_3$ was reported.[11] A method for synthesizing polyfluorinated carbonates in methanol was patented.[12] These procedures involve the use of toxic, explosive and corrosive reagents that produce a harmful detrimental effect on the environment. Importantly, no IR, NMR spectroscopy and elemental analysis data for the products were reported in these sources. In view of this, the transesterification of diphenyl carbonate with alkanols in the presence of amines to give dialkyl carbonates[13] deserves attention. However, this procedure is suitable for the synthesis of only non-fluorinated products. On the other hand, polyfluorinated carbonates were obtained by transesterification of dimethyl carbonate,[14] a modern ‘green’ reagent,[15] with 2,2,3,3-tetrafluoropropan-1-ol, while carbonates containing more than four carbon atoms in a poly-fluoroalkyl substituent could not be similarly accessed.

We have previously described the successful use of stoichiometric amounts of titanium(IV) alkoxides for the synthesis of carbonates based on 2,2,3,3-tetrafluoropropan-1-ol.[16] That process comprised a nucleophilic addition–removal mechanism.[17] In this work, those findings are extended towards a series of other polyfluoroalkanols, and a new phosgene-free synthesis of symmetric polyfluorinated dialkyl carbonates is suggested. Trihydroperfluoroalkyl alcohol telomers **1a–c** (Scheme 1) were subjected to alkyl exchange with titanium(IV) alkoxides to give mixed orthotitanates **A**, which played the roles of both catalysts and reagents. The thus generated *in situ* orthotitanates **A** underwent transesterification with diphenyl carbonate.

The first stage of transesterification results in non-symmetric alkyl polyfluoroalkyl carbonates **2a–i**, which are then converted into the target compounds, *i.e.* symmetric bis(polyfluoroalkyl) carbonates **3a–c**. The secondary products of the process are non-fluorinated dialkyl carbonates **4a–c**, with the overall yield of **2** + **3** + **4** approaching 90% with respect to diphenyl carbonate.† It is important that phenol was never detected among the reaction products due to formation of stable titanium(IV) tetraphenoxide. The ratio between the reaction products was estimated by GLC and ^1H NMR spectroscopy (Table 1).



Scheme 1

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† *Compounds* **3a–c** *(general procedure)*. A mixture of trihydroperfluoroalkyl alcohol **1a–c** (0.439 mol of **1a**, 0.270 mol of **1b**, or 0.175 mol of **1c**) and titanium alkoxide (0.044 mol) was heated to boiling, and the alkanol that formed was distilled off in a mixture with excess **1a–c**. After that, diphenyl carbonate (0.075 mol) was added to the mixed titanium alkoxide **A** formed *in situ*, and the mixture was distilled to collect the mixture of carbonates **2–4**. Individual products were isolated by rectification.

Bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**. Yield 51%. Colourless liquid, bp 181–182 °C, n_D^{20} 1.335. *Bis(2,2,3,3,4,4,5,5-octafluoropentyl) carbonate* **3b**. Yield 64%. Colourless liquid, bp 234–235 °C, n_D^{20} 1.324. *Bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) carbonate* **3c**. Yield 71%. Colourless liquid, bp 300–301 °C, n_D^{20} 1.325. For the spectral and elemental analysis data, see Online Supplementary Materials.

Table 1 Transesterification of diphenyl carbonate with titanium alkoxides.[a]

Entry	Polyfluoro-alkanol	Strating titanate	Product ratio[b]			Total yield[c] (%)
			2	**3**	**4**	
1	**1a**	$Ti(OEt)_4$	40	56	4	78
2	**1a**	$Ti(OPr^i)_4$	22	58	20	88
3	**1a**	$Ti(OBu)_4$	49	0	51	53
4	**1b**	$Ti(OEt)_4$	28	72	0	83
5	**1b**	$Ti(OPr^i)_4$	24	73	3	85
6	**1b**	$Ti(OBu)_4$	40	44	16	60
7	**1c**	$Ti(OEt)_4$	19	81	0	84
8	**1c**	$Ti(OPr^i)_4$	12	83	5	85
9	**1c**	$Ti(OBu)_4$	47	45	8	67

[a] Molar ratios **1**/$Ti(OR)_4$/$(PhO)_2CO$: for **1a**, 10 : 1 : 1.7; for **1b**, 6.15 : 1 : 1.7; for **1c**, 4 :1:1.7. [b] GC data. [c] Calculated with respect to diphenyl carbonate.

The optimal polyfluoroalkanol / titanate / diphenyl carbonate molar ratio for providing the highest yields of products **3a–c** (see Table 1) was determined experimentally. Taking into account that transesterification is an equilibrium reaction, a large excess of 2,2,3,3-tetrafluoropropan-1-ol **1a** with respect to titanates is needed because it forms various azeotropic mixtures with ethanol or isopropanol produced, which reduces its amount in the reaction mixture. The maximum extent of transesterification of $Ti(OR)_4$ with polyfluoroalkanols **1** was observed in cases of R = Et or R = Pr^i (60 and 68%, respectively).[17] In the case of $Ti(OBu)_4$, the extent of transesterification does not exceed 50% since liberating butan-1-ol probably forms azeotropic mixtures with a polyfluoroalkanol, which promotes its removal from the reaction mixture. In particular, even in the case of a large excess of 2,2,3,3-tetrafluoropropan-1-ol **1a** and $Ti(OBu)_4$ the yield of compound **3a** was close to 0% (entry 3) since alcohol **1a** having boiling point (107 °C) lower than that of butan-1-ol (117 °C) is readily distilled off the reaction mixture without giving a transesterification product of type **A**. Varying the **1** / $Ti(OR)_4$ molar ratio and the nature of R (see Table 1) makes it possible to control the selectivity of the formation of alkyl polyfluoroalkyl carbonate **2** or bis(polyfluoroalkyl) carbonate **3**.

To conclude, sequential transesterification of titanium(IV) alkoxides, polyfluoroalkanols and diphenyl carbonate results in mixtures of alkyl polyfluoroalkyl carbonates and bis(polyfluoroalkyl) carbonates, the yields of the latter being 50–80%. This new environmentally friendly synthesis of symmetric polyfluorinated carbonates that are practically useful fluorine-containing compounds seems promising.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.038.

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