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New Synthetic Approach to Polyfluorinated Carbonates

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Abstract—Transesterification of commercial titanium(IV) alkoxides with 2,2,3,3-tetrafluoropropan-1-ol, followed by in situ transesterification of mixed titanium(IV) alkoxides thus formed with diphenyl carbonate, afforded alkyl 2,2,3,3-tetrafluoropropyl carbonates and bis(2,2,3,3-tetrafluoropropyl) carbonate in up to 60% yield. The degree of transesterification decreased in the series $(i\text{-PrO})_4\text{Ti} > (\text{EtO})_4\text{Ti} > (\text{BuO})_4\text{Ti}$ and did not exceed 68%. The selectivity for alkyl 2,2,3,3-tetrafluoropropyl carbonates and bis(2,2,3,3-tetrafluoropropyl) carbonate was found to change depending on the composition of mixed titanium(IV) alkoxide formed in situ.

Keywords: transesterification, titanium alkoxides, tetrafluoropropan-1-ol, dialkyl carbonates

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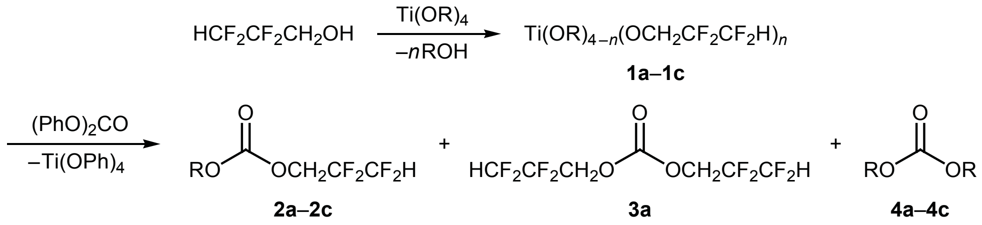
Organic carbonates are among the most promising “green” candidates for replacement of common toxic solvents and fuel additives, as well as for the design of innovative intermediate products in pharmaceutics, lubricants, and polymers [1]. Fluorinated dialkyl carbonates are poorly studied compounds, but they attract interest since introduction of fluorine into organic molecules strongly affects physicochemical properties of the latter [2]. The presence of fluorine atoms in carbonates makes it possible to use them as solvents in electrochemical power sources; fluorinated carbonates have a high dielectric permittivity and a low viscosity in comparison to hydrocarbon analogs, which favor improved solubility of alkali metal salts as electrolyte components. Furthermore, they are characterized by extended operational temperature range [3–6]. Polyfluorinated carbonates are also important as highly reactive intermediate products in the synthesis of other derivatives, e.g., carbamates [7, 8].

Dialkyl carbonates, including fluorinated ones, are traditionally synthesized by reactions of the corresponding alcohols with phosgene [9]. Alternative methods such as reaction of 2,2,3,3-tetrafluoropropan-1-ol with carbon tetrachloride in the presence of AlCl_3 [10] and pyrolysis of ortho esters [11] have also been reported. However, in both cases toxic, explosive, and aggressive reagents are used, which adversely affect the environment. In this connection, the synthesis of polyfluorinated carbonates via transesterification of dimethyl carbonate [12], which is a modern green reagent [13], with 2,2,3,3-tetrafluoropropan-1-ol seems experimentally more efficient since since it requires no specific conditions. It was found that the best catalyst for the synthesis of alkyl 2,2,3,3-tetrafluoropropyl carbonates was tetramethylammonium hydroxide which provided 81% selectivity for methyl 2,2,3,3-tetrafluoropropyl carbonate at 50% conversion of dimethyl carbonate [12]. Titanium tetraethoxide showed a low activity despite the known ability of titanium(IV) alkoxides to catalyze transesterification reactions [14, 15].

Taking into account successful use of stoichiometric amounts of titanium(IV) alkoxides for the synthesis of dialkyl carbonates [16], herein we propose a new phosgene-free synthesis of polyfluorinated dialkyl carbonates via successive transesterifications involving titanium(IV) alkoxides.

We previously described cross-transesterification of propylene carbonate with commercial titanium(IV) alkoxides as an alternative phosgene-free method of synthesis of dialkyl carbonates [16]. Titanium tetrakis(2,2,3,3-tetrafluoropropoxide) has not been reported previously. Therefore, we initially tried to synthesize it by transesterification of commercial Ti(IV) alkoxides with 2,2,3,3-tetrafluoropropan-1-ol (Scheme 1). However, we failed to achieve complete transesterification even with alcohols boiling at a lower temperature than

Scheme 1.



R = Et (**a**), *i*-Pr (**b**), Bu (**c**).

2,2,3,3-tetrafluoropropan-1-ol (Table 1). Analysis of the distillate composition showed that 2,2,3,3-tetrafluoropropan-1-ol was distilled off from the reaction mixture together with the corresponding aliphatic alcohol, so that the degree of transesterification decreased. In the case of titanium tetrabutoxide, there were no reasons to increase the amount of 2,2,3,3-tetrafluoropropan-1-ol.

Mixed titanium(IV) alkoxide **1a**–**1c** formed in situ was treated with diphenyl carbonate (Scheme 1). Propylene carbonate turned out to be effective in transesterification with non-fluorinated titanium(IV) alkoxides [16], but no dialkyl carbonates were formed in its reactions with alkoxides **1a**–**1c**. Presumably, chelating properties of propane-1,2-diol as a weak Brønsted acid do not compensate increased acidity of 2,2,3,3-tetrafluoropropan-1-ol. Phenol is a stronger Brønsted acid than 2,2,3,3-tetrafluoropropan-1-ol and, as follows from our results, is capable of replacing all alcohols in mixed alkoxides **1a**–**1c**. The reactions of **1a**–**1c** with diphenyl carbonate afforded 80–90% of mixtures of three products, alkyl 2,2,3,3-tetrafluoropropyl carbonate **2a**–**2c**, bis(2,2,3,3-tetrafluoropropyl) carbonate (**3a**), and dialkyl carbonate **4a**–**4c**. The product ratio (Table 1) depended not only on the composition of mixed alkoxide **1a**–**1c** but also on the structure of aliphatic alcohol. The overall amount of fluorinated carbonates **2a**–**2c** and **3a** increased in parallel with the degree of transesterification. In the case of ethoxide **1a**, the amount of diethyl carbonate (**4a**) significantly decreased, whereas the amount of diisopropyl carbonate (**4b**) almost did not change. Despite selective formation of butyl 2,2,3,3-tetrafluoropropyl carbonate **2c**, we failed to separate it from dibutyl carbonate (**4c**) by fractional distillation.

Thus, we did not succeed in obtaining tetrakis(2,2,3,3-tetrafluoropropoxy)titanium(IV) by transesterification of titanium(IV) alkoxides with 2,2,3,3-tetrafluoropropan-1-ol. The degree of transesterification decreases in the series $(i\text{-PrO})_4\text{Ti} > (\text{EtO})_4\text{Ti} > (\text{BuO})_4\text{Ti}$, and it does not exceed 68%. Mixed titanium(IV) alkoxides **1a**–**1c** generated in situ demonstrate a high reactivity toward diphenyl carbonate, giving rise to mixtures of dialkyl carbonates. Variation of the ratio of 2,2,3,3-tetrafluoropropan-1-ol and aliphatic alcohol moieties in titanium(IV) alkoxide **1a**–**1b** makes it possible to control the selectivity for alkyl 2,2,3,3-tetrafluoropropyl carbonate and bis(2,2,3,3-tetrafluoropropyl) carbonate.

In summary, we have developed procedures for the synthesis of ethyl 2,2,3,3-tetrafluoropropyl carbonate and bis(2,2,3,3-tetrafluoropropyl) carbonate by transesterification of commercially available titanium(IV) alkoxides with 2,2,3,3-tetrafluoropropan-1-ol, followed by treatment of mixed titanium(IV) alkoxides formed

Table 1. Successive transesterifications of titanium(IV) alkoxides with 2,2,3,3-tetrafluoropropan-1-ol and diphenyl carbonate

R	$HCF_2CF_2CH_2OH–Ti(OR)_4$ molar ratio	Degree of transesterification, %	Product ratio		
			2	**3**	**4**
Et	2:1	30	67	12	21
Et	4:1	47	61	25	14
Et	10:1	60	40	56	4
i-Pr	2:1	43	43	39	18
i-Pr	4:1	52	42	42	16
i-Pr	10:1	68	22	58	20
Bu	2:1	14	40	2	58
Bu	4:1	22	46	0	54
Bu	10:1	25	49	0	51

in situ with diphenyl carbonate. Isopropyl 2,2,3,3-tetrafluoropropyl carbonate and butyl 2,2,3,3-tetrafluoropropyl carbonate could not be isolated from the reaction mixtures. The proposed approach based on successive transesterifications can be regarded as an alternative phosgene-free method of synthesis of dialkyl carbonates, including fluorinated ones.

EXPERIMENTAL

2,2,3,3-Tetrafluoroprpropan-1-ol (98%, manufactured by *GaloPolimer Perm*) and other commercially available reagents (Alfa Aesar) were used without further purification.

The ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in DMSO-d_6 on Bruker Avance-500 and DRX-400 spectrometers. The ^{1}H and ^{19}F NMR chemical shifts were measured relative to tetramethylsilane and hexafluorobenzene, respectively, used as internal standards; the ^{13}C chemical shifts were measured relative to the solvent signal (δ_C 39.5 ppm). The IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 6700 spectrometer with Fourier transform equipped with a diamond ATR accessory. The elemental compositions were determined with a Perkin Elmer 2400 automated CHN analyzer. Chromatographic analyses were carried out on a Shimadzu GC2010 gas chromatograph equipped with a flame ionization detector and a ZB-5 capillary column, 30 m×0.25 mm, film thickness 0.25 μm; carrier gas nitrogen, split ratio 1:30; oven temperature programming from 40°C (3 min) at a rate of 10 deg/min to 280°C (15 min); injector temperature 250°C, detector temperature 300°C.

General procedure for the synthesis of alkyl 2,2,3,3-tetrafluoropropyl carbonates. A mixture of 2,2,3,3-tetrafluoropropan-1-ol (0.38 mol) and tetraethyl or tetraisopropyl titanate (0.19 mol) was heated to the boiling point with simultaneous removal of the liberated alcohol by distillation. Diphenyl carbonate (0.32 mol) was added to the residue, and the mixture was heated to the boiling point while distilling off the resulting carbonates which were then separated by fractional distillation.

General procedure for the synthesis of bis(2,2,3,3-tetrafluoropropyl) carbonate. A mixture of 2,2,3,3-tetrafluoropropan-1-ol (0.95 mol) and tetraethyl or tetraisopropyl titanate (0.095 mol) was heated to the boiling point with simultaneous removal of the liberated alcohol by distillation. Diphenyl carbonate (0.162 mol) was added to the residue, and the mixture was heated to the boiling point while distilling off the resulting carbonates. Bis(2,2,3,3-tetrafluoropropyl) carbonate was isolated from the product mixture by fractional distillation.

Ethyl 2,2,3,3-tetrafluoropropyl carbonate (2a). Yield 58%, colorless liquid, bp 155–156°C, n_D^{20} = 1.340. IR spectrum (KBr), ν, cm^{-1}: 2990 (C–H), 1762 (C=O), 1271 (C–F), 1108 (C–O). ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3, *J* = 7.1 Hz), 4.20 q (2H, $OC\mathbf{H}_2CH_3$, *J* = 7.1 Hz), 4.65 t (2H, OCH_2CF_2, *J* = 14.2 Hz), 6.61 t.t (1H, CF_2H, *J* = 51.8, 5.2 Hz). ^{19}F NMR spectrum, δ_F, ppm: 23.89 d.t (2F, CF_2H, *J* = 51.8, 5.2 Hz), 37.5 t.q (2F, OCH_2CF_2, *J* = 14.2, 5.2 Hz). ^{13}C NMR spectrum (126 MHz), δ_C, ppm: 13.79 (CH_3), 62.38 t ($O\mathbf{C}H_2CF_2$, *J* = 26.8 Hz), 64.78 ($O\mathbf{C}H_2CH_3$), 109.23 t.t (CF_2H, *J* = 248.0, 33.3 Hz), 114.27 t.t ($OCH_2\mathbf{C}F_2$, *J* = 249.4, 26.7 Hz), 153.62 (CO). Found, %: C 35.10; H 3.95; F 37.03. $C_6H_8F_4O_3$. Calculated, %: C 35.31; H 3.95; F 37.23.

Bis(2,2,3,3-tetrafluoropropyl) carbonate (3a). Yield 51%, colorless liquid, bp 181–182°C, n_D^{20} = 1.335. IR spectrum (KBr), ν, cm^{-1}: 2983 (C–H), 1778 (C=O), 1279 (C–F), 1108 (C–O). ^{1}H NMR spectrum, δ, ppm: 4.77 t (2H, OCH_2CF_2, *J* = 14.2 Hz), 6.63 t.t (1H, CF_2H, *J* = 51.8, 5.2 Hz). ^{19}F NMR spectrum, δ_F, ppm: 23.95 d.t (2F, CF_2H, *J* = 51.8, 5.2 Hz), 37.55 t.q (2F, OCH_2CF_2, *J* = 14.2, 5.2 Hz). ^{13}C NMR spectrum (126 MHz), δ_C, ppm: 63.41 t ($O\mathbf{C}H_2CF_2$, *J* = 26.7 Hz), 109.22 t.t (CF_2H, *J* = 248.1, 33.2 Hz), 114.14 t.t ($OCH_2\mathbf{C}F_2$, *J* = 249.7, 26.9 Hz), 152.97 (CO). Found, %: C 28.95; H 2.07; F 52.21. $C_7H_6F_8O_3$. Calculated, %: C 28.98; H 2.08; F 52.39.

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CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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