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> SHORT COMMUNICATIONS =

New Synthesis of Dialkyl Carbonates from Alkylene Carbonates and Titanium Alkoxides

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Dialkyl carbonates are used in industry as organic solvents, fuel additives, lubricants in refrigerating units, and heat carriers. A conventional procedure for the preparation of dialkyl carbonates is based on the reaction of alcohols with phosgene which is very toxic. Phosgene-free syntheses of organic carbonates are extensively developed; they include oxidative carbonylation of alcohols [1, 2], reactions of alcohols with urea [3, 4], reactions of oxiranes with carbon dioxide [5, 6], and reactions of inorganic carbonates with alkyl halides [5] or alcohols [7, 8]. Also, mutual transformations of alkyl carbonates are possible.

We now propose a new phosgene-free synthesis of dialkyl carbonates via reaction of alkylene carbonates with titanium alkoxides. An advantage of the proposed procedure is that it ensures simultaneous preparation of two important products, dialkyl carbonate and alkyl titanate derivative [dialkyl alkanediyl titanate or bis-(alkanediyl) titanate]. The latter can be used as curing agent for epoxy resins or as precursor for the synthesis of nanosized titanium dioxide. The titanium-containing residue can be decomposed by treatment with dilute sulfuric acid to regenerate the diol.

The reactions were carried out with a number of alkyl titanates and alkylene carbonates.





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A mixture of 45.62 g (0.2 mol) of tetraethyl titanate and 40.8 g (0.4 mol) of propylene carbonate was slowly heated and distilled through a column, and a fraction boiling in the range from 120 to 130°C was collected. Yield of diethyl carbonate 40.59 g (86%), $n_{\rm D} = 1.384$ (published data [9]: $n_{\rm D} = 1.384$). Found, %: C 50.84; H 8.45. Calculated, %: C 50.85; H 8.47.

The undistillable residue was partly hydrolyzed bis-(propane-1,2-diyl) titanate. Yield 38.97 g (99%). Found, %: C 36.69; N 6.11; Ti 24.56. Calculated, %: C 36.76; N 6.17; Ti 24.42.

The reaction with equimolar amounts of the reactants was carried out in a similar way using 45.62 g

Synthesis of dialkyl carbonates by transesterification of tetraalkyl titanates with alkylene carbonates

Alkylene carbonate	R in Ti(OR) ₄	n ^a	Yield, %
Propylene carbonate	R = Et	1	77
		2	86
	R = Pr	1	86
		2	87
	R = i-Pr	1	25
		2	2
	R = Bu	1	92
		2	96
Ethylene carbonate		1	48
		2	57
Trimethylene carbonate		1	88
		2	95

^a *n* is the number of moles of alkylene carbonate per mole of tetraalkyl titanate. (0.2 mol) of tetraethyl titanate and 20.4 g (0.2 mol) of propylene carbonate. Yield of diethyl carbonate 18.17 g (77%), $n_D = 1.384$ (1.384 [9]). Found, %: C 50.85; H 8.46. Calculated, %: C 50.85; H 8.47. The undistillable residue was partly hydrolyzed diethyl propan-1,2-diyl titanate. Yield 41.09 g (97%). Found, %: C 38.68; H 7.52; Ti 23.30. Calculated, %: C 39.65; H 7.60; Ti 22.57.

The reactions with tetrapropyl, tetraisopropyl, and tetrabutyl titanates, as well as with ethylene and trimethylene carbonates, were carried out in a similar way. The results are collected in table. Following an analogous procedure, diethyl carbonate can be obtained from tetraethyl titanate and dibutyl carbonate. This is a rare example of the transformation of a higher ester into lower. Any alkyl carbonate may be converted in turn into alkylene carbonate. For this purpose, a catalytic amount of titanium alkoxide is sufficient, though the best catalysts are sodium alkoxides. Such transformation sequence ensures preparation of trimethylene carbonate from diethyl or dimethyl carbonate.

The products were identified by GLC, as well as by refractometry and elemental analysis. The GC/MS identification was performed using an Agilent GC 7890A MSD 5975C inert XL EI/CI instrument (quadrupole mass-selective detector; electron impact, 70 eV). The refractive indices were measured using an IRF-22 refractometer. The elemental compositions were determined using a Perkin Elmer automatic analyzer.

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