

## Review

# Conventional synthesis methods of short-chain dialkylcarbonates and novel production technology via direct route from alcohol and waste CO<sub>2</sub>

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## ABSTRACT

The aim of this work is to review different synthesis methods of dialkylcarbonates with special emphasis on diethyl carbonate synthesis methodologies. The novel synthesis route for dimethyl carbonate and diethyl carbonate based on the utilization of alcohol and carbon dioxide as the raw materials, together with heterogeneous catalysts, is presented.

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## 1. Introduction

Carbon dioxide next to water vapor, methane, nitrous oxide, freons, halocarbons and ozone is one of the most important and prominent greenhouse gases, which could result in a climate change by increasing solar warming of the earth's atmosphere. Combustion of fossil fuels, such as coal, oil and gas in power plants, emissions from transportation and industrial production, are the largest sources of CO<sub>2</sub> emissions globally. The levels of carbon dioxide alone in the atmosphere have risen more than 30% since the Industrial Revolution in the 1700s. Continuous temperature increase on the Earth, caused by increasing levels of CO<sub>2</sub> in the atmosphere might, consequently, result in melting of the arctic ice, increased forest fires, rising sea levels, expansion of deserts, loss of animal habitat, spreading of tropical diseases and more frequent and severe storms. Therefore, it is not surprising, that green processes based on chemical fixation of carbon dioxide have recently attracted much attention in industrial chemistry from the standpoint of the protection of environment. CO<sub>2</sub> is recognized to be a cheap, recyclable and non-toxic carbon source that sometimes can replace toxic chemicals such as phosgene, isocyanates or carbon monoxide [1–4]. In addition, carbon dioxide is also an attractive C1 building block in organic synthesis producing useful organic compounds [5–7]. The industrial synthesis of urea, salicylic acid and methanol already involve carbon dioxide as a reactant. Recently, there has been much effort put on the development of new synthesis methods based on CO<sub>2</sub> as a feedstock for organic carbonates due to their excellent properties and apparent commercial applications [8]. Another reason is that their production is historically dominated by extremely poisonous phosgene chemistry.

Short-chain dialkylcarbonates such as dimethyl carbonate (DMC) or diethyl carbonate (DEC) are gaining popularity as replacements for hazardous chemical reagents or reactive solvents. Longer chain and branched dialkylcarbonates also find extensive use in lubricant, cosmetic, plasticizer, fuel and pharmaceutical compositions. The present interest towards the development of DMC synthesis methods and applications due to its versatility as a reagent and solvent and also its moderate toxicity for human health and environment is witnessed by a growth of literature and patents references, mainly in the most recent years [9,10]. In contrast, literature search on the preparation of DEC points out only a few patents and publications with an increase since the year 2000. Therefore, in this paper the special emphasis is put on DEC synthesis methodologies.

Diethyl carbonate, the second homologue of dialkylcarbonate family is one of the most important green chemicals in carbonate esters also called ethyl carbonate, carbonic acid diethyl ester or Eufin. It is a colorless, transparent liquid under the normal conditions and has a mild toxicology profile [10]. Some properties of DEC are summarized in Table 1.

When released into the environment, DEC will slowly biodegrade to carbon dioxide and ethanol [11–13]—a fact rendering it a significant advantage over other fuel oxygenates such as methyl *tert*-butyl ether (MTBE). DEC, by the presence of two ethyl groups and one carbonyl group in its structure, represents a viable alternative to both ethyl halides and phosgene for ethylation and carbonylation processes. Hence, it has lately attracted much inter-

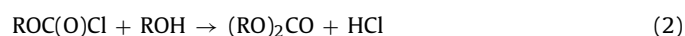
est in the chemical industry and in the motor fuel industry. Because of its high oxygen content (40.6 wt%), diethyl carbonate has been proposed as a replacement for MTBE as an attractive oxygen-containing fuel additive. Moreover, gasoline/water distribution coefficients are more favorable for DEC when compared to dimethyl carbonate and ethanol [10]. DEC can also be used as a raw material for manufacturing of polycarbonates [14], and it is as an excellent solvent and an intermediate for various pharmaceuticals such as antibiotics and phenobarbital [15,16]. Furthermore, DEC is applied as a solvent of polyamide, polyacrylonitrile and diphenol resin in the synthetic fiber industry, as solvents of cellulose ether, synthetic and natural resin in the textile printing and dyeing industry and as a paint remover. It is worth to mention that DEC is widely used as an electrolyte in lithium ion batteries. The world-wide production and consumption of dialkylcarbonates is estimated to be several tens of thousands of tonnes per year, whereas the annual production capacity of DEC, at present, is estimated to be 6000 mt/year industrial grade and 1200 mt/year battery grade [17,18].

## 2. Conventional diethyl carbonate production technologies

### 2.1. Phosgenation of ethanol

The phosgene (COCl<sub>2</sub>)-ethanol process is the oldest method of producing DEC as has been reported by Muskat and Strain in 1941 [19]. Currently, the phosgenation is the most important industrial method for producing carbonic acid esters. It should be, however, mentioned that since the 1980s the oxidative carbonylation reaction has replaced the phosgenation as the main method of DMC synthesis (the EniChem and Ube process). Nevertheless, the application of this production technology for longer chain alcohols such as ethanol still faces several technical challenges. Therefore, DEC is manufactured almost exclusively by reacting ethanol with phosgene using technology developed in the 1940s [20].

The majority of the production processes for dialkylcarbonates follow a similar route, according to Eqs. (1) and (2) [21].



Phosgene reacts with an alcohol to form chloroformates which react further with another molecule of alcohol to form carbonate. The process occurs in anhydrous solvents such as toluene, dichloromethane or benzene with excess of pyridine, which act as a hydrochloric acid trap in order to shift the equilibrium of the reaction towards formation of dialkylcarbonates [19]. Pyridine is only one among many acid acceptors (dimethyl aniline, quaternary ammonium bases or inorganic bases such as oxides, hydroxides and carbonates) that may be used. The temperature of the reaction depends on the nature of the alkaline reagent. In the presence of pyridine or caustic soda, a temperature below room temperature is required in order to obtain higher yields of carbonic acid esters. On the other hand, when calcium carbonate is used, the reaction temperature should be above 50 °C. Moreover, in the absence of base, the reaction requires high temperature to proceed (50–150 °C) and results in poor carbonate yields.

The main disadvantage of this method is the use of an extremely hazardous phosgene as a reactant. It decomposes in the lungs to form carbon monoxide and hydrochloric acid. Phosgene is classified by the U.S. Department of Transportation (DOT) as a class "A" poison. Therefore, in order to match the principles of "Green Chemistry" towards the lowest impact on human health and environment, there is an urgent need to develop alternative, more convenient and safe routes for those processes that are based on phosgene, its derivatives or the use of carbon monoxide. Synthesis methods for DEC via oxidative carbonylation of ethanol, reaction

**Table 1**  
Physical properties of diethyl carbonate.

Melting point	−43 °C
Boiling point	126–128 °C
Density	0.975 g/cm <sup>3</sup>
Flash point	25 °C
Water solubility	Insoluble
Toxicology	Mildly toxic

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