



## DIALKYL CARBONATE SYNTHESIS: RECENT SCIENTIFIC AND TECHNOLOGICAL ADVANCEMENTS

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### Abstract:

Dialkyl Carbonates (DAC's) are essential organic compounds (structurally seen as esters of carbonic acid) that have gained significant importance over the last few decades. They can be used as solvents, reagents, and for the synthesis of various organic compounds such as 5-6 membered heterocyclic compounds, indolines, and piperidines. They are highly versatile since they are used in the pharmaceutical, cosmetic, petrochemical, and agricultural industries. They are also used as solvents in Li-ion batteries, pesticides, fertilizers, polymer synthesis, beauty products, paints and coatings. This article analyses the different synthetic methods of DAC's, technological advancements in their syntheses, and the innovation with respect to discoveries of catalysts for these syntheses. It also includes its applications in various industries and uses in other reactions.

**Keywords:** dialkyl carbonates, green solvent, catalysis, modern methods of synthesis

### 1. Introduction

Dialkyl Carbonates are known as 'Green solvents' due to their biodegradability, low toxicity, and being safe to handle compounds. They are commonly used as polar solvents and reagents as they are stable under ambient conditions and thus are used as substitutes to toxic and corrosive compounds in the synthesis of various heterocyclic compounds<sup>1</sup>. The industrially important DACs, especially short-chain symmetrical DACs, are all colourless, transparent and flammable liquids with a pleasant odour and are relatively less toxic<sup>26</sup>. Due to the versatility and numerous applications of DAC's their synthesis is an important factor in industrial chemistry. The market

for DMC (Dimethyl Carbonate) was estimated in 2014 to be approximately 390 million USD. The market for DMC has been estimated to reach 690 million USD in 2023, expanding at a compound annual growth rate of 6.6% from 2015 to 2023<sup>2</sup>. There has been significant growth in the demand for DMC in Asia due to its wide range of applications. Thus, important methods of synthesis of DAC's have been developed over the years, such as the phosgene method, oxidative carbonylation, conversion through CO<sub>2</sub>, along with valuable development in the catalysts applied in these methods.

## 2. Methods of synthesis

### 2.1. Phosgene Method

Until 1980, the traditional industrial method for the synthesis of symmetrical dialkyl carbonates was

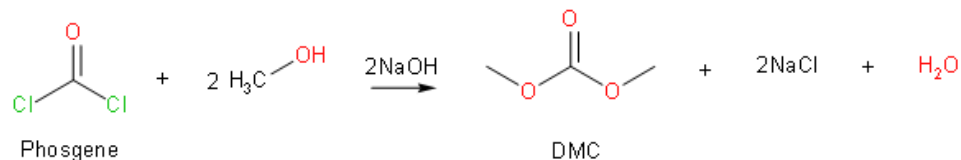


Fig 1.1. Synthesis of DMC *via* phosgene alcoholysis

This reaction is done in the presence of bases such as pyridine or NaOH to neutralize the acid formed by the initial reaction of phosgene and methanol. Despite a good yield of DMC, this method has its drawbacks, such as safety concerns regarding the use of phosgene, and disposal of the excess amount of salt produced upon neutralizing the acid<sup>4</sup>. Chloroformate Esters are intermediates formed, and they can undergo disproportionation leading to the production of phosgene along with the DAC<sup>5</sup>. Phosgene, being a toxic gas, is very risky and hazardous to be used for large-scale synthesis, and its use has been phased out in modern times. Thus, alternate methods were developed which eliminate the use of phosgene and are more sustainable.

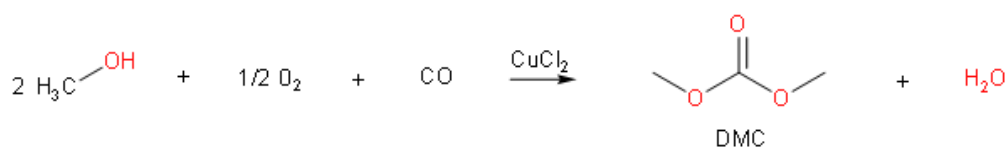


Fig 1.2. Synthesis of DMC *via* oxidative carbonylation

The liquid phase method saw much success at the industrial level due to the ready availability of raw materials and a favourable thermodynamic route with relatively moderate operating conditions. However, this method faces the problem of rapid catalyst deactivation, low selectivity, requirement of high temperature and pressure, and equipment corrosion<sup>3,4</sup>. However, the latter has been

done *via* phosgene alcoholysis<sup>27</sup>. A typical example of this is the synthesis of DMC, where methanol reacts with phosgene in the presence of a base to form DMC and NaCl<sup>3</sup>.

### 2.2. Oxidative Carbonylation

In the 1980s, a greener synthesis route was developed based on the direct oxidative carbonylation of alcohols using CO<sub>2</sub> and Oxygen, in the presence of Cu catalysts. This was classified into gas-phase (by the Dow Chemical Company, 1988) or liquid-phase (by the Enichem Company, 1983) depending on the state of the alcohol<sup>3</sup>. The liquid phase reaction is commonly done in the presence of CuCl<sub>2</sub> catalyst, and takes place in 2 steps. In the 1<sup>st</sup> step, Cu gets oxidized to form copper methoxy chloride in the presence of methanol, which then reacts with CO to form DMC, regenerating CuCl<sub>2</sub><sup>4</sup>.

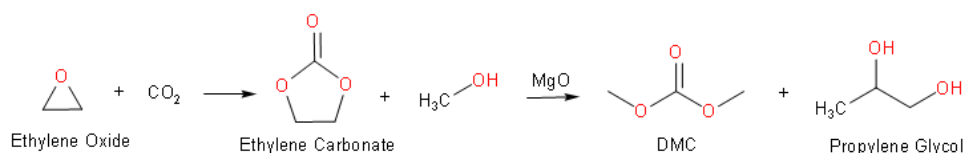
improved over time by using zeolite-encapsulated cobalt complexes such as Co-salophen catalyst, Co-schiff base, and selective reactions *via* alkali metal selenites and many other catalysts<sup>6</sup>.

### 2.3. Alkyl nitrite carbonylation

UBE Industries, a chemical company in Japan developed this method in 1978. In this process, nitric oxide

(NO) is used as a redox coupling agent with alkyl nitrite being used as an oxidizing agent. This process is divided into two parts that avoid formation of a ternary azeotrope <sup>4</sup>. The 1<sup>st</sup> step is the synthesis of alkyl nitrite by reacting NO, O<sub>2</sub>, and alcohol, in the absence of a catalyst. In the 2<sup>nd</sup> step, CO reacts with the alkyl nitrite in the presence of a catalyst to form the DAC and nitric oxide without forming any H<sub>2</sub>O <sup>7</sup>. Pd-based catalysts such as Pd/NaY, PdCl<sub>2</sub>, and Pd/C <sup>8</sup> are commonly used. However, the yield of the DAC formed is not great, and alkyl nitrites and NO<sub>x</sub> compounds formed are corrosive and toxic. Also, Pd is an expensive metal, and high pressure is required in the 2<sup>nd</sup> step <sup>2</sup>. Not much research is done on this method due to the fact that synthesis of DMC from CO<sub>2</sub> (something we will explore in the next section) is a cheaper, more efficient, and greener method of synthesis as compared to nitrile carbonylation.

## 2.4. Modern methods of synthesis from CO<sub>2</sub>



**Fig 1.3.** Synthesis of DMC by transesterification reaction

Since transesterification of cyclic carbonates and alcohols to generate dialkyl carbonates follows a nucleophilic substitution mechanism, basic compounds are considered as promising catalysts, and the strength of nucleophilicity plays a crucial role in their activity <sup>3</sup>. Selective catalysts are utilized in these reactions on the basis of the product required. For example, the synthesis of glycerol

Methods where CO<sub>2</sub> is directly and indirectly used for the synthesis of DAC's are important areas of research and production of DAC's. This is because they are 'greener' as they use CO<sub>2</sub> and urea as raw materials for the production of industrially essential chemical compounds. They are cheaper, more abundantly available feedstock and the future of DAC production <sup>3</sup>.

There are three ways of DAC synthesis *via* CO<sub>2</sub>. They are as follows:-

### 2.4.1. Transesterification reaction

A greener, modern way of producing DAC's is by transesterification of cyclic and alcohols. This is done by first reacting epoxides with CO<sub>2</sub> in the presence of a catalyst to form a cyclic carbonate (such as EC or PC) <sup>1</sup>, which is then reacted with an alcohol by a transesterification substitution reaction in the presence of a base catalyst <sup>9</sup>.

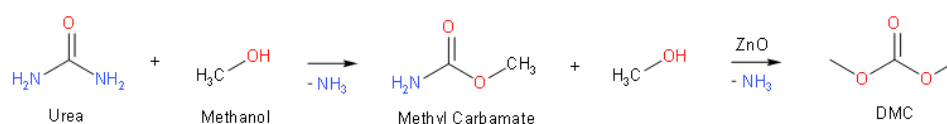
carbonate can use catalysts that are oxides of Mg/Al <sup>10</sup> such as MgO. MgO can also be used for the synthesis of DMC <sup>15</sup>, so can other catalysts such as Amberlyst A2 (a resin) <sup>11</sup>, DABCO-derived (1, 4-diazabicyclo 2.2.2 octane) basic ionic liquids <sup>12</sup>, Na- and K-dawsonites (NaAlCO<sub>3</sub>(OH)<sub>2</sub>) <sup>13</sup>, and Sodium alkoxides. Samarium trifluoromethanesulfonate

(Sm(OTf)<sub>3</sub>) is a catalyst that can be used for the synthesis of DPC<sup>14</sup>. Research regarding catalysts like these is an important field of innovation that can help propel this method to new heights, as they are essential in improving the yield and selectivity of the product. This reaction can also be done via a "one-pot method" resulting in low energy consumption and cheaper costs<sup>3</sup>. This approach is a promising, greener way of converting CO<sub>2</sub> to high-value chemicals. It also forms glycols as by-products, which can be utilized as antifreeze, coolant, and for polyester fibre synthesis<sup>4</sup>. However, the production of the epoxides represents a constraint and cost driver in production of the carbonates. Moreover, it also involves hazardous compounds and some risk of explosion.

Regardless, this method is one of the primary methods used for production of DACs and DMC in modern times.

#### 2.4.2. Urea Alcoholysis

This process has gained significant importance since the 2000s as it employs cheap raw materials, mild oxidation conditions, and an overall 'greener' synthesis with valuable by-products. This is an indirect reaction of CO<sub>2</sub>, where urea is reacted with an alcohol to give symmetric DAC's through the formation of an alkyl carbamate intermediate with ammonia as a by-product. This ammonia can then be reused in urea synthesis<sup>16</sup>. Long-chain DAC's (for example, Dinonyl Carbonate) can be effectively formed by this method



**Fig1.4.** Synthesis of DMC by urea alcoholysis with methyl carbamate intermediate

This process has been revolutionized and can be really effective due to the use of suitable catalysts, increasing the %yield from ~10% with MgO and CaO to more than 35% with Zinc based catalysts like ZnO, ZnFeO, ZnCl<sub>2</sub>, and some other transition metal compounds<sup>3</sup>. ZnO is considered to be the model homogeneous catalyst here due to its amphoteric properties and non-toxic

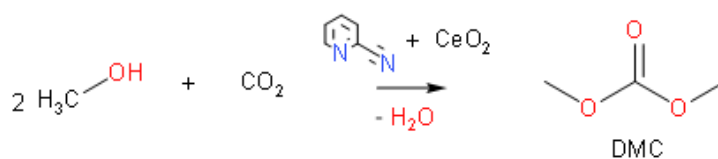
nature. It is considered to be a precursor to the homogenous catalyst Zn(NH<sub>3</sub>)<sub>2</sub>(NCO<sub>2</sub>)<sub>2</sub><sup>19, 28</sup>. It has to be dissolved in the reaction solution at 150-200°C as it is not soluble in alcohol at room temperature<sup>17</sup>. This is also an incredibly efficient catalyst, with experiments showing that it could be reused up to 4 times without deactivation<sup>17</sup>. Another active catalyst that could be

used here is  $2\text{CaO/CeO}_2$ , due to its insolubility in the reaction medium and very high efficiency resulting in more than 50% yield and 98% selectivity<sup>16</sup>. Dibutyltin oxide catalyst is also an effective catalyst, which is used in the synthesis of long-chained DAC's<sup>18</sup>. As this is an environmentally friendly and highly efficient method of synthesis, it is gaining momentum industrially for commercial production of DAC's, with lots of scope for research with respect to heterogeneous catalysts due to easier post-reaction separation<sup>3</sup>.

#### 2.4.3. Directly with alcohol

Differing from other synthetic routes, the carbonyl group is directly derived from reacting  $\text{CO}_2$  with alcohol, forming the DAC without any other intermediates.  $\text{CO}_2$  is a non-toxic, non-corrosive, non-flammable, and abundant gas, which makes its use as a raw material very attractive from an industrial standpoint. It has the same atom economy as oxidative carbonylation<sup>4</sup>. However, some major drawbacks of this method are the low yield of DAC's, limitations in thermodynamic equilibrium, and requirements of high pressure for the reaction to occur. Removal of the water

formed in the reaction as a by-product is another way to shift the thermodynamic equilibrium towards the DAC. Thus, the development of efficient dehydrating agents and catalysts is an important area of research in modern times<sup>20</sup>. Heterogeneous catalysts are usually preferred over homogenous catalysts due to their ease of separation and recyclability of the catalyst. Metal oxides of Mg, Al as well as of transition metals like Ni, V can be used here, but they give low yields as well as selectivity, even under high pressure<sup>3</sup>. However, work by Japanese researchers Tomishige and Fujimoto showed the potential of amphoteric metals oxides like  $\text{ZrO}_2$  and  $\text{CeO}_2$ <sup>29</sup>, and significant breakthroughs were achieved by the implementation of dehydrating agents alongside them. In 2009 experiments focusing on nitrile groups as dehydrating agents were conducted<sup>20</sup>. Water capture with nitriles leads to amides, which can later be converted back to the corresponding nitrile and enable the regeneration of the dehydrating species<sup>30</sup>. After several experiments, the best results were shown upon using  $\text{CeO}_2$  as a catalyst in the presence of 2-cyanopyridine<sup>20</sup>.



**Fig 1.5.** Synthesis of DMC by direct conversion of CO<sub>2</sub>

With this system (5MPa, 120°C, 12h), the yield and selectivity for DMC were extraordinarily high, reaching levels of 94% and 96%, respectively <sup>21</sup>. The scope of this method is also not only limited to the synthesis of DMC, and can also be used for other DAC's. The use of these catalysts makes this method a solid contender to be used for large-scale commercial production of DAC's. Studies are being conducted on the feasibility of this reaction on a commercial

scale and with low Greenhouse gas emissions, and the ability to reactivate the CeO<sub>2</sub> by washing it with methanol at 393 K for 1h and calcining it with dry air at 573 K for 12h after its initial deactivation are advantages of this method <sup>22</sup>. Also, the ability to use CO<sub>2</sub> as a feedstock to important chemicals makes this an environmentally sustainable method of DAC production. This method has the most potential to be implemented on a large scale with lots of sustainability and good yields of products.

### **3. Applications of DAC's**

#### **3.3.1. As solvents**

As mentioned earlier, DAC's are non-toxic, easy to handle versatile 'green' solvents due to their low biodegradability, and thus can be used as alternative solvents to ethers and ketones. Also, their boiling points can easily be modified by changing the length and properties of the alkyl group 1. They are considered as aprotic dipolar solvents. They can also be used as non-aqueous electrolytes. They are used in Li-ion batteries and react with the Li to give lithium alkyl carbonates which form the solid electrolyte interphase (SEI) <sup>23</sup>.

#### **3.3.2. As reagents**

DAC's are easier to handle and thus can easily be used as substitutes to phosgene in alkoxyacylation reactions and as alkylating agents in place of alkyl halides and dimethyl

sulphates. They also follow HSAB principles, which helps in understanding its reaction mechanisms more easily 1.

#### **3.3.3. As a fuel additive**

DAC's generally have high oxygen content, and DMC has especially has a higher oxygen content (53.3% on a weight basis) as compared to other fuel additives such as dimethyl ether (35%), methanol (50%), methyl tert-butyl ether (MTBE) (17.6%), etc. and is thus used as a gasoline additive <sup>24</sup>. By adding DMC to diesel in IC engines, engine emissions and NO<sub>x</sub> emissions were reduced; however, CO emissions remain close to the same. It reduces the combustion duration due to the lower boiling point of DMC, and increases the brake thermal efficiency as compared to pure diesel <sup>24, 25</sup>.

#### 4. Discussion

Over the course of the last 60-70 years, DAC's have become incredibly important chemicals in industrial chemistry. Throughout the years, newer, more efficient, and environmentally friendlier methods of synthesis for DAC's have been developed through the contributions of many scientists and researchers. Recent discoveries of more efficient and selective catalysts have propelled the production of DAC's to new heights, owing to its increase in global demand, and thus production. Their versatility in multiple industries makes them some of the most important modern-day chemical compounds and explains their significance.

#### 5. Conclusion

This review hopes to highlight the advancements made in DAC synthesis,

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