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Organic Carbonates[†]

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Contents

I. Introduction

Carbonic acid which is unstable at room temperature has been isolated in its pure state at lower temperature and characterized spectroscopically.[1,2] The diesterification of carbonic acid with hydroxy compounds leads to the formation of stable organic compounds known as organic carbonates. Depending upon the nature of hydroxy compounds, the resulting carbonates are either dialkyl, diaryl, or substituted dialkyl diaryl carbonates. Among the various types of organic carbonates, the simplest one is dimethyl carbonate. The production of dimethyl carbonate[3,4] on an industrial scale by catalytic oxycarbonylation of methanol has provided a great impetus to its use as a safe analog for phosgene or dimethyl sulfate in the manufacture of many useful organic compounds.

In spite of burgeoning applications, there is no compilation of the literature on the synthesis and utility of organic carbonates. The present review, therefore, attempts to provide a comprehensive survey of the currently available literature on organic carbonates.

II. Synthesis, Isolation, and Characterization of Carbonic Acid

Carbonic acid (H_2CO_3) is of special importance in nature. It is a key compound in CO_2-HCO_3/CO_3^{2-} proton transfer reactions in biological and geochemical carbonate-containing systems.[5-8] Carbonic acid is known to be present to the extent of about 0.4% in water containing dissolved CO_2. The equilibrium between carbonic acid with carbon dioxide and water and its significance are well recognized and have been thoroughly studied (eq 1).

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \qquad (1)$$

It is believed that "carbonic acid" cannot exist in the free state.[9] It was not isolated in its pure state and characterized spectroscopically until 1960. Later it was possible to prepare the ether adducts of carbonic acid $H_2CO_3 \cdot R_2O$[10] ($R = CH_3$, C_2H_5) at temperature below −30 °C, and a solid crystal of the complex was obtained at −78 °C. This was achieved by the addition of an ether solution of anhydrous HCl to a suspension of finely divided sodium bicarbonate in ether at −30 °C. In solution, the adducts decompose into H_2O, CO_2, and R_2O above 5 °C. The dissociation constant of carbonic acid is large in

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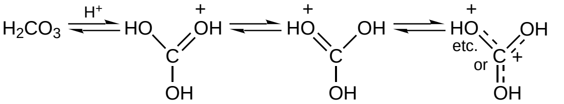
comparison with those of the hydrates of other carbonyl compounds,[11] and this has been taken to reflect the high stability of the unhydrated species, CO_2. However, an activation energy of 16.5 kcal/mol for the dissociation reaction of carbonic acid to water and carbon dioxide suggests that it should be possible to observe carbonic acid in its free state.[12] Olah and White have shown that protonated carbonic acid is remarkably stable in superacidic media.[13] It was obtained by simply dissolving carbonates or hydrogen carbonates in $FSO_3H{-}SbF_5$ (or other superacids). The solutions decompose at about 0 °C to give hydronium ion and CO_2 (eq 2). The protonated carbonic acid is highly resonance stabilized (eq 3).

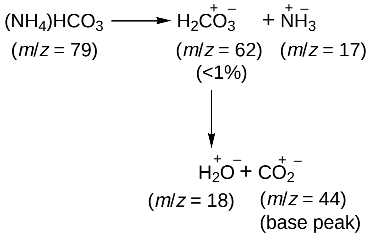
$$CO_3^{2-} \text{ or } HCO_3^- \xrightarrow[-80\ ^\circ C]{FSO_3H{-}SbF_5/SO_2} H_3CO_3^+ \xrightarrow{-10 \text{ to } 0\ ^\circ C} CO_2 + H_3O^+ \quad (2)$$



(3)

Protonated carbonic acid was characterized by ^{1}H- and ^{13}C-NMR spectroscopy. Olah and co-workers have recently isolated carbonic acid at low temperature in methanolic solution and characterized it by ^{13}C-NMR, ab initio, and ILGO studies.[1] Simultaneously, carbonic acid was synthesized and isolated by a new cryogenic technique in methanol solvent and characterized by FTIR spectroscopy.[2] This cryogenic technique is useful for isolation of many other short-lived intermediates and is suitable for nonvolatile reactants such as salts which can not be vaporized without decomposition.

The reaction of CO_2 and H_2O in the gas phase has been studied in detail by ab initio calculations.[14] Several calculations on the gas phase reaction of carbon dioxide with H_2O and hydroxide ion have focused mainly on accurate reaction energies.[15] These predict that a sizeable activation energy (>40 kcal/mol) is involved in the formation and dissociation of carbonic acid, and thus the free carbonic acid should exist as a stable molecule. The existence of a stable free carbonic acid in the gas phase was evidenced by mass spectral study of the thermolysis products of $(NH_4)HCO_3$.[16] The presence of a stable carbonic acid radical cation, $CH_2O_3^{\cdot +}$ species in the mass spectral study was observed. This was further confirmed by collision activation (CA) mass spectroscopy experiments and neutralization reionization (NRMS) experiments ($CH_2O_3^+$ ion remains intact upon neutralization followed by reionization) (eq 4).



(4)

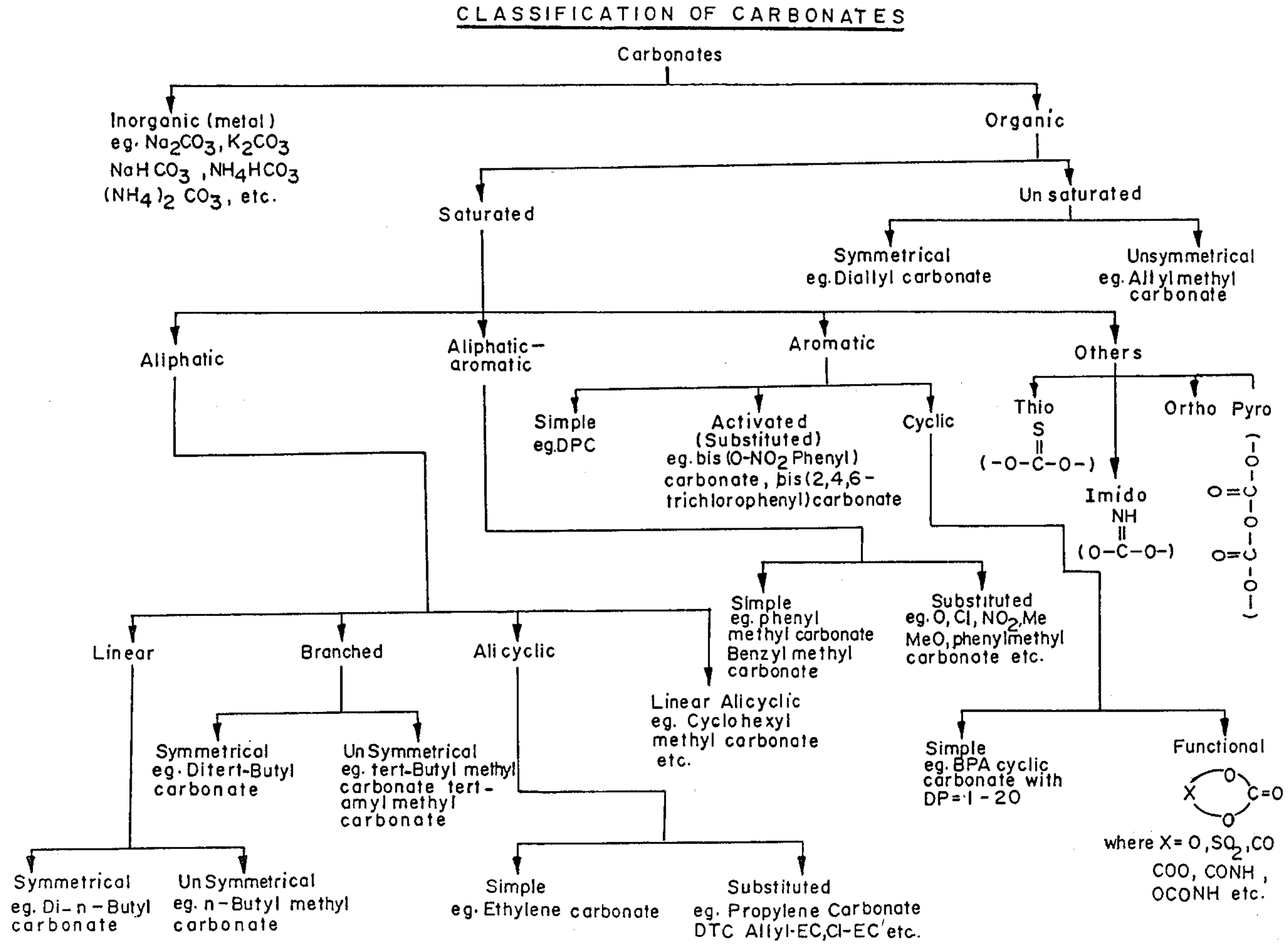
$$\begin{tikzcd}[column sep=small] (NH_4)HCO_3 \arrow[r] & \overset{+\,-}{H_2CO_3} & + \overset{+\,-}{NH_3} \\ (m/z = 79) & (m/z = 62)\ (<1\%) \arrow[d] & (m/z = 17) \\ & \overset{+\,-}{H_2O} + \overset{+\,-}{CO_2} & \\ & (m/z = 18)\quad (m/z = 44)\ \text{(base peak)} & \end{tikzcd}$$

Thus the decomposition of carbonic acid to CO_2 and H_2O in solution was attributed to the acid/base and also catalysis by solvents. This increases the rate of hydration of CO_2 and the dissociation of carbonic acid to such an extent that carbonic acid is inaccessible.

III. Carbonates

The monoester of carbonic acid, known as hemicarbonic acid, is formed by the reaction of alcohol with carbon dioxide. This is also unstable and decomposes to alcohol and carbon dioxide. Hemicarbonic acid can only be isolated as salts (with inorganic metal such as sodium and potassium), simple anhydrides, or mixed anhydrides with carboxylic acids.[17] The inorganic salts of hemicarbonic acid are solid, stable, and high-melting compounds. This monosalt can be converted to disalt which is known as a metal carbonate. Hemicarbonic acid upon esterification with another molecule of hydroxy compound forms

Chart 1



stable organic carbonates. The simplest organic carbonate is dimethyl carbonate.

IV. Classification of Carbonates

Carbonates can be mainly classified into two groups, namely, inorganic (metal) and organic carbonates. Depending on the structural variation, organic carbonates can be further subdivided as shown in Chart 1.

V. Physical Properties of Organic Carbonates

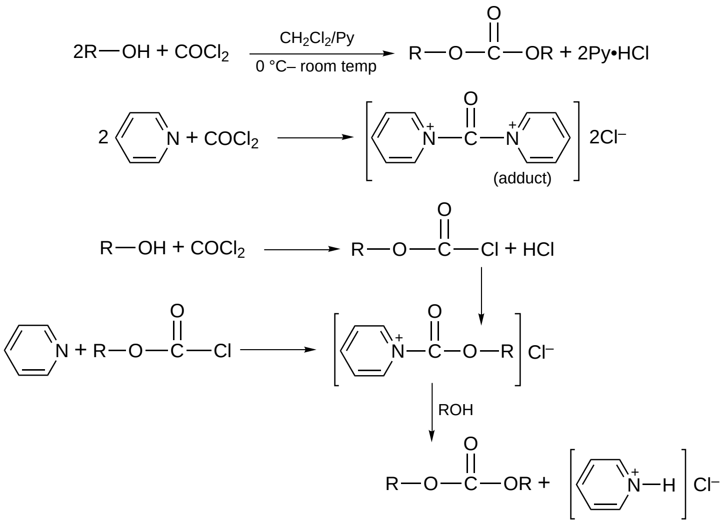
The industrially important dialkyl carbonates are all colorless liquids. Most of them have a pleasant odor. The aromatic carbonates, on the other hand, are solids. Ethylene carbonate is infinitely soluble in water. Propylene carbonate is soluble in water only to the extent of 25.0 g of propylene carbonate/100 g of water (at 25 °C). Butylene carbonate is less soluble, yet in water, only 7.0 g of butylene carbonate dissolves in 100 g of water (at 25 °C). Dimethyl carbonate and diethyl carbonate are sparingly soluble in water. The other carbonates, including aromatic carbonates, are nearly insoluble in water. They are soluble in many organic solvents, particularly polar solvents, such as esters, ketones, ethers, alcohols, and aromatic hydrocarbons. The lower aliphatic carbonates form azeotropic mixtures with several organic solvents.[18] Ethylene carbonate finds extensive use as a solvent for aromatic compounds, polymers, and inorganic salts. In many applications, ethylene and propylene carbonate offer a safe and clean alternative to more hazardous dipolar aprotic solvents. Inorganic carbonates are white, crystalline compounds, with high melting points. They are soluble in water and insoluble in most of the organic solvents. They easily react with compounds containing acidic proton, e.g., acid, phenol, etc. They are useful in many organic reactions.

VI. Methods of Preparation of Organic Carbonates

A. Phosgenation Technique

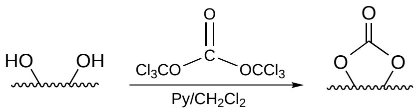
In this method, hydroxy compounds (aliphatic, aromatic) are dissolved in a single or a mixture of inert, anhydrous solvent (dichloromethane, chloroform, benzene, toluene) with excess pyridine and phosgenated at or below room temperature. Pyridine acts as an acid acceptor and reacts with phosgene, and an ionic adduct is formed. The adduct formed is more reactive than the corresponding chlorocarbonic acid esters.[19] Pyridine is only one among the acid acceptors that may be used. Nearly all the organic carbonates (except few like ortho- and pyrocarbonate) can be prepared by this method (Scheme 1). Symmetrical carbonates are obtained in one step, whereas unsymmetrical, alkyl aryl, or substituted alkyl aryl carbonates are obtained by a two-step reaction. Aromatic hydroxy compounds[20] are much

Scheme 1. Synthesis of Organic Carbonates by Phosgenation Method[a]



[a] Where R = alkyl, aryl, and substituted alkyl and aryl.

Scheme 2. Synthesis of Organic Carbonates by Phosgenation Method[a]



[a] Where ∼ = 2,4-dihydroxypentane, 2,4-dihydroxy-2,4-dimethylpentane, and *cis*-8-*trans*-1,2-dihydroxycyclohexane.

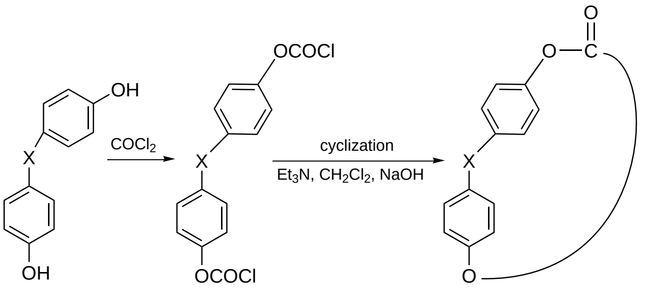
slower to react with phosgene than aliphatic hydroxy compounds. The more acidic hydroxy compounds are less reactive toward phosgene. For example, halogenated phenols react slower than phenol. Substitution in the ortho position also decreases the reactivity. The conversion of hydroxy compounds to carbonates can be completed in a short period of time. Therefore, the reaction can be carried out continuously without any difficulty, and good yields of carbonates are obtained.

The reaction mixture is washed with dilute HCl (to neutralize excess pyridine) and then with water (to remove salt). Pure organic carbonate is obtained either by distillation or recrystallization from a suitable solvent or solvent mixtures. Good yields of 5- or 6-membered cyclic carbonates of 1,2- and 1,3-dihydroxy compounds are also obtained by this method.[21] Sterically hindered dialkyl carbonates such as di-*tert*-butyl carbonate can also be prepared in 50% yield.[22] For the preparation of carbonates, phosgene can be substituted by compounds such as chloroformic acid trichloromethyl ester (diphosgene) and bis(trichloromethyl) carbonate. For example, 1,2- and 1,3-diols were easily converted to cyclic carbonates with triphosgene in CH_2Cl_2 and pyridine at 70 °C[23] (Scheme 2).

Recently, an aromatic dihydroxy compound, namely, bisphenol-A, has been selectively converted to cyclic carbonate under pseudo-high-dilution conditions employing triethylamine-catalyzed hydrolysis/condensation reaction of bisphenol-A bis(chloroformate) using CH_2Cl_2 and NaOH.[24] Similarly, functionalized bisphenols were converted to functionalized aromatic cyclic carbonates[25] (Scheme 3).

In the absence of an organic base, the direct reaction of hydroxy compounds with phosgene requires higher temperature (50−150 °C) and results in poor yields of carbonates along with unreacted chlorocarbonates.[26] This also leads to the formation of unwanted products.

Scheme 3. Synthesis of Organic Carbonates by Phosgenation Method[a]



[a] Where X = $-C(CH_3)_2-$, $-SO_2-$, −CO−, −O−, −C(O)−O−, −CO−NH, −O−C(O)−, and −O−C(O)−NH−.

The advantages of the phosgenation method are (a) high yields of carbonates and (b) functionalized carbonates such as cyclic and activated carbonates that can be prepared, which are useful monomers for the preparation of high molecular weight polymers. The main drawbacks of this reaction are (a) the process involves the use of toxic and hazardous chemicals like pyridine and phosgene, (b) excess pyridine has to be neutralized, and (c) the byproducts salt has to be completely removed and disposed. This involves additional purification steps.

B. Oxidative Carbonylation of Alcohols/Phenols

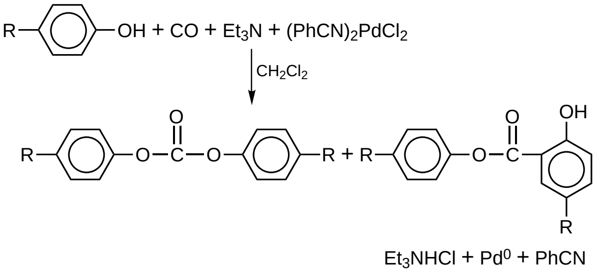
The formation of dialkyl carbonates from the reaction of alcohols and carbon monoxide has been reported to be promoted by transition metal compounds (in particular palladium, mercury, and copper) and post-transition-metal compounds.[27] In the case of palladium and mercury, however, the reaction does not seem to be selective and involves reduction to the metal, which can not be reoxidized directly. The reactivity of copper is of greater interest since through a redox process with oxygen and carbon monoxide it gives a system which functions catalytically. Romano et al.[28] explored the synthesis of dimethyl carbonate by oxidative carbonylation of methanol using a copper salt such as copper chloride as catalyst. The reaction takes place in two steps, in which cuprous chloride is oxidized to cupric methoxy chloride, and this is reduced with carbon monoxide to form dimethyl carbonate and regenerate cuprous chloride (eq 5).

$$2\mathrm{CuCl} + 2\mathrm{CH_3OH} + {}^1/_2\mathrm{O_2} \rightarrow 2\mathrm{Cu(OCH_3)Cl} + \mathrm{H_2O}$$

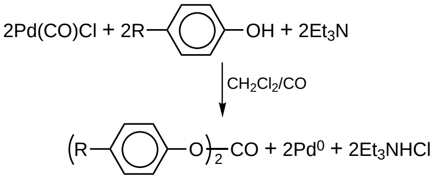
$$2\mathrm{Cu(OCH_3)Cl} + \mathrm{CO} \rightarrow \mathrm{(CH_3O)_2CO} + 2\mathrm{CuCl} \quad (5)$$

A number of patents report the synthesis of dimethyl carbonate by treatment of methanol, CO, and oxygen using various catalysts and reaction conditions.[29] Good conversion to dimethyl carbonate is achieved with high selectivity. Dimethyl carbonate is also produced by a continuous gas phase reaction of alkyl nitrites (RONO) with CO in the presence of a catalyst comprised of a platinum halide or a complex with alkali metal or alkaline earth metal halides.[30] Dimethyl carbonate is produced in 70−80% yield with a selectivity in the range of 80−90%. Dimethyl carbonate is produced industrially by oxidative carbonylation of methanol by Enichem Synthesis,[3] Dow Chemical,[4] and Ube Industries Ltd. Enichem Synthesis has the capacity to produce about 8800 tons/year dimethyl carbonate.[31a]

The analogous oxidative carbonylation of aromatic hydroxy compound has met with less success. Diphenyl carbonate was formed in moderate yield from phenol and carbon monoxide in the presence of a base and a stoichiometric quantity of a group VIIIb metal salt.[32] Hallgren and Mathews[33] reported the reaction of phenols with carbon monoxide at atmospheric pressure and room temperature in the presence of palladium chloride and a tertiary amine to produce a mixture of diaryl carbonates and aryl salicylates (eq 6, where R = H, −CH_3, −Cl, CH_3O−). Only diaryl carbonates were produced when palladium carbonyl chloride was substituted for palladium chloride (eq 7).



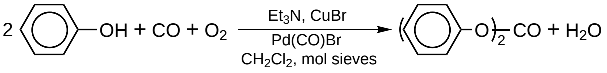
(6)



(7)

The same reaction was made catalytic[34] using an oxidation cocatalyst in which the palladium metal was oxidized to Pd(II) species. A variety of copper, vanadium, cobalt, and manganese salts were effective cocatalysts, although in many cases side products were produced. Using catalytic quantities of manganese salt with palladium, up to 100 mol of diphenyl carbonate/mol of palladium was achieved. This reaction requires longer time to achieve higher conversion of phenol.

A number of attempts have been made to produce diaryl carbonate by the direct oxidative coupling of phenols with carbon monoxide or by direct condensation with carbon dioxide.[35] Oxidation of phenols with carbon monoxide and molecular oxygen is carried out in the presence of catalysts containing palladium compounds, alkyl ammonium halide, and an organic or inorganic base under pressure of 4−30 kg/cm^2, at 100−200 °C, for 1−13 h. Diphenyl carbonate is obtained in 4−30% yield with 90−96% selectivity. Use of molecular sieves such as 3 Å is also found to have favorable effect on yield and selectivity.[36] Diphenyl carbonate in 39.5% yield with 99% selectivity is produced by a continuous process in a multistage distillation column in which water formed in the reaction is removed as steam by distillation[37] (eq 8).

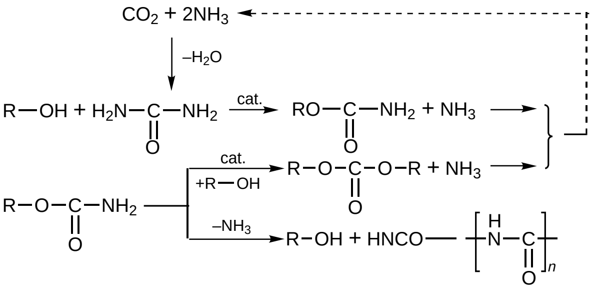


(8)

Lower basicities of phenols, expensive catalysts, low yields, and low catalyst turnover efficiencies have precluded a commercial process based on oxidative carbonylation of phenols. In this context, it is generally acknowledged that the discovery of a convenient and less expensive route to diaryl carbonates would be a revolutionary development.

C. Reaction of Urea with Alcohols/Phenols

The reaction of urea with alcohols which leads to the formation of carbamates using metal salts like zinc acetate and lead acetate was discovered by Paquin.[38] Prolongation of the reaction or the addition of triphenylphosphine as a cocatalyst results in the formation of carbonate. Isocyanuric acid is a major byproduct of this reaction (eq 9).

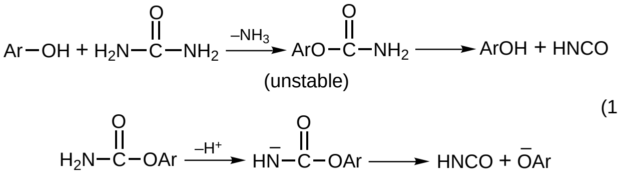


(9)

The decomposition of the carbamate to form isocyanic or isocyanuric acid, which is observed with catalyst systems such as zinc acetate/triphenylphosphine, does not occur if titanium, aluminum, or zirconium alkoxides are used in combination with suitable cocatalysts.[39] Besides these, catalysts such as dibutyltin oxide, dibutyltin dimethoxide, and triphenyltin chloride have been found to give high yields of carbonates. Even heterogeneous catalysts such as antimony trioxide and aluminum trioxide can be used. This reaction is carried out at 150−195 °C for 4.5 h and at 195–220 °C for 14 h depending upon the catalyst system.

The yields of carbonates are >99%.[40] The ammonia which is liberated during the reaction can be, in principle, recycled for the synthesis of urea. Primary, secondary, and low-boiling alcohols can be converted into carbonates. Kinetic studies have shown that the formation of dialkyl carbonate from urea and aliphatic hydroxy compound proceeds in two steps.[40] At a constant temperature of 160 °C, 50% of the expected amount of ammonia is formed fast; the urea is completely transformed into carbamate in the presence of catalyst. Even on raising the temperature from 165 to 180 °C, the rate of the subsequent reaction to dialkyl carbonate remains much lower than that of the first. The carbamate that is formed as intermediate is thermally stable at the reaction condition and is transformed into dialkyl carbonate.

The reaction of urea with aromatic hydroxy compounds was also investigated with temperatures ranging from 150 to 195 °C for 4.5 h using various combinations of catalysts. Aryl carbamates are formed as intermediates and are thermally unstable. They decompose to isocyanuric acid and phenols at the reaction condition (eq 10). The formation and stability of aryl carbamate is also affected by the nature of substituent, catalysts, and reaction medium.[40] The formation of aryl carbamate is accelerated by electron-donating groups and slowed by electron-withdrawing groups. In nonpolar solvents such as tetralin or dibutyl ether, the decomposition proceeds much more slowly than in polar solvents such as DMF, NMP, and HMPA. Decomposition is enhanced by bases (e.g., triethylamine, pyridine), and weak acids cause a slow decomposition. The use of mineral acids results in a fast decomposition. Nevertheless, the reaction of phenyl carbamate with phenol under these conditions (similar to aliphatic hydroxy compound) resulted in the formation of only 1% diphenyl carbonate.



$$\mathrm{Ar{-}OH} + \mathrm{H_2N{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2} \xrightarrow{-\mathrm{NH_3}} \underset{\text{(unstable)}}{\mathrm{ArO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2}} \longrightarrow \mathrm{ArOH} + \mathrm{HNCO}$$

$$\mathrm{H_2N{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OAr} \xrightarrow{-\mathrm{H^+}} \mathrm{H\bar{N}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OAr} \longrightarrow \mathrm{HNCO} + \mathrm{\bar{O}Ar}$$

(10)

D. Reaction of Oxiranes with Carbon Dioxide

The chemistry of carbon dioxide has received much attention in recent years. It has been considered as a monomer in polymerization and polycondensation reactions.[41] The reaction of carbon dioxide with oxiranes to produce cyclic carbonates has been of interest as a useful method for its fixation by a chemical process.[42] Synthesis of cyclic carbonates from the reaction of carbon dioxide with oxiranes has been accomplished using Lewis acids, transition-metal complexes, organometallic compounds, or poly(siloxane)-supported metal halides as catalysts under high pressure.[43] Rokicki and Kuran[44] reported the reaction of oxiranes with carbon dioxide catalyzed by alkali metal salts in the presence of phase transfer agents such as crown ethers or quaternary ammonium salts. The reaction gave the corresponding cyclic carbonates in high yields under high pressure at 80–120 °C; however, the yield was very small at atmospheric pressure. Ratzenhofer and Kisch[45] performed the synthesis of cyclic carbonate from the reaction of oxirane with carbon dioxide in the presence of mixtures of triphenylphosphine with the halides of aluminum, molybdenum, or iron at room temperature under atmospheric pressure. The yield of cyclic carbonate was not satisfactory.

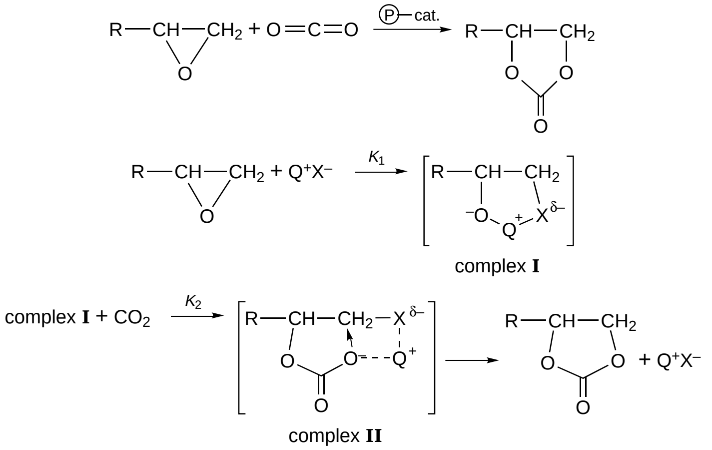
Baba et al.[46] found an excellent new catalyst system composed of organotin halides with quaternary ammonium or phosphonium salts, in which the reaction of oxiranes with carbon dioxide proceeded smoothly to give the corresponding cyclic carbonates in high yields at atmospheric pressure at 40–100 °C; however, neither organotin halide nor tetrabutylphosphonium halide individually showed any catalytic activity. This method was also useful for the reaction of inactive or acid sensitive oxiranes with carbon dioxide to produce cyclic carbonates under neutral and mild reaction conditions.

Recently, Nishikubo et al.[47] reported the synthesis of cyclic carbonates by the addition reaction of oxiranes with carbon dioxide using insoluble polystyrene beads containing pendant quaternary ammonium or phosphonium as catalysts at atmospheric pressure. The reaction of oxiranes with CO_2 proceeded smoothly catalyzed by 1–2 mol % polymer-supported quaternary onium salts to give the corresponding cyclic carbonates in high yields at 80–90 °C. In this reaction system, the catalytic activity of the polymer-supported quaternary onium salts was strongly affected by the following three factors: (i) degree of ring substitution of the onium salt residues to the polymer, (ii) degree of cross-linking of the polystyrene beads and chain length of the alkylene spacer between the polymer backbone and the onium salt, and (iii) hydrophobicity of the alkyl group on the onium salts and the kind of onium salts. Thus, the polymer-supported quaternary phosphonium salts with low degree of ring substitution, low degree of cross-linking, and long alkylene spacer chain were found to have higher catalytic activity. The polymer-supported catalysts can easily be separated at the end of a reaction by filtration and be reused. Kinetic study revealed that the rate of reaction was proportional to the products of catalyst concentration and oxirane concentration. The mechanism of reaction of oxirane with carbon dioxide catalyzed by the polymer-supported onium salt is shown in Scheme 4.

E. Use of Metal Carbonate

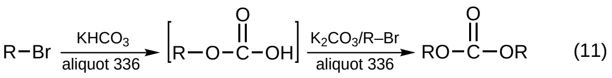
Little is known about the transformation of inorganic (metal) carbonates to organic carbonates, except the reaction of silver carbonate with alkyl iodide.[48] This may be due to insolubilities of inorganic carbonates even in aprotic organic solvents. Recent work reported in the patent literature describes the alkylation of metal carbonate with alkyl halides at high temperature and in dipolar aprotic solvents using various catalysts.[49] Lissel and Dehmlow[50] reported the preparation of dialkyl carbonates

Scheme 4. Reaction Mechanism of Oxiranes with Carbon Dioxide by Polymer-Supported Catalyst[a]



[a] Where R = $PhOCH_2-$, $C_4H_9-O-CH_2-$, $CH_2=CH-O-CH_2-$, and $CH_2=CH-CH_2-O-CH_2Ph-$. $K_1 \gg K_2$.

in a phase transfer catalytic reaction from primary alkyl halides (bromides) with a mixture of dry potassium hydrogen carbonate and dry potassium carbonate in nonpolar solvents. The yields of organic carbonates ranged from 67% to 86%. The reaction was ineffective in the absence of potassium hydrogen carbonate and a phase transfer catalyst (eq 11, where R = n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_4H_{19}, n-$C_{11}H_{23}$, $C_{15}H_{31}$, $PhCH_2^-$, (o-Me)$PhCH_2^-$, (m-Cl)$PhCH_2^-$).

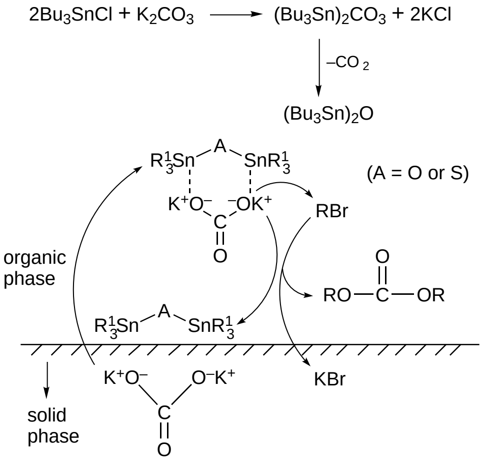


$$\mathrm{R{-}Br} \xrightarrow[\text{aliquot 336}]{\mathrm{KHCO_3}} \left[\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}OH}\right] \xrightarrow[\text{aliquot 336}]{\mathrm{K_2CO_3/R{-}Br}} \mathrm{RO{-}\overset{O}{\overset{\|}{C}}{-}OR} \qquad (11)$$

Fujinami et al.[51] reported the preparation of dialkyl carbonates by the heterogeneous reaction of solid potassium carbonate with alkyl bromides in dimethylformamide or dimethyl sulfoxide in the presence of organostannyl compound such as hexabutyldistannoxane or chlorotirbutylstannane as catalyst.

The reaction of alkyl bromide was studied using various tin compounds. The reaction was carried out at 40−100 °C for 8−80 h. Dialkyl carbonate was obtained in 19−89% yield. The alkylation reaction was distinctly accelerated by the addition of a phase transfer catalyst such as 18-crown-6. The reaction was complete in 10 h at 80 °C in less polar solvents such as acetonitrile and benzene. This dramatic effect is explained by involving the reaction of triorganotin chloride with metal carbonate to form bis(triorganotin) carbonate which is decarboxylated to hexabutyldistannoxane or hexaalkyldistannthiane. This is an efficient catalyst, interacts with the carbonate anion, and forms an organic soluble intermediate. This organotin derivative acts as a solid−liquid phase transfer catalyst. Organostannyl catalyst acts as a Lewis acid and interacts with carbonate ion and the crown ether as a Lewis base to associate with potassium ion. This undergoes efficient reaction with alkyl bromide in organic solvent retaining organic carbonate in the organic phase with separation of metal bromide (Scheme 5). Cella and Bacon[52] prepared dialkyl carbonates by the phase transfer-catalyzed alkylation of alkali metal carbonate and bicarbonate salts in nonpolar and polar solvents. The reaction of alkali metal alkyl carbonate salts with alkyl halides in dipolar solvents produces mixed alkyl carbonates in good yields. The major limitation of this method was the failure of activated aryl halides or electronegatively substituted alkyl halides (e.g., 2,2,2-trifluoroethyl bromide) to produce carbonates due to the labile nature of the intermediate alkoxy carbonate salts.

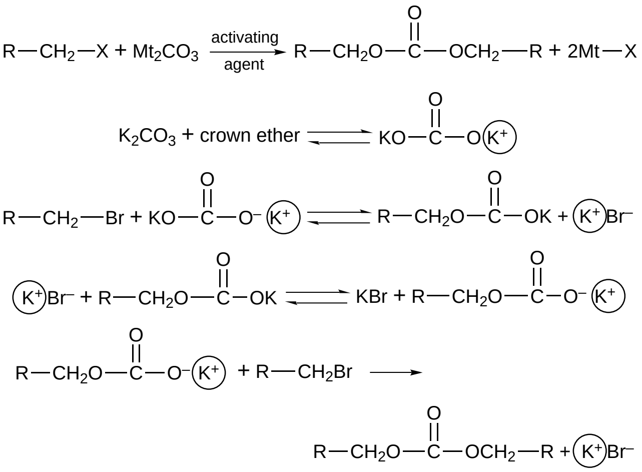
Scheme 5. Formation of Dialkyl Carbonate from Potassium Carbonate and Alkyl Bromide Using Organostannyl Catalyst



A number of carbonates $(RCH_2O)_2CO$ (R = CH_3, C_2H_5, $CH_2=CH$, C_3H_7, C_5H_{11}, C_6H_5) have been synthesized by the reaction of alkali metal carbonates with the corresponding halogen derivatives in the presence of activating agents such as crown ethers, polyglymes, polyamines, and triethylbenzylammonium chloride. The effects of various parameters (type of the halogen derivative, metal carbonate, activating agent, solvent, and reaction time) on the reaction have been studied by Rokicki et al.[53] Although group I and II alkali metal carbonates were used in alkylation reactions with primary alkyl halides, $K_2CO_3^-$ with benzyl bromide at 70−80 °C for 24 h using 0.1 mol % 18-crown-6-ether and triethylbenzylammonium chloride as activating agent was found to give >90% yield. Acetonitrile and ethers such as diglyme and dioxane were the best solvents for this reaction. The mechanism proposed for this reaction is shown in Scheme 6.

Under ordinary conditions, K_2CO_3 is insoluble even in polar solvents such as DMSO or DMF which readily solvate cations, and a reaction with benzyl

Scheme 6. Phase Transfer-Catalyzed Reaction of Alkyl Halides with Metal Carbonate[a]



[a] Where Mt − K and Na; R = C_6H_5−, $-CH_2{=}CH$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, and $-C_5H_{11}$, X = Br and Cl.

bromide does not take place. The introduction of activating agents such as crown ethers results in the formation of a complex of increased liophilicity, and the "naked" carbonate anion undergoes nucleophilic substitution with an alkyl bromide. The reaction of alkyl bromides with activated potassium carbonates is reversible, and the yield of alkylpotassium carbonates depends on the amount of excess of bromo derivatives used and the difference in nucleophilicity of the carbonates and bromide anions. The greater reactivity of the alkyl bromides compared to the corresponding chlorides in reactions with K_2CO_3 is due to the lower basicity and nucleophilicity of the bromide anion.

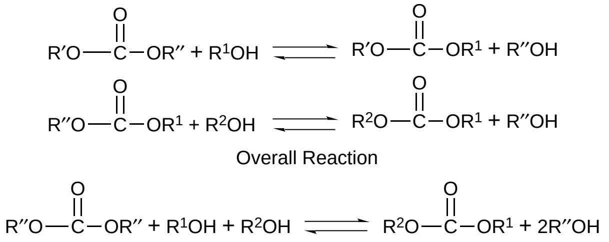
This method suffers from the following disadvantages. (i) Reactions of inorganic carbonates with alkyl halides are sluggish even at elevated temperatures. (ii) This reaction requires a long time, and yields obtained are also low but can be improved under specific reaction conditions. (iii) This reaction works satisfactorily only with alkyl bromide and K_2CO_3. It is difficult to prepare organic carbonates, using alkyl chloride and iodide with Na_2CO_3, and other group II metal carbonates. (iv) The solubility of most metal carbonates in nonpolar solvents is negligible, and the solubility is not appreciably better in dipolar aprotic solvents. (v) This method is not applicable for the preparation of diaryl and activated dialkyl carbonates. (vi) In the preparation of dialkyl carbonates by this process, side products such as dialkyl ethers are produced.

F. Carbonate Interchange Reaction

Carbonate interchange reaction can be defined as a process wherein one carbonate is converted to another carbonate by which one or both the acyl oxygen parts of the parent carbonate are displaced by an appropriate alkoxide/aryl oxide to produce a different carbonate with the aid of a suitable catalyst (Scheme 7).

Carbonate interchange reaction between carbonates and hydroxy compounds adheres to the following rule:[54] The more nucleophilic hydroxy compound displaces the less nucleophilic compound, and if both hydroxy compounds have similar nucleophilicity, then the less volatile compound displaces the more volatile one. Hence, even with lower mass alcohols, diaryl carbonates form dialkyl carbonates and the less nucleophilic phenols, but lower mass dialkyl carbonates react with higher mass alcohols to give the higher mass dialkyl carbonates; the lower boiling alcohol is removed by distillation. In this case carbonate interchange reaction occurs in steps with the intermediate formation of a mixed carbonate. The reaction of dialkyl carbonates with phenols to give diaryl carbonates occurs contrary to the above rule and can be achieved by using suitable catalysts. It proceeds, however, at a relatively slow rate. This reaction is analogous to transesterification reaction involving the reaction of hydroxy compound with an ester.[55]

Scheme 7. Carbonate Interchange Reaction[a]



[a] Where R″ = alkyl, aryl, or substituted alkyl or aryl; R^1, R^2 = alkyl, aryl, same, or different.

1. Dialkyl to Dialkyl Carbonates

The carbonate interchange reaction of aliphatic dihydroxy compounds of the general formula $HO-(CH_2)_n-OH$, where $n = 1-9$, 11−14, and 18, diethylene glycol, trimethylene glycol, and *p*-xylene glycol with diethyl carbonate or dibutyl carbonate was carried out by Carothers, Van Natta, and Hill.[56] They carried out reactions at temperatures between 120 and 160 °C, utilizing the catalytic action of sodium alcoholates. They obtained ethylene carbonate from ethylene glycol and trimethylene carbonate from 1,3-trimethylene glycol. However, the aliphatic dihydroxy compounds in which the −OH groups were separated by more than three $-CH_2-$ groups resulted in polycarbonates with molecular weight below 3000. Sarel and co-workers[57] investigated the influence of reaction conditions and structure of the aliphatic dihydroxy compounds on the formation of cyclic carbonates. Peterson[58] modified the carbonate interchange reaction used by Carothrs to eliminate the influence of alkaline catalyst. He used sodium alcoholates and an equivalent amount of carboxylic acid ester as catalysts.

Therefore, it was concluded that dialkyl carbonates will not undergo carbonate interchange reaction with aliphatic dihydroxy compounds in the absence of catalysts even at elevated temperatures. The reaction occurs readily in the presence of basic catalysts and is a convenient method for the synthesis of dialkyl carbonates and poly(alkyl carbonate)s. Morgan[59] prepared ethylene carbonate by the reaction of ethylene glycol with diethyl carbonate using anhydrous potassium carbonate as catalyst. Various

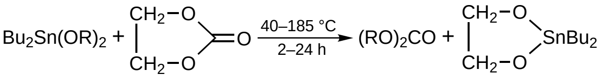
Table 1. Carbonate Interchange Reaction of Ethylene Carbonate with Alcohols

Chem. Abstr. no. (Co. name)	hydroxy compd	catalyst	reaction conditions: temp (°C)/time (h)/pressure (kg/cm^2)	product carbonate	yield (%)
76:99140z (Dow Chem. Co.)	$C_2H_5OH^a$	C_2H_5ONa	175/3/103	DEC	13
90:168058g (Bayer AG)	CH_3OH	NaOH	reflux/1.5/na	DMC	na
90:186365j (Bayer AG)	CH_3OH	$ClCH_2CO_2Na$	150/2/na	DMC	60
90:186366k (BayerAG)	CH_3OH	Tl_2O_3	150/0.5/na	DMC	25
92:214901t (Nisso Petrochem. Ind. Co. Ltd.)	C_4H_9OH	$Ti(OC_4H_9)_4$	120/5/na	DBC	68
93:147990k (Nisso Petrochem. Ind. Co. Ltd.)	C_4H_9OH	Ph_3P	120/5/na	DBC	65
93:149791m (Nisso Petrochem. Ind. Co. Ltd.)	C_2H_5OH	$ZnCl_2$, Et_3N	reflux/5/na	DEC	70
110:74823g (Asahi Chem. Ind. Co. Ltd.)	CH_3OH	anion exchange resin (Dowex MSA-1)	100/na/7	DMC	48
116:193723h (Asahi Chem. Ind. Co. Ltd.)	CH_3OH	PbO	100/1/na	DMC	38
118:254406x (Bayer AG)	CH_3OH	KOH	80/continuous process	DMC	45

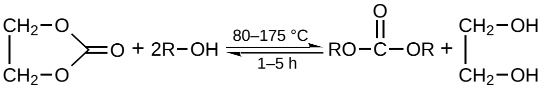
[a] Propylene carbonate was used; na = data not available.

methods are available for the synthesis of ethylene carbonate. It can be conveniently prepared from carbon dioxide and oxiranes.[44-47]

Sakai et al.[60] have reported the carbonylation of butylstannyl alkoxides with ethylene carbonate under nitrogen at atmospheric pressure. The corresponding dialkyl carbonates are obtained in 27−73% yield (eq 12, where R = CH_3, C_2H_5, n-C_4H_9, t-C_5H_{11}, i-C_3H_7, i-C_4H_9, t-C_4H_9). More emphasis has been given to the synthesis of higher alkyl carbonates by carbonate interchange reaction between ethylene carbonate and aliphatic hydroxy compounds (eq 13, where R = $-CH_3$, $-C_2H_5$, n-C_4H_9, polyhydroxy compound, e.g., D-mannitols). Most of the patented information reveals the use of basic inorganic compounds as catalysts which include alkali metal derivatives, such as hydroxides,[61] alkoxides,[62] hydrides, and alcoholate amides, and alkali metal salts formed from weak acids, such as acetates,[63] carbonates, and bicarbonates. Organic bases such as triethylamine[63] and triphenylphosphine[65] and phase transfer catalysts such as benzyltrimethylammonium chloride[64] and tetrabutylphosphonium bromide are also used. All the catalysts are used in the range of 0.1−0.01 wt % based on the weight of the reaction mixture. Reaction temperature varies from 175 to 225 °C. Lower temperature leads to low yields, even with relatively long reaction times. Some side reactions also take place in the case of alkyl carbonates which are less stable. They readily split off carbon dioxide and ethers. Such side reactions take place between ethylene carbonate and 1,2-glycols. The side products formed are alkyl glycol ethers and polyglycols such as di-, tri-, and tetraglycols. These reactions can be prevented by the use of a combination[66] of Lewis acid and organic base.



(12)

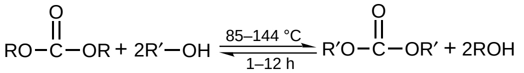


(13)

Carbonate interchange reactions between ethylene carbonate and aliphatic hydroxy compounds were also catalyzed by the use of organometallic catalysts such as titanium n-butoxide,[67] lead oxide,[68] thallium oxide[69] (Tl_2O_3), and zinc tetraacetoacetate.[70] All the reactions are conducted under homogeneous condition with or without the use of solvent, and good yields of corresponding carbonates are obtained. Recently a process based on the carbonate interchange reaction of ethylene carbonate with methanol producing dimethyl carbonate and ethylene glycol has been developed by Texaco Chemical Co.[71] The available patent information of carbonate interchange reaction of ethylene carbonate with hydroxy compounds (R−OH) is shown in Table 1.

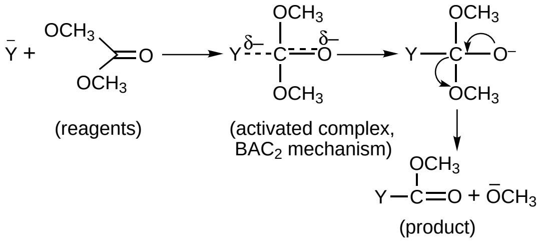
Dialkyl carbonates are also prepared by using basic ion exchange resin[72] containing quaternary ammonium groups. For example, dimethyl carbonate is produced from ethylene carbonate and methanol by passing the reactants through Dowex MSA-1 at 100 °C under 7 kg/cm^2 gauge in 48% conversion and 99% selectivity. Carbonate interchange reaction of ethylene carbonate with polyhydroxy compounds[73] such as 1-O-(p-nitrobenzoyl)- and 1-O-benzylglycerols, 1,2:3,4-di-O-isopropylidene-D-mannitols, 1,2-O-isopropylidene-α-D-glucofuranose, uridine, 1,2:5,6-di-O-isopropylidene-D-mannitol, and D-mannitol was carried out at 140−160 °C for 15−40 min, 30 mmHg, and corresponding cyclic carbonates were obtained in the range of 65−90% yield. Organosilyl carbonates[74] ($R_3SiO-CO-OSiR_3$), useful as water repellents, were prepared by reaction of trialkylsilane with ethylene carbonate using $NiCl_2$ as catalyst.

Dimethyl carbonate and diethyl carbonate can also be used in carbonate interchange reactions with aliphatic hydroxy compounds because the byproduct formed is a low-boiling point alcohol which can be easily removed from the reaction as an azeotrope with hydrocarbon solvent. Bondav et al.[75] have tabulated the conditions for the carbonate interchange reaction of diethyl carbonate with R−OH for C_{4-10} normal alcohols using metal hydroxides (NaOH, KOH, $Ca(OH)_2$) as catalysts, and 66−84% yields of corresponding carbonates were obtained. Dialkyl carbonates containing allyl double bonds,[76] which are useful as materials for optical glasses, are also prepared by carbonate interchange reaction between dimethyl carbonate and allyl alcohol. This is interchanged with different diols,[77] and double-bond-containing carbonate compounds are obtained which have high refractive index. A variety of simple[78] and substituted[79] alkyl carbonates are obtained by carbonate interchange reaction between dimethyl carbonate/diethyl carbonate and substituted alcohols (eq 14, where $R = -CH_3, -C_2H_5$; $R' =$ normal C_4-C_{10} alcohols, substituted alcohols, alcohols containing double bonds) (Table 2).



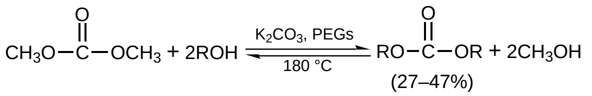
$$RO-\overset{O}{\overset{\|}{C}}-OR + 2R'-OH \underset{1-12\text{ h}}{\overset{85-144\text{ °C}}{\rightleftharpoons}} R'O-\overset{O}{\overset{\|}{C}}-OR' + 2ROH \quad (14)$$

Carbonate interchange reaction of dimethyl carbonate with alcohols was also carried out under bas−liquid phase transfer catalysis[80] (GL-PTC) conditions in which potassium carbonate bearing PEGS are able to catalyze reactions that usually require strong basic media. Under such conditions the hard anions (nucleophiles) generated attack the carbonyl carbon according to a BAC_2 mechanism (eq 15).



(15)

It is well known that dimethyl carbonate behaves as an ester in solution where solvation may be high. Therefore, it reacts with nucleophiles according to a BAC_2 mechanism yielding carbonate interchange product with alcohols. Primary alcohols react better than secondary ones, and tertiary alcohols are almost inactive under GL-PTC. Carbonate interchange reaction in GL-PTC is controlled by an alkoxide anion intermediate. In fact basicity trends in alkoxides follow the order tertiary > secondary > primary, so the first ones are present at equilibrium in lower concentrations than the last ones. The steric hindrance due to the alkyl chain is increased, and the conversion decreases. The yields of dialkyl carbonates obtained by this method vary from 27% to 47% (eq 16, where $R = -C_2H_5$, n-C_3H_7, n-C_4H_9, i-C_4H_9).



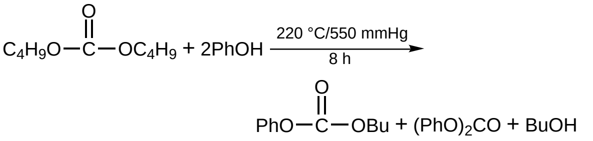
$$CH_3O-\overset{O}{\overset{\|}{C}}-OCH_3 + 2ROH \underset{180\text{ °C}}{\overset{K_2CO_3,\text{ PEGs}}{\rightleftharpoons}} \underset{(27-47\%)}{RO-\overset{O}{\overset{\|}{C}}-OR} + 2CH_3OH \quad (16)$$

The unsymmetrical[81a] dialkyl carbonates such as *tert*-butyl methyl carbonate and *tert*-amyl methyl carbonate, which are useful octane enhancers for gasoline, were prepared by carbonate interchange reaction with dimethyl carbonate. The reaction was carried out using inorganic base (cesium carbonate) with phase transfer catalyst (PEG-2000) under pressure at 125 °C for 5 h. For example, *tert*-butyl methyl carbonate was obtained in 43% yield with 95% selectivity from dimethyl carbonate and *tert*-butyl alcohol.

Recently, the carbonate interchange reaction of alcohols with dimethyl carbonate has been reported at atmospheric pressure under homogeneous conditions using di-*n*-butyltin oxide compound as catalyst.[81b] This reaction does not suffer from severe thermodynamic constraints and is therefore more facile. The reaction results in the formation of a mixture of unsymmetrical and symmetrical carbonates in good yields. Alcohols containing bulky groups and electron-withdrawing groups are unreactive (Table 3). The observed reactivities of alcohols and phenols toward carbonate interchange reaction with dimethyl carbonate are best understood in terms of a mechanism involving the formation of an alkoxy/aryloxy carbonate intermediate (Scheme 8).

2. Dialkyl to Alky Aryl Carbonate

The reaction of hydroxy compound (aliphatic or aromatic) with phosgene results in the formation of corresponding chloroformate in the presence of an acid-binding agent such as organic base. Reaction with another 1 mol of hydroxy compound (aromatic or aliphatic) gives alkyl aryl carbonate. Alkyl aryl carbonate can also be prepared by carbonate interchange reaction of phenol with dimethyl carbonate. This reaction is slow and unfavorable from an equilibrium and thermodynamic point of view. Therefore, it has to be carried out using appropriate catalyst and reaction conditions. Yamazaki et al.[82] have carried out the reaction of excess phenol with dibutyl carbonate at 220 °C and 550 mmHg pressure for 8 h using dialkyltin aryl oxide catalyst. It resulted in the formation of butyl phenyl carbonate in the range of 30−45% with a selectivity of 40−70% (eq 17). In this reaction diphenyl carbonate was also formed due to the reaction of butyl phenyl carbonate with excess phenol. In order to obtain higher selectivity of phenol to butyl phenyl carbonate, the reaction has to be carried out at lower temperature, and this can be achieved by the use of excess dibutyl carbonate.



$$C_4H_9O-\overset{O}{\overset{\|}{C}}-OC_4H_9 + 2PhOH \xrightarrow[8\text{ h}]{220\text{ °C}/550\text{ mmHg}} PhO-\overset{O}{\overset{\|}{C}}-OBu + (PhO)_2CO + BuOH \quad (17)$$

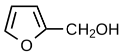
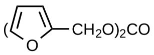
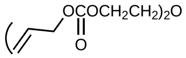
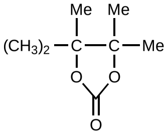
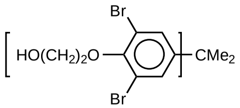
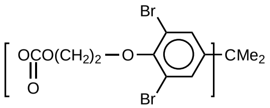
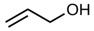
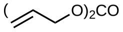
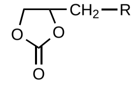
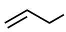
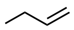
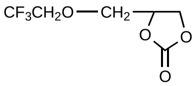
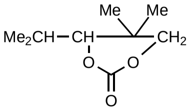
yield = 30–45%

selectivity = 40–70%

Dimethyl carbonate was reacted with phenol in the presence of titanium tetraphenoxide[83] catalyst at 180 °C and 6.6 atmospheric pressure with the continuous removal of methanol−dimethyl carbonate azeotrope; 53% phenyl methyl carbonate was obtained with 95% selectivity.

Recently[81b] the ortho- and meta-substituted phenols were selectively converted to the corresponding phenyl methyl carbonate by carbonate interchange reaction with dimethyl carbonate using di-*n*-butyltin

Table 2. Carbonate Interchange Reaction of Dimethyl Carbonate/Diethyl Carbonate with Various Hydroxy Compounds[a]

Chem. Abstr. no. (Co. name)	DMC/DEC	hydroxy compd	catalyst	reaction conditions: temp (°C)/time (h)/pressure (kg/cm^2)	product carbonate	yield (%)
83:11345f (Chemetron Corp.)	DEC		K_2CO_3	93−120/3/0.4/xylene		na
91:38943b (BASF AG)	DMC	C_2H_5OH	KOH	60/1/na	DEC + $C_2H_5OCO_2Me$	70
98:142969v (Anic SPA)	DMC	$CH_2{=}CH{-}CH_2OH + (HOCH_2CH_2)_2O$	NaOMe	reflux/na/na		91
99:53768g (Neos Co. Ltd.)	DEC	$Me_2CHC(Me)(OH)C(Me)(OH)Me$	*p*-$MeC_6H_4SO_3H$	110 na/na/na		93
103:123146a (Tokuyama Soda Co. Ltd.)	DEC		$CH_2{=}CHCH_2ONa$	90 na/na/7		83
110:215192q (Societe Francaise dorgano)	DMC		11,4,7,10,13-pentaoxa-cyclopentadecene	reflux/na/na/hexane		95
105:42777a (Neos Co. Ltd.)	DEC	3-(1-pyrrolidino)-1,2-propanediol	K_2CO_3	reflux/3/na	 R = 3-C-pyrrolidino	97
108:56767w (Hoechst AG)	DMC	 + $C_6H_{13}(CH_2)_2OH$	NaOMe	85−130/na/1	$C_6H_{13}(CH_2)_2OCO_2$ 	84
110:23867s (Neos Co. Ltd.)	DEC	$CF_3CH_2OCH_2CH(OH)CH_2OH$	K_2CO_3	reflux/1/na		70
111:23523x (Mitsui Petrochem. Ind. Ltd.)	DMC	$Me_2CHCH(OH)C(Me)(CH_2OH)Me$	NaOH	144/12/na		100

[a] na = data not available.

Table 3. Reaction of Alcohols (R−OH) with Dimethyl Carbonate

sr no.	R−	reaction time (h)	conversion (%)	dialkyl carbonate (%)	alkyl methyl carbonate (%)	selectivity to dialkyl carbonate (%)	mol of product/mol of catalyst
1	$Ar-CH_2-$	8	93	64	29	69	61
2	n-C_4H_9-	12	84	72	12	86	48
3	s-C_4H_9-	18	84	55	29	65	56
4	t-C_4H_9-	24	−	−	−	−	−
5	$CH_2{=}CH-CH_\infty-$	12	70	41	29	58.5	50
6	CF_3-CH_2-	24	−	−	−	−	−

[a] Catalyst: di-*n*-butyltin oxide, 1 mol % based on alcohol; − = no reaction.

Scheme 8. Mechanism of Carbonate Interchange Reaction in the Presence of Tin Catalyst

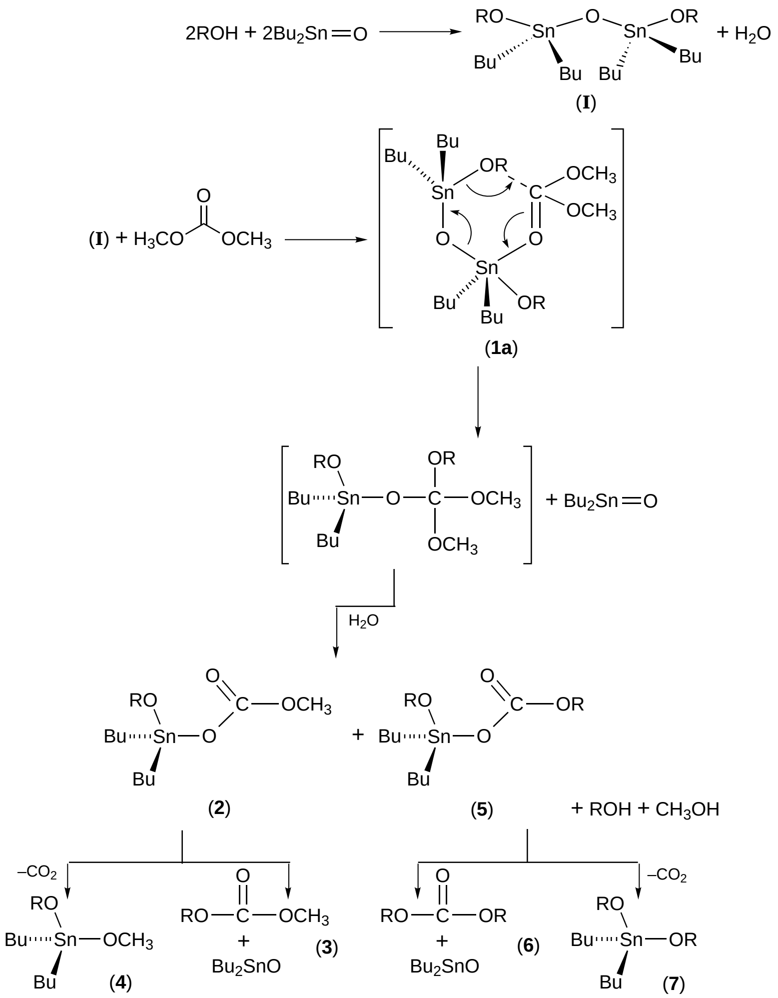


Table 4. Reaction of Phenol and Substituted Phenols with Dimethyl Carbonate[a]

sr no.	substituent	conversion (%)	diaryl carbonate (%)	aryl methyl carbonate (%)	selectivity to diaryl carbonate (%)	mol of product/mol of catalyst
1	H	37	33	4	90	20
2	p-CH_3	39	30	9	77	24
3	p-OCH_3	63	52	11	82	36
4	p-Cl	51	45	6	88	28
5	m-CH_3	25	−	25	0	25
6	m-OCH_3	25	−	25	0	25
7	o-CH_3	11	−	11	0	11
8	o-Cl	9	−	9	0	9
9	−CHO	−	−	−	−	−
10	$-COOCH_3$	−	−	−	−	−

[a] Catalyst: di-*n*-butyltin oxide (1 mol % catalyst based on phenol and substituted phenols). Reaction time: 12 h (for sr no. 1−8), 24 h (for sr no. 9); − = no reaction.

oxide as catalyst at atmospheric pressure (Table 4, entries 5−8).

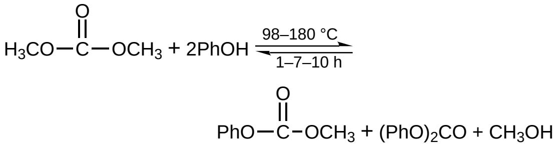
A large number of patents[84] have appeared in the literature which report the preparation of phenyl methyl carbonate. The detailed information about catalysts, time, percent conversion, and selectivity to phenyl methyl carbonate is shown in Table 5. Phenol is converted to phenyl methyl carbonate in 12−48%

Table 5. Preparation of Phenyl Methyl Carbonate (PhMeC) by Carbonate Interchange Reaction of Dimethyl Carbonate with Phenol

Chem. Abstr. no. (Co. name)	catalyst	reaction conditions: temp (°C)/time (h)/pressure (kg/cm^2)/solvent	PhMeC (%)	DPC (%)	selectivity to PhMeC (%)
90:186577e (Bayer AG)	$Ti(OC_4H_9)_4$	160/45/na/heptane	na	na	94
90:186578f (Bayer AG)	$(n\text{-}C_4H_9)_2Sn(OPh)_2$	155/na/na/heptane	na	na	98
91:92272v[a] (Mitsubishi Chem. Ind. Co. Ltd.)	$(n\text{-}C_4H_9)_2Sn(OBu)_2$	150/na/vacuum/na	40	2.3	95
95:42628c (Snam Progetti SPA)	$TiCl_3$	98/na/na/na	na	na	100
98:106994r (Asahi Chem. Ind. Co. Ltd.)	$Zr(acac)_4$	130/10/na/na	47.8	2.2	95
98:125616k (Asahi Chem. Ind. Co. Ltd.)	$Pb(OH)_2PbCO_3 + LiCl$	130/4/na/na	27.2	na	100
99:213037y (Gen. Elec. Co.)	$(C_8H_{17})_2SnO + Ti(OC_3H_7)_4 +$ 5 Å mol sieves	100/na/na/na	20	na	100
104:50646b[b] (Gen. Elec. Co.)	$(n\text{-}C_4H_9)_2Sn(C_2H_2O_2)_2 + CH_3SO_3H$	180/1−7/na/na	14	7	67
112:157845h (Mitsui Petrochem. Ind. Ltd.)	$Ti(OC_3H_7)_4$	280/0.5/na/na	18	2	88
112:178360m (Mitsui Petrochem. Ind. Ltd.)	$(AcOSnBu_2)_2O$	250/0.5/na/na	11	na	100
119:203159g (Ube Industries)	$YbCl_3$	170/1.5−7/na/na	16	0.7	95
119:270820d (Bayer AG)	$Ti(OC_3H_7)_4$	reflux/4/na/na	12	4	75

[a] Dibutyl carbonate was used. [b] DEC was used; na = data not available.

yield and in >90% selectivity (eq 18).

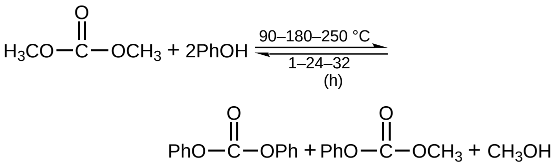


$$H_3CO-\overset{O}{\overset{\|}{C}}-OCH_3 + 2PhOH \xrightleftharpoons[1\text{–}7\text{–}10\ h]{98\text{–}180\ °C} PhO-\overset{O}{\overset{\|}{C}}-OCH_3 + (PhO)_2CO + CH_3OH \qquad (18)$$

yield = 12–47%
selectivity = 95–100%

3. Dialkyl to Diaryl Carbonates

The oxidative carbonylation of phenol with carbon monoxide and carbon dioxide is not an effective method to prepare diphenyl carbonate. The best method as of now appears to be through the carbonate interchange reaction between dialkyl carbonate and aromatic hydroxy compound, in spite of the fact that this reaction is slow and possesses unfavorable equilibrium and thermodynamics. This reaction takes place in two steps. In the first step dialkyl carbonate reacts with 1 mol of aromatic hydroxy compound to form alkyl aryl carbonate. Reaction with another 1 mol of hydroxy compound leads to the formation of diaryl carbonate (eq 19). This reaction is carried out in the liquid phase under homogeneous condition with soluble catalysts. Catalysts employed for the preparation of diaryl carbonate are organometallic compounds such as titanium, tin,[85] silicon,[86] lead, iron,[87] lithium,[88] and aluminum[89] which are used as alkoxides, oxides, and acetates. Tin compounds are used as stannoxane,[90] and polymeric tin compounds such as poly(oxydioctylstannylene)[91] are also used. A wide temperature range is reported (150−250 °C) for the carbonate interchange reaction between dialkyl carbonate and aromatic hydroxy compound. Byproduct formed in the reaction is removed in the form of azeotrope with the hydrocarbon solvent, or it is removed as azeotrope with dialkyl carbonate. Therefore, in this reaction dialkyl carbonate is used in excess. A number of patents are extant on the catalytic carbonate interchange reaction of phenol with dimethyl carbonate. They reveal the use of titanium and organotin catalysts. A maximum conversion of phenol to diphenyl carbonate is obtained in the range of 34−36% with 100% selectivity. The use of specific catalysts, temperature, yield of the product, and selectivity to diphenyl carbonate is given in Table 6.



$$H_3CO-\overset{O}{\overset{\|}{C}}-OCH_3 + 2PhOH \xrightleftharpoons[1\text{–}24\text{–}32\ (h)]{90\text{–}180\text{–}250\ °C} PhO-\overset{O}{\overset{\|}{C}}-OPh + PhO-\overset{O}{\overset{\|}{C}}-OCH_3 + CH_3OH \qquad (19)$$

yield = 12–45%
selectivity = 50–100%

The carbonate interchange reaction of various para-substituted phenols with dimethyl carbonate was studied at atmospheric pressure using di-*n*-butyltin oxide as catalyst. Para substituent gave predominantly diaryl carbonate with a low percentage of para-substituted phenyl methyl carbonate. Electronic effects of the substituents appeared important in obtaining good conversion and selectivity to product carbonate. Phenols possessing electron-withdrawing groups were unreactive, and higher nucleophilic phenols were found to be more reactive in this reaction[81b] (Table 4, entries 9, 10, 1−4).

A continuous process is also described for the preparation of diphenyl carbonate from dimethyl

Table 6. Preparation of Diphenyl Carbonate by Carbonate Interchange Reaction of Dimethyl Carbonate with Phenol

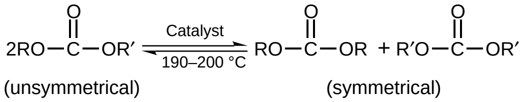
Chem. Abstr. no. (Co. name)	catalyst	reaction conditions: temp (°C)/time (h)/pressure (kg/cm^2)/solvent	DPC (%)	PhMeC (%)	selectivity to DPC (%)
92:58427K (Mitsubishi Chem. Ind. Co. Ltd.)	Si−Ti complex	250/3/4/N_2	12.5	6.3	66
95:80505t (Nisso Petrochem. Ind. Co. Ltd.)	Li_2O_3[a]	150−220/10/na/na	17.2	12.7	57
104:50647c (Gen. Elec. Co.)	poly(oxydioctylstannylene)[a]	180/1−24/na/na	32.2	9.1	78
106:67825y (Daicel Chem. Ind. Ltd.)	$Fe(OAc)_3$	155−185/8/na/benzene	34.3	na	100
109:210720e (Daicel Chem. Ind. Ltd.)	$(BuSn(OAc)_2)O$	reflux/8/na/na	5.3	na	100
116:193904t (Daicel Chem. Ind. Ltd.)	$Al(OPh)_3$ or $Al(OMe)_3$	85−90/8/na/na	36.5	na	100
119:162809y (Tianrangi Huagong)	$MgCl_2$−$Ti(OBu)_4$−organotin	190/32/na/benzene	36.4	na	100
119:180523e (Daicel Chem. Ind. Ltd.)	$(n\text{-}C_4H_9)_2Sn(OBu)_2$	reflux/8/na/benzene	45	42	51

[a] DEC was used; na = data not available.

carbonate. Reaction is carried out in the presence of catalyst such as titanium phenoxide[92] and in three successive reaction zones. Conditions were selected to maximize the formation of aryl alkyl carbonate in the first two zones, while conversion to diphenyl carbonate was favored in the third zone. The vapors from the first two zones were separated by distillation to give recyclable streams. A similar continuous process is also described for the preparation of diphenyl carbonate using PbO[93] catalyst; 885 g/kg/h diphenyl carbonate with 99% selectivity is obtained. It is reported that Enichem Synthesis (Italy) produces 4000 tons of diphenyl carbonate per year by carbonate interchange reaction of dimethyl carbonate with phenol.[31] This process has been licenced to GE Plastics in Japan.[31b]

4. Alkyl Aryl Carbonate to Diaryl Carbonate

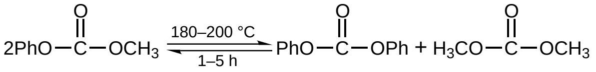
Alkyl aryl carbonate can be converted to diaryl carbonate by reaction with another molecule of aromatic hydroxy compound using a suitable catalyst. This reaction is slow and thermodynamically unfavorable. Only one patent reports the reaction of phenyl methyl carbonate with phenol in benzene solvent in the presence of catalyst, and byproduct methanol was removed as an azeotrope. In this reaction phenyl methyl carbonate was converted to diphenyl carbonate in 48.4% yield and 95% selectivity.[94] Alkyl aryl carbonates can be conveniently converted to diaryl carbonate by self-condensation or disproportion reaction in presence of Lewis acid catalysts. Williams et al.[95a] have studied the disproportion of various unsymmetrical carbonates by heating in the presence of different catalysts (eq 20, where R, R′ = alkyl, aryl).



$$2RO{-}\overset{O}{\overset{\|}{C}}{-}OR' \underset{190\text{–}200\ °C}{\overset{\text{Catalyst}}{\rightleftharpoons}} RO{-}\overset{O}{\overset{\|}{C}}{-}OR + R'O{-}\overset{O}{\overset{\|}{C}}{-}OR' \quad (20)$$

(unsymmetrical) (symmetrical)

Mixed ethyl and aryl or aryl alkyl carbonates disproportionate in the presence of catalysts such as sodium methoxide, titanium tetrachloride, titanium butoxide, sodium hydrogen titanium butoxide, strontium methoxide, magnesium methoxide, aluminum isopropoxide, tetraethyl tin, lead borate, and sodium phenoxide. Usually diethyl carbonate was formed, and other symmetrical carbonates were isolated. However, the loss of CO_2 and other side reactions were also observed. The course of the reaction was dependent upon the structure of the carbonates and on the catalyst. The more alkaline catalysts such as sodium methoxide and lithium aluminum ethoxide promoted more side reactions. Titanium butoxide was reported to be the best catalyst for this reaction. Phenyl methyl carbonate was converted to diphenyl carbonate using aluminum-based Lewis acid catalysts, and anisole was also formed due to decarboxylation reaction.[95b] It is evident from the patent literature[96,84j,k] that phenyl methyl carbonate is converted to diphenyl carbonate using various Lewis acid catalysts at 180−195 °C with or without the use of hydrocarbon solvent to remove dialkyl carbonate (eq 21). A summary of available information is presented in Table 7.



$$2PhO{-}\overset{O}{\overset{\|}{C}}{-}OCH_3 \underset{1\text{–}5\ h}{\overset{180\text{–}200\ °C}{\rightleftharpoons}} PhO{-}\overset{O}{\overset{\|}{C}}{-}OPh + H_3CO{-}\overset{O}{\overset{\|}{C}}{-}OCH_3 \quad (21)$$

5. Use of Activated Carbonates

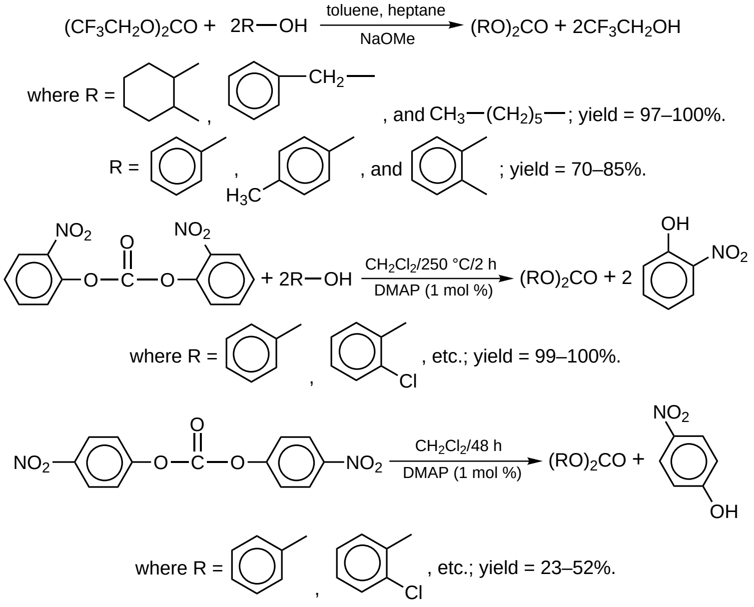
In the case of esters, transesterification is accelerated due to the electron-withdrawing substituents on either the alkyl or alkoxy group of the ester. Likewise carbonate interchange reaction can also be accelerated by the presence of electron-withdrawing groups in dialkyl and diaryl carbonates. Dialkyl carbonates containing fluorine groups and diaryl carbonates containing $-NO_2$, $-Cl$, or $-CN$ in the ortho position with respect to the carbonate linkage are more reactive in carbonate interchange reaction. These carbonates are known as activated carbonates. Diaryl carbonates such as bis(4-nitrophenyl) carbonate, bis(2,4-dinitrophenyl) carbonate, and bis(2,4,6-trichlorophenyl) carbonate are also activated carbonates but are less reactive than bis(2-nitrophenyl) carbonate.

Table 7. Self-Condensation of Phenyl Methyl Carbonate to Diphenyl Carbonate

Chem. Abstr. no. (Co. name)	catalyst	reaction conditions: temp (°C)/time (h)/solvent	conversion (%)	selectivity to DPC (%)
85:46222g (Anic SPA)	$Ti(OPh)_4$	180/4/ethylcyclohexane	70	95
87:5655y (Anic SPA)	$Ti(OPh)_4$	180/4/na	40	95
112:178360m (Mitsui Petrochem. Ind. Ltd.)	$Mn_2(CO)_{10}$	200/1/na	na	na
117:130915x (Asahi Chem. Ind. Co. Ltd.)	Na_2WO_4	195/5/na	74	93
117:192542g (Idemitsu Kosan Co. Ltd.)	$Ti(OBu)_4$	80/na/na	na	99
118:105312m (Asahi Kasei Kogyo KK)	PbO	180/3/na	89	99

[a] na = data not available.

Scheme 9. Synthesis of Dialkyl and Diaryl Carbonates by Carbonate Interchange Reaction with Activated Dialkyl and Diaryl Carbonates



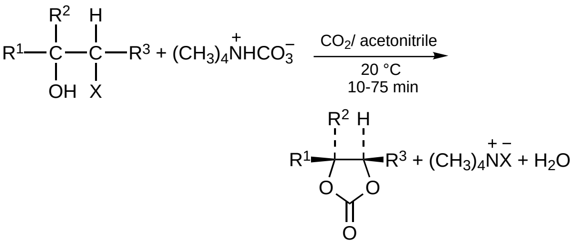
Brunelle synthesized bis(2,2,2-trifluoroethyl) carbonate[97] and bis(2-nitrophenyl) carbonate[98] by the reaction of corresponding hydroxy compounds with phosgene. Other di- or trisubstituted carbonates were synthesized by reaction with triphosgene.[99] These activated carbonates reacted with various hydroxy compounds, and the corresponding carbonates were obtained in good yields. The carbonate interchange reaction of activated dialkyl carbonate[100] was carried out with alcohols and phenols using hydrocarbon solvent at the reflux temperature in the presence of base (Scheme 9). Carbonate interchange reactions of bis(2-nitrophenyl)carbonate[101] and bis(4-nitrophenyl)carbonate with various phenols were carried out at room temperature using an organic base such as triethylamine, and the rate of reaction was accelerated by the use of hypernucleophilic 4-(dimethylamino)pyridine as catalyst (Scheme 9).

Bis(4-nitrophenyl) carbonate was found to be less effective in carbonate interchange reaction for preparing diaryl carbonates. Bis(2-nitrophenyl) carbonate in the presence of 4-(dimethylamino)pyridine as a catalyst shows a unique reactivity. This was mainly attributed to the unusual stabilization of the tetrahedral intermediate formed by the attack of 4-(dimethylamino)pyridine on the bis(2-nitrophenyl) carbonate.[101] These activated carbonates are also useful in the synthesis of high molecular weight polycarbonates in the presence of 4-(dimethylamino)pyridine as catalyst.[99]

G. Other Methods of Synthesis of Dialkyl Carbonates

1. From Halohydrins

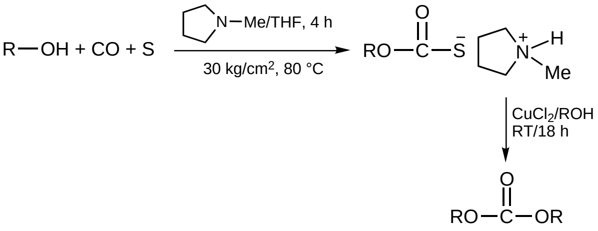
Alicyclic carbonates were prepared from *vic*-halohydrins using sodium hydrogen carbonate[102] and sodium alkyl carbonates.[103] These methods require high temperature and pressures to obtain good yields of the carbonates. Alicyclic carbonates can be prepared in high yields, in short reaction times, under mild conditions and without the above-mentioned drawbacks by simply stirring the corresponding *vic*-halohydrins with tetramethylammonium[104] hydrogen carbonate in acetonitrile. Tetramethylammonium hydrogen carbonate was easily obtained by saturating the commercially available methanol solution of tetramethylammonium hydroxide with carbon dioxide (eq 22, where R^1, R^2, R^3 = $-H$, $-CH_3$, $-C_6H_5$; X = $-Cl$, $-Br$). Bromohydrins react faster than the corresponding chlorohydrins.



(22)

2. From Alcohols and Carbon Monoxide by Elemental Sulfur

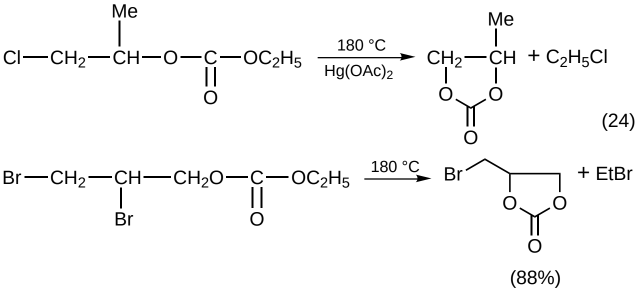
Several cyclic and acyclic carbonates were synthesized from the corresponding alcohols using carbon monoxide in good to excellent yields. Carbonates are formed by carbonylation of alcohol with carbon monoxide and elemental sulfur[105] in the presence of triethylamine or 1-methylpyrolidine at 30 kg/cm^2, 80 °C, for 4 h to afford the corresponding ammonium salts of *O*-alkyl thiocarbonates followed by treatment with copper(II) chloride at room temperature (eq 23, where R = $-CH_2-CH-Ph$, $-CH_2-CH_2-$, $-CH_2-CH(CH_3)-$, n-$C_6H_{13}-$, n-C_4H_9-, i-C_4H_9-, $Ph-CH_2-$).



(23)

3. Alicyclic Carbonate from Halogenated Carbonates

Mono-[106] or dihalogenated[107] alkyl carbonates were heated with or without catalyst at 180–200 °C for 1–4 h. Cyclic carbonates were obtained in 82–90% yields with the formation of alkyl halide byproduct (eq 24).

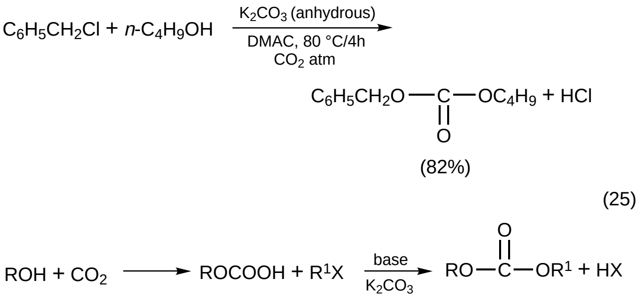


(24)

4. From Carbon Dioxide

Recent interest in the utilization of carbon dioxide as a synthetic building block has prompted investigations toward preparation of carbonates from carbon dioxide.

a. From CO_2, Alcohol, and Alkyl Halide.[108] In this reaction alcohol and carbon dioxide reversibly react to form monoalkylcarbonic acid, which in turn affords monoalkyl carbonate in the presence of potassium carbonate. The monoalkyl carbonate thus formed reacts with alkyl halide to produce carbonate. The key to this reaction is the use of K_2CO_3 as base (eq 25).



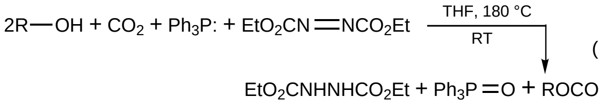
$$C_6H_5CH_2Cl + n\text{-}C_4H_9OH \xrightarrow[\text{DMAC, 80 °C/4h, } CO_2 \text{ atm}]{K_2CO_3 \text{ (anhydrous)}} C_6H_5CH_2O-\underset{\underset{\displaystyle O}{\|}}{C}-OC_4H_9 + HCl \quad (82\%)$$

(25)

$$ROH + CO_2 \longrightarrow ROCOOH + R^1X \xrightarrow[K_2CO_3]{\text{base}} RO-\overset{\overset{\displaystyle O}{\|}}{C}-OR^1 + HX$$

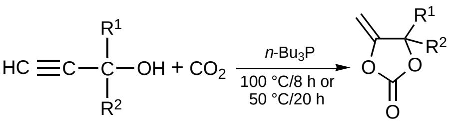
This method is useful for the preparation of symmetrical and unsymmetrical dialkyl carbonates in good yields. The reaction is efficient with primary and secondary alcohols and primary butyl bromides and iodides.

b. From CO_2, Alcohol, and Triphenylphosphine. In this reaction, an alcohol reversibly adds to carbon dioxide, and hemicarbonic acid is formed. This reacts with triphenylphosphine–diethyl azodicarboxylate complex, and further reaction of another 1 mol of alcohol results in the formation of dialkyl carbonate with the liberation of triphenylphosphine oxide and dicarbethoxyhydrazine. This reaction is characterized by mildness, simplicity, and good yield under ambient conditions (eq 26a, where R = i-C_4H_9-, $C_5H_{11}-$, $CH_3-CH(CH_3)-(CH_2)_4-$, $CH_2{=}CH-CH_2-$).[109a]



$$2R-OH + CO_2 + Ph_3P{:} + EtO_2CN{=}NCO_2Et \xrightarrow[\text{RT}]{\text{THF, 180 °C}} EtO_2CNHNHCO_2Et + Ph_3P{=}O + ROCO_2R \quad (26a)$$

Dixneuf and Bruneau[109]1b have reported a one-step transformation of substituted propargyl alcohols with CO_2 and a phosphine catalyst to a cyclic carbonate in 98% yield (eq 26b, where $R^1 = -CH_3$; $R^2 = -CH_3$, $-C_2H_5$, $-C_6H_5$, $-n$-C_4H_9, $-CH{=}CH_2$). The reaction occurs with tertiary alcohols. The α-methylene cyclic carbonates are useful intermediates for the synthesis of β-oxopropyl carbonates and oxazolidinones.



(26b)

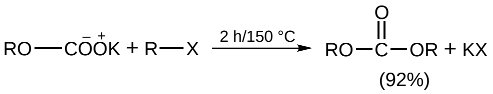
c. From CO_2, Alcohol, and Dialkoxydibutyltin. Reactions of carbon dioxide with dibutyltin dialkoxides have been studied by Sakai et al.[110] This method was also studied by Yamazaki et al.[82] who showed the preparation of dialkyl carbonates from CO_2 and alcohols in the presence of dialkoxydibutyltin. The reactions were carried out under pressure of CO_2. It is assumed that carbon dioxide is inserted into the Sn–O bond of $Bu_2Sn(OR)_2$ followed by alcoholysis yielding carbonate and $Bu_2Sn(OH)_2$, which is again esterified by alcohol, so that the tin catalyst is reused. Removal of most of the water produced from the reaction mixture is necessary to give higher yields of carbonates (eq 27,where R′ = $-CH_3$, $-C_2H_5$, $-C_4H_9$, $-C_5H_{11}$).

$$2R'OH + CO_2 \xrightarrow[100-170\ °C/24\ h]{Bu_2Sn(OR')_2} (R'O)_2CO + H_2O \quad (27)$$

d. Fixation of CO_2 by Metal Salt.[111] Ethanol is added to a reactor filled with CO_2, and the reaction is catalyzed by $Hg(OAc)_2$. Diethyl carbonate is obtained in 58% yield. Reaction of a mixture of alcohols with CO_2 is also catalyzed by nitronium salt. For example, propargyl alcohol and methanol are reacted with CO_2 in the presence of $Ru(CO)_{12}$ and triethylamine for 120 h at room temperature. Propargyl methyl carbonate was obtained in 76% yield.

5. Alkylation of Alkali Metal Carbonate[112]

Alkali metal carbonate, e.g., ethyl potassium carbonate, was obtained by passing CO_2 through an alcoholic solution of potassium ethanolate. Alkylation with alkyl halide gives dialkyl carbonate (eq 28, where R′ = $-CH_3$, $-C_2H_5$, $-C_4H_9$, $-C_5H_{11}$).



$$RO{-}C\overset{-}{O}\overset{+}{O}K + R{-}X \xrightarrow{2\text{ h}/150\ ^\circ\text{C}} RO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR + KX \quad (28)$$

(92%)

VIII. Applications of Organic Carbonates

A. Application of Dimethyl Carbonate as Alkylating Agent under GL-PTC

Even though dimethyl carbonate can be used to introduce a carbonate linkage by carbonate interchange reaction, it is also a useful chemical for a variety of synthetic and industrial applications under different reaction conditions. The various applications of dimethyl carbonate and other organic carbonates are detailed in this section.

Dimethyl carbonate is an intermediate whose reactivity makes it useful as a substitute for phosgene and dimethyl sulfate. These are used as intermediates in several industrial applications. In many organic chemical transformations, dimethyl carbonate offers a safe and cleaner reaction, free of solid wastes.

Dimethyl carbonate, under appropriate operating conditions, is active toward various substrates in carbonylation[113] and methylation.[114,115] The potential areas of utilization are numerous, and it covers a large part of the present industrial uses of phosgene and dimethyl sulfate. The use of dimethyl carbonate as an alkylating agent has been thoroughly studied using various catalysts and conditions and appears to be the reagent of choice for the methylation of phenols.

Phase transfer catalysis (PTC) has been used for a long time by organic chemists to catalyze many organic reactions. PTC has become in recent years one of the most widely used techniques in organic synthesis and is applied to a great number of organic reactions.[116,117] Alkylation of phenols and substituted phenols with dimethyl carbonate is also carried out under PTC using K_2CO_3 and crown ethers.[118] But the yields of the product obtained were low (eq 29).

$$R_1{-}PhOH \xrightarrow[\substack{180\ ^\circ C\\ DMC}]{K_2CO_3/18\text{-crown-}6} R_1{-}PhOR \qquad (29)$$

where R_1 = alkyl.

PTC reactions can be carried out by different methods. The first method involves flow of a gaseous reagent through a solid bed bearing a liquid catalyst (SL-PTC).[119−122] Several reactions of industrial importance are carried out under such conditions. Examples of such reactions are the oxidation of SO_2 to SO_3, aromatic alkylation, and oxychlorination. However, activated anions were never allowed to react in classical organic synthesis under SL-PTC.

The second method involves the flow of gaseous reagents through a molten phase transfer catalyst supported on a solid. This is known as gas−liquid phase transfer catalysis (GL-PTC). This new method was extensively studied by Tundo et al.[123]

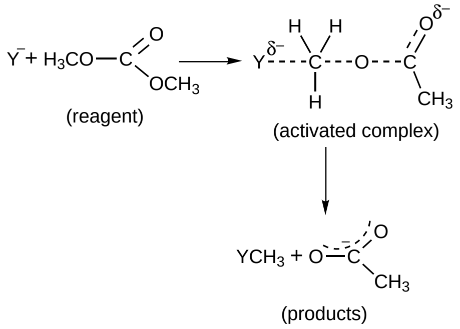
GL-PTC technique has many advantages over the classical PTC technique. (i) A continuous process can be carried out in a gas phase. (ii) It is useful for highly selective synthesis, and gas phase reactions occur at a high rate due to the absence of solvation of the anions. For example, nucleophilic substitution reaction occurs around 10^7 times faster in the gas phase than in solution. (iii) Activated anions have high free energy in the unsolvated state. (iv) No solvent is used in this reaction. In GL-PTC reactions, both reagents and products, which are in gaseous phase, are reversibly adsorbed on liquid film. This in turn is supported on a solid. The liquid film constitutes the phase in which the reaction occurs because the liquid actually is a molten phase transfer catalyst. It allows the activation of anions.

Catalysts able to provide reactions under GL-PTC conditions include both ionic substances such as quaternary onium salts and neutral ligands like crown ethers, cryptands, or poly(ethylene glycol)s. In GL-PTC, poly(ethylene glycol)s (PEGs) are extensively used because PEGs are thermally stable upto 200 °C and they have a high adjustable vapor pressure depending on their mean molecular weight. Finally, PEGs are cheap and nontoxic substances.

In GL-PTC some problems can arise from the limited stability with time and/or temperature because gas phase processes are usually performed at high temperatures in order to volatilize the organic reagents and speed up the reaction. Under such conditions, decomposition or partial volatilization of the catalyst may take place. Therefore an important prerequisite for a GL-PTC catalyst is that it must have high thermal stability at the reaction conditions.

The GL-PTC technique has been extensively used for a variety of organic reactions. This includes alkylation of weak acidic compounds such as phenols and mercaptans with alkyl halides using K_2CO_3 as a base,[124] transhalogenations in alkyl halides,[125,126] and production of primary alkyl halides from primary alcohols.[127]

As dimethyl carbonate is a low-boiling (bp 90 °C) compound, it can be easily volatilized at lower temperature and is thermally stable. Therefore dimethyl carbonate meets the conditions of GL-PTC technique. Dimethyl carbonate is used in GL-PTC for alkylation of weakly acidic compounds such as phenols, thiophenols, aromatic amines, malonic acid esters, and arylacetonitriles. Under GL-PTC conditions the anions generated attack the saturated carbon of dimethyl carbonate. In this reaction a broader delocalization results during the transition state, and the corresponding ether is formed by a base-catalyzed bimolecular alkyl–oxygen fission (BAL_2) mechanism (eq 30).



(30)

1. Reaction with Phenol and Thiophenol

Under GL-PTC conditions when a mixture of dimethyl carbonate and phenols or mercaptans flows through a catalytic bed of K_2CO_3/PEGs, only anisole is produced[128] (eqs 31 and 32).

$$ArOH + CH_3OCOOCH_3 \xrightarrow{\text{PEGs, } K_2CO_3} ArOCH_3 + CH_3OH + CO_2 \quad (31)$$

$$RSH + CH_3OCOOCH_3 \xrightarrow{\text{PEGs, } K_2CO_3} RSCH_3 + CH_3OH + CO_2 \quad (32)$$

In GL-PTC potassium carbonate-bearing PEGs as catalysts are able to catalyze reactions that usually require strong basic media. Under these conditions, reactions of soft nucleophiles like ArO^- and RS^- are strongly promoted. Mercaptans are more easily obtained than alkoxides by reaction with a base and so undergo a faster nucleophilic displacement. On the other hand, the nucleophilic strength of anions is enhanced under GL-PTC conditions as they attack the methyl group rather than the carbonyl one. The overall reaction pathway is as follows:

$$PhOH + B \rightarrow BH^+ + PhO^-$$

$$PhO^- + CH_3OCOOCH_3 \rightarrow PhOCH_3 + CH_3OCOO^-$$

$$BH^+ + CH_3OCOO^- \rightarrow B + CO_2 + CH_3OH$$

$$\text{Overall reaction: } PhOH + CH_3OCOOCH_3 \rightarrow PhOCH_3 + CO_2 + CH_3OH$$

Anion activation and deficiency in solvation during the transition state enables ArO^- anions to shift the nucleophilic attack forward to the methyl group according to the BAL_2 mechanism. The leaving group, namely, the methoxycarbonate anion, is not stable and spontaneously decomposes into CO_2. The acidity is removed from the reaction environment, the base is regenerated, and the process continues. Alkylation with dimethyl sulfate or alkyl halides requires the use of a base in stoichiometric amounts because the leaving group (SO_4^{2-} or Hal^-) can not be removed from the reaction medium.

2. Reaction with Primary Aromatic Amines

Under GL-PTC conditions aromatic amines produce selectively *N*-methylanilines. The overall process is described as follows (eq 33).

$$ArNH_2 + CH_3OCOOCH_3 \xrightarrow{\text{PEGs, } K_2CO_3} ArNHCH_3 + CH_3OH + CO_2 \quad (33)$$

The reaction does not occur in the absence of PEGs. Besides, in the absence of K_2CO_3, the reaction produces only urethane ($ArNHCOOCH_3$). Therefore, it is the base that promotes the subsequent alkylation reaction. At 90% conversion and a dimethyl carbonate/aniline molar ratio of 10, <1% *N,N*-dimethylaniline is produced. *N*-Methylaniline is produced industrially by the monoalkylation of aniline with methanol in gas phase. High temperatures (up to 400 °C), high pressures, or long contact times are needed. This results in the formation of a mixture of mono- and dimethylanilines and unreacted aniline.

3. Reaction with Arylacetonitriles

Very high selectivities in monoalkylation arise when dimethyl carbonate is reacted with carbanions, under GL-PTC condition. Arylacetonitriles and malonic acid esters give only methylation, through a BAL_2 mechanism. Moreover, only mono-C-alkylation occurs (eq 34).

$$ArCH_2CN + CH_3OCOOCH_3 \xrightarrow[\substack{\text{conv} = 97.5\% \\ \text{select} = 99.5\%}]{\text{PEGs, } K_2CO_3} ArCH(CH_3)CN + CH_3OH + CO_2 \quad (34)$$

When arylacetonitriles are reacted with alkyl halides in the presence of strong bases, alkylation is not quite as selective and yields large amounts of dialkyl derivatives as byproducts under classical or PTC conditions.

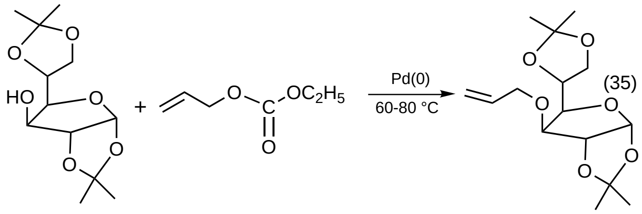
Owing to anion activation and presumably due to their microenvironmental effects, dimethyl carbonate reacts differently in batch and in continuous flow conditions. The results are as follows:

	products	
reagents	batch	GL-PTC
ArOH	$ArOCOOCH_3$	$ArOCH_3$
ArSH (RSH)	$ArSCH_3$(−)	$ArSCH_3$ ($RSCH_3$)
$ArNH_2$	$ArNHCOOCH_3$	$ArNHCH_3$
ROH	$ROCOOCH_3 + (RO)_2CO$	$ROCOOCH_3 + (RO)_2CO$
$ArCH_2CN$	$ArCH(CN)COOCH_3$	$ArCH(CN)CH_3$

Such differences might be attributed not only to anion activation but also to temperature effects. GL-PTC derives different products from reactions carried out in solution often in a very selective way. Thus the results attest that dimethyl carbonate can readily replace the highly toxic dimethyl sulfate as safe methylating agent when the reactions are carried out under GL-PTC conditions in a continuous flow process. The detailed information based on this aspect (GL-PTC) is described by Tundo et al. in a review article.[129]

Dimethyl carbonate can be used under GL-PTC for alkylation of various compounds containing acidic hydrogen. The reaction, however, takes place in the gaseous phase. Dimethyl carbonate can also be used in solution to carry out the alkylation reaction using (dimethylamino)pyridine,[130] Lewis acids such as Al(III) compounds,[131] quaternary ammonium salts,[132] and guanidine bases[133] as catalysts at 100−180 °C. Alkylation reactions can be carried out using lower temperatures and neutral conditions using palladium(0) as catalyst.

Lakhmiri et al.[134] converted primary and secondary alcohols of the carbohydrate series into allyl ethers using allyl ethyl carbonate in the presence of Pd(0) at 60−80 °C (eqs 35 and 36). Anomeric hydroxyl as well as functionalized compounds like hydroxyl esters were also allylated (eq 37).



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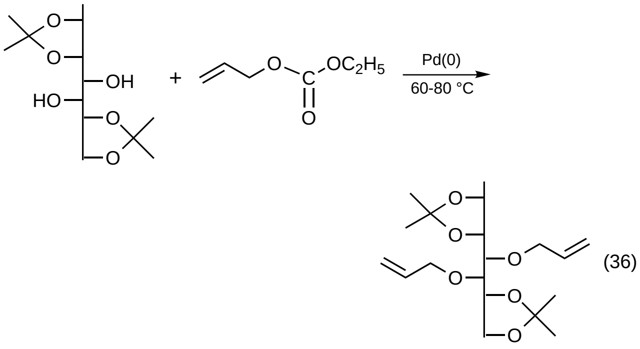

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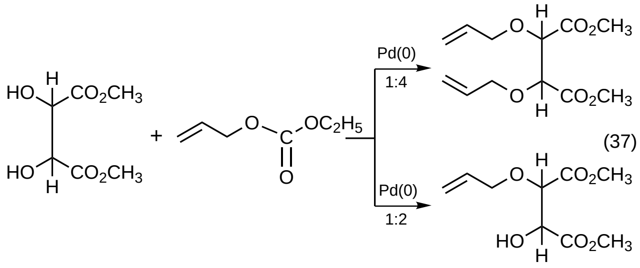
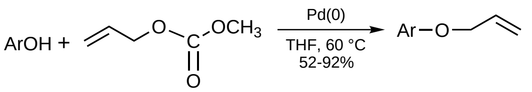


(37)

Substituted phenols can also be converted to allyl aryl ethers in the presence of Pd(0) catalysts[135] (eq 38, where Ar = $-C_6H_5$, p-$CH_3O-C_6H_4-$, 2,6-$(CH_3)_2-C_6H_3-$, p-$Cl-C_6H_4-$, p-$NO_2-C_6H_4-$). This reaction has been extended to bisphenols recently (eq 39, where R = $-C(CH_3)_2)$).[136] Bisallyl ethers of bisphenol-A are important intermediates and find use in a variety of polymer-forming reactions. Allyl carbonates can be used to alkylate ethyl acetoacetate in the presence of a catalytic amount of ruthenium in N-methylpiperidine[137] (eq 40).

Phenyl acetonitriles and ketone oximes react with dimethyl carbonate in the presence of a base like K_2CO_3 to yield the corresponding monoalkylated product and cyclic oxazolin-2-ones respectively[138,139] (eqs 41 and 42). Reaction of norbornene with acetyl ethyl carbonate gave a cyclopropane derivative[140] (eq 43).



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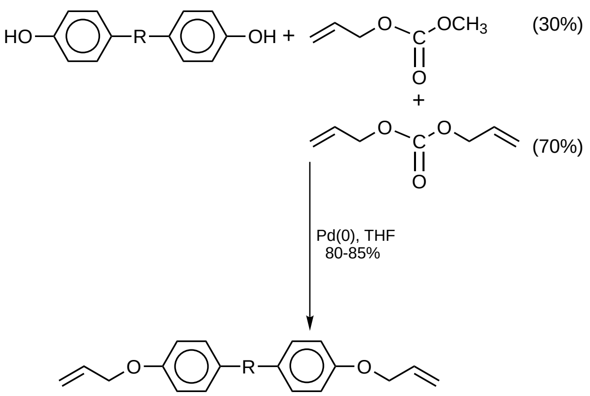

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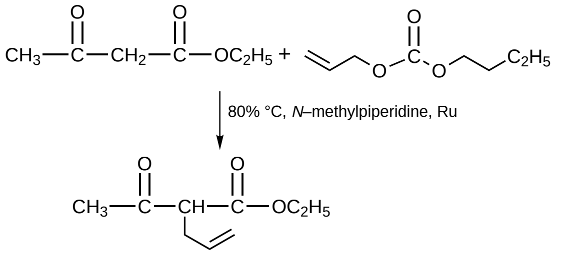

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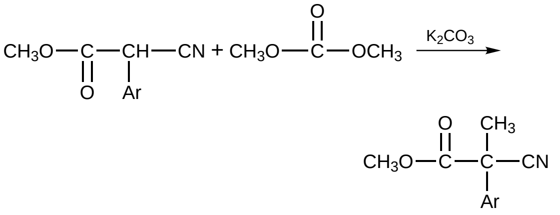
The reaction presumably involves an oxidative addition followed by dicarboxylation.



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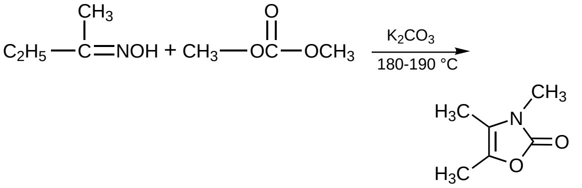

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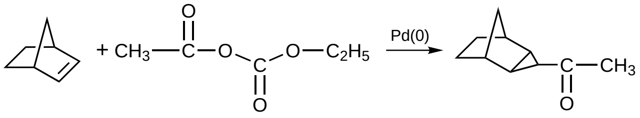

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B. Other Applications of Organic Carbonates

1. Dimethyl and Diethyl Carbonates

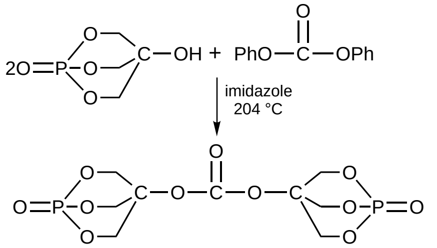
The carbonate linkage plays a dominant role in determining the chemical properties of dimethyl and diethyl carbonate. The carbonate interchange reaction can be used to obtain higher symmetrical and unsymmetrical alkhl aryl and diaryl carbonates using suitable reaction conditions.

Diethyl carbonate is an excellent solvent in the midboiling range. This has been used as a medium evaporating solvent for cellulose nitrate and finds applications where a pure neutral/acquer solvent is required. Diethyl carbonate finds substantial use as an intermediate for various pharmaceuticals, notably phenobarbital where it is used to prepare diethyl phenylmalonate. Diethyl and dimethyl carbonate are used in the production of urethanes, ureas,[141,142] and other aliphatic carbonic acid esters such as alkyl carbonates,[143] cyclic carbonates,[144] and oxetanes.[145] Carbonate interchange reaction with N-acylated 2-aminoethanols followed by elimination of carbon dioxide leads to polymerizable *N*-vinyl compounds.[146]

Dimethyl carbonate has been reacted with rice hull ash using 5 wt % alkali at 352 °C to obtain tetramethoxysilane.[147] Dimethyl carbonate can be used to introduce a carbonate linkage in a polymer by suitable carbonate interchange reaction. For example, diphenyl carbonate[81b] can be produced from dimethyl carbonate (eq 19) which in turn can be used for the manufacture of an engineering polymer such as poly(aryl carbonate)s based on bisphenol-A. The latter reaction is thermodynamically favorable and has been extensively studied during the past few years[8] (eq 2). Considerable research efforts have gone into the synthesis of poly(aryl carbonate)s by direct carbonate interchange reaction of bisphenol-A or its diesters with dimethyl carbonate[149] (eq 3). Poly(alkyl carbonate)s can also be prepared by carbonate interchange reaction of aliphatic dihydroxy compounds with dimethyl carbonate using suitable catalysts.[150]

2. Diphenyl Carbonate

Diphenyl carbonate is used as an intermediate for the synthesis of low molecular weight aliphatic monoisocynates starting from the corresponding ureas or allophenates.[151] Dicarboxylic acids react with diphenyl carbonate to eliminate carbon dioxide and form diphenyl esters, which are the starting materials for the production of high molecular weight aromatic polyesters.[152,153] Diphenyl carbonate can be used to increase the viscosity of polycondensates such as polyamides and polyesters.[154] The reaction of pentaerythritol phosphate alcohol with diphenyl carbonate in the presence of imidazole catalyst at 204 °C in an isopropylated triphenyl phosphate solvent at 70 mmHg with distillation of phenol gave an 87% yield of bis(pentaerythritol phosphate) carbonate[155] (eq 44).



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3. Allyl Carbonates

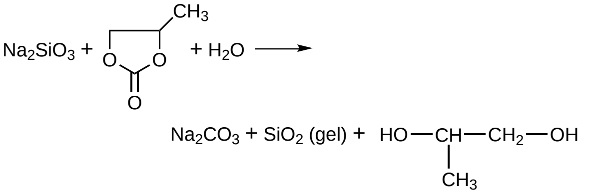
Plastics having excellent optical clarity and usefulness in lens applications are obtained by polymerizing a bis(allyl carbonate) such as diethylene glycol bis(allyl carbonate).[156,157] Allyl carbonates can be used to modify other vinyl polymers.[158,159] Diallyl carbonate is effective as a blossom-thinning agent for fruit trees.[160]

4. Cyclic Carbonates

Five-membered cyclic carbonates are polar and, for this reason, are excellent solvents, e.g., for poly(acrylonitrile).[161] They are also important for the extractive separation of mixtures[162] and as additives for hydraulic fluids.[163] They are often used in oxyalkylation reactions of —OH, —SH, or aromatic —NH groups in place of oxiranes, which are more difficult to handle.[162,164] They readily react with carboxylic acids to form 2-hydroxyethyl esters,[165] e.g., bis(2-hydroxylethyl) terephthalate, which is a monomer for poly(ethylene terephthalate). Primary and secondary amines are converted into urethanes[166] or ureas.[167] Polymerization of ethylene carbonates yields poly(ether carbonate)s because of the partial elimination of carbon dioxide.[168] The hydrolysis of 5-membered cyclic carbonates produces high yields of very pure 1,2-diols.[169] Some specific applications of cyclic carbonates are described in the following sections.

a. Curing of Phenol—Formaldehyde Resins.[170] Phenol—formaldehyde (PF) resins are used as thermosetting wood adhesives and foundary core binders. Cyclic carbonates accelerate the curing of alkaline PF resins. PF resin curing, which is believed to be accelerated by the formation of phenate ions, is instead slowed down by increasingly alkaline pHs and accelerates in the presence of esters and carbonates. This has been attributed to the strength and dissociation of the acid involved in the ester which determines the rate of curing of the resin. This correspondence between rate of cure and pK_a of the acid ester is the first clear indication of some sort of acid—base mechanism. The cure acceleration of PF resins is faster in the presence of carbonates compared with esters. This was due to the fact that the cyclic carbonate gives more functionality on the phenolic nuclei. Esters are monoprotic acids, whereas carbonates are diprotic, similar to carbonic acid. A mechanism has been proposed for cure acceleration by cyclic carbonates.[170] The cure acceleration of PF resins using cyclic carbonate is widely used by plywood and chipboard industry.

b. Accelerators for Curing Silicate Systems Used as Foundry Sand Binders. Silica sand is widely used in foundries to produce molds and cores. If the sand has to be reclaimed successfully, then the reclamation process must not only restore the condition of the sand by breaking down agglomerates and removing metal particles but also enable the sand to be reused with the same type of binding agent as before. It is reported that sand bonded with aqueous sodium silicate and hardened with cyclic alkylene carbonate can be reclaimed to provide an acceptable reclaimed sand by means of an attrition process.[171] Typically, dry sand is mixed with 3.5 wt % of a 45—50% aqueous sodium silicate solution and 0.35 wt % propylene carbonate. The sand hardens, presumably due to the formation of SiO_2 gel (eq 45).



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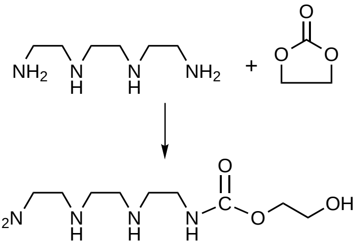
c. Acceleration of Epoxy Resin Curing. Use of cyclic carbonates as reactive diluents for epoxy resins has been reported.[172–174] Studies have shown that use of cyclic carbonate results in decrease in gel time due to the lower viscosity and higher polarity of the medium.[175,176] Furthermore the reaction of amine with carbonates is exothermic, and this evolved heat also increases the cure rate. The carbonates also significantly influence the cured resin's thermal and mechanical properties. Amines reacts with carbonates to form carbonates or urethanes (eq 46) which result in the replacement of some of the epoxy reactive groups with unreactive groups. These materials do, however, provide physical cross-link sites because of their association through hydrogen bonding and thus give cured resins with better room temperature mechanical properties.



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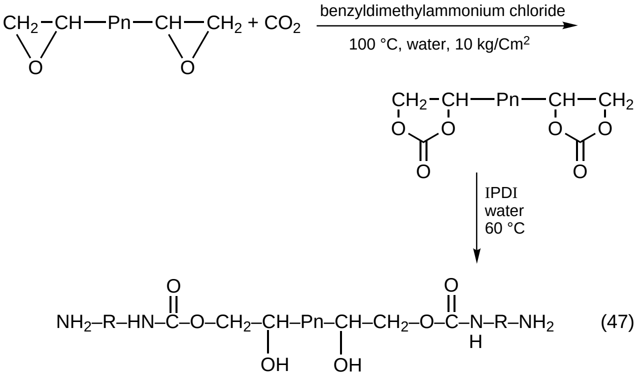
d. Reactive Doluents/Compatibilizers in Polyurethanes.[177] Reaction injection molded (RIM) polyurethanes are made from relatively high molecular weight polyethers which contain amine groups, diamine chains extensively, and isocyanates. Several advantages are seen in using cyclic carbonates such as propylene carbonates in RIM polyurethanes: Cyclic carbonate causes significant lowering of viscosity of the product. Excellent heat sag properties are also realized. The highly polar carbonate dissolves in the hard block phase causing a significant decrease in the stiffness at elevated temperatures. It is also found that the systems containing propylene carbonate react slowly. This property is desirable because it allows for the complete filling of larger RIM parts.

e. Synthesis of Polyurethanes.[178] The synthesis of urethanes and polyurethanes is carried out without using diisocyanates. In this method an epoxide resin or polyfunctional epoxy compound is reacted with carbon dioxide in the presence of quarternary ammonium salt as catalyst (eq 47). It is desirable for at least some of the molecules in the epoxide resin to have more than two epoxy groups. The helps to promote cross-linking in the final product. The oligomer is further reacted with a diamine to form a urethane oligomer which contains a urethane and a hydroxyl group. This reaction take place in aqueous solution. The resulting urethane-containing oligomers with amine end groups can serve as amine solidifiers for epoxy resins and as solidifiers for other compounds, which have the ability to react with amine or hydroxyl end groups.



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By this method the end user can mix the urethane oligomer with epoxy resins, apply it on a substrate, and allow the cross-linking to occur on site, in the pores of substrate so that the resulting polyurethane fills the pores of substrate. This results in a strong bond between the polyurethane and the substrate. This method provides a material that has a combination of all the advantages of known epoxy resins plus the hardness, strength, and flexibility of polyurethane.

f. Flexible Polyurethanes for Coating.[179] Polyisocyanates have been used successfully as chipboard binders. Since in this process absorption of polyisocyanates occurs on the wood particles, the quantity of polyisocyanates needed to bind a certain amount of wood chips is relatively high. The efficiency of polyisocyanates is greatly improved by using a polyisocyanate composition containing an organoclay and a cyclic alkylene carbonate. The cyclic alkylene carbonate acts as a polar activator. This composition provides excellent adhesion to the wood particles, exhibits a desirable regel time, and can be easily sprayed.

g. Thermosetting Resins.[180] Thermosetting resins can be obtained by polymerization of a cyclic carbonate with a polyvalent isocyanate compound in the presence of potassium fluoride as the catalyst. Poly(ethylene oxide), cryptands, or quarternary ammonium salts are additionally used to activate the reaction. It is possible to complete the hardening reaction within several minutes without producing any appreciable amount of gas. The resulting thermosetting resins have relatively high transparency and excellent impact strength.

h. Hot Melt Polyurethane Composition.[181] Hot melt polyurethane compositions are prepared from poly(butylenediol adipate), tosyl isocyanate, methylenediphenyl diisocyanate (MDI), and propylene carbonate by heating in the presence of dibutyltin dilaurate as catalyst. This composition is useful as a bonding agent in the footwear industry.

i. Superior Cleaning Solvent.[182] Solvent compositions having superior cleaning power can be formulated using cyclic carbonate as one of the key components. Such solvents exhibit low toxicity are nonflammable, pH neutral, essentially nonvolatile, and aprotic. For example, a solvent composition comprising of ethylene carbonate, ethylene diacetate, triethanolamine, and/or *N*-methyl-2-pyrrolidone exhibit superior cleaning for a wide range of residues and are environmentally and physiologically safe. These may be diluted with water for cleaning tasks that are insensitive to corrosion. Such a solvent effectively removes residues such as oils, greases, epoxy resins, organic adhesives, waxes, photoresist, inks, fingernail enamel, and nonpolymeric paints and coatings. These are also useful for removing evaporative drying finishes like lacquer or varnish from solid substrates including wood, plastic, metal, and ceramics.

j. Thermal Recording Materials.[183] Cyclic carbonate compounds having an electron-donating compound and an electron-accepting compound are useful as thermal recording materials. These materials show high thermal response and good storage stability for colored images.

k. Electrolytes.[184] Propylene carbonate is widely employed as an organic solvent in electrolytes for high-energy density batteries and electrolytic capacitors, due to its good solvent properties, high dielectric constant, low pour point, and high boiling point. Mixtures of propylene carbonate and ethylene carbonate are also used. Use of cyclic carbonates extends capacitor life and is often superior to the conventional glycol-based dielectrics.

l. Extraction of Metals.[184] Propylene carbonate is used for the extraction of metals. The metals are extracted from acidic solutions as salts or complexes formed with propylene carbonate. Metals that can be extracted include bismuth, cadmium, cerium, cobalt, copper, gold, iridium, iron, lead, mercury, molybdenum, palladium, rhodium, uranium, vanadium, and zinc.

m. Cosmetics and Personal Care.[184] Propylene carbonate is an excellent polar additive for montomorillonite or bentonite clay gellants. These gellants are widely used as gel bases for lipstick, skin cleaners, antiperspirants, eye shadow, mascara, hair conditioners, and other cosmetic products.

n. Miscellaneous.[184] Ethylene carbonate is used in photosensitive compositions for preparing lithographite plates. Plasticizers for thin acrylic films also incorporate ethylene carbonate. Ethylene carbonate may be employed as a liquid fuel for jet or turboprop engines, either alone or in combination with ethylene oxide and nitroalkanes. A propylene carbonate—methanol—amine mixture is an effective detergent for bearing components. Propylene carbonate is used in fire extinguishing compounds and antifoam agents for antifreeze. Either propylene or ethylene carbonate may be used in hydraulic brake fluids having low hydroscopicity and low viscosity at reduced temperatures. Ethylene carbonate can be utilized as a solvent in the separation of different aromatic amines. Propylene carbonate is used as a pretreatment in metal-plating processes and as a plating medium. It can also be used in the bleaching of wood. Other applications of ethylene carbonate in reactions such as hydroxyethylation, hydroxyethyl carbonate formation, and polymerization by both condensation and ionic methods have been described in a technical brochure published by Dow Chemical Co.[185]

5. Dialkyl Carbonates as Lubricants

Aliphatic carbonates possessing ether groups are used as lubricants and hydaulic fluid.[186] Oligocarbonates containing ether groups are also useful as lubricant compositions for refrigerators. These oligomers have low hygroscopicity, high detergency, and good compatibility with non-ozone-destroying halofluorocarbons.[187,188] Lubricating greases useful at low temperatures are made from carbonates thickened with metal soap.[189] Various complex carbonates are especially useful as components of greases and lubricating oils because they do not form corrosive acids when pyrolyzed.[190] Addition of carbonates to fuels and lubricating oils is a means of reducing the accumulation of engine deposits.[191] Applications of dialkyl carbonates in the fields of synthetic lubricants have been reviewed by Fisicaro and Gerbar in a recent review.[192]

6. Agricultural Applications

Various mixed alkyl chlorinated aryl carbonates find use as herbicides and seed disinfectants. Carbonates active as herbicides are customarily obtained from alkynols,[193] and those active as acaricides, fungicides, and insecticides are obtained from (dinitroalkyl)phenols.[194,195] Dihalogenocyanophenyl alkyl carbonates[196,197] and alkyl phenyl carbonates possessing a fluorinated aliphatic group can also be used to make pesticides.[198] Alkyl carbonates containing the oxime functional group are active as fungicides.[199]

7. Applications in Medicinal Chemistry

Alkoxy carbonylation of amines is of considerable interest in medicinal chemistry. Di(2-pyridyl) carbonate is used for the synthesis of various protected carbonates.[200] *N,N′*-Disuccinimidyl carbonate has been reorganized as versatile reagent for active ester synthesis.[201] *N,N′*-Disuccinimidyl carbonate has been found to be a highly effective alkoxy-carbonylating agent for a variety of primary and even sterically hindered secondary alcohols and are subsequently converted to functionalized carbonates.[202] These are pharmacologically important organic molecules.[203] Iodoalkyl carbonates[204] are useful as esterification agents for cephalosporin, penicillin, β-lactam, etc.

8. Miscellaneous Applications

Higher dialkyl carbonates are useful as lubricants, solvents for cellulosic compounds, and additives.[205] Unsymmetrical carbonates such as methyl *tert*-butyl carbonate and methyl *tert*-amyl carbonate are useful as octane enhancers for gasoline.[81a] Salts of carbonic acid monoesters can be used to carboxylate compounds such as ketones.[206,207]

Some carbonates are suitable for use as flavor and fragrance sources, e.g., 4-isopropyl-5,5-dimethyl-2-oxo-1,3-dioxane which is used to enhance the aroma of foods, perfumes, and cosmetic and provides the product with an aroma like that of coumarin or tobacco.[208] Mixed aromatic and aliphatic carbonates are used to produce a softer poly(vinyl chloride).[209] They also serve as aids in the dyeing of textiles.[210]

Biodegradable compositions containing dialkyl carbonates are used as textile softners.[211] Dialkyl carbonates are useful as oil components for cosmetics and pharmaceuticals.[212] Ethoxylated carbonates can be used as rolling oil in the manufacture of rolling sheets.[213] Some special carbonates have acquired importance as protecting groups in peptide synthesis, e.g., bis(pentafluorophenyl) carbonate[214] is used for the synthesis of several pentafluorophenyl esters of amino acids. Di-*tert*-butyl iminodicarbonates are useful for the introduction of protected amino functionalities.[215] Acrylate-terminated carbonates having molecular weight in the range of 720−1500 are useful for the preparation of cross-linked carbonate-containing polymers.[216]

Esters of carboxylic acids were readily synthesized from alkyl or aryl halides by reacting the corresponding Grignard reagents with dimethyl and diphenyl carbonates. Cyclic carbonate was also used and produced alkyl, aryl, or hydroxyalkyl esters by this method. This is useful for the synthesis of carboxylic esters in one step from the corresponding halides.[217]

C. Economic Aspects[194]

Large amounts of carbonates do not reach the market but are utilized as intermediates and further processed. The world-wide production and consumption is estimated to be tens of thousands of tons per year. The kilogram price is $2−5. The importance of carbonates is shown not so much by these figures as by the fact that they are used in the synthesis of high-quality products.

VIII. Future Perspectives

This review has summarized the methods available for the synthesis of organic carbonates. Dialkyl carbonates have come to occupy an important position as useful intermediates for a variety of industrial and synthetic applications.

The synthesis of diaryl carbonates by oxidative carbonylation of phenols does not appear to be very promising at the present time. The preferred alternative appears to be the carbonate interchange reaction of phenol with dialkyl carbonate. More emphasis is warranged toward gaining a mechanistic understanding of this reaction. Newer ideas in catalysis need to be invoked to overcome the unfavorable equilibrium and thermodynamics. It is generally acknowledged that the discovery of a convenient and cheap direct production process for diaryl carbonates without the use of phosgene would be a revolutionary development with wide applications to both organic chemical and polymer industries. The use of ethylene carbonate for the synthesis of dimethyl carbonate is extremely promising as ethylene carbonate utilizes for its synthesis abundantly available carbon dioxide. Substantially more work is warranted to fully explore and exploit the utility of ethylene carbonate in organic chemical synthesis.

IX. Acknowledgement

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