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Applications of Dimethyl Carbonate for the Chemical Upgrading of Biosourced Platform Chemicals

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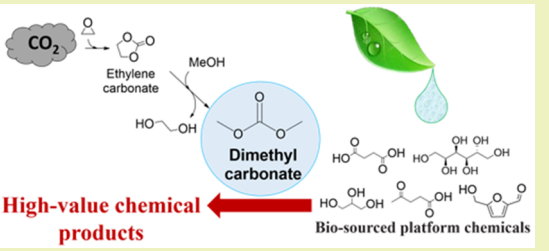
ABSTRACT: Dimethyl carbonate (DMC) is a nontoxic compound currently prepared from CO_2 as a building block, which displays a versatile reactivity for multiple applications including, particularly, the implementation of sustainable protocols for the conversion of biosourced substrates. Among them, this paper will survey representative cases of DMC-mediated methylation and carboxymethylation reactions by which platform chemicals including glycerol and its derivatives, succinic and levulinic acids, furan-derived compounds as 5-HMF and FDCA, and sorbitol are transformed into added-value compounds. By their intrinsic nature, these processes typify genuine green archetypes combining the upgrading of renewables with the use of safe reagents, catalysis, recycle, minimal, if any, production of wastes, and solvent-less conditions.



KEYWORDS: *Dimethyl carbonate, Biomass-derived platform molecules, Methylation, Carboxymethylation, Catalysis, Biorefinery*

INTRODUCTION

The growing awareness of modern society for global environmental issues mostly including the finite availability of fossil resources and climate change is changing life styles moving consumers toward more responsible choices of products (plastics, materials, fuels, and even food) with reduced or neutral carbon footprint.[1,2] In this respect, the development of biorefineries able to process biomass and further convert the biosourced substrates of the primary transformation into high-value chemical products is a highly desirable target for a sustainable management of the natural carbon cycle.[3] The analysis of this scenario, however, highlights significant challenges associated on one side with the economic sustainability of biomass conversion which needs to integrate the production of chemicals to that of biofuels, and on the other side with a deficiency of technologies for the upgrading of renewables, an aspect which is further exacerbated by the large number of potentially accessible biobased compounds. Plastics are among the best models exemplifying how the choices of feedstocks and processing technologies not only affect the economics of the productive chain but also medium−long-term impact on the environment. Indeed, a new promising plastic typically requires 2−3 years for preliminary applications, 2−6 years to reach a platform position, and up to 20−40 years for market penetration in the production of materials with enhanced technical functions on a scale over 100 000 tonnes.[4] A cogent strategy to cope with these issues and combine safety and environmental protection with economics is by tailoring syntheses in which clean reagents and solvents are used for the catalytic upgrade of renewable platform chemicals. CO_2 and its derivatives, particularly dialkyl carbonates, can play a remarkable role in this respect. Indeed, regarding biomass originated by atmospheric carbon dioxide which is converted into chemicals with sustainable (sunlight) energy, the approach aims at squaring the carbon cycle.[5] The model case of dimethyl carbonate (DMC), the simplest term of the dialkyl carbonates series, well illustrates the concept. Since the synthesis of DMC has been extensively reviewed even in recent times,[6−8] evolution and details of these studies will not be further commented here except for stressing that the industrial production of DMC integrated in the Asahi−Kasei process for the manufacturing of polycarbonat, represents one of the best examples of green and sustainable transformations available on a large scale (Scheme 1).[9]

CO_2 is initially used as a safe building block for the insertion of into ethylene oxide, producing ethylene carbonate which, in turn, undergoes a transesterification reaction with methanol carried out in a continuous mode. Pure dimethylcarbonate is thus achieved. Then, in the same plant, DMC is used for a second transesterification reaction to synthesize diphenylcarbonate which is the last intermediate for the manufacture of polycarbonate. The overall sequence proceeds with high yields and selectivities in all steps; intermediate products including ethylene carbonate, DMC, MeOH, diphenylcarbonate (DPC), and PhOH are used as reactants toward the final polymer, all

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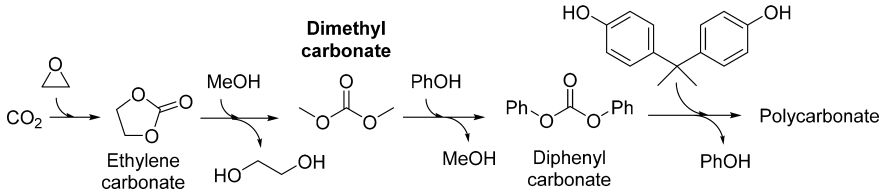
Scheme 1. Synthesis of DMC Integrated in the Polycarbonate Manufacture from Asahi−Kasei Process



processes are catalytic reactions with no wastes, and no water is required for disposal treatments. As another remarkable feature, DMC is obtained as a nontoxic reagent.

From the chemical standpoint, DMC behaves as an ambident electrophile due to the presence of two active centers, the methyl and the carbonyl carbons, in the molecule. Both methylation and methoxycarbonylation reactions are therefore observed with several types of O-, S-, C-, N-, and P-nucleophiles including phenols and alcohols, methylene active compounds, amines and phosphines.[10−12] Conditions and the nature of the catalysts help to differentiate the two reaction paths: below or at the refluxing temperature (90 °C), DMC acts primarily as a methoxycarbonylating agent yielding carbonate interchange products (e.g., asymmetrical methyl alkyl carbonates, high dialkyl carbonate homologues, and carbamates), while at $T \geq 160$ °C, methylation reactions preferentially occur forming methyl ethers and tioethers and with high selectivity, mono-*N*-methyl amines. Of note, DMC-mediated reactions are (i) catalyzed by both bases (alkaline carbonates, organo-bicyclo compounds as TBD, DBU, and DABCO, hydrotalcites, etc.) and protic- or Lewis-acid systems, (ii) often do not require additional solvents since DMC serves both as a reagent and a reaction medium, and (iii) coproducts are methanol, recyclable to the synthesis of DMC, and CO_2 (only in the case of methylations), which do not involve disposal issues.[13]

Overall, the nontoxicity, the favorable physicochemical profile, and the versatile reactivity make DMC an ideal vector of both CO_2 and methyl functions and also for the valorization of biobased derivatives.

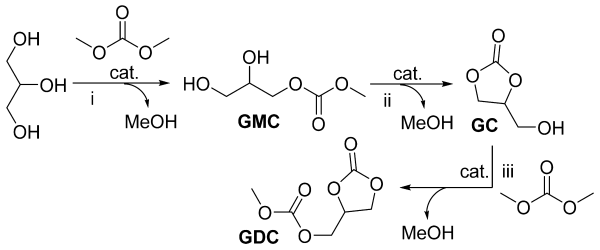
DMC FOR THE UPGRADING OF TOP PLATFORM CHEMICALS

In the past 15 years, massive efforts have been addressed to the identification of the most promising biomass-derived compounds. Starting from the first extensive analysis carried out in 2004 by U.S. Department of Energy,[14] selection criteria of substrates have been more and more refined over the years to include and examine market attractiveness and competitiveness, technologies for high volume products, potential for supply chain integration and replacement of existing petrochemical derivatives, etc.[3,15−18] However, the current list of the so-called top biobased platform chemicals still includes most of the originally identified compounds, particularly ethanol, functionalized mono- and dicarboxylic acids (lactic-, levulinic-, hydroxypropionic-, and succinic- acid), furan-based products as furfural, hydroxymethylfurfural (HMF), and furan dicarboxylic acid (FDCA), biohydrocarbons derived from isoprene, glycerol and derivatives, and other sugars such as sorbitol and xylitol. This review will examine representative examples in which some of such platform molecules have been upgraded by using DMC as a methylating or a methoxycarbonylating agent.

GLYCEROL AND DERIVATIVES

Glycerol. DMC readily undergoes interchange carbonate reactions (transcarbonations) with glycerol to produce either glycerol carbonate (GC) or the corresponding glycerol dicarbonate (GDC) (Scheme 2).[19]

Scheme 2. Transcarbonation Reactions of Dimethyl Carbonate with Glycerol



Up to three subsequent transcarbonations may occur. The first two processes (i, ii) however, often take place almost concurrently: the intermediate glyceryl methyl carbonate (GMC) is not isolated due to easy cyclization reaction which yields GC with very high selectivity and yields, both typically >90%, at 40−80 °C in a few hours. The formation of GDC instead requires an excess of DMC and longer reaction times.

The broad spectrum of applications of GC as a low toxic solvent in cosmetic, personal care, medicinal uses, and as an excellent electrophilic partner for reactions of alcohols and phenols, has fueled an enormous attention for the reaction of Scheme 2 which certainly represents one of the most investigated uses of DMC for the upgrading of renewable substrates. This scenario is further witnessed by the role of GC as a key product for sustainability in the portfolio of industrial giants as Huntsmann and UBE.[20,21]

Base catalysts are by far more effective for the synthesis of GC than acid systems, due to their ability of activating glycerol through the formation of a glyceroxide anion which acts as a powerful nucleophile on DMC (see Scheme 2). Starting from seminal works proposing K_2CO_3 for the transcarbonation of DMC with glycerol,[22] several bases have been reported, mostly as heterogeneous systems including NaOH/γ-Al_2O_3, KF supported on Al_2O_3, SiO_2, ZnO, ZrO_2, H-beta, and carbon, K-exchanged zeolites, and metal-doped calcined hydrotalcites.[23−26] The literature, however, highlights a pre-eminent role of commercially available CaO to catalyze the reaction: features and performance of CaO have demonstrated its potential for the implementation of the synthesis of GC even on an industrial scale.[27,28] The process typically offers quantitative (glycerol) conversion at 95 °C, with GC yield of 95%. Although the catalyst may deactivate by forming calcium hydroxycarbonate $[Ca_x(OH)_y(CO3)_z]$, this has a negligible impact on the tecno-economic feasibility of the synthesis

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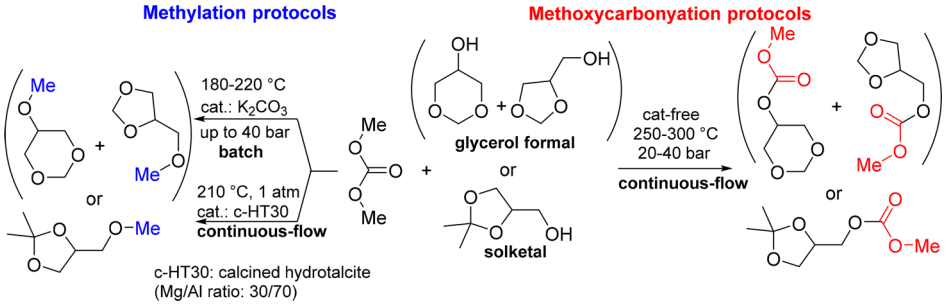
Scheme 3. Upgrading of Glycerol Acetals by DMC



because fresh commercial CaO is a cheap material and the disposal of the exhausted catalyst does not pose any environmental issue. Of note, CaO has been recently proposed for the synthesis of GC from DMC and crude glycerol under MW-irradiation. At 65 °C, a 91% conversion of the crude reagent (glycerol, MeOH, and NaOMe as residues of biodiesel manufacture) was achieved after only 5 min, with 85% yield of GC.[29]

Biocatalysts have also been investigated for the transcarbonation of DMC with glycerol. A major hurdle for the setup of the reaction is the poor mutual solubility of reactants which imposes either additional solvents (i.e., *t*-BuOH, acetonitrile, MTBE) or surfactants (i.e., Tween 80 and Brijs) able to avoid or minimize the preferential adsorption of hydrophilic glycerol on the enzyme surface.[30,31] *Candida antarctica* (CAL) immobilized on polyacrylic resin (Novozym 435) has been reported as one of the most active and selective biocatalysts. Interestingly, a protocol has described the use of this enzyme also under solventless conditions to carry out two sequential DMC-promoted transesterification reactions by which soybean oil was first converted into biodiesel and glycerol, while the latter was concurrently transformed into GC. The overall process was optimized at 60 °C yielding conversion and selectivity to GC of 92.5% and 96.4%, respectively.[32] A similar approach was followed to implement also the continuous-flow synthesis of GC using lipase B from *Candida antarctica* immobilized on Accurel MP1000 (CalBAcc) as a catalyst.[33] At 60 °C, CalBAcc proved effective to obtain GC starting either from a solution of pure glycerol, DMC, Brij 76 as a surfactant, and *t*-BuOH as a solvent, or a mixture of DMC−soybean oil and MTBE as a cosolvent.[34] Varying the residence time up to 176 min, quantitative conversion and selectivity were claimed, but isolated yields of GC were not indicated. In this respect, recent reviews have stressed how the availability of immobilized enzymes is currently opening a new frontier for continuous-flow applications of biocatalysis.[35,36]

The application of continuous-flow technologies to perform these types of reactions could offer significant advantages as compared to batch reactor designs. Continuous-flow systems allow for higher control over reaction conditions, quick and efficient reagent mixing, shorter reaction times, and enhanced heat and mass transfer and process intensification. Due to the aforementioned advantages, continuous-flow conditions can significantly promote processes by increasing yields and/or selectivities, as compared to batch processes. These technologies also improve safety and facilitate scale up for certain applications.[37,38]

Thermal, catalysts-free conditions were also explored for the reaction of DMC with glycerol. It should be noted that in the perspective of large-scale productions, the energetic demand of protocols requiring high temperatures is significantly alleviated by integrating such processes in modern biorefinery units in which the recovery or exchange of (waste and excess) heat is managed by heat-sinks as part of cogeneration plants.[39] In the batch mode, the thermal transcarbonation protocol for the synthesis of GC was productive at 300 °C and 20 MPa, yielding GC in a 98% yield after 15 min. Both the use of lower pressure ≤5 MPa or a crude reagent [mixture of glycerol water (10 wt %), salts (20 wt %), and soaps (35 000 ppm)] decreased yields to 40−60%, because the contact of reagents as condensed phases was less effective, and at the same time, alkaline impurities of crude glycerol favored the decomposition of GC into glycidol.[40,41] The thermal reaction of DMC with glycerol was investigated also by one of us who highlighted how the products selectivity and yields could be tuned by changing the reaction conditions, specifically the reactant ratio and time in the batchwise mode and the pressure and the residence time in the continuous-flow mode:[42] accordingly, in an autoclave at 180 °C (batch), either GC or glycerol dicarbonate (GDC) were obtained selectively in 84% and 80% yield, respectively; while at 230−250 °C and 50 bar (flow rate 0.1 mL min^{-1}), the flow-reaction yielded GC as the primary product (83−92% yield).

Glycerol Acetals. The most studied acetals of glycerol (GAs) are the simplest terms of the series, namely glycerol formal and solketal, which are obtained by acid-catalyzed condensation of glycerol with formaldehyde and acetone, respectively. These model GAs find applications as such in the field of biobased and nontoxic solvents and fuel additives, but they also display a typically alcohol-like reactivity which allows their chemical upgrading into the corresponding ethers and esters.[43,44] In this respect, DMC has been extensively investigated by our group, as both a methoxycarbonylating and a methylating agent of GAs in a variety of conditions including catalytic, thermal (cat-free), batch, and continuous-flow modes. Results are summarized in Scheme 3.

A thermal (catalyst-free) transcarbonation was effectively performed under continuous-flow conditions, at 275−300 °C and 20−40 bar.[45] GAs yielded the corresponding monotransesterification products with a selectivity up to 98% at a substantially quantitative conversion (Scheme 3, right). The reaction was remarkably affected by the pressure whose effect was consistent with the partition of DMC from the vapor to the liquid phase. Accordingly, an abrupt improvement of the conversion (from 1−2% to ∼85%) was observed at ∼35 bar.

Since DMC-mediated methylation reactions display an activation barrier higher than methoxycarbonyl (transcarbonation) processes, the etherification of GAs required both temperatures as high as 180−220 °C and the compulsory

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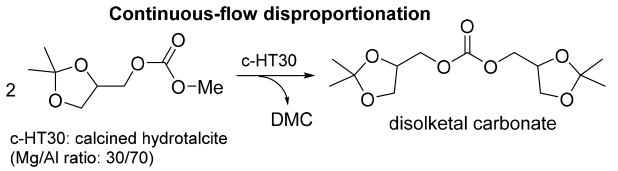
presence of a catalyst (Scheme 3, left). Such reaction was first reported under batch conditions in the presence of K_2CO_3 as a basic catalyst.[40] Although excellent selectivity and yields up to 99% and 86−99%, respectively, were achieved toward the methyl ethers of both glycerol formal and solketal, a slow kinetics was noticed, and an extensive side-decarboxylation of DMC took place generating a high autogenous pressure. The reaction outcome was greatly improved in the continuous-flow mode by using a catalyst (c-HT30) composed of a mixture of Mg/Al oxides obtained by the calcination of a hydrotalcite precursor (Scheme 3, left, bottom).[46] Under such conditions, quantitative conversion and O-methylation selectivities were reached at atmospheric pressure, and even more importantly, the productivity of the process (~2 $g_{prod}\ g_{cat}^{-1}\ h^{-1}$) was up to 200 times higher than that of the previous batchwise method. Moreover, the flow-mode protocol proved effective also for the etherification of glycerol carbonate and tetrahydrofurfuryl alcohol, the latter deriving from sugars dehydration.

To conclude this section, recently, a continuous-flow procedure was implemented to further convert asymmetrical methyl alkyl carbonates obtained from GAs and DMC, into the corresponding symmetrical dialkyl carbonates.[47] Scheme 4 illustrates the model case of the solketal derivative.

Scheme 4. Catalytic Disproportionation of Solketal Methyl Carbonate



At 210 °C and atmospheric pressure, in the presence of the same catalyst above-mentioned (c-HT30), a disproportionation reaction took place yielding disolketal carbonate with selectivity and productivity up to 92% and 152 $mg_{prod}\ g_{cat}^{-1}\ h^{-1}$, respectively (residence time: 2.5 min). The procedure proved robust and suitable to several biobased methyl alkyl carbonates, thereby further confirming the effective role of the chemistry promoted by DMC in this area.

BIOBASED CARBOXYLIC ACIDS

Succinic Acid. Microbial-based productions of renewable succinic acid afford the corresponding salt, often as a disodium species, which must be neutralized and further converted into other derivatives, especially esters, before any use.[48] With the aim of avoiding these upstream operations that consume a stoichiometric acid and produce waste salt, an original approach was proposed by integrating recovery and chemical upgrading of succinate using DMC as an alkylating agent.[49] The concept is illustrated in Scheme 5.

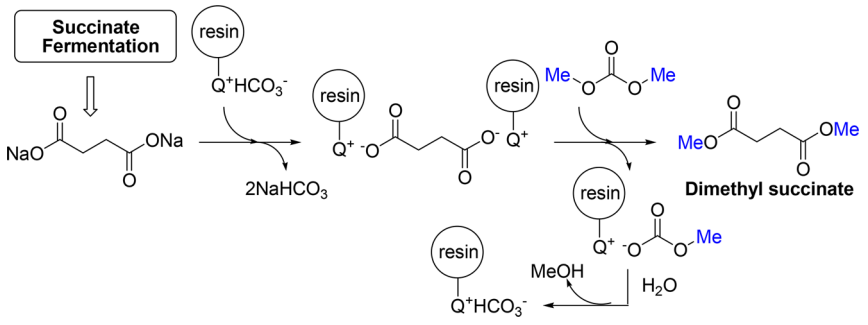
First, succinate disodium salt is captured from an aqueous fermentation broth by an anion exchange resin in a (bi)carbonate form releasing the respective (bi)carbonate salt. Then, at 100−120 °C, sorbed succinate undergoes an O-methylation reaction mediated by DMC and catalyzed by quaternary ammonium groups (Q+) of the resin. This exemplifies a low-temperature alkylation pathway, unusual for DMC, which according to further study of the same group is affected by the nature and hydrophobicity of ammonium cations.[50] In the presence of water, the resulting methoxycarbonate anions exchanged on to resin, decompose thereby restoring the original bicarbonate-based resin and releasing methanol. It should be noted that here few other studies are available for the O-methylation of carboxylic acids by DMC: in those cases, either superbases as DBU or combined systems as K_2CO_3/tetrabutylammonium chloride and K_2CO_3/DMSO were used as catalysts.[51−53]

Levulinic Acid. Levulinic acid (LA) comes from saccharides through an acid-catalyzed sequence yielding at first 5-(hydroxymethyl)furfural (HMF) which, in turn, yields an equimolar mixture of LA and formic acid.[54] Among biobased carboxylic acids, LA has probably the highest potential for the market including personal care products, lubricants, adsorbents, electronics, photography, batteries, and drug delivery systems. Moreover, due to the progressive drop of its price from 8.8 to 13.2 $/kg in 2000 to 5−8 $/kg in 2015, a steady growth of applications and uses of LA is expected in the near-future.[55]

The reactivity of levulinic acid with DMC has been extensively investigated by our group. In the presence of basic catalysts, multiple products including methyl levulinate, dimethyl succinate, and methyl 4,4-dimethoxypentanoate (i.e., dimethyl ketal of methyl levulinate) were achieved.[56] However, tuning of reaction conditions, mostly by changing temperature and cosolvents, allowed to a certain degree a control of the products distribution. This is shown in Scheme 6.

At 160 °C, the K_2CO_3-catalyzed reaction of LA with DMC produced selectively methyl levulinate (ML, eq a), while increasing temperature (up to 200 °C) and adding MeOH prompted the unique formation of the dimethyl ketal of ML (eq b). Finally, moving to stronger bases as DBU, induced the formation of dimethyl succinate (DS) which was isolated in a ~30% yield (eq c). Mechanistic hypotheses for such reactions are formulated in Scheme 7.

Scheme 5. Recovery of Dimethyl Succinate from Fermentative Broths, via Methylation with DMC



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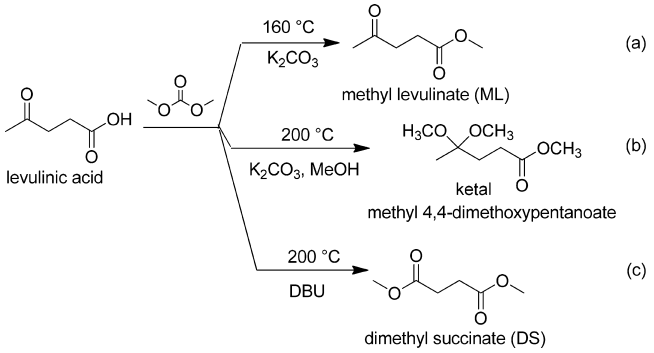
Scheme 6. Multiple Products from the Reaction of Levulinic Acid and DMC



The formation of DS has been explained through a sequence comprised of: (i) the base-catalyzed condensation of DMC with enolate of ML; (ii) nucleophilic attack of methoxide anion to the carbonyl group; (iii) reverse Claisen reaction by which a β-ketoester species is split into DS and methyl acetate (Scheme 7, top). A similar oxidation-like pathway was proposed also for the reaction of DMC with benzyl ketones.[57] On the other hand, in the presence of MeOH, a nucleophilic attack of methoxide anion to the carbonyl group followed by a catalytic O-methylation mediated by DMC accounts for the ketal formation (Scheme 7, bottom).

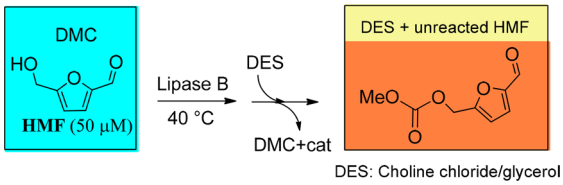
Interestingly, another DMC-mediated process was implemented to upgrade γ-valerolactone (GVL) which is one of the most significant derivative of LA. At 220 °C, the K_2CO_3-catalyzed reaction of GVL with DMC yielded the α-monomethyl derivative of the lactone [dihydro-3,5-dimethyl-furan-2(3H)-one] with >90% selectivity at complete conversion.[58]

Lactic Acid. To the best of our knowledge, protocols for the upgrading of lactic acid as such by DMC have not been reported yet. Nonetheless, an interesting study has been described using the solution blow spinning (SBS) technique to prepare nonwoven fiber sheets of polylactic acid (PLA) starting from solutions of PLA in DMC solvent.[59]

Biobased Furan-Derived Compounds. Biosourced furanics have been referred to as "Sleeping Giants" because of their enormous market potential, as evidenced also by DuPont and DSM, and confirmed by Avantium that discovered an innovative catalytic process by which furanics are obtained starting from carbohydrates derived from a variety of crops.[60] In this area, the most versatile building blocks are 2,5-furandicarboxylic acid (FDCA) for polymer applications and 5-hydroxymethylfurfural (HMF) that can be valorized by conversion into monomers, fuels, additives, surfactants, and fungicides.

HMF. The high intrinsic reactivity of HMF makes its esterification challenging since (self-)oligomerization, rehydration to levulinic acid and humin formation may be concurrent side-reactions. However, it was discovered that in the presence of a commercially available immobilized lipase B from *Candida antarctica* as a biocatalyst, a highly selective transcarbonation of HMF was achieved at 40 °C by using dimethyl carbonate both as a reagent and a solvent.[61] The product, 5-methoxycarbonyl derivative of HMF, was isolated in a 91% yield through an inventive approach by which deep-eutectic solvents based on choline-derived salts were the separation agents (Scheme 8)

Scheme 8. Synthesis and Isolation of Methoxycarbonyl Derivative of HMF by Dimethyl Carbonate and DES

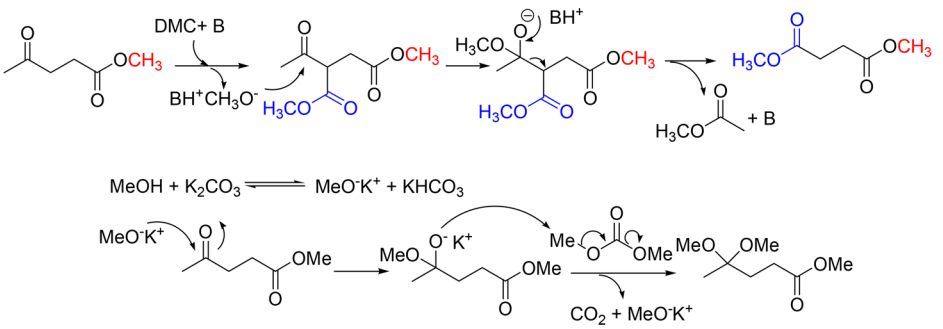


Other applications reported the used of DMC as a solvent for the synthesis of HMF. In a first example, the extraction capacity of DMC solvent was used to recover HMF from aqueous solutions.[62] At 150 °C (autogenous pressure), the dehydration of fructose to HMF was carried out in a biphasic system of DMC/water in the presence of a Ce-based heterogeneous catalyst $[(Ce(PO_4)_{1.5}(H_2O)\text{-}(H_3O)_{0.5}(H_2O)_{0.5})]$. 5-HMF was isolated in >99% purity and 70% yield in the DMC phase. Even more recently, the same dehydration of fructose was explored starting from a mixture of dimethyl carbonate and tetraethylammonium bromide (DMC:TEAB weight ratio of 10−20:1) as a reaction medium.[63] In this case, conventional acid catalysts as Amberlyst resins and $BF_3O(Et)_2$ were used to obtain HMF in 80% yield under mild conditions (90 °C and ambient pressure).

FDCA. A very recent patent by DuPont described a general reactive distillation protocol by which diesters of FDCA were obtained in the presence of variety of acid catalysts:[64] among other reactants, DMC was used to obtain the corresponding dimethyl ester (FDME), a valuable monomer for polyesters.

The same esterification of FDCA by DMC was used in an application similar to that above-described for the recovery of disodium succinate from fermentative broths (see Scheme

Scheme 7. Mechanisms for the Formation of Dimethyl Succinate (top) and ML-Ketal (bottom)



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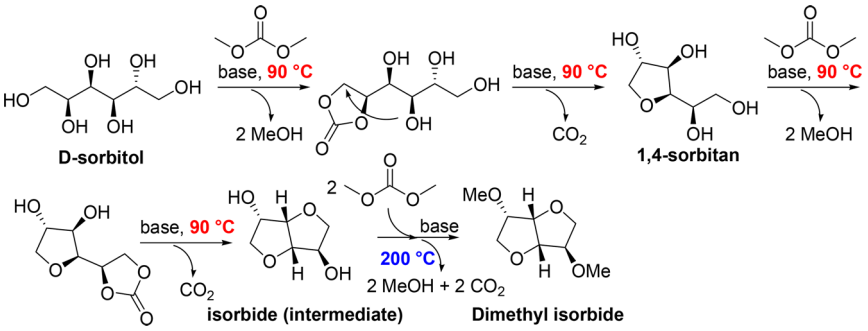
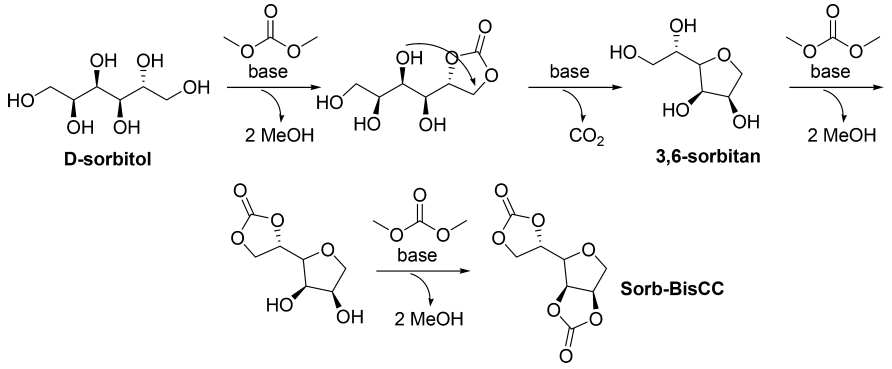
Scheme 9. One-Pot Two-Step Sequence for the Synthesis of Dimethyl Isosorbide from Sorbitol and DMC



Scheme 10. Formation of Sorb-BisCC from D-Sorbitol and DMC



5).[65] In this case, disodium 2,5-furandicarboxylate (Na_2FDCA_2) was produced by whole cell biotransformation of 5-(hydroxymethyl)furfural (HMF) by a recombinant *Pseudomonas putida*. The salt was exchanged on a macroporous Dowex resin, with a capacity up to 0.30 g $FDCA_2^-$ per g dry resin, and finally, methylation was performed in an autoclave at 100 °C with excess DMC (30 g DMC/g loaded resin). The reaction yielded 0.77 mol FDME per mol of FDCA. Authors claimed the need for a high reaction temperature to favor the alkylation kinetics, but a hurdle for this improvement was the thermal stability of the resin.

Sorbitol. The major interest for D-sorbitol as a biobased platform chemical is mostly due to its conversion to isosorbide (1,4:3,6-dianhydro-D-glucitol), an anhydro cyclic derivative which finds applications and potential uses as a building block for new polymers and functional materials, new organic solvents, intermediate for medicinal and pharmaceutical sectors, and even for fuels or fuel additives.[66,67] Among different methods for the synthesis of isosorbide, an appealing protocol has been conceived through the straightforward reaction of D-sorbitol and DMC in the presence of base catalysts (K_2CO_3, MeONa, DBU).[68−70] The overall cyclization process proceeds via two sequential DMC-mediated reactions, specifically a methoxycarbonylation followed by an intramolecular alkylation, in which DMC acts both as a leaving group and a sacrificial molecule. In an extension of this study, a procedure was implemented to perform in one-pot both the preparation of isosorbide and its further upgrading to the corresponding dimethyl derivative, a green industrial solvent of interest also for pharmaceutical additives and products for personal-care (Scheme 9).

The reaction required a careful control of temperature, by first heating reactants mixture at 90 °C to allow the quantitative cyclization of D-sorbitol to the isosorbide intermediate, and then at 200 °C for the second methylation step affording dimethylisosorbide. In the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst, the product was isolated in a 69% yield which is relevant if one considers to the scant reactivity of secondary hydroxyl groups of isosorbide. Authors proposed that the molecule backbone of isosorbide, particularly its rigid V-shaped configuration, allowed the formation of strong intramolecular H-bonds affecting the reactivity.

Another interesting product coming from the base-catalyzed reaction of sorbitol and DMC is the bis-cyclocarbonate derivative, Sorb-BisCC (1*R*,4*S*,5*R*,6*R*)-6-(1,3-dioxolan-2-one-4-yl)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane), that is a useful building block for short and long polyols, or novel biobased nonisocyanate polyurethanes (NIPU)[65,71,72] (Scheme 10).

In this case, a transcarbonation of DMC starting from a primary hydroxyl group at position 6 forms a cyclic carbonate intermediate which, upon nucleophilic attack by a secondary hydroxyl and subsequent decarboxylation, yields 3,6-sorbitan. Two further transcarbonation reactions of additional DMC and residual hydroxyl functions give Sorb-BisCC as a final product in a 40%yield. The reaction outcome was controlled by temperature and solvation effects; specifically, the onset of competitive formation of isosorbide (Scheme 9) was observed above 80 °C and favored by cosolvents (e.g., dioxane and MeOH).

CONCLUSIONS

This paper has reviewed recent advances on the use of DMC as a transcarbonation and a methylation reagent for the upgrading of biosourced platform chemicals focusing the discussion of synthetic strategies on the choice of catalysts and reaction conditions including both continuous-flow and thermal (noncatalytic) processes. Dimethyl carbonate often offers one

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of the best options to meet not only criteria of safety but also to intensify the process by improving productivity, minimizing the use of solvents, and optimizing downstream operations (recycle, separation, and purification methods). It should be noted that coproducts of DCM-mediated transformations are MeOH and CO_2 (the latter only for methylation reactions), which can be directly or indirectly recycled for the synthesis of DMC itself or easily conveyed to other uses. Although costs of DMC and energy demand for its reactions may still not be competitive with respect to processes carried out by conventional (and highly dangerous/toxic) carboxylating and methylating agents as phosgene, methyl halides, and dimethylsulfate), a concrete perspective to alleviate this issue can be devised by integrating synthesis and use of DMC in a biorefinery plant with modern technologies for recovery/recycle of waste heat and reagents/solvent.

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Notes

The authors declare no competing financial interest.

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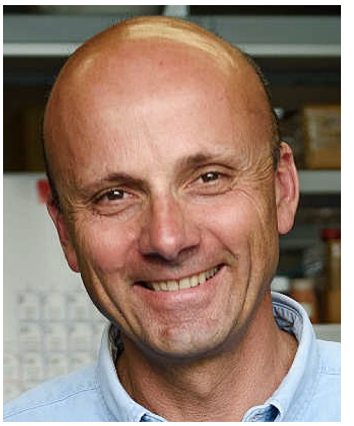
Maurizio Selva is a full professor of Organic Chemistry at the Department of Molecular Sciences and Nanosystems, University Ca' Foscari Venezia (Italy). Since the beginning of his academic career in the early 90s, his main research interests focused on the implementation of eco-friendly organic syntheses based on clean reagents, catalysts, and solvents. More specifically, the development of green catalytic techniques for the upgrading of bio-based platform chemicals using dense CO_2 and dialkyl carbonates and multiphase systems assisted by ionic liquids are among the current topics of research of Prof. Selva.



Alvise Perosa earned his Ph.D. in Chemistry from Case Western Reserve University in 1996 and is currently associate professor of Organic Chemistry at Ca' Foscari University Venice. He was Fulbright Fellow at Case Western Reserve University, Endeavour Research Fellow at the University of Sydney and is currently a Fellow of the Royal Society of Chemistry. Alvise sits on the Editorial Advisory Boards of Green Chemistry (RSC) and ACS Sustainable Chemistry and Engineering (ACS). Alvise's interests include research, teaching, and outreach in green chemistry with specific focus on chemicals from renewable resources, green chemicals from carbon dioxide, ionic liquids, catalysis, supercritical fluids, and multiphase reaction systems.

Daily Rodríguez-Padrón is a Ph.D. student at the Universidad de Cordoba (Group FQM-383). She received her Degree in Chemistry at the University of Havana, Cuba in 2013, and her Master's Degree at the University of Córdoba, Spain in 2016. After finishing her undergraduate studies, she worked at the Center of Genetic Engineering and Biotechnology, in Cuba, for one year, especially on synthesis of peptides. As part of her Ph.D. investigations in the Group FQM-383 "Nanochemistry and biomass Valorization" she has worked on the design of nanomaterials through mechanochemical grinding processes, the functionalization of nanoparticles with proteins, and their applications in catalysis, green chemistry, biomass valorization, and electrochemistry with a strong sustainable character looking forward to ameliorate climate change.

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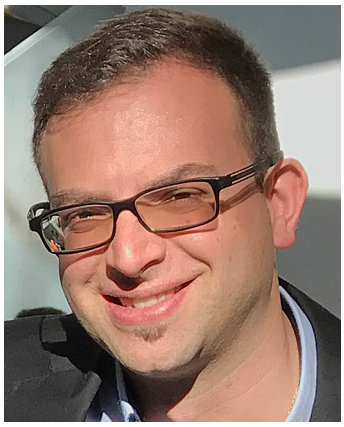

Rafael Luque is full professor from Departamento de Quimica Organica at Universidad de Cordoba (Spain), where he graduated in 2005, after spending a postdoctoral stay at The Green Chemistry Center of Excellence from the University of York. With various positions held in China (Chinese Academy of Sciences, Xiamen University), Brazil (Universidade Federal de Pelotas), France (Sorbonne Universites UTC), and Russia (RUDN University) as visiting/distinguished professor, Rafael, 2018 Highly Cited Researcher, belongs to group FQM-383 which has extensive expertise in nanoscale chemistry, heterogeneous catalysis, green chemistry, and biomass and waste valorization.

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