

Catalytic Processes Combining CO₂ and Alkenes into Value-Added Chemicals



Synthesis of Cyclic Carbonates, Lactones, Carboxylic Acids, Esters, Aldehydes, Alcohols, and Amines

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Abstract The present chapter comprises an overview on catalytic pathways to synthesize a highly desired variety of common compounds/chemicals starting from carbon dioxide as C1 building block and simple alkenes. After a summary of the corresponding pioneering work of the past, the authors focus on state-of-the-art

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protocols. New transformations based on simple and non-activated starting materials containing a C–C double bond functionality leading to a broad product portfolio are covered. Overall, this chapter embraces sustainable routes, reagents, and apparatus to produce value-added products starting from CO₂ and alkenes as cheap and readily available building blocks.

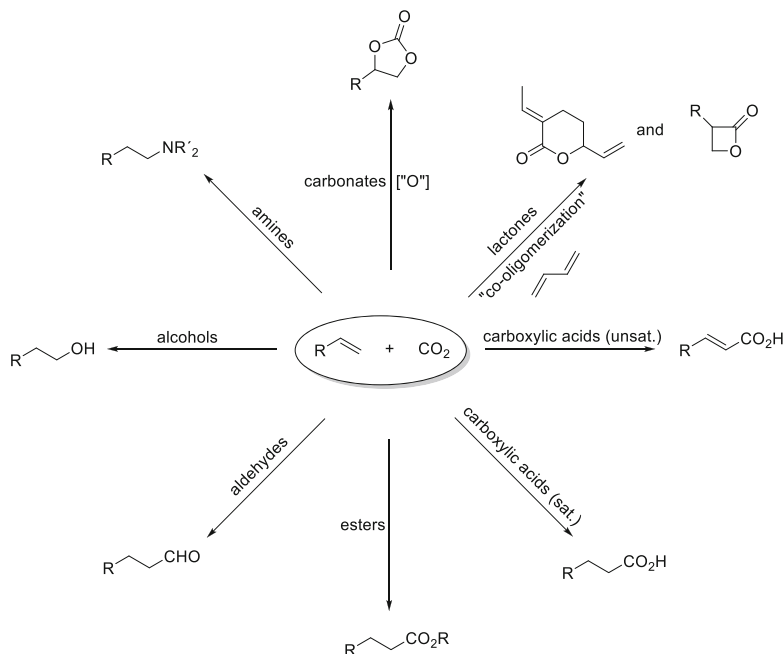
Keywords Alcohols · Aldehydes · Alkenes · Amines · Carbon dioxide · Carbonates · Carbon–carbon bond formation · Carboxylic acids · Esters · Homogeneous catalysis · Lactones · Reverse water-gas shift reaction

1 General Introduction

Fossil fuels are currently the world's main source of carbon, with 93% used for energy and transportation purposes and the remaining 7% being used for chemical production [1]. Challenges associate with the use of fossil fuels are their finite nature and their release of greenhouse gases into the atmosphere by combustion. To address these problems, researchers have turned to CO₂ as an alternative, abundant, and green carbon source. While enormous amounts of CO₂ are released annually from anthropogenic sources, only about 0.3% is being utilized today [2]. Pursuing new routes to utilize CO₂ would allow further exploitation of the vast and ubiquitous carbon source.

Researchers have successfully incorporated CO₂ into simple compounds like urea and formic acid and into complex compounds like polyurethanes [3, 4]. In addition, CO₂ has reacted effectively with numerous substrates, including alcohols, epoxides, aromatics, and alkynes, to produce molecules of industrial importance. In detail, this embeds the synthesis of fuels, bulk chemicals, commodities, and even fine chemicals and pharmaceuticals [5, 6]. The use of CO₂ in their synthesis can significantly reduce the carbon footprint of chemical production, when coupled with renewable energy input [3, 7–10].

Among many conceivable target products, carbonates, lactones, carboxylic acids, esters, aldehydes, alcohols, and amines appear highly attractive. Their general structure implies a close relationship to the CO₂ molecule. At the same time, their synthesis is particularly challenging as they mostly require formation of new carbon–carbon bonds. While CO₂ reacts readily with *O*- and *N*-nucleophiles to give carbonic and carbamic acids, reactions to form C–C bonds require typically stoichiometric use of carbanions such as Grignard reagents or other metal alkyl and aryl species. Alternative pathways involving catalytic combinations of alkenes with CO₂ are of great interest to synthesize the mentioned target molecules (Scheme 1), especially when the transformed alkene can be provided from biomass, e.g., by selective dehydration of the corresponding alcohol [11, 12]. According to the principles of Green Chemistry and Engineering, the synthesis of the target molecules will involve essentially a (molecular metal) catalyst and a highly intensified process scheme. Different classes of highly important chemical products are outlined in the next sections.



Scheme 1 Schematic overview of the target molecules and the systems illustrated in this book chapter

2 Reaction Products from CO₂ and Alkenes

2.1 Cyclic Carbonates

Cyclic carbonates are generally stable compounds which can guarantee a long-term fixation of CO₂ [13]. Carbonates are employed in a wide variety of industrial applications. Fluorinated carbonates are used in batteries production (as electrolytes additives) [14, 15]. Other carbonates, i.e., dimethyl carbonate, are used as solvents, considered greener compared to traditional VOCs [13, 16]. They are employed for the synthesis of compounds such as diols (i.e., ethylene glycol), carbamates, methanol, heterocyclic compounds, and ionic liquids [13]. In addition, carbonates are useful precursors for the synthesis of different polymers for various applications [17, 18]. Polycarbonates are thermoplastic polymers of high importance, finding application in the electrical sector, building, and automotive fields as well as data storing (i.e., CDs) and optical equipment (i.e., laboratory goggles) [19].

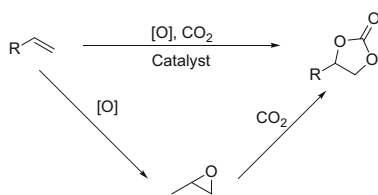
Traditionally, the production of carbonates requires the use of the highly toxic phosgene [16]. Recently, many protocols coupling epoxides and CO₂ have been reported leading to a greener synthesis of carbonates [16, 18, 20, 21]. Nevertheless, some of the used epoxides (i.e., propylene oxide) are considered toxic, and they usually require to be synthesized from alkenes [16, 22]. Starting directly from alkenes,

a safe oxidant, and CO_2 can lead to a greener synthesis of these useful compounds, eliminating the need of toxic reagents such as phosgene and corresponding epoxides.

The synthesis of carbonates from alkenes is considered as oxidative carboxylation since it involves an oxidation step (to epoxides) followed by the carboxylation of the intermediate (Fig. 1). Different oxidants and different catalysts (homogeneous, heterogeneous, and nonmetallic) have been reported in the literature. The present literature deals mainly with the production of cyclic carbonates starting from alkenes, while other types of carbonates synthesis are not well represented by the current research. Linear carbonates can also be obtained by coupling CO_2 with alcohols; however, this approach is reviewed elsewhere [23, 24]. Herein, the authors report a list of significant examples dealing with the production of cyclic carbonates starting from alkenes, CO_2 , and different types of oxidants.

The group of Aresta reported about a rhodium complex able to perform the transformation of olefins to carbonates in the presence of O_2 and CO_2 [25]. The homogenous system suffered from very low activity ($\text{TON} = 3$); therefore they decided to implement the system using a heterogeneous catalyst. Different heterogeneous catalysts known to perform a first epoxidation step and a following carboxylation were tested. Nb_2O_5 showed good catalytic activity but resulted in only low yields of the desired product (4.5%) [26]. Titanosilicate molecular sieves coupled with H_2O_2 or *tert*-butyl hydroperoxide (TBHB) oxidants were able to catalyze the oxidative carboxylation of alkenes in organic solvents with yields up to 52% [27]. The system was further implemented using ionic liquids as solvents, abolishing the need of organic volatile solvents [28]. More elaborated heterogeneous catalytic systems were developed more recently based on the gained mechanistic knowledge. In 2015, Jain et al. reported the immobilization of a cobalt complex and triphenylphosphonium bromide on chitosan [22]. The catalyst was able to convert alkenes, CO_2 , and O_2 into carbonates, providing yields up to 85%. In addition, the catalyst was recyclable up to four times by simple magnetic separation. The same year the group of Han developed a polyoxometalate-based homochiral metal-organic framework (MOF) able to produce even enantiomerically pure carbonates [29]. The catalyst consists of a pyrrolidine moiety as chiral organocatalyst and Keggin-type anions (Zn(II)-based polyoxometalate) as oxidation catalyst. This moiety can convert the alkene into a chiral epoxide, using TBHB as oxidant. The MOF contains an amine-bridged ligand to adsorb and activate CO_2 and therefore be able to perform the following transformation of the epoxide into the carbonate. Yields up to 92% for

Fig. 1 General oxidative carboxylation of alkenes to carbonates. [O] = general oxidant (i.e., H_2O_2 , O_2 , etc.)



enantiomerically pure carbonates were achieved using this multifunctional catalytic system [29].

In addition to metal-based catalyst, other systems were reported. In 2007, Li et al. reported the transformation of alkenes to carbonates using CO₂, H₂O₂ as oxidizing agent and bromides in catalytic amounts to activate the transformation [30]. The system is highly active and can lead to yields of carbonates of 89%. Recently, other examples of nonmetallic catalysts performing similar transformations were reported. For example, homoallylic alcohols and CO₂ can lead to the enantioselective synthesis of cyclic carbonates with the aid of a dual Brønsted acid/base organocatalyst [31].

The reported examples represent an interesting step forward toward the development of technologies able to fix CO₂ in valuable chemicals such as cyclic carbonates. In addition, the use of alkenes and CO₂ for these processes would lead to substitute processes using highly toxic reagents (phosgene) and allow to elude the additional transformation step of alkenes via epoxides.

2.2 Lactones

Due to the formal relation in their synthetic pathway from CO₂ and an alkene functionality or diene moiety, respectively, lactones and co-oligomerization products like 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one are discussed together within this section. Both products embody a 1-oxacycloalkan-2-one unit which is known to be abundant within comonomers for plastics, in flavors and fragrances, or for sesquiterpenoids in plants and in drugs. Apart from α - and β -lactones, these compounds are mostly made by an internal esterification of an alcohol and a carboxylic acid functionality under the release of one equivalent of water. Another typical method of producing lactones is the Baeyer-Villiger oxidation. Cyclic ketones are oxidized with peroxy-carboxylic acids under ring expansion. The Baeyer-Villiger oxidation of cyclohexanone provides ϵ -caprolactone, which is industrially produced in considerable quantities as starting material for the preparation of polyesters and polyethers. However, the formation of lactones starting from simple alkenes in combination with renewable CO₂ is so far rare in literature. Yet, the formation of β -lactones has never been observed experimentally.

Early catalytic reactions with CO₂ in the formation of γ -lactones were carried out by Inoue et al. in 1979 [32]. For methylenecyclopropanes, 2.4 mol% of, e.g., [Pd(dpa)₂] (dba = dibenzylideneacetone), in the presence of a phosphine ligand (2.0–4.0 eq.) catalyzed the reaction with CO₂ (40 atm) and provided successfully a mixture of five-membered lactones in good yields (Fig. 2, up to 77%, **2** and **3**). They were able to influence the selectivity between **2** and **3** by changing from PPh₃ to a chelating dppe ligand. They suggest that the transformation with CO₂ proceeds via a trimethylenemethane species **4** (Fig. 2) which has been suggested for the Pd-catalyzed cycloadditions of methylenecyclopropanes to alkenes before [33]. However, a methyl-substitution in positions 3 and 3' instead of position 1 was not tolerated

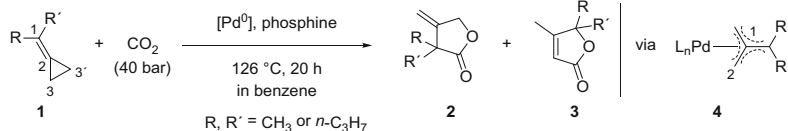


Fig. 2 Reaction of methylenecyclopropanes with CO₂ catalyzed by palladium(0) complexes [32]

since no conversion was observed. Further details on the mechanism and on catalyst reusability remain unknown.

Subsequently, Binger and Weintz described the dependence on the reaction conditions like temperature, pressure, ligand concentration, and substrate amount on the desired formation of products **2** and **3**. During their investigations, even co-oligomerization products from **3** and **1** were observed which were already known for Pd⁰-catalyzed alkylations of CH-acidic compounds [34, 35]. Based on their experiments and optimizations (precursor, cyclopentadienyl allyl palladium, DMF, 165 °C, PPh₃), they were even able to yield compound **3** (R, R = H) with 80% yield from methylenecyclopropane and proposed a plausible reaction pathway involving the insertion of CO₂ into a Pd–C bond forming a palladalactone with the mentioned consecutive reactions. The few protocols herein reported are still unique examples to produce simple five-membered γ -lactones **2** and **3** from monoenes and CO₂ under catalytic conditions.

Compared to monoenes, reactions of dienes with CO₂ have been studied more deeply. Regarding the coupling of dienes with CO₂, lactones can be synthesized in the so-called co-oligomerization or telomerization (“linear dimerization”) reactions. In particular with conjugated dienes, transition metal compounds can readily form complexes via coupling reactions with CO₂. Early publications from the 1970s reported about the first telomerization of dienes with CO₂. In general, telomerizations can be considered as dimerization of two dienes in the presence of a suitable nucleophile, for example, alcohols, resulting in the case of 1,3-butadiene in substituted octadienes (1-substituted-2,7-octadienes, 3-substituted 1,7-octadiene). These products are useful intermediates, for example, in the total synthesis of natural products, precursors for plasticizer alcohols, solvents, corrosion inhibitors, and herbicides. From an industrial point of view, 1,3-butadiene and methanol are the most attractive starting materials due to their availability and low price. However, carbon dioxide can be used as suitable coupling partner as well for this reaction. Thus, Inoue et al. and Musco et al. found in the 1970s that highly functionalized organic compounds, γ - and δ -lactones, can be prepared by homogeneously Pd-catalyzed telomerization of 1,3-butadiene with CO₂ [36–38]. In 1980, Döhring and Jolly introduced 1,2-butadienes (methylallene) as substrates [39]. However, these transformations suffered from low selectivity for the lactone products, since open esters, carboxylic acids, and higher alkenes can be formed, too [40]. With immobilized palladium catalysts, prepared from [Pd(η^5 -Cp)(η^3 -C₃H₅)] and polymer-bound phosphines, the group around Dinjus was able to produce up to 72% selectivity of δ -lactone 2-ethylidene-6-heptene-5-olide, albeit at low conversion

(7%) [41]. The resulting δ -lactone is a highly functionalized compound and may be used for producing various products and as intermediate for consecutive reactions, e.g., like hydrogenations, hydroformylations, hydroaminations, or polymerizations [42, 43].

Recently, Behr et al. discussed in detail the mechanistic pathways for the synthesis of γ - and δ -lactones with palladium-phosphine catalysts [42, 44] (Fig. 3). After coupling of two butadiene molecules, the equilibrium between bis- η^3 -allyl- and mono-allyl-species complex allows insertion of carbon dioxide to the allylic carbonate species. Reductive elimination leads to the lactone isomers depending on the C–O formation. During an intensive investigation of this reaction [41], the same group published about their improvements toward a mini-plant with up to 95% selectivity of the δ -lactone at a conversion rate of 45% butadiene (Fig. 4) [42].

The group developed a stable and robust process enabling recycling of the by-products and closing all solvent and catalyst loops. In a continuously stirred tank reactor, butadiene and carbon dioxide are mixed together with acetonitrile and the catalyst system Pd(acac)₂/PPh₃. The product mixture is continuously fed into a thermal separation and a connected distillation unit to remove the gaseous phase and recycle the feeds. Thus, in their mini-plant, δ -lactone was obtained maintaining the catalyst activity over 70 h of continuous operation and with a constant product stream of 8 g h⁻¹ with an overall yield of 30% and a selectivity of 85% [45].

In the rhodium-catalyzed reaction of butadiene and carbon dioxide, a C13 γ -lactone-2-ethyl-2,4,9-undecatrien-4-olide is formed by a combination of three molecules of butadiene with one CO₂, besides the C9-lactones generated as in the case of palladium catalyst system [46]. Inspired by the given literature basis and results of the group of Nozaki in 2014 (Pd-catalyzed one-pot/two-step co-/terpolymerization

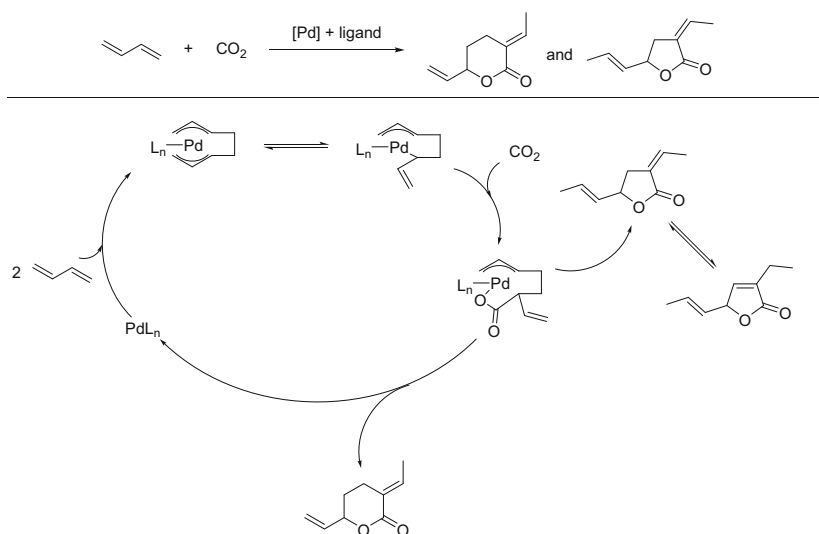


Fig. 3 Pd-catalyzed transformation of 1,3-butadienes into lactones [42]

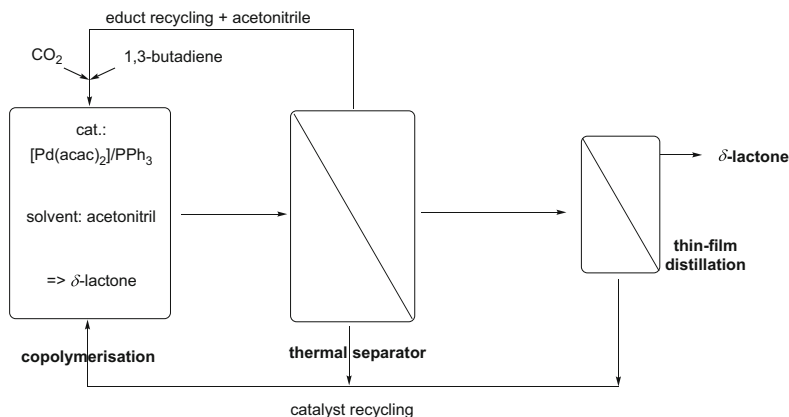


Fig. 4 Flow scheme of the production process for the δ -lactone (6 h, 80°C) [42, 44, 45]

of carbon dioxide and 1,3-dienes) [47], the group of Beller improved the yield of the δ -lactone up to 67% [48]. They reported a system comprised of $\text{Pd}_2\text{dba}_3/\text{TOMPP}$ (tris-(*o*-methoxyphenyl)-phosphine) as catalyst showing high productivity at low loadings and under mild conditions (0.06 mol% [Pd], 0.18 mol% ligand, 80°C, TONs up to 1,500). Most recently, Bayón and Dupont developed a similar catalyst system, in the presence of an ionic liquid additive giving an increased TON of 4,540 of lactone with 96% selectivity after 5 h at 70°C [49].

2.3 Carboxylic Acids and Derivatives

Carboxylic acids and their derivatives are highly important for the synthetic utilization in the production of, e.g., polymers, pharmaceuticals, solvents, and food additives (commodities) [50]. Presently, the global market for carboxylic acids is predicted to grow each year ca. 5% [51]. Carboxylic acids are especially produced for applications in polymer industry as both monomers and additives, e.g., as polyvinyl acetate (glue) from acetic acid [52, 53], PET (polyethylene terephthalate) [54], nylon fibers (polyamides) [55] based on adipic acid, and amines or acrylic/methacrylic polymers [56]. For modifying the properties of synthetic polymers, long-chain carboxylic acids ($>\text{C}_9$) are used as additives for alkyd resin films [57]. Apart from the polymer sector, carboxylic acids are widely used as solvents [58], for the textile and leather industry [59, 60]; in agrochemical industry to provide herbicides, fungicides, and rodenticides [58]; in pharmaceutical industry [51, 61, 62]; and for the food and feed industry [58, 63]. Moreover, Shell reported the use of valeric acid derivatives as biofuels [64], while formic acid is discussed as hydrogen carrier/storage [7, 65, 66]. Today, the majority of aliphatic ($\text{C}_4\text{--C}_{13}$), aromatic carboxylic, and dicarboxylic acids are produced via oxidation of the corresponding aldehydes usually obtained by the oxo synthesis (alkene hydroformylation).

Oxidation catalysts are usually Co or Mn salts, and O₂ (or HNO₃, KMnO₄) is used as oxidant [58, 67]. Small-chain acids like formic acid or acetic acid [53, 68, 69] are mainly produced by carbonylation, using, e.g., alcohols [70] or alkenes [71, 72], as substrates. Pivalic acid and other tertiary carboxylic acids can be obtained from alkenes by the Koch synthesis [58, 73]. Industrially, carboxylic acid esters can be synthesized by alkoxycarbonylations of alkenes, since it produces esters in a single step without coupling agents [74], or more generally via esterification reactions [75]. Stereoselective hydroesterification processes, mostly palladium- or rhodium-catalyzed, also enable the access to a variety of compounds which are widely used not only in the pharmaceutical field [76, 77]. For production of biodiesel, large quantities of fatty acid methyl esters are produced by transesterification of vegetable oils (mostly soybean, rapeseed or palm oil) with methanol [78].

The use of CO₂ as C1 building block for industrial production of carboxylic acids is implemented for decades in the synthesis of salicylic acid according to Kolbe [79] and Schmitt [80], converting phenol with CO₂ in the presence of a base (NaOH). However, this reaction has limited synthetic scope being applicable to phenolic type substrates and is based on a stoichiometric approach.

The examples discussed in this section focus on catalytic reactions where free acids are isolated as the products (if appropriate, after acidic hydrolysis) using mainly simple and non-activated alkenes as substrates.

According to Fig. 5, two basic routes (1) and (2) toward carboxylic acids based on an alkene moiety in combination with CO₂ can be envisaged.

Following pathway (1), acrylic acid as important platform chemical is one of the major target molecules provided by this transformation [81]. Preliminary work in this field was carried out in particular by the group of Hoberg. They studied the oxidative coupling of different alkenes like ethene [82], 1,3-butadiene [83], or styrene [84] with CO₂-forming metalla-lactone intermediates in the presence of [Ni(cod)₂] and a stabilizing base additive (DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene). Starting from the isolated and stable Ni-lactone, further saturated (e.g., propionic acid) and unsaturated carboxylic acids were accessible after hydrolysis. However, β-H elimination toward acrylic acid was not feasible at that time. These kinetic and thermodynamic constraints were computationally investigated by DFT calculations in 2007 [85]. A breakthrough for the catalytically Ni-promoted synthesis of acrylates was shown by Lejkowski et al. in 2012 [86, 87]. They developed a robust nickel catalyst for the direct carboxylation of simple alkenes, like ethene, styrene, and

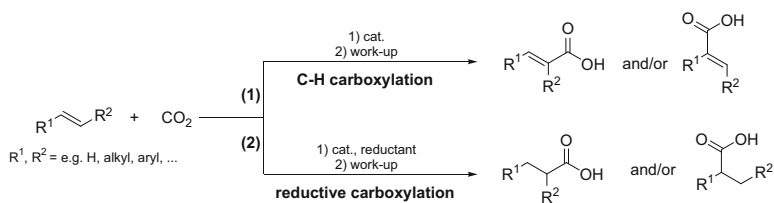


Fig. 5 Possible routes to carboxylic acids from alkenes and CO₂

1,3-dienes with CO_2 to their corresponding linear α,β -unsaturated carboxylic acid salts (TONs up to 116 for butadiene carboxylation) by the usage of an electron-rich bisphosphine ligand (BenzP*) and a suitable base (sodium 2-fluorophenoxide).

Vogt and coworkers were also able to develop a catalytic procedure for the synthesis of acrylate with diphosphine nickelalactones in the presence of Et_3N as base (with TONs up to 21) [88].

In addition to transition metal catalysts, such as Ni, Mo, and W, especially Pd offers new promising strategies to generate acrylic acid [88–90]. Most recently, the group of Schaub enhanced the TON to sodium acrylate to 514 using a Palladium system in an amide solvent (CHP: *N*-cyclohexylpyrrolidone) with a basic additive (alcoholates) [91, 92]. Additionally, the system was found suitable for other alkenes like propene and cyclopentene (TONs up to 92). In a semicontinuous reaction setup, they could show good results for the ethene conversion to acrylate with a total TON from 2 cycles of 235 in combination with an integrated catalyst recycling stream (Fig. 6).

The second pathway (2) to combine alkenes with CO_2 to yield carboxylic acids involves an overall reductive process, whereby saturated aliphatic acids are obtained as the final products (Fig. 5). One of the first examples in literature for the homogeneous catalytic conversion of ethene with CO_2 to the free propionic acid dates back to 1978. Lapidus et al. carried out the transformation in 38% yield in the presence of Wilkinson's catalyst under harsh reaction conditions (180°C , 700 bar) [93]. An exact mechanism of this transformation has so far remained unclear as no reduction equivalents required for product formation are specified in the described protocol.

Based on the approach from pioneering work by Hoberg [82–84] as well as Walther and Dinjus [94] to regenerate reactive metal species for alkene/ CO_2 coupling, Rovis and coworkers reported about the first nickel-catalyzed reductive

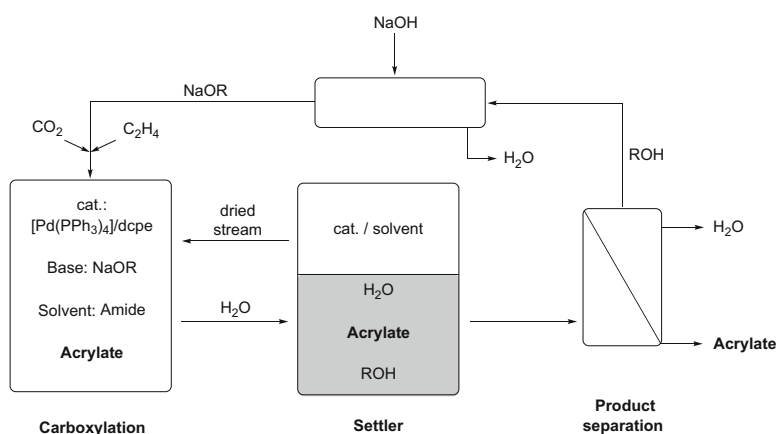


Fig. 6 Semicontinuous process scheme for Pd-catalyzed synthesis of sodium acrylate from ethene and CO_2 [91]

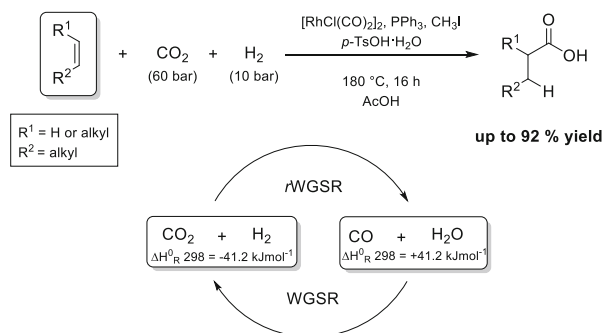
carboxylation of styrenes using CO₂ under ambient conditions (23°C, 1 bar CO₂) [95]. The transformation led regioselectively to saturated α -substituted carboxylic acids (phenylacetic acid derivatives). However, transmetallation of nickel by Et₂Zn was required to regenerate the active species in this hydrocarboxylation. Under comparable reaction conditions (r.t., 1 bar CO₂, THF), an iron-catalyzed system with similar regioselectivities of the formed α -aryl carboxylic acids has been reported in 2012 using an excess of a Grignard reagent (EtMgBr) as reductant [96, 97]. For aryl carboxylation reactions, light-driven transformations [98] or generally photo-redox catalytic systems [99, 100] have also attracted interest recently.

In 2013 the group of Leitner reported the rhodium-catalyzed formal hydrocarboxylation of alkenes. The reaction of olefins with CO₂ and H₂ leads to the corresponding one-carbon-atom elongated carboxylic acids (Fig. 7) [101]. Saturation of the C–C double bond provides an important energetic driving force, but competing hydrogenation poses also mechanistic challenges on the transformation [102].

With a [RhCl(CO)₂]₂/PPh₃ system and a promoting iodide reagent, very high to excellent yields (up to 92%) for the free acids were obtained for a range of cyclic and linear alkenes. For internal olefins, the ratio of regioisomeric acids is largely independent of the original position of the double bond. Mechanistic studies including isotopic labeling studies with ¹³CO₂, D₂, and H₂¹⁸O demonstrated that the formal hydrocarboxylation results from the effective interconnection of two catalytic cycles. In the first step, catalytic reverse water-gas shift reaction (*r*WGSR) generates carbon monoxide and water, which consecutively get converted in a subsequent Reppe-type hydroxycarbonylation cycle to yield the free carboxylic acid (Fig. 7).

In 2016 the group of Mikami published ambient synthesis of α -aryl carboxylic acids from CO₂ and styrene derivatives via rhodium-catalyzed hydrocarboxylation (precursor, [RhCl(cod)₂]) [103]. Depending on the substrate, yields up to 95% were obtained. As reduction equivalents, 1.2 eq. of ZnEt₂ per mol substrate was most suitable. Remarkably, they were able to perform the catalytic asymmetric hydrocarboxylation of α,β -unsaturated esters synthesize with ee values up to 66% employing a

Fig. 7 Overall hydrocarboxylation of alkenes involving the *r*WGSR followed by the consecutive hydroxycarbonylation [101]



cationic rhodium complex with (*S*)-(-)-4,4'-bi-1,3-benzodioxole-5,5'-diylbis(diphenylphosphine) [(*S*)-SEGPHOS] as a chiral diphosphine ligand (Fig. 8).

The group of R. Martin has reported a variety of carboxylation reactions of diverse starting materials like allylic alcohols [104], styrenes [105], 1,3-dienes [106], halogenated aliphatic hydrocarbons [107, 108], unsaturated hydrocarbons [109–111], and others [112, 113]. They were able to control regioselective hydrocarboxylation of aryl- and alkyl-substituted C–C bonds with a catalytic system based on a nickel precursor, a bipyridine-based ligand, and a reducing reagent (metallic manganese) (Fig. 9) [109]. Even more recently, the same group published about the 1,4-dicarboxylation of 1,3-dienes (e.g., butadiene) using the Ni-based reaction system in Fig. 9 [106]. This multiple CO₂ incorporation into abundant 1,3-dienes gives access to adipic acids from simple and available precursors. The salient features of this method are its excellent regio- and chemo-selectivity, mild conditions, and ease of execution. The (over-)stoichiometric use of a metal-based reducing agent is, however, a major limitation for large-scale application.

Clearly, the principle outlined in Fig. 7 utilizing a combination of CO₂ and H₂ as source for in situ formed CO (and H₂O, respectively) offers the most attractive strategy for alkene transformations. Meanwhile, protocols were published about carboxylation-, alkoxy-carboxylation- or hydroformylation-related reactions and may open new strategies in CO₂ utilization [89, 114, 115]. Notably, the required hydrogen may also come from organic substrates, in particular alcohols, as most catalysts active in these reactions are generally active for dehydrogenation or reforming processes.

In 2012 the group of García reported the first example of catalytic reductive hydroesterification reaction of styrenes using CO₂ as a C1 source and methanol as a reductant catalyzed by nickel complexes [116]. Yields up to 71% for the linear isomer were obtained using complex [(dippe)Ni(μ-H)]₂ for styrenes bearing σ-electron-withdrawing groups. The corresponding TON was limited, however, as high catalyst loadings (20 mol%) were required.

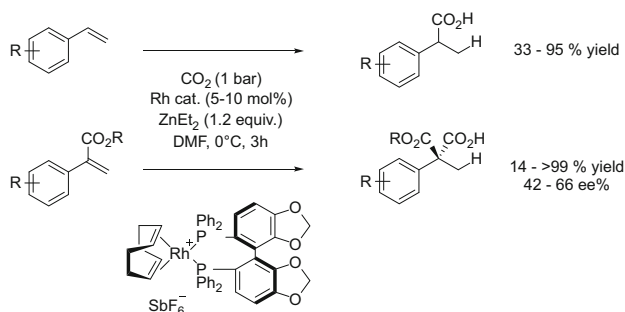


Fig. 8 Rh-catalyzed hydrocarboxylation of alkenes with CO₂ and ZnEt₂ [103]

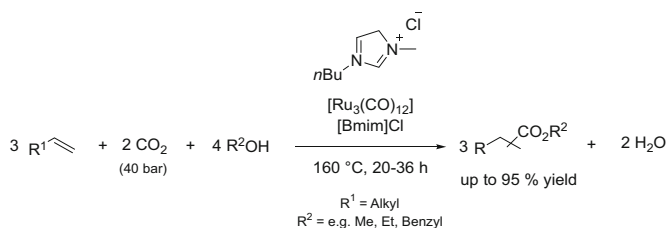


Fig. 10 Ru-catalyzed alkoxy-carbonylation of alkenes with carbon dioxide and methanol [117]

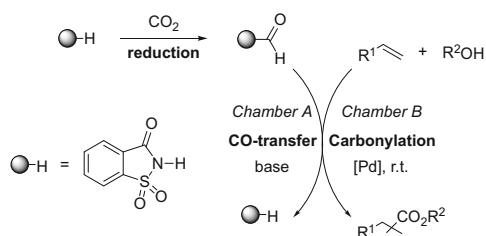


Fig. 11 Indirect utilization of CO₂ as a C1 source under ambient reaction conditions using *N*-formylsaccharin as a CO transfer reagent [119]

2.4 Further Reduced Target Molecules

The following section summarizes the state of the art for the use of CO₂ as a C1 building block in combination with alkenes for the generation of more strongly reduced functional groups such as aldehydes, alcohols, and amines. It covers synthetic protocols comprising, e.g., hydroformylation, hydrohydroxymethylation, and hydroaminomethylation, using CO₂/H₂ as synthon to generate useful compounds. The target molecules are highly important for a lot of different applications like pharma, agriculture, or health care as well as for further chemical transformations by addressing compounds like APIs, solvents, lubricants, dyeing reagents, or plastics. Considering their usual synthetic routes, a change from common C1 building blocks to CO₂ opens new fields and opportunities for upcoming synthetic pathways and transformations.

2.4.1 Aldehydes

While CO₂ is long known as a possible C1 source in technical hydroformylation, its application has found more widespread attention in organic synthesis only most recently. In 2017, the research groups of Xia and Ding used the readily available and inexpensive poly(methylhydrosiloxane) (PMHS, $M_w = 1900$) as alternative

reductant to high pressure H₂ for hydroformylation of alkenes and CO₂ [120]. The desired aldehydes from alkyl- and aryl-based substrates were isolated in moderate to good yields (up to 70%) and with good selectivity to the linear product (l:b = up to 89:11). From their mechanistic studies, they found that CO₂ was inserted preferentially into the Si–H bond to form the corresponding silyl formate [Si]OC(O)H which either decomposes into CO and silanols [Si]OH or is hydrolyzed to formic acid subsequently releasing CO and H₂O. With the production of CO, aldehydes could then be formed by established Rh-catalyzed hydroformylation chemistry [121]. Interestingly, an excess of CO₂ hindered the further reduction of the formed aldehyde toward the alcohol moiety (Fig. 12) [120].

2.4.2 Alcohols

Pioneering work in this area has been reported in 2000 by Tominaga and Sasaki, who used CO₂ as building block with various ruthenium cluster complexes to obtain C₁-elongated alcohols from different alkenes (Fig. 13) [122]. The highest yield of 88% alcohol was achieved using [H₄Ru₄(CO)₁₂], a well-known rWGSR catalyst. The nature and performance of the required alkali salt additive were intensively studied together with investigations about the active species [123–126]. An immobilized system was also reported [127]. Although the inferred primary product of this reaction is the aldehyde obtained by hydroformylation of the alkene, these intermediates were not observed in high yield due to rapid further reduction. This system proved effective for several substrates. When CO was used instead of CO₂, the yield of the alcohol was either significantly decreased or comparable to the

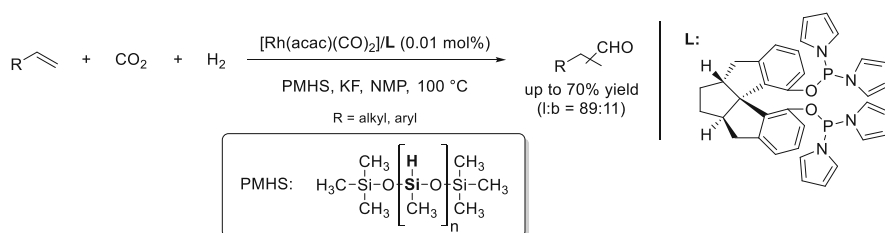


Fig. 12 Hydroformylation of alkenes with CO₂, silane, and H₂ [120]

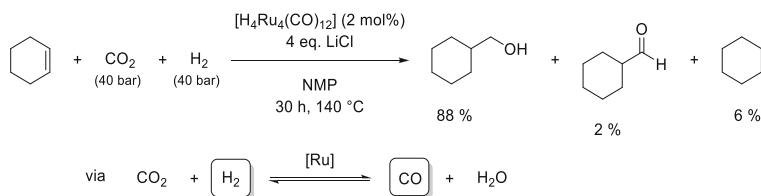


Fig. 13 Ru-catalyzed hydroformylation/reduction of cyclohexene using CO₂ [122]

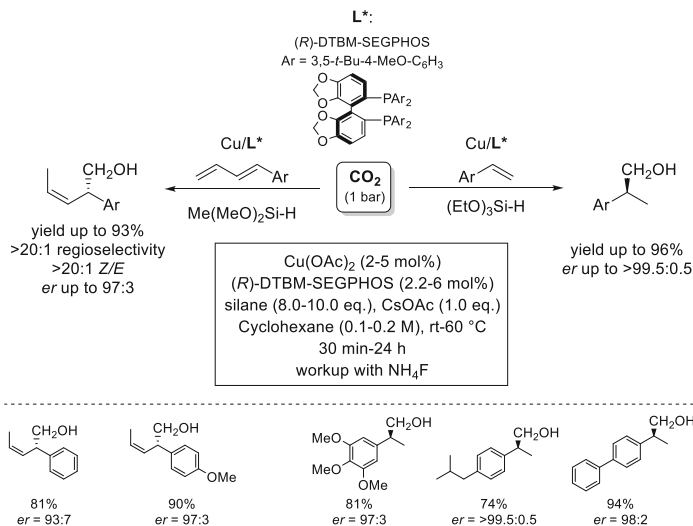


Fig. 15 Enantioselective hydrohydroxymethylation with CO₂ to give chiral alcohols [131]

the silyl ether which released the alcohol product after treating with NH₄F. Thus, these studies suggest that pathways without involving the *r*WGS equilibrium may also be possible to exploit the CO₂/H₂ synthon.

2.4.3 Amines

Amines are large-scale industrial products or intermediates that are often produced by multistep processes [70]. To provide amines in a single-unit operation, the hydroaminomethylation reaction approach can lead to the formation of C1-elongated amines from alkenes [132]. An initial hydroformylation of the alkene forms the aldehyde that gets further converted in a second step with an amine toward an enamine/imine from which the final amine is formed through subsequent reduction. The group of Eilbracht demonstrated already in 2009 the possibility to use CO₂ as a CO surrogate for the conversion of alkenes with secondary amines and aniline [133]. The use of the *r*WGS catalyst system [Ru₃(CO)₁₂]/LiCl/BTAC (BTAC = benzyltrimethylammonium chloride) proved to be an efficient system for the in situ formation of CO from CO₂ and H₂. Optimization of the four-step tandem reaction was successfully demonstrated using cyclopentene and morpholine as substrates (Fig. 16). The combination of promoting salts revealed a synergetic effect on the yield and selectivity, with the phase-transfer catalyst enhancing the solubility of LiCl in toluene. Isomeric mixtures (1:b up to 64:36) of secondary and tertiary amines were formed effectively from a variety of alkenes with yields in the range of 35–98%.

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