CATALYTIC CARBOXYLATIVE CYCLIZATION OF TERMINAL ACETYLENIC ALCOHOLS WITH CO_2: MODERN APPROACHES TO GREEN SYNTHESIS

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The catalytic carboxylative cyclization of terminal acetylenic alcohols with carbon dioxide represents an atom-efficient approach to the synthesis of α-alkylidene cyclic carbonates. Among terminal alkynols, propargylic alcohols are particularly suitable substrates because the adjacent hydroxyl and C≡C groups enable CO_2 incorporation followed by intramolecular cyclization. This review summarizes the development of homogeneous metal catalysts, organocatalysts, ionic liquids, heterogeneous metal-containing materials, and continuous-flow approaches. Particular attention is paid to reaction temperature, CO_2 pressure, catalyst recyclability, solvent requirements, and substrate scope. Comparative analysis indicates a progressive transition from high-pressure and noble-metal systems toward atmospheric-pressure, solvent-free, recyclable, and process-intensified catalytic technologies. Current achievements and remaining challenges in the sustainable production of α-alkylidene cyclic carbonates are discussed.

Introduction

Carbon dioxide is an attractive renewable C1 feedstock; however, its high thermodynamic stability requires efficient activation strategies. The reaction of CO_2 with propargylic alcohols is particularly attractive because incorporation of CO_2 and intramolecular cyclization produce α-alkylidene cyclic carbonates with high atom economy. An early important advance was the CuCl/ionic-liquid system reported by Gu *et al.*, which

enabled the synthesis of α-methylene cyclic carbonates under comparatively mild conditions [1]. Silver catalysis subsequently expanded the substrate scope and demonstrated efficient activation of propargylic C≡C bonds [2], while carboxylative cyclization in supercritical CO_2 established CO_2 as both reagent and reaction medium [3].

In general, the catalytic process involves activation of the hydroxyl group and/or CO_2, formation of a carbonate-type intermediate, activation of the alkyne moiety, and intramolecular cyclization to the five-membered carbonate. The exact sequence depends strongly on catalyst type. Consequently, development of greener processes has focused on simultaneous activation of CO_2 and the propargylic alcohol while decreasing temperature, CO_2 pressure, catalyst loading and solvent consumption.

Development of catalytic approaches

Metal-free catalysis represented an important step toward more sustainable CO_2 fixation. Kayaki *et al.* demonstrated that N-heterocyclic carbenes can efficiently promote CO_2 incorporation into propargylic alcohols [4]. Bicyclic guanidines were subsequently used for carbonate formation in supercritical CO_2, confirming that strong organic bases can replace transition metals in appropriate systems [5]. These studies established activation of CO_2 by nucleophilic organocatalysts as an alternative to direct metal–alkyne activation.

Silver catalysts nevertheless remain among the most effective systems because of the strong affinity of Ag(I) for alkynes. Bifunctional Ag(I) complexes enabled α-methylene cyclic carbonate synthesis under ambient conditions [6]. Immobilization of small Ag nanoparticles on hierarchically porous supports provided a heterogeneous and recyclable alternative and demonstrated efficient cyclization at ambient temperature and pressure [7].

Replacement of noble metals has also received considerable attention. The ZnI_2/NEt_3 combination efficiently converted propargylic alcohols and CO_2 at room temperature under solvent-free conditions, with yields reaching up to 99% for suitable substrates [8]. The synergistic action of Zn(II) and triethylamine was attributed to complementary activation of the reacting components.

Ionic-liquid-based systems constitute another important green strategy because the medium can participate in CO_2 capture and activation. By controlling ionic-liquid basicity, Chen *et al.* achieved efficient cyclic carbonate formation at atmospheric CO_2 pressure [9]. A highly active AgOAc/quaternary-ammonium system subsequently demonstrated that cooperative Lewis acid–base catalysis could provide high turnover numbers without an additional conventional ligand or base [10].

Further improvement was achieved with a recyclable AgI/OAc^- system that operated at atmospheric CO_2 pressure and retained activity over repeated catalytic cycles [11]. Tetrabutylphosphonium-based ionic liquids were then designed with multiple CO_2-interaction sites, allowing simultaneous CO_2 activation and promotion of the propargylic substrate under ambient conditions [12]. Fine structural tuning of simple ammonium salts showed that tetrabutylammonium oxalate could produce α-alkylidene cyclic carbonates

rapidly and selectively under solvent-free conditions at relatively low organocatalyst loading [13].

Modern green catalytic strategies and comparative assessment

The major trend in recent catalyst development is the combination of mild conditions, inexpensive catalytic components and recyclable reaction media. A CuI/ionic-liquid system containing a biomass-derived levulinate anion enabled carboxylative cyclization at 25 °C, illustrating the possibility of combining renewable catalyst components with CO_2 utilization [14]. In comparison with silver systems, copper offers economic advantages but often requires careful optimization of ligands, counterions or cocatalysts. A significant advance was the N-heterocyclic-carbene Cu(I) catalyst reported for the direct synthesis of α-alkylidene cyclic carbonates at room temperature and atmospheric CO_2 pressure [15]. Importantly, the protocol was applicable not only to tertiary substrates but also to primary and secondary propargylic alcohols, demonstrating that catalyst design can overcome important substrate-reactivity limitations.

Heterogeneous catalysis has become particularly important from a green-chemistry perspective. In 2024, an Ag(I)-functionalized polyoxoniobate-based coordination polymer was applied to solvent-free carboxylative cyclization at room temperature [16]. Such systems combine alkyne activation by Ag(I) with a solid framework capable of catalyst recovery, reducing downstream separation requirements. Process intensification represents the next stage of development. Stiernet *et al.* demonstrated continuous-flow coupling of CO_2 with propargylic alcohols, achieving quantitative conversions in short residence times and substantially increasing space–time productivity compared with conventional batch processing [17]. The flow strategy also decreased the amount of CO_2 required and provided a route toward scalable production of α-alkylidene cyclic carbonates.

Most recently, porous organic polymers have been used as supports for highly dispersed silver nanoparticles. An Ag/POP catalyst reported in 2026 promoted efficient CO_2 cyclization with propargylic alcohols under mild conditions and combined catalytic activity with stability and recyclability [18]. This development reflects the current movement toward catalysts that integrate CO_2-philic porous environments with accessible alkyne-activating metal sites.

Review findings

Comparison of the reported approaches shows a clear evolution of carboxylative cyclization technology. Early homogeneous Cu and Ag systems established high synthetic efficiency but frequently depended on specialized solvents, elevated CO_2 pressure, or difficult catalyst separation. Organocatalysts and ionic liquids reduced dependence on noble metals and enabled CO_2 capture and conversion within the same medium. Zn- and Cu-based systems further demonstrated that efficient reactions are possible using comparatively inexpensive metals. From a sustainability perspective, no single catalyst property is sufficient to define the optimal process. High product yield should be considered together

with CO_2 pressure, temperature, solvent demand, catalyst loading, recyclability, substrate scope and ease of product separation. Current heterogeneous Ag-containing catalysts offer excellent activity and recycling potential, whereas metal-free ionic liquids and organic salts avoid metal contamination. Cu-based catalysts provide a balance between cost and activity, while continuous-flow processing offers an important advantage in productivity, CO_2 efficiency and future scale-up.

The literature therefore indicates that the most promising strategy is cooperative catalysis, in which different active sites simultaneously activate the hydroxyl group, CO_2 and the C≡C bond. Combining such multifunctional catalysis with solvent-free conditions, recyclable porous materials and continuous-flow technology is likely to provide the greatest improvement in the overall sustainability of the process.

Conclusion

Carboxylative cyclization of terminal propargylic alcohols with CO_2 has developed from conventional metal-mediated reactions into an efficient platform for sustainable α-alkylidene cyclic carbonate synthesis. Modern systems can operate at room temperature and atmospheric CO_2 pressure, and considerable progress has been achieved in solvent elimination, catalyst recycling and replacement of expensive metals. The transition from homogeneous Ag catalysts to ionic liquids, organocatalysts, Cu- and Zn-based systems, multifunctional heterogeneous materials and continuous-flow processes demonstrates the rapid evolution of this field. Future research should focus on lowering metal loading, using dilute or industrial CO_2 streams, broadening the scope toward less reactive terminal alkynols, improving long-term catalyst stability and integrating CO_2 capture directly with catalytic conversion.

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