有机小分子催化的炔丙醇与二氧化碳羧化环化反应

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摘要 对有机小分子催化二氧化碳(CO_2)与炔丙醇羧化环化合成环状碳酸酯的反应体系进行概述, 重点介绍离子液体、 CO_2 加合物和有机膦在催化炔丙醇羧化环化反应中的研究进展. 有机小分子化合物能够与 CO_2 生成 CO_2 加合物或者亲核进攻炔丙醇中碳碳三键生成两性离子中间体, 从而活化 CO_2 和(或)炔丙醇底物, 催化此羧化环化反应. 本文对有机小分子催化此羧化环化反应的机理进行了简要分析和探讨, 希望为进一步发展更加高效、绿色的有机小分子催化体系提供一点思路.

关键词 二氧化碳, 有机小分子催化剂, 炔丙醇, 羧化环化

二氧化碳(CO_2)是一种廉价、无毒、储量丰富的碳一资源^[1-5], 其作为合成子可以通过构建C-C、C-O、C-N、C-S键转化为高附加值产品^[6-9]. CO_2 资源化利用符合绿色化学、可持续发展的要求, 已经成为快速发展的研究热点之一^[10-12]. 例如, CO_2 可以转化为甲酸、甲醇、一氧化碳等能源性产品, 也可以用于合成碳酸酯、氨基甲酸酯、水杨酸等精细化学品^[13,14]. 但是, CO_2 中碳处于最高价态, 具有热力学稳定性和化学惰性, 不利于 CO_2 的化学转化和广泛利用. 目前, 开发高效的催化剂用来活化 CO_2 , 降低反应能垒, 已成为 CO_2 转化的关键和难点. 在化学工作者的不懈努力下, 一系列高效的催化剂不断被报道, 并应用于 CO_2 的催化转化领域^[15,16].

炔丙醇羧化环化反应制备五元环 α -亚烷基碳酸酯是 CO_2 利用的一类重要的化学转化反应, 原子利用率100%, 符合绿色化学的要求^[16-20]. 产物 α -亚烷基碳酸酯是一类重要的杂环化合物, 在有机合成中具有广泛的应用前景. 目前炔丙醇与 CO_2 羧化环化反应的相关研究发展迅速, 一系列新颖的反应体系陆续被报道, 用于催化此羧化环化反应. 在炔丙醇与 CO_2 羧化环化反应

中, 研究最多的催化体系为过渡金属催化体系, 如过渡金属银(Ag^I)^[21,22]、铜(Cu^I)^[23]、锌(Zn^{II})^[24]盐被广泛应用于炔丙醇羧化环化反应的研究中. 过渡金属盐能够有效地活化炔丙醇结构中的碳碳三键, 有利于烷基碳酸阴离子对碳碳三键的进攻, 生成目标产物. 虽然过渡金属催化剂能够高效地催化此羧化环化反应, 但是同时也存在一些缺点, 比如成本高、容易造成金属残留等. 因此, 开发无过渡金属的有机小分子催化体系在 CO_2 化学转化反应领域受到了越来越广泛的关注. 一系列有机小分子试剂, 如有机膦、超强碱^[17]、离子液体、二氧化碳加合物(氮杂环卡宾等)等应用于此羧化环化反应(图1). 本文概述了有机小分子催化剂在炔丙醇羧化环化反应中的应用, 并重点探究其反应机理, 期望为后续更高效有机催化体系的建立提供一点思路.

1 反应体系

1.1 离子液体体系

离子液体具有较低的蒸汽压、良好的稳定性、溶

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端炔丙醇: $R = H$
内炔丙醇: $R = \text{alkyl, Ar} \dots$

Organocatalysts: 离子液体、 CO_2 加合物、有机磷、超强碱等

图1 (网络版彩色) 炔丙醇与 CO_2 的羧化环化反应

Figure 1 (Color online) The carboxylative cyclization of propargyl alcohol and carbon dioxide

解性、结构可设计性等特点, 被广泛地应用于有机催化反应^[25~27]。离子液体是一类高效绿色的催化剂, 其在催化二氧化碳与炔丙醇类化合物羧化环化反应的应用也逐渐成为研究热点之一。基于离子液体中阴阳离子可以设计的特性, 在离子液体结构中引入一个或多个 CO_2 活化位点与 CO_2 相互作用, 能够活化 CO_2 , 提高 CO_2 与炔丙醇的反应效率^[28~33]。

在离子液体的阴离子结构中引入一个或多个二氧化碳活化位点, 能够将直线型 CO_2 分子转变成碳酸根负离子、氨基甲酸负离子等弯曲型离子, 从而达到活化 CO_2 的效果^[28~31]。图2为部分离子液体活化 CO_2 的示意图, 四正丁基磷(tetrabutylphosphonium, $[\text{Bu}_4\text{P}]^+$)类离子

液体中阴离子能够高效地活化 CO_2 。在炔丙醇羧化环化反应中, 离子液体阴离子的选择对反应至关重要, 尤其是阴离子的碱性。四正丁基磷(2,4-OPym-5-Ac: 2,4-二羟基嘞啶-5-羧酸阴离子) $[\text{Bu}_4\text{P}]_3[2,4\text{-OPym-5-Ac}]$ 中阴离子对应酸的 $\text{p}K_{\text{a}1}$ 数值为9.13, 催化效果最好(收率79%)。当 $\text{p}K_{\text{a}1}$ 值升高至9.97($[\text{Bu}_4\text{P}]_3[2,4\text{-OB-Ac}]$, 2,4-OB-Ac: 2,4-二羟基苯甲酸阴离子)时, 收率降低至66%。当 $\text{p}K_{\text{a}1}$ 值降低至5.45(四正丁基磷2,6-OPy-4-Ac: 2,6-二羟基吡啶-4-羧酸阴离子) $[\text{Bu}_4\text{P}]_3[2,6\text{-OPy-4-Ac}]$ 时, 收率降低至15%。这些结果说明, 阴离子的碱性对反应至关重要。碱性过强容易导致副反应, 碱性偏弱则导致催化活性降低。只有恰当的碱性才能得到最佳的反应收率^[28,32]。另一方面, 虽然离子液体不能像过渡金属催化剂那样直接与炔丙醇的碳碳三键相互作用、活化碳碳三键, 但是某些离子液体的阴离子能够与炔丙醇分子的羟基形成氢键(图1), 从而通过诱导效应间接地活化碳碳三键, 有利于烷基碳酸负离子中间体对三键的亲核加成, 最终生成 α -亚烷基碳酸酯^[28,33]。例如, 刘志敏课题组^[29]发现 $[\text{Bu}_4\text{P}]_3[2,4\text{-OPym-5-Ac}]$ 与炔丙醇底物混合后, 核磁共振氢谱中炔丙醇羟基氢的化学位移由5.30移动至5.82, 在核磁共振碳谱中碳碳三键的化学位移由88.6和

图2 (网络版彩色) 炔丙醇羧化环化反应体系的部分离子液体

Figure 2 (Color online) Partial ionic liquids of propargyl alcohol carboxylative cyclization reaction system

70.3分别移动至89.4和68.9处. 他们认为[2,4-OPym-5-Ac]阴离子与炔丙醇羟基通过生成氢键从而活化羟基, 并导致碳碳三键上电子的重新分配, 即通过诱导效应间接活化碳碳三键, 有利于碳酸负离子中间体对三键的亲核加成. 炔丙醇底物分为内炔丙醇和端炔丙醇两类, 一般认为端炔丙醇的活性较高. 在表1中的4种离子液体中, [DBUH][MIm](1,8-diazabicyclo-[5.4.0]-7-undecenium 2-methylimidazolidine)能够较好地适用于内炔丙

醇类底物, 收率为68%~88%. 这也可能是此反应体系中[DBUH][MIm]用量较高(200mol%)的原因. 离子液体的循环利用能力也是评价离子液体性能的重要指标. 表1中[DBUH][MIm]、[TBDH][TFE]可以重复使用5次, 不丧失催化活性和选择性; [Bu₄P]₃[2,4-OPym-5-Ac]、[Bu₄P][2-MIm]两种离子液体未进行循环使用实验.

图3为[Bu₄P]₃[2,4-OPym-5-Ac]催化炔丙醇羧化环化反应的反应机理. 首先CO₂被离子液体中的阴离子捕

表1 不同种类离子液体催化CO₂与炔丙醇羧化反应体系

Table 1 Different kinds of ionic liquids catalyze reaction system of CO₂ and propargyl alcohol

离子液体	用量(mol%)	反应条件	CO ₂ 压力(MPa)	底物适用性	收率(%)	循环次数 ^{b)}	文献
[Bu ₄ P] ₃ [2,4-OPym-5-Ac]	10	30°C, 20 h	0.1	端炔丙醇较好	60~97	-	[28]
[Bu ₄ P][2-MIm]	5	80°C, 24 h	0.1	端炔丙醇	51~95	-	[29]
[DBUH][MIm]	200	60°C, 24 h	2.5	内炔丙醇	68~88	5	[30]
[TBDH][TFE] ^{a)}	15	80°C, 12 h	0.1	端炔丙醇	24~99	5	[31]
[nBu ₄ N] ₂ O _x	2.5	80°C, 6 h	5.0	端炔丙醇	12~99	-	[32]

a) 2-氨基乙醇和端炔丙醇为原料, 生成的α-亚烷基碳酸酯与2-氨基乙醇反应转化为2-恶唑烷酮和邻羟基酮; b) “-”表示无数据

图3 (网络版彩色)[Bu₄P]₃[2,4-OPym-5-Ac]催化体系反应机理^[28]

Figure 3 (Color online) Reaction mechanism of [Bu₄P]₃[2,4-OPym-5-Ac] catalytic system^[28]

获得碳酸酯中间体**a**，而后 $[2,4\text{-OPym-5-Ac}]^3-$ 阴离子与炔丙醇中的羟基形成氢键，从而活化羟基并通过诱导效应间接活化炔丙醇的碳碳三键。随后，中间体**a**亲核进攻炔丙醇碳碳三键得到中间体**b**，醇羟基上的氢经过质子转移得到中间体**c**，最后中间体**c**中的醇羟基亲核进攻**c**中的羰基碳原子完成关环得到 α -亚烷基环状碳酸酯和用于下一个催化循环的离子液体(图3)。

1.2 CO₂加合物体系

活化CO₂是炔丙醇与CO₂羧化环化中不可缺少的一步，但是CO₂具有热力学稳定性和动力学惰性。活化甚至打破CO₂分子需要大量能量，而断裂CO₂中的 π 键所需要的能量较低。富电性亲核试剂能够进攻CO₂分子中的碳原子，生成CO₂加合物，将直线型CO₂分子转变成弯曲的两性化合物或阴离子从而活化CO₂。这为CO₂加合物应用于炔丙醇羧化环化反应奠定了理论基础。一系列CO₂加合物不断被报道，如*N*-杂环卡宾-CO₂加合物(NHC-CO₂)、*N*-杂环烯烃-CO₂加合物(NHO-CO₂、ANHO-CO₂)、碳二卡宾-CO₂加合物(CDCs-CO₂)、咪唑甜菜碱-CO₂加合物(AFIB-CO₂)、四氢嘧啶-2-亚烷基-CO₂加合物(THPE-CO₂)和磷叶立德-CO₂加合物(P-yiled-CO₂)等(图4)，并用于催化炔丙醇与CO₂生成 α -亚烷基碳酸酯的反应^[34-40]。在这些加合物中，O-C-O键角由CO₂分子中直线型结构转变为弯曲几何结构，如NHO-CO₂加合物中O-C-O键角为127.7°~129.9°，THPE-CO₂加合物中O-C-O角为127.50°~129.5°，AFIB-CS₂中S-C-S的键角为126.6°~126.9°(CS₂代替CO₂)，P-yiled-CO₂加合物中O-C-O键角为127.7°^[41]。弯

曲型结构的“CO₂”比气体CO₂更活泼。

N-杂环卡宾的C₂为具有较强的亲核能力，能够亲核进攻CO₂生成NHC-CO₂加合物。5mol%的NHC-CO₂加合物在60°C，4.5 MPa CO₂，无溶剂条件下能够高效催化炔丙醇与CO₂羧化环化得到相对应的 α -亚烷基碳酸酯，收率可达到99%。在反应过程中，加合物的稳定性(捕获CO₂与脱羧的平衡能力)与其催化活性关系密切，而且取决于加合物具体的结构。NHO-CO₂加合物稳定性略低于NHC-CO₂加合物，但是NHO-CO₂加合物的催化活性提高近10倍，甚至在0.1 MPa CO₂压力下环状碳酸酯的收率依然能够维持在63%。将NHO-CO₂加合物 α -碳烷基化后得到的ANHO-CO₂加合物，相对于NHO-CO₂加合物热稳定性更高，供电子能力更强。其催化能力也更强，反应时间可以缩短至3 h，对于含有各种内部和末端官能化的炔丙醇底物可以以高收率和选择性得到相对应的产物。相对于NHO-CO₂、NHC-CO₂加合物，碳二卡宾-CO₂加合物(CDCs-CO₂)更容易热脱羧，将其应用于炔丙醇羧化环化反应，内部和末端炔丙醇都能够以较高收率转化为对应的碳酸酯。作者认为热脱羧后游离的CDCs对于反应的进行起着至关重要的作用，CDCs强Lewis碱性可以活化炔丙醇底物，催化反应中烷基碳酸阴离子的生成，从而加快反应的进行。

另一方面，THPE-CO₂加合物具有高热稳定性，在DMSO溶液中100°C下能够保持稳定，不分解。这与NHO-CO₂、NHC-CO₂、CDCs-CO₂加合物的热稳定性不同。而且，THPE-CO₂加合物能够高效催化炔丙醇羧化环化反应，对于含有不同官能团的炔丙醇底物具有很高的适用性(表2)。THPE-CO₂极高的催化活性得益于

图4 不同种类的CO₂加合物

Figure 4 Different kinds of CO₂ adducts

表2 不同种类CO₂加合物体系下的炔丙醇羧化环化反应Table 2 Propargyl alcohol carboxylative cyclization reactions of different kinds of CO₂ adducts

加合物	用量(mol%)	反应条件	CO ₂ 压力(MPa)	底物适用性	收率(%)	文献
NHC-CO ₂	5.0	60°C, 5~45 h	4.5	内、端炔丙醇	51~99	[34]
NHO-CO ₂	5.0	60°C, 12 h	2.0	内、端炔丙醇	56~98	[35]
ANHO-CO ₂	5.0	60°C, 3 h	2.0	内、端炔丙醇	55~96	[36]
CDCs-CO ₂	5.0	80°C, 12 h	2.0	内、端炔丙醇	51~94	[38]
AFIB-CO ₂	2.0	60°C, 5 h	2.0	端炔丙醇	75~94	[38]
THPE-CO ₂	5.0	60°C, 2 h	2.0	内、端炔丙醇	57~96	[39]
P-yiled-CO ₂	5.0	80°C, 12 h	2.0	内炔丙醇	90~96	[40]

THPE-CO₂加合物本身可以充当有机亲核试剂引发炔丙醇与CO₂的羧化环化,并且THPE中的碱性离子可以稳定反应中的烷基碳酸阴离子,催化烷基碳酸阴离子亲核进攻炔丙醇炔三键完成闭环得到 α -亚烷基环状碳酸酯(图5)。

CO₂加合物体系作为一种成熟的催化体系广泛应用于炔丙醇与CO₂的羧化环化反应,是一种无过渡金属参与的绿色高效体系。但是不同CO₂加合物的结构存在着一定的差异,其热稳定性也影响着加合物的催化活性,所以CO₂加合物的稳定性可能会制约其发展。而且结构不同也造成CO₂加合物在反应过程中脱羧环节的速率差异,这也可能会影响反应的效率,从而制约CO₂加合物的工业化应用。虽然CO₂加合物实现工业化还有一段很长的路要走,但是现阶段作为一种无过渡金属参与的催化体系它依然发挥着重要的作用,具有广阔的发展前景。

1.3 有机膦体系

有机膦是一类亲核性的有机小分子催化剂,广泛用于多种有机反应中。Dixneuf使用三正丁基膦(PBu₃, 8mol%)为催化剂合成 α -亚烷基环状碳酸酯(5.0 MPa CO₂, 100°C, 8 h)^[42,43]。2007年, Ikariya课题组^[44]在超临界CO₂(ScCO₂)溶剂中利用PBu₃(5mol%)催化与炔丙醇羧化环化得到 α -亚烷基环状碳酸酯,并且对于具有不同官能团的炔丙醇底物有良好的适用性。基于PBu₃强亲核性的特点,在反应体系中PBu₃可能与CO₂生成Bu₃P⁺CO₂⁻加合物,也可能亲核进攻碳碳三键生成两性离子中间体(图6(a))。为稳定可能生成的两性离子中间

图5 (网络版彩色)THPE-CO₂催化体系反应机理^[39]Figure 5 (Color online) Reaction mechanism of THPE-CO₂ catalytic system^[39]

体,2019年Sun等人^[45]在炔丙醇结构中引入强拉电子酮基,获得 γ -羟基炔酮底物。实验发现酮基的引入使反应条件更加温和,在室温、常压CO₂条件下,一系列 γ -羟基炔酮底物以高收率转化为目标产物。可能的反应机理如图7所示,首先,PBu₃亲核进攻 γ -羟基炔酮的碳碳三键,生成两性离子中间体A。拉电子酮基的存在有利于稳定中间体A。随后,中间体A中碳负离子夺取羟基的氢原子生成新的中间体B。中间体B亲核进攻CO₂并发生环化反应,生成最终产物 α -亚烷基环状碳酸酯并重新生成PBu₃。随后作者开发了双功能氨基酸衍生的

图6 有机磷反应体系. (a) PBu_3 作催化剂; (b) 手性有机磷小分子作催化剂

Figure 6 Organic phosphorus reaction system. (a) PBu_3 as catalyst; (b) chiral organic phosphine molecule as catalyst

图7 PBu_3 催化 γ -羟基炔酮与 CO_2 羧化环化反应机理^[45]

Figure 7 Reaction mechanism of the carboxylative cyclization of γ -hydroxyacetylene and carbon dioxide catalyzed by PBu_3 ^[45]

手性有机磷小分子催化剂(图6(b)), 此手性有机磷小分子具有大空间位阻和高亲核性, 能够催化外消旋的 γ -羟基炔酮底物*rac*-1高选择性(*s*-Factor为24.6)地获得

49%收率, 81% ee值的产物(*R*)-2, 并以46%的收率和91% ee值回收获得未反应的(*R*)-1.

2 总结与展望

在 CO_2 资源化利用的进程中, CO_2 与炔丙醇的羧化环化反应是一种绿色环保的 CO_2 转化方式. 而有机小分子, 如离子液体、 CO_2 加合物和有机磷等, 通过活化 CO_2 和炔丙醇等方式高效地催化 CO_2 羧化环化反应的进行. 并且得益于这些有机小分子优异的催化性能, 其在 CO_2 资源化利用方面发展迅速, 结构新颖、性能优异的小分子催化剂不断被报道和发展. 但是目前也存在一些问题, 如较高的制备成本、重复使用能力、结构稳定性等. 因此, 基于对有机小分子催化剂活化 CO_2 和炔丙醇底物机理的认识, 合理设计、开发低成本(降低反应体系的成本)、高活性(提高催化活性)、净工艺(开创更环保的生产工艺)、可循环利用、高收益的有机小分子催化剂, 对实现在更加温和条件下更高效地催化此环化羧化反应至关重要, 将会促进炔丙醇与 CO_2 羧化环化反应的不断发展.

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Summary for “有机小分子催化的炔丙醇与二氧化碳羧化环化反应”

The carboxylative cyclization of propargyl alcohol and carbon dioxide catalyzed by organocatalysts

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Carbon dioxide (CO₂), as a cheap, non-toxic, and abundant C1 resource, can be transformed into high value-added chemicals by constructing C–C, C–O, C–N, and C–S bonds, which is in agreement with the requirements of green chemistry and sustainable development. For example, CO₂ can not only be transformed into fuel-related formic acid, methanol etc., but also serves as raw materials for the synthesis of fine chemicals such as carbonates, carbamates and salicylic acid. However, CO₂ has the disadvantage of thermodynamic stability and chemical inertness, which can hinder its chemical conversion and utilization. It has become one of the research hotspots to develop efficient catalysts of activating CO₂ and reducing the reaction energy barrier in the field of CO₂ conversion. Under the continuing efforts of chemists, a series of highly efficient catalysts have been developed and applied in the catalytic conversion of CO₂. The carboxylative cyclization of propargyl alcohol to prepare α -alkylidene cyclic carbonates is one of desired chemical reaction in CO₂ fixation, which presents 100% atomic utilization and meets the requirements of green chemistry.

Now, investigations on the carboxylative cyclization of propargyl alcohol and CO₂ have been developing rapidly, and a series of novel reaction systems have been reported. In the carboxylative cyclization, transition metals are extensively studied. Various transition-metal catalytic systems, including silver (Ag^I), copper (Cu^I), zinc (Zn^{II}), are closely investigated in the carboxylative cyclization. The transition-metal salts can effectively activate the carbon-carbon triple bond in the propargyl alcohol structure, facilitating the subsequent attack of carbon-carbon triple bonds by alkyl carbonate anions to generate the target products. Although the transition metals are efficient catalysts in this cyclization reaction, their disadvantages, such as high cost and transition-metal residues, are not favourable.

Recently, transition metal-free organocatalysts have been becoming one hotspot in the catalysis field, and found wide applications in the field of CO₂ conversion, burgeoning in the literature. A series of organocatalysts, such as ionic liquids (ILs), organic strong bases, phosphines and CO₂ adducts, have been reported in this carboxylation cyclization reaction. Herein, an overview about the research progresses of organocatalyst-catalyzed carboxylative cyclization is provided, with a particular emphasis on the application of ionic liquids, CO₂ adducts and phosphines, and their corresponding mechanisms. Rationally designed CO₂-reactive site-containing ILs could activate CO₂ effectively, in which the anion is the main contributor, while the cations make a lower contribution. By introducing one or more CO₂-reactive sites into the anion structure of ILs, linear CO₂ molecules can transformed into active carbonate anions and carbamate anions, thereby achieving the effect of activating CO₂. In virtue of CO₂-reactive sites, ILs-catalyzed carboxylation cyclization is realized under mild conditions. Strong nucleophiles are found to easily react with CO₂ molecule to generate CO₂ adducts, such as *N*-heterocyclic carbenes-CO₂ adducts (NHC-CO₂), *N*-heterocyclic olefins-CO₂ adducts, alkylated *N*-heterocyclic olefins CO₂-adducts (ANHO-CO₂), carbodicarbenes-CO₂ adducts (CDCs-CO₂), alkoxide-functionalized imidazolium betaines CO₂-adducts(AFIB-CO₂) and so on, which can serve as efficient organocatalysts in the carboxylative cyclization reaction. Phosphines also present strong nucleophilicity, can activate CO₂ and propargyl alcohol molecules by nucleophilic addition to CO₂ and carbon-carbon triple bonds of propargyl alcohols. Furthermore, chiral phosphines can act as chiral organocatalysts to afford optically active functionalized cyclic carbonates. Taken together, these rationally designed organocatalysts exhibited excellent performance, obtaining a series of α -alkylidene cyclic carbonates in good yields.

In this paper, the mechanisms of the carboxylative cyclization promoted by organocatalysts are closely discussed, hoping to pave a way for the design of more efficient and green organocatalysts.

carbon dioxide, organocatalyst, propargyl alcohol, carboxylative cyclizationdoi: [10.1360/TB-2020-0399](https://doi.org/10.1360/TB-2020-0399)