

CO₂ 参与构筑 C-N, C-C 键合成化学品

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摘要 CO₂作为一种储量丰富、廉价易得、环境友好的可再生C₁资源, 将其转化为高附加值的化学品和能源产品已成为一个具有吸引力的研究领域. 本文综述了近年来以CO₂为C₁组分参与构筑C-N, C-C键, 合成高附加值化学品方面的研究进展, 重点介绍了CO₂参与合成噁唑啉酮、喹唑啉二酮、脲、异氰酸酯、咪唑啉酮、苯并咪唑、芳香酸和芳香醛等化合物的相关反应以及催化反应机理研究, 并对该领域的研究前景进行了展望.

关键词

二氧化碳
噁唑啉二酮
苯并咪唑
咪唑啉酮
芳香酸
芳香醛

自人类社会步入工业化时代, 大气中的CO₂浓度急剧增加, 导致全球温度升高和气候恶化等问题. 因此, 节能减排、CO₂的捕集利用引起了世界各国政府的广泛重视, 化学转化是其资源化利用的有效途径. 从分子结构看, CO₂是直线型分子, C原子上的2个未参加杂化的p轨道与sp杂化轨道成直角, 分别与2个氧原子的p轨道肩并肩地发生重叠, 生成2个3中心4电子的离域 π 键^[1]. 由于碳原子与氧原子的电负性差异, CO₂分子中含有2个极性C=O双键, 其电子结构式可表示为O^{- δ} -C^{+2 δ} -O^{- δ} , 亲核试剂易进攻碳原子, 而亲电试剂易进攻氧原子. 原则上CO₂作为储量丰富、廉价易得、无毒、可再生的C₁资源可用于有机合成中. 但由于CO₂的热力学稳定性和动力学惰性, 实现其化学转化通常采用以下4种策略^[2]: (1) 使用高能原料, 如环氧化合物、氢气、炔烃、烯烃和胺类等物质; (2) 将CO₂转化生成低能量产物, 如碳酸盐、氨基甲酸盐、芳香酸和酯等物质; (3) 通过移除反应中的其他产物以移动反应平衡, 促进目标产物的生成; (4) 提供额外的能源如光能或电能. 在CO₂化学转化中催化剂起到关键作用, 迄今已经发展了多种催化体系, 包括过渡金属类催化剂^[3-5]、胺类催化剂^[6]、氮杂环卡宾类

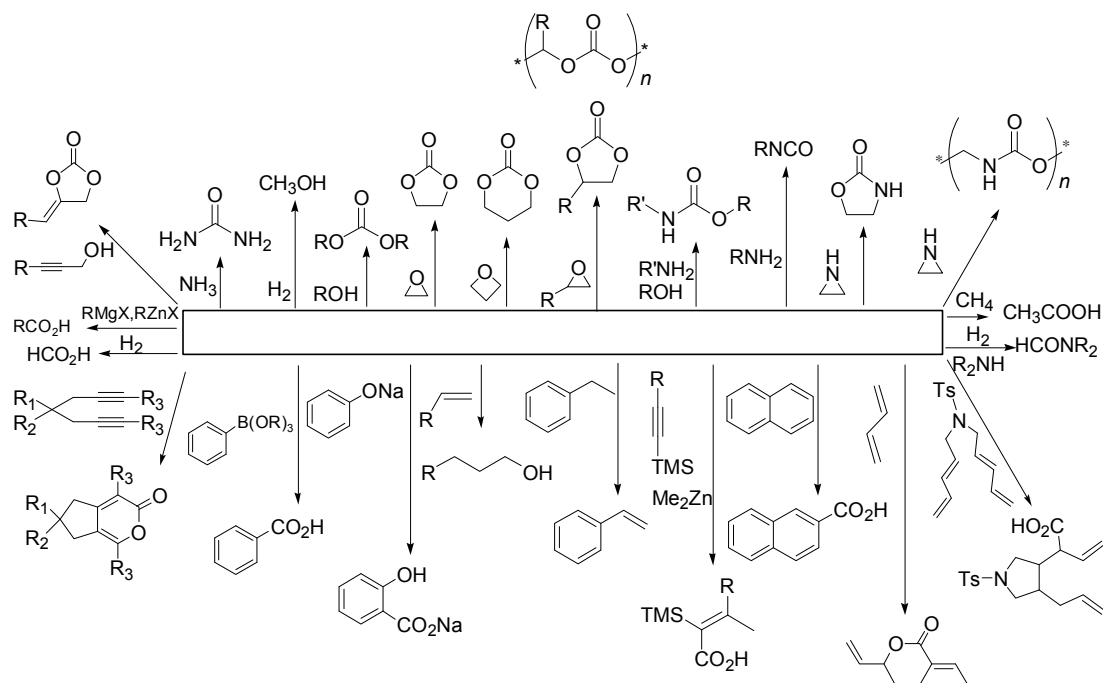
催化剂^[7]和“受阻的路易斯酸碱对”类催化剂(frustrated lewis pairs, FLPs)^[8]等. 相应地发展了多种CO₂参与合成高附加值化学品的新途径^[9], 获得不同种类的化学品(图1). 例如, 合成环状碳酸酯、碳酸二甲酯、尿素、甲醇、甲酸及其衍生物、聚碳酸酯、聚脲和氨基甲酸甲酯等. 尽管在CO₂化学转化方面已开展了大量研究工作, 但它在温和条件下的转化仍存在着诸多挑战. 本文将概括介绍以CO₂为C₁组分参与构筑C-N和C-C键, 合成高附加值化学品方面的研究进展, 重点介绍CO₂参与合成噁唑啉酮、喹唑啉二酮、脲、咪唑啉酮、苯并咪唑、芳香酸和芳香醛等化合物的相关反应以及催化反应机理, 并对该领域的研究前景进行展望.

1 CO₂参与C-N键形成的反应

生成C-N键的反应是有机合成中的一个重要领域, 通过C-N键的生成可制备众多具有生物活性和药物活性的重要化合物和中间体. 近年来CO₂参与有机反应形成C-N键为合成具有高附加值化学品提供了新思路和新方法. 下面将从合成产物的种类出发, 介绍近年来以CO₂为原料通过构筑C-N键制备噁唑啉

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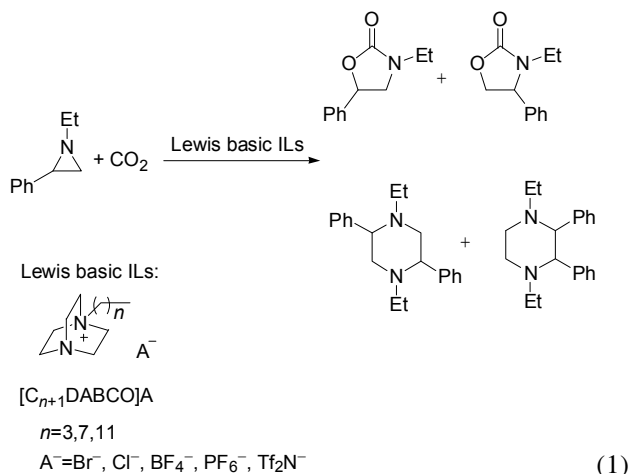
图1 CO_2 转化为高附加值化学品Figure 1 Chemical conversion of CO_2 into high value-added chemicals

酮、喹啉二酮、脲、异氰酸酯、咪唑啉酮、苯并咪唑类化合物等的反应途径及其反应机理。

1.1 噁唑啉酮类化合物的合成

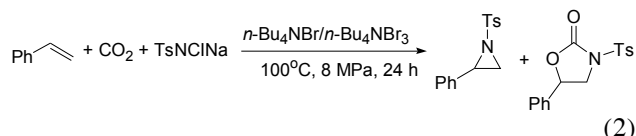
噁唑啉酮类化合物是一类重要的杂环化合物，被广泛用作有机合成中间体和手性助剂。氮杂环丙烷是一类氮取代的环丙烷，可作为高能活性物质与惰性的 CO_2 反应，通过构筑C-N键合成噁唑啉酮类化合物。目前，已经报道了多种有效催化 CO_2 与氮杂环丙烷环加成反应的催化体系。例如，SalenCr(III)/*N,N*-二甲基4-氨基吡啶(DMAP)^[10]或者酚/DMAP^[11]双组分催化体系、碱金属卤代物和四烷基卤化铵盐体系^[12,13]、氨基酸^[14,15]、离子液体^[16,17]、氯化氧锆^[18]和非均相类催化体系^[19]等。值得注意的是，当体系处于 CO_2 超临界状态下，单质碘对该反应有很高的催化活性^[20]。另外，在电化学条件下， CO_2 与氮杂环丙烷的环加成反应也能顺利进行^[21]。针对该类环加成反应，何良年课题组^[16]设计了一系列1,4-二氮杂二环[2.2.2]辛烷(DABCO)型离子液体催化体系，高效催化了无溶剂、无添加剂条件下氮杂环丙烷与 CO_2 的环加成反应，得到5-芳基-2-噁唑啉酮(式(1))。研究发现，卤素阴离子(Cl^- , Br^-)具有很好的催化活性，而

Tf_2N^- , PF_6^- 和 BF_4^- 等其他阴离子则没有活性。这类路易斯碱催化剂容易制备，连续循环使用后反应活性和产物选择性均没有明显降低。

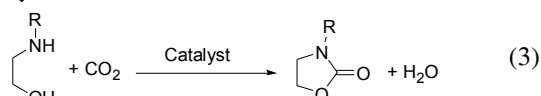


氮杂环丙烷通常是由烯烃与含氮化合物反应得到，因此直接使用烯烃、含氮化合物和 CO_2 3组分反应是合成噁唑啉酮的一条理想反应路径。何良年课题组^[22]使用 $n\text{-Bu}_4\text{NBr}_3/n\text{-Bu}_4\text{NBr}$ 双组分催化体系，实现了由烯烃、氯胺-T和 CO_2 3组分一锅法、高选择性合成噁唑啉酮的新途径(式(2))。研究表明，该反应途径经历了烯烃与氯胺-T反应生成氮杂环丙烷，以

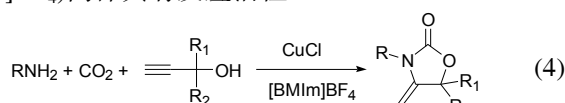
及氮杂环丙烷进一步与CO₂反应生成目标产物. 这种新的合成路线使用便宜的原料和简单的催化体系, 简化了噁唑啉酮的合成过程.



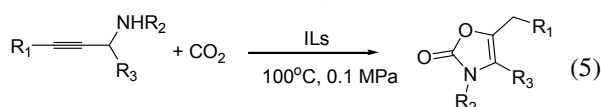
随着对噁唑啉酮类化合物合成途径研究的深入, 人们发现邻氨基醇与CO₂反应也能得到噁唑啉酮产物(式(3)). 但是由于副产物水的生成, 反应速率大大降低. 因此, 反应体系的脱水成为提高该反应速率的关键. 目前, 已经报道的催化体系有Ph₃SbO/3A分子筛^[23]、Ph₃P/PySH^[24]、R₃P/DBAB^[25]、*n*-Bu₂SnO^[26]和CeO₂^[27]等.



炔丙醇、脂肪伯胺和CO₂ 3组分反应同样可以得到5-亚甲基噁唑啉酮产物(式(4)). 使用正三丁基磷可以催化该类反应, 形成反应中间体环状碳酸酯. 然而, 使用这种催化体系时, 反应条件苛刻、产率低、反应时间长, 并且大量使用有毒叔磷化合物. 针对这些问题, 邓友全课题组^[28]采用CuCl/[BmIm][BF₄]催化体系成功催化了炔丙醇、伯胺与CO₂的3组分一锅法反应, 合成带有环外双键的5-亚甲基噁唑啉酮产物. 离子液体既作为反应介质, 也作为促进剂, 避免了有毒磷化合物的使用. 其他离子液体, 如([BmIm]PF₆)和([BPy]BF₄)同样具有反应活性.

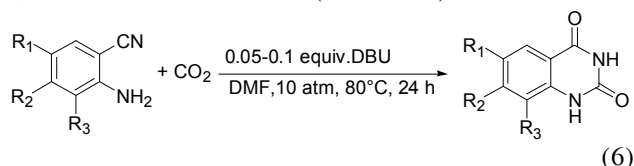


为发展无金属催化的合成路线, 韩布兴课题组^[29]采用[Bmim][OAc]/[Bmim][Tf₂N]双离子液体催化体系, 实现了丙炔胺化合物与CO₂反应合成噁唑啉酮类化合物的新途径(式(5)). 该过程可在常压下进行, 离子液体既作为高效、稳定的催化剂, 也作为反应溶剂. 实验结果与理论计算表明反应历经2步, 先是通过环加成反应得到反应中间体, 然后反应中间体异构化得到最终产物. 机理研究表明, 阴离子[OAc]⁻改变了氢的转移, 促进了CO₂的亲电进攻、分子内环化和双键的异构化等步骤的进行.

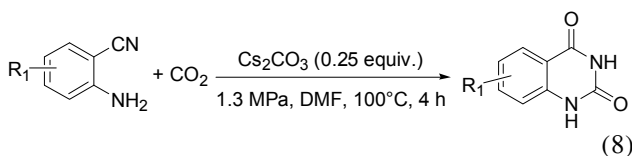
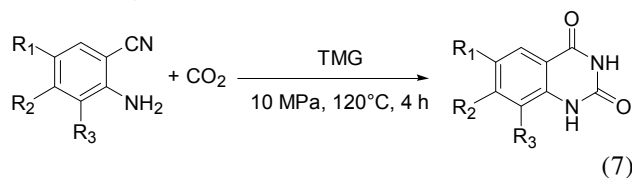


1.2 噁唑啉-(1*H*,3*H*)-2,4-二酮类化合物的合成

噁唑啉-(1*H*,3*H*)-2,4-二酮类化合物具有很高的生物活性和药物活性, 被广泛用于抗肿瘤、抗高血压的药物方面^[30]. 传统的合成方法主要包括邻氨基苯甲酰胺与光气反应^[31]、邻氨基苯甲酸与脲^[32]、异腈酸钾^[33]或氯磺酸异氰酸酯反应^[34]等. 另外, 文献[35,36]还报道了微波辅助的噁唑啉-(1*H*,3*H*)-2,4-二酮的合成方法. 然而, 由于高毒性试剂的使用或反应条件的苛刻, 限制了上述反应的广泛应用. 近年来, 研究人员发展了CO₂与2-氨基苯腈直接反应合成噁唑啉-(1*H*,3*H*)-2,4-二酮类化合物的绿色新途径. Miyata课题组^[37]采用化学计量的有机碱1,8-二氮杂二环十一碳-7-烯(DBU), 在*N,N*-二甲基甲酰胺(DMF)中使CO₂与2-氨基苯腈直接反应. 该反应可在常温常压下进行, 噁唑啉-(1*H*,3*H*)-2,4-二酮收率可达90%. Isino课题组^[38]将反应温度增至80℃, CO₂压力增至10 atm (1 atm = 101325 Pa), 使用催化量的DBU, 即可高产率地得到噁唑啉二酮产物(82%~99%).



何良年课题组^[39]报道了胍催化的CO₂与2-氨基苯腈在无溶剂条件下的反应, 考察了一系列含有给电子基团和吸电子基团的底物的反应情况, 均得到较高的噁唑啉-(1*H*,3*H*)-2,4-二酮产率(60%~95%, 式(7)). Bhanage课题组^[40]报道了无机碱碳酸铯催化的该反应, 也得到了相应的噁唑啉-(1*H*,3*H*)-2,4-二酮(产率51%~94%, 式(8)). 该过程具有操作简单、步骤少、废液少、固体催化剂Cs₂CO₃容易处理和底物适用范围广等优点.



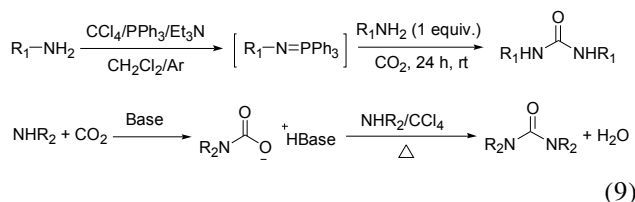
本课题组^[41]通过有机强碱(DBU)和弱质子给体三氟乙醇(TFE)的中和反应, 合成了一种新型质子型

离子液体([HDBU⁺][TFE⁻])。该离子液体可在常温常压下催化邻氨基苯腈及其衍生物与CO₂的反应,无论是给电子基还是吸电子基的邻氨基苯腈底物分子均能高产率地得到相应的喹唑啉-(1*H*,3*H*)-2,4-二酮。通过对比实验和核磁研究,提出了可能的离子液体催化机理(图2):其阴离子活化CO₂分子,其阳离子通过氢键作用活化邻氨基苯腈底物分子,形成的中间体进一步反应生成最终产物。

1.3 脲类化合物的合成

脲及其衍生物是一类重要的羰基化合物,作为中间体广泛应用于药物合成、农业化学品和染料合成、燃气运输中的抗氧化剂和塑料添加剂^[42]等。传统的合成方法涉及光气和异氰酸酯^[43]等剧毒化学品的使用,因此利用CO₂替代光气和异氰酸酯等合成脲类化合物无疑是最具前途的绿色反应途径。由于CO₂参与的合成脲类化合物的反应多数涉及水的生成,因此已报道的催化体系主要包括2种:含脱水剂的催化体系^[44,45]和不含脱水剂的催化体系^[46~48]。主要包括RuCl₃·3H₂O/炔醇体系、三苯基氧化锑(Ph₃SbO)/3A分子筛体系、三苯基氧化锑(Ph₃SbO)/P₄S₁₀体系等。Dinsmore课题组^[49]报道了DBU与Mitsunobu试剂催化胺与CO₂反应,得到不对称脲衍生物。该反应过程中,DBU先催化胺与CO₂反应得到氨基甲酸中间体,然后与Mitsunobu试剂(DBAD, PBu₃)脱水得到异氰酸酯中间体,最后再与胺分子反应得到不对称的脲衍生物。Marsura课题组^[50]进一步简化了对称脲衍生物的合成方法。他们采用PPh₃/CCl₄试剂,以伯胺代替叠氮化合物,在碱催化下先生成磷酰亚胺,然后与CO₂反应,

原位脱除氯化氢得到对称的脲衍生物(式(9))。该方法被认为是一条有价值的环境友好合成路线。



韩布兴课题组^[46]使用碱性离子液体[BMIIm]OH作为催化剂,在无溶剂条件下由胺和CO₂直接合成双取代的对称脲,该反应中没有使用脱水剂。他们提出了可能的反应机理(图3):首先CO₂与胺反应得到氨基甲酸盐,然后与[BMIIm]OH发生离子交换,氨基甲酸阴离子被[BMIIm]⁺活化,胺阳离子在羟基存在下脱水得到脲,最后重新生成离子液体[BMIIm]OH和产物脲,完成催化循环。

1.4 异氰酸酯的合成

异氰酸酯是一类含有-N=C=O基团的重要化合物,广泛用作合成高附加值化学品的反应中间体,如脲、聚氨酯和异氰化物^[51,52]等。传统的合成方法使用一氧化碳或光气为C₁组分。Melillo课题组^[53]报道了碱催化CO₂、伯胺或仲胺、三氯氧磷或亚硫酸氯三组分反应合成了异氰酸酯的新方法(式(10))。机理研究表明,在碱的存在下,CO₂与伯胺或仲胺反应生成氨基甲酸盐,然后与三氯氧磷或亚硫酸氯反应得到中等产率的异氰酸酯(45%~75%)。

Mitsunobu试剂同样适用于催化伯胺与二氧化碳反应得到烷基和芳基异氰酸酯化合物^[54](式(11))。在

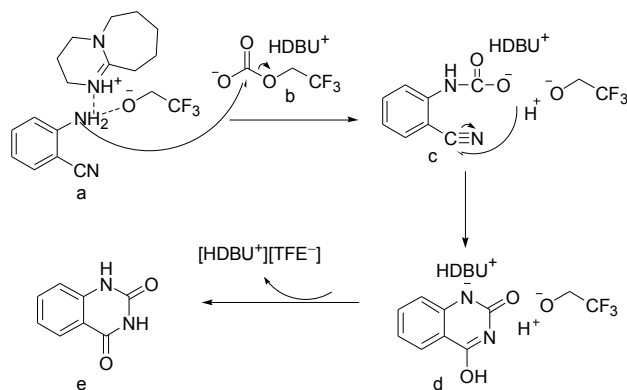


图2 离子液体[HDBU⁺][TFE⁻]的催化机理

Figure 2 Catalytic mechanism of ionic liquid [HDBU⁺][TFE⁻]

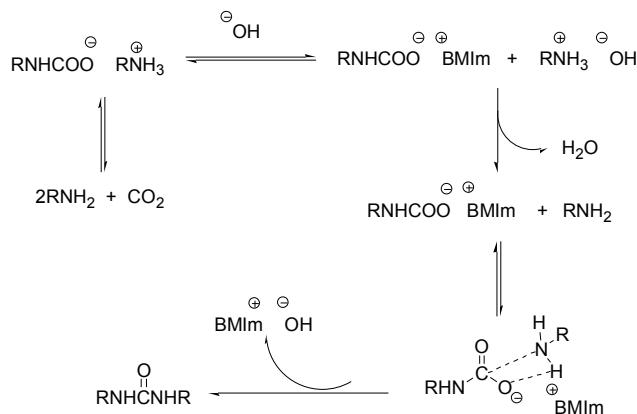
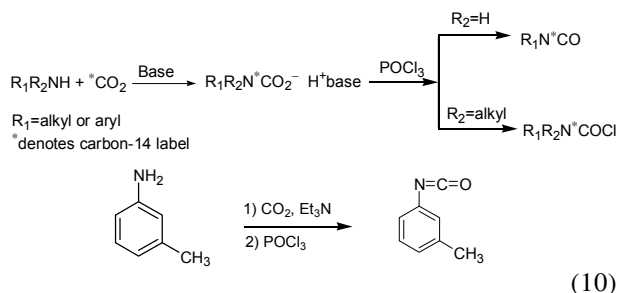
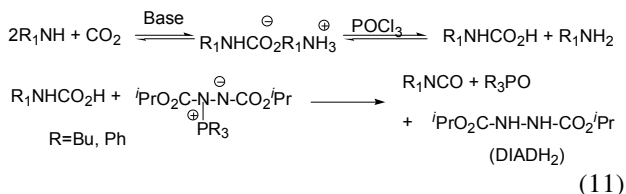


图3 碱性离子液体[BMIIm]OH的催化机理

Figure 3 Catalytic mechanism of basic ionic liquid [BMIIm]OH



二氯甲烷溶液中, 伯胺与 CO_2 反应生成氨基甲酸盐; 然后偶氮二羧酸二异丙酯加入 $n\text{-Bu}_3\text{P}$ 或 Ph_3P 的二氯甲烷溶液中得到Mitsunobu两性离子, 最后与氨基甲酸反应得到异氰酸酯。



1.5 咪唑啉酮类化合物的合成

1,3-二甲基咪唑啉酮(DMI)是一类稳定的极性溶剂, 对无机物和有机物均有较高的溶解能力^[55]. Seki和Ikariya^[56]用商用MCM-41或HMS型介孔二氧化硅有效催化了超临界 CO_2 与 N,N' -二甲基乙二胺(DMEDA)的反应, 获得1,3-二甲基咪唑啉酮, 并提出了反应机理(图4): DMEDA与 CO_2 反应得到环状氨基甲酸盐, 然后经过分子内脱水得到DMI。

苯并咪唑啉酮是一类含有N, O原子的杂环化合物, 主要用作苯并咪唑啉酮类有机颜料合成的中间体。本课题组^[57]以 CO_2 作为羰基化试剂, 通过设计合成双功能离子液体催化剂[HDBU][OAc], 发展了 CO_2 与邻苯二胺反应直接合成苯并咪唑啉酮及其衍生物的新路线, 提出了离子液体的催化机制(图5): 其阳离子活化 CO_2 , 阴离子通过分子间氢键作用活化邻苯二胺, 最终导致产物的生成。在 120°C , 9 MPa条件下, 考察了一系列含有给电子基团和吸电子基团的邻苯二胺底物与 CO_2 的反应, 均获得相应的目的产物, 其

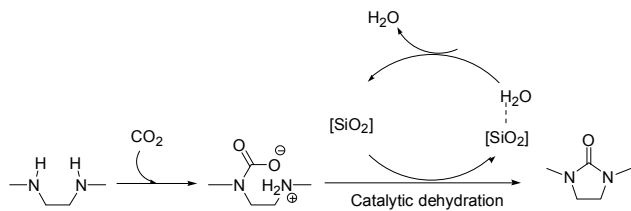


图4 DMEDA与超临界 CO_2 反应合成DMI

Figure 4 Synthesis of DMI from DMEDA react with supercritical CO_2

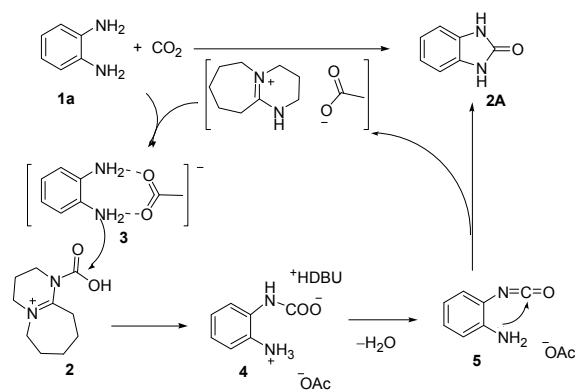


图5 [HDBU][OAc]催化邻苯二胺与 CO_2 反应生成苯并咪唑啉酮

Figure 5 Synthesis of benzimidazolone from *o*-phenylenediamine and CO_2 catalyzed by [HDBU][OAc]

收率为73%~95%。此外, 离子液体循环使用5次, 其催化活性没有降低。该反应在无溶剂、无金属参与条件下进行, 副产水, 是一条绿色反应路线。

1.6 苯并咪唑类化合物的合成

苯并咪唑及其衍生物是一类重要的药物中间体, 具有良好的生物活性, 广泛应用于药物合成。传统方法是通过邻苯二胺与羧酸及其衍生物的缩合反应来制备苯并咪唑类化合物, 但是往往反应条件比较苛刻, 需要高温、强酸和很长的反应时间等。本课题组^[58]采用 $\text{RuCl}_2(\text{dppe})_2$ ($\text{dppe}=1,2\text{-二(二苯膦基)乙烷}$)为催化剂, 发展了基于 CO_2 、邻苯二胺和氢气反应合成苯并咪唑的新途径。考察了一系列含有给电子基团和吸电子基团的邻苯二胺底物与 CO_2/H_2 的反应, 均获得很好的产物选择性和产率。通过核磁研究, 提出了可能的反应机理(图6): 邻苯二胺本身作为有机碱促进了 CO_2 加氢产物的生成, 该产物进一步与邻苯二胺发生分子内缩合脱水, 最终得到产物苯并咪唑。

同时, 为了发展更加简单、绿色的合成过程, 本课题组^[59]采用 Au/TiO_2 为催化剂, 以2-硝基苯胺为反应原料, 直接与 CO_2 , H_2 反应, 获得一系列苯并咪唑

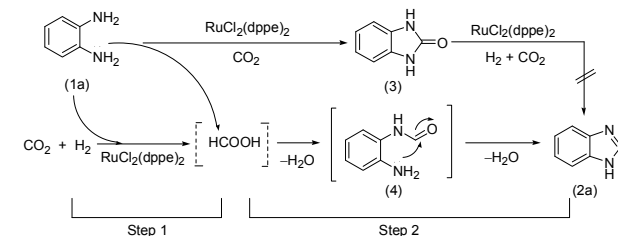
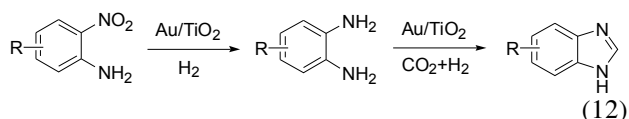


图6 $\text{RuCl}_2(\text{dppe})_2$ 催化邻苯二胺与 CO_2 反应生成苯并咪唑

Figure 6 Synthesis of benzimidazole from *o*-phenylenediamine and CO_2 catalyzed by $\text{RuCl}_2(\text{dppe})_2$

类化合物. 反应途径历经2步, 首先2-硝基苯胺在Au/TiO₂催化下被还原为邻苯二胺中间体, 然后进一步与CO₂, H₂反应得到最终环化产物.

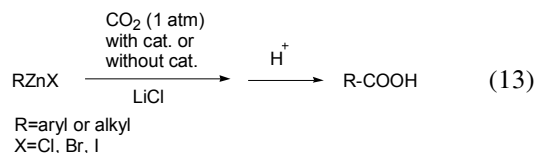


2 CO₂参与C-C键形成的反应

在经典的CO₂参与的C-C键生成反应中, 仅有机锂试剂和格式试剂等高活性反应物能与CO₂反应^[60]. 如何将更多的碳亲核试剂引入活化CO₂生成C-C键, 一直是个挑战性的研究课题. 近年来, 以CO₂为羧基化试剂的羧化反应得到了广泛研究, 研究者通过构筑不同的催化体系, 采取多种反应策略, 不仅合成路线更加简单高效, 实现了温和条件下的CO₂羧化反应, 而且获得了众多有用、特殊的羧酸衍生物. 下面对近年来关于CO₂参与C-C键生成的反应研究进展进行简单介绍.

2.1 有机锌试剂与CO₂的羧化反应

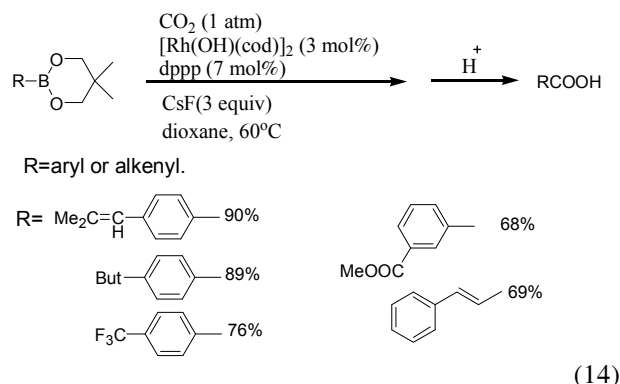
为了替代格氏试剂和有机锂试剂, 亲核性较弱的有机锌化合物被用来与CO₂反应. Ochiai等人^[61]以Ni(acac)₂-PCy₃(acac=乙酰丙酮)和氯化锂为催化剂, 采用碘代烷基锌为反应底物, 在四氢呋喃中与CO₂反应, 生成了相应的羧酸产物. 他们研究发现, 在反应体系中氯化锂的加入是必需的, 而镍催化剂的加入则大大提高了产物收率. 当体系中没有镍催化剂时, 反应仅得到36%的苯甲酸. Yeung和Dong^[62]报道了镍和钯催化剂催化的溴代烷基锌化合物与CO₂的耦合反应, 该反应条件温和, 底物官能团适用范围广. 而Kobayashi和Kondo^[63]则在不使用任何过渡金属催化剂情况下, 仅在DMF溶剂中通过增大氯化锂的使用量, 实现了这类反应, 并且反应底物广泛适用于卤代的烷基或芳香基有机锌试剂(式(13)).



2.2 有机硼酸酯类化合物与CO₂的羧化反应

有机硼酸酯是一类很容易通过多种方法制得的化合物, 大量用于有机反应的反应底物. Iwasawa课

题组^[64]报道了芳基硼酸酯和烯基硼酸酯与CO₂的反应. 他们构筑了相对复杂的催化体系, 包括[Rh(OH)(cod)]₂(3 mol%, cod=1,5-环辛二烯)、Ph₂P(CH₂)₃PPh₂(dppp, 7 mol%)和CsF(3 equiv.), 使得反应在相对温和条件下(60℃, 1 atm)进行, 高产率得到相应的羧酸产物(68%~90%).



为了实现该羧化反应在更加温和的条件下进行, Hou课题组^[65]采用卡宾铜作为催化剂, 并且将底物范围扩大至醛类、烯烃类、卤代烃类、环氧乙烷类、含硝基类和炔烃类化合物等. 值得一提的是, 他们获得了铜催化活性物种的单晶, 并通过单晶结构分析, 结合DFT模拟计算, 提出了可能的反应机理: CO₂插入Cu-Ar键是关键, 芳基亲核进攻CO₂生成新的C-C键(图7).

2.3 烯烃、二烯烃类化合物与CO₂的羧化反应

Takimoto和Mori^[66]开发了1,3-二烯和丙二烯与CO₂的羧化反应. 他们发现1,3-二烯先与Ni(cod)₂、

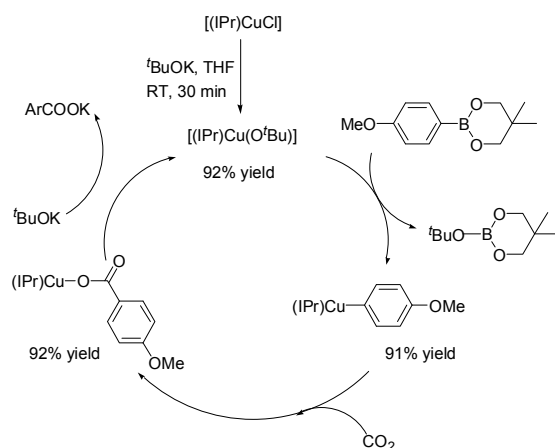
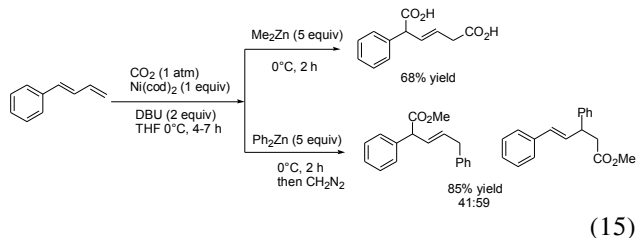
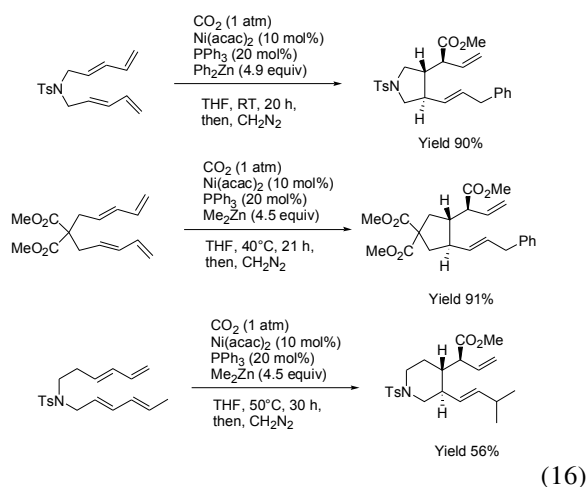


图7 [(IPr)CuCl]催化有机硼酸酯与CO₂的羧化反应机理
Figure 7 Reaction mechanism of carboxylation of organic borate esters with CO₂ catalyzed by [(IPr)CuCl]

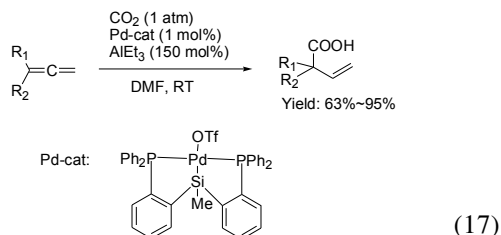
DBU在CO₂气氛下反应,然后再与二甲基锌反应,最终得到1,4-二羧基产物(式(15)).当使用芳基锌代替甲基锌时,反应可得到单羧酸产物.这类反应过程简单、时间短、条件温和.



此外,为了解决1,3-二烯与CO₂的共聚反应选择性差的问题,Takimoto和Mori^[67]使用双-1,3-二烯为底物,通过控制分子内发生共聚反应,成功得到立体选择性和区域选择性都很高的闭环产物(式(16)).反应过程历经CO₂插入双- Π -烯丙基镍中间体,然后生成的环镍羧酸化合物与有机锌试剂发生金属交换,最终得到目标产物.该反应具有反应条件温和、产率高、区域选择性和立体选择性高等优点.

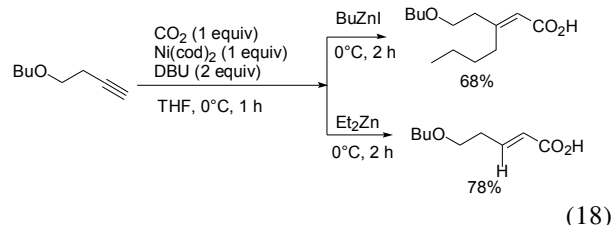


Takaya和Iwasawa^[68]报道了甲硅烷基螯合型钯催化剂催化丙二烯类化合物与CO₂发生氢羧化反应.反应中AlEt₃被用作还原剂,并且通过钯中间体的 β -氢消除起到氢源的作用(式(17)).该方法不仅是一种固定CO₂的反应,而且是一种高效的、底物适用范围较广的合成 β,γ -不饱和羧酸的方法.

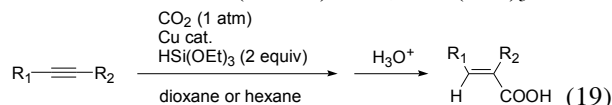


2.4 炔类化合物与CO₂的羧化反应

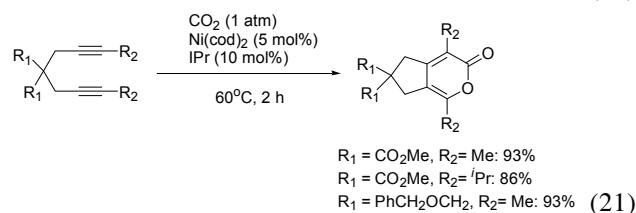
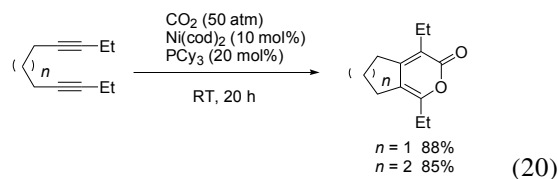
Yamamoto课题组^[69]报道了Ni(cod)₂和DBU催化的端炔与CO₂的反应,高区域选择性和高化学选择性制备了羧酸化合物.Mori课题组^[70]报道了类似的镍催化的反应,研究发现当烷基锌试剂或芳基锌试剂加入Yamamoto反应体系中,炔烃发生烷基化和芳基化的羧化反应.有趣的是,使用BuZn试剂时,得到丁基化产物68%;而使用EtZn试剂时,通过 β 氢消除反应得到加氢羧化产物78%(式(18)).



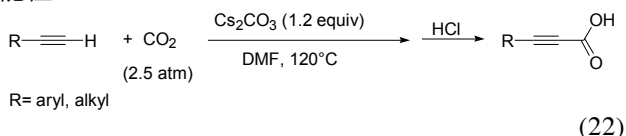
为了发展利用CO₂直接生成C-C键的反应,还原剂的使用必不可少.迄今,高活性和易燃试剂,如二乙基锌^[71-73]和三乙基铝^[74]等,常用于化学计量的和催化量的反应中.Tsuji课题组^[75]采用稳定、易于处理的氢硅烷为还原剂,应用于铜催化的炔羧化反应中.例如,以三乙氧基氢硅烷[HSi(OEt)₃]为还原剂,含有不同官能团的炔烃均能与CO₂发生羧化反应(式(19)).在这类反应中,也可以使用更加便宜的工业副产物聚甲基氢硅氧烷(PMHS)来代替HSi(OEt)₃.



Tsuda等人^[76]发现在镍-膦配体催化剂存在下, α,ω -二炔与CO₂反应得到双环 α -吡喃酮(式(20)).在同样的转化反应中,使用1,3-双(2,6-二异丙基苯基)咪唑-2-烯(IPr)配体代替膦配体时,显示更高的活性,反应可在常压下进行,得到相同的羧化产物,并且其收率得到提高(86%~93%,式(21))^[77].

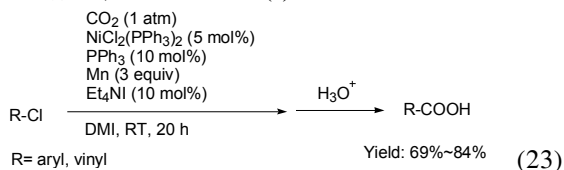


研究发现, CuBr, AgI, AgNO₃都能催化端炔、溴代烷与CO₂的反应, 可用于一锅法制备芳基羧内酯化合物^[78]. 当使用IPrCuCl催化剂时, 反应可在较低温度下进行(60℃)^[79]; 而以CuI/PEt₃为催化剂, 反应甚至可在室温下发生^[80]. 在Cu或Ag催化下, 无需溴代烷, CO₂可直接插入端炔的C-H键, 生成羧化产物. Zhang课题组^[81]仅采用Cs₂CO₃催化剂, 在120~160℃的温度条件下实现了该反应(产率80%~96%, 式(22)), 反应过程更加简单, 为实现工业化应用提供了可能性.



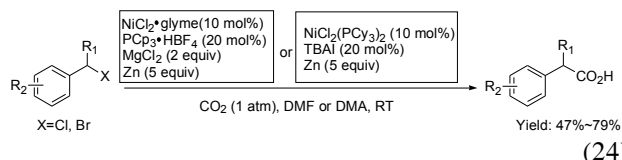
2.5 卤代芳烃化合物与二氧化碳的羧化反应

如前所述, 芳基锌和芳基硼酸酯可用于CO₂的羧化反应, 而这些化合物是由相应的卤代芳烃化合物制备而得. 因此, 人们尝试将卤代芳烃化合物直接应用于与CO₂进行羧化反应. 首例报道的卤代芳烃与CO₂的直接羧化反应, 是通过镍和钯催化的电化学过程实现的^[82]. 然而, 反应效果并不理想, 底物普适性也比较差. 后来, 人们发展了在化学计量的零价镍化合物和2,2'-联吡啶催化下, 氯代或溴代芳烃化合物与CO₂直接羧化反应^[83]. 最近, 又实现了溴代芳烃化合物与CO₂在催化量钯作用下的直接羧化反应^[84]. 但是反应催化剂活性低, 只能催化活化的溴代芳烃化合物, 而非活化的溴代芳烃化合物和活化的氯代芳烃化合物不发生反应. 只有在高活性的二乙基锌为还原剂, 40℃和10 atm压力条件下, 反应才能得到较高的收率. Tsuji课题组^[85]构建了由NiCl₂(PPh₃)₂, PPh₃, Mn粉和Et₄Ni组成的催化反应体系, 使得氯代芳烃化合物和氯代乙烯基化合物与CO₂的羧化反应在常温常压下得以进行(产率68%~84%, 式(23)), 并且底物适用范围广, 多种类型芳烃氯代物均可转化为相应的羧酸化合物. 机理研究表明, 反应中Mn粉起还原剂作用, 并检测到Ni(I)物种.



Martin课题组^[86]也报道了一种新型的、直接的、高效的镍(NiCl₂·glyme(glyme=甘醇二甲醚)), NiCl₂

(PCy₃)₂(PCy₃=三环己基膦))催化伯、仲和叔类苄基卤代物与CO₂的羧化反应, 通过活化sp³碳卤键制备了一系列苯乙酸化合物(式(24)). 该合成方法操作简单、反应条件温和、化学选择性高. 与其他类似的合成方法不同, 该方法不需要特定复杂结构、高活性的有机金属试剂.



在研究卤代芳烃化合物与CO₂的羧化反应制备芳香酸的同时, 为了进一步拓展CO₂在生成C-C键反应中的应用, 本课题组^[87]以CO₂为甲酰化试剂, 通过Pd/C和DBU协同催化, 发展基于碘代芳烃化合物与CO₂、聚甲基氢硅烷(PMHS)直接甲酰化反应, 合成芳香醛化合物的新途径. 通过核磁检测与实验研究提出了可能的反应机理(图8). 零价钯活化碘代芳烃化合物, 形成二价钯化合物, 然后与由CO₂和PMHS反应得到的中间体硅酸甲脂发生亲核加成, 最终生成产物芳香醛. 其中, DBU一方面活化了CO₂, 另一方面中和了反应过程中生成的HI, 拉动反应向正向进行.

2.6 含有酸性C-H键的芳烃化合物与CO₂的羧化反应

由酚盐和CO₂直接制备水杨酸的Kolbe-Schmitt反应是最早活化酸性C-H键羧化的例子. 最近, Boogaerts和Nolan^[88]报道了(IPr)AuOH可以活化缺电子芳烃的酸性C-H键(图9). 他们发现一价金化合物在芳香酸C-H键(pK_a值< 30)与CO₂的羧化反应中活性很高, 并通过化学计量实验确定了反应机理.

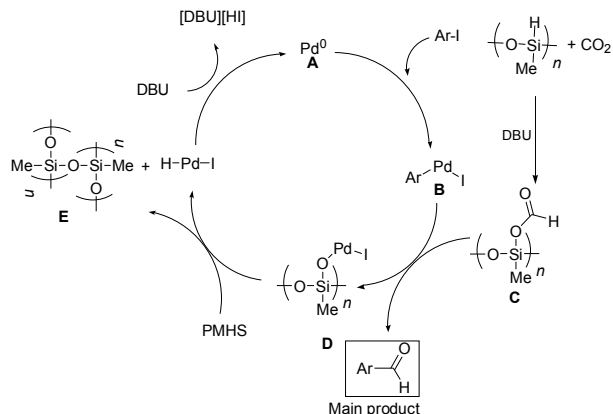


图8 Pd/C与DBU的协同催化机理

Figure 8 Synergistic catalytic mechanism of Pd/C and DBU

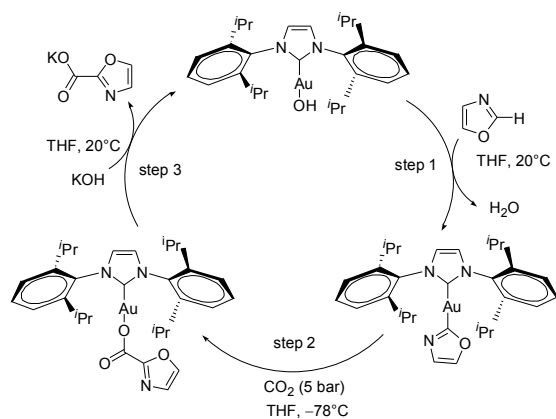
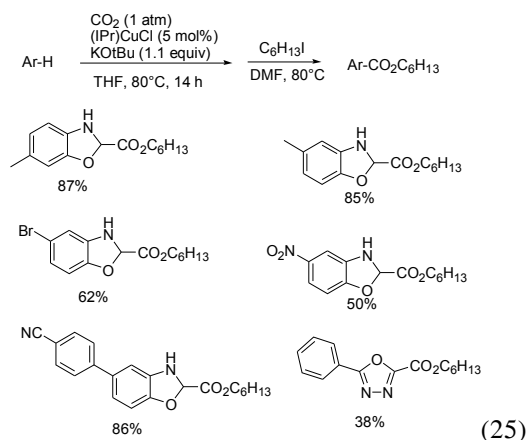


图9 (IPr)AuOH的催化机理

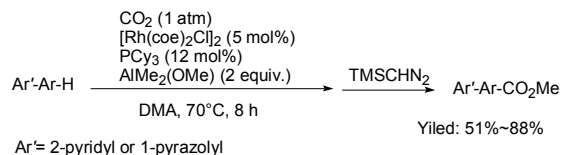
Figure 9 Catalytic mechanism of (IPr)AuOH

Hou课题组^[89]和Nolan课题组^[90]几乎同时报道了铜催化剂高效催化酸性C-H键的直接羧化反应(式(25))。该方法具有独特的优点,如使用CO₂为羧化试剂、简单的杂环化合物为底物(不需要制备前驱体)、更加经济性和环境友好。他们分离得到关键中间体,如苯并恶唑铜化合物和羧酸铜化合物,并且通过X射线单晶衍射确定了其结构,为研究机理提供了重要的证据。



(25)

Iwasawa课题组^[91]发现首例通过螯合作用辅助活化酸性C-H键的羧化反应。在催化剂[Rh(coe)₂Cl]₂ (coe=环辛烯)和助剂AlMe₂(OMe)存在下,一系列2-芳基吡啶和1-芳基吡唑化合物与CO₂反应得到相应的羧化产物(式(26))。催化循环过程包括C-H键活化、还原消除、CO₂亲核加成和转移金属化4个步骤。



(26)

3 结论与展望

综上所述,以CO₂为C₁资源,通过构筑C-N和C-C键,在合成噁唑啉酮类、唑啉二酮类、脲类、异氰酸酯、咪唑啉酮类、苯并咪唑类、芳香酸类和芳香醛类化合物等方面已经取得重要进展。尤其通过构建不同的催化体系,如离子液体催化体系等,使CO₂参与的一些反应在温和条件下得以实现。尽管已经取得了诸多进展,然而温和条件下的CO₂活化及其转化仍然是一个挑战性难题,CO₂化学转化的工业应用仍然任重道远。

今后将着重在以下2方面开展工作:(1) 设计开发高效的催化体系,使已有反应途径的反应条件更加温和化,反应过程更加简单,以便早日实现工业化;(2) 揭示CO₂的活化机理,探索更多原子经济性高的绿色有机反应过程,拓展CO₂的官能化应用,以获得更多具有高附加值的化学品和能源产品。随着研究的不断深入,CO₂化学转化作为CO₂资源化利用的有效手段,不但能获得重要的化学品或能源产品,而且可实现碳的化学循环,成为自然界碳循环的有力补充。

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CO₂-involved synthesis of chemicals by the construction of C–N and C–C bonds

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The emission of CO₂ continues to cause serious environmental problems, and there has therefore been a considerable increase in the number of researcher working towards the development of new technologies for the capture and utilization of CO₂. As a green, abundant, cheap and renewable C₁ resource, CO₂ could participate in a wide range of chemical reactions, and could therefore be converted into various value-added chemicals. The conversion of CO₂ into other value-added chemicals therefore represents an important way to use CO₂, although it contributes very little to reducing the concentration of CO₂ in the Earth's atmosphere. The green features of CO₂-involved chemical processes are of critical importance from the perspective of sustainable development. However, only a few industrial processes have been reported that use CO₂ as a raw material because CO₂ is thermodynamically stable and chemically inert. To achieve chemical transformations with CO₂, a high energy input is generally required, which can be achieved using highly reactive chemicals, specific catalytic systems and high temperature/pressure conditions. Based on these rules, research towards the development of CO₂ chemical conversion processes has made great progress. CO₂ has been successfully used as a green C₁ building block for the production of a variety of different value-added chemicals via the construction of C–H, C–C, C–O and C–N bonds. In particular, CO₂ hydrogenation processes and reactions involving the formation of C–O bonds have been widely investigated. Furthermore, the CO₂-based synthesis of chemicals via the construction of C–N and C–C bonds has recently attracted considerable attention from numerous researchers, and many excellent results have been reported in literature. For example, aziridines, amino alcohols, acetylenic amines, primary amines, secondary amines, 2-aminobenzonitrile, 1,2-diamines and o-phenylenediamines have all been reacted with CO₂ as nitrogen-containing nucleophiles to give the corresponding oxazolidinones, ureas, quinazolines, imidazolidones and benzimidazoles via the formation of C–N bonds. Organozinc compounds, organoboronic esters, dienes, alkenes, alkynes, aryl halides and arenes bearing acidic C–H bonds have also been reacted as nucleophiles with CO₂ to give the corresponding aromatic acids and aromatic aldehydes via the construction of C–C bonds. In most cases, it has been demonstrated that catalysts can play a crucial role in the transformation of CO₂. It is noteworthy that the chemical transformation of CO₂ can be achieved under mild conditions, even at room temperature under atmospheric pressure, through the design of highly efficient catalytic systems. This review will provide a summary of recent advances in the field of CO₂-based C–N and C–C bond formation processes for the production of oxazolidinones, quinazolinones, ureas, isocyanates, imidazolinones, benzimidazoles, aromatic acids and aromatic aldehydes, with particular emphasis on the catalytic systems used to achieve these transformation and possible catalytic reaction mechanisms. This review should therefore provide basic ideas with regard to the use CO₂ as an ideal and attractive C₁ source in organic synthesis to generate value-added chemicals.

carbon dioxide, quinazolinones, benzimidazoles, imidazolinones, aromatic acids, aromatic aldehydes

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