

Photoredox-catalyzed α -C-H alkylation of (poly)-hydroxylated substrates mediated by CO_2

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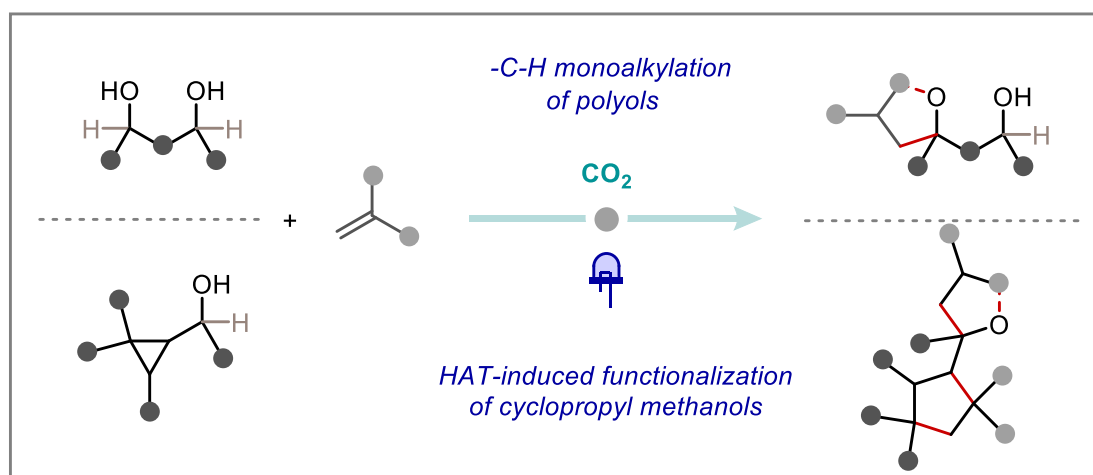
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Carbon dioxide (CO_2) is an overproduced, inexpensive and non-toxic gas which can reversibly bind chemical functions with sufficient Lewis basicity. Consequently, it can be used to modify temporarily the reactivity of the corresponding molecules.^[1] For instance, CO_2 -promoted photoredox processes have been developed to achieve the α -C-H alkylation of aliphatic amines.^[2] Our investigations in this area focus on using CO_2 to transiently modulate the reactivity of hydroxylated molecules in order to develop original photoredox-catalyzed transformations. Recently, we have demonstrated that the catalytic and reversible carbonation of aliphatic polyols under CO_2 atmosphere constitutes a unique strategy to perform the α -C-H monoalkylation of these abundant feedstocks by photocatalytic hydrogen atom transfer (HAT).^[3] Experimental and theoretical mechanistic studies have demonstrated an activation resulting from an intramolecular hydrogen bonding between the carbonate and the remaining alcohol.

In the meantime, we have discovered that CO_2 could be used to slow down keto-enol tautomerism in complex radical cascades.^[4] This observation was applied to the design of an unprecedented cascade triggered by photocatalytic HAT and allowing the conversion of cyclopropyl methanol derivatives into elaborate building blocks in one step.



[1] P. K. Sahoo, Y. Zhang, S. Das, *ACS Catal.* **2021**, *11*, 3414.

[2] a) J. Ye, I. Kalvet, F. Schoenebeck, T. Rovis, *Nat. Chem.* **2018**, *10*, 1037; b) Y. Qin, R. Cauwenbergh, S. Pradhan, R. Maiti, P. Franck, S. Das, *Nat. Commun.* **2023**, *14*, 7604.

[3] G. Archer, R. Meyrelles, I. Eder, N. Kovács, Boris Maryasin, M. Médebielle, J. Merad, *Angew. Chem. Int. Ed.* **2024**, *63*, e202315329.

[4] K. Song, Q. Ordan, M. Médebielle, J. Merad, *manuscript in preparation*.