Organic chemistry: Carbon dioxide tamed

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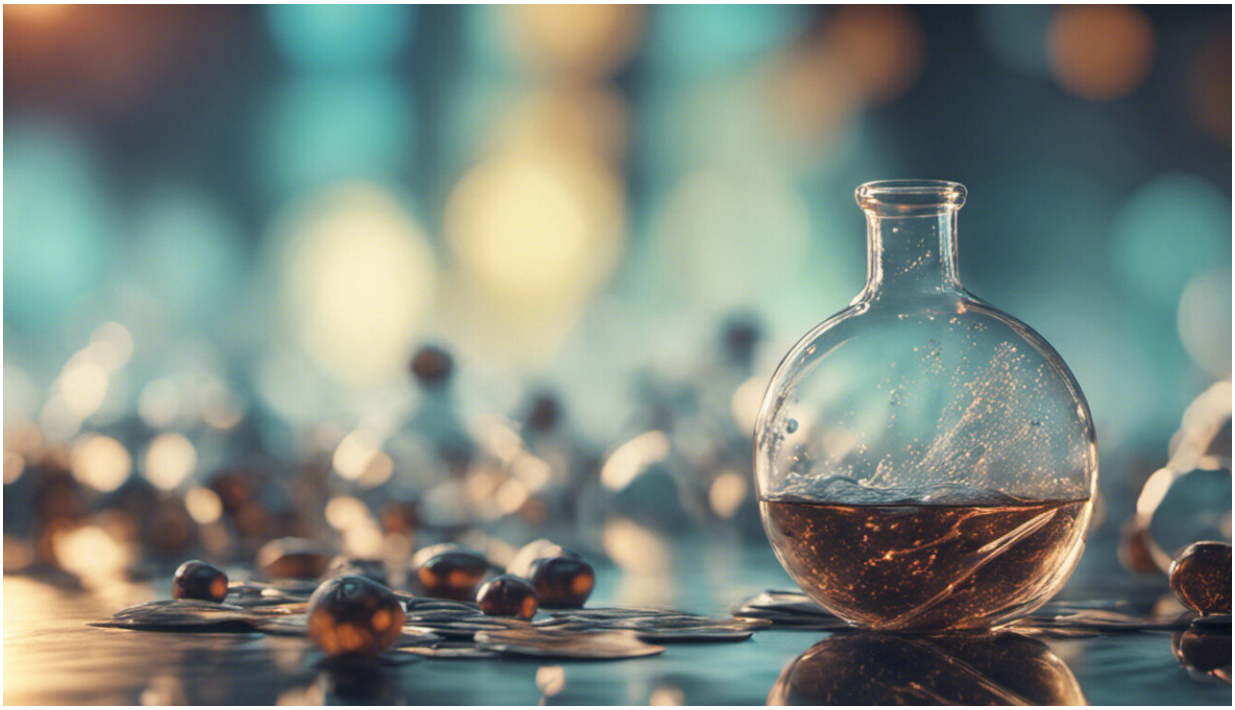

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Carbon dioxide has become notorious as a troublesome greenhouse gas produced by burning fossil fuels. Now, this gas could also offer a cheap, abundant and nontoxic source of carbon for the chemical reactions that synthesize products such as plastics and pharmaceuticals.

Only a few industrial processes currently use carbon dioxide as a reagent because it takes a lot of energy to break its strong chemical bonds. For

example, to synthesize salicylic acid, a precursor of aspirin, carbon dioxide must be squeezed to 100 times atmospheric pressure and the reaction mixture heated to 125 ºC.

Hung Duong of the A*STAR Institute of Chemical and Engineering Sciences in Singapore and co-workers have shown that a copper catalyst can incorporate carbon dioxide into organic molecules under much milder conditions. The commercially available catalyst consists of a copper atom joined to a bulky ligand called 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr).

Some reactions involving carbon dioxide require high-energy starting materials that contain reactive metals such as lithium or magnesium. However, these metals often destroy other sensitive chemical groups in the molecule during the reaction. Milder starting materials that contain tin tend to be highly toxic, "so we looked at the use of more environmentally benign organoborons," says Duong.

The researchers tested a range of molecules that feature a carbon–carbon double bond close to a boron-containing chemical group. They assumed that the copper catalyst works by knocking the boron group off the molecule and briefly taking its place so that it can shepherd carbon dioxide into the right position to bond with the molecule. The products of the reaction contain a carbon–carbon double bond and a carboxylic acid group, arranged in a very predictable pattern. "These are highly versatile building blocks for organic synthesis," explains Duong.

The reaction generally produced good yields of products when run at just 70 ºC and atmospheric pressure, although it was less successful in those cases where particularly large chemical groups were attached to one end of the starting material.

The reaction also needed relatively large amounts of catalyst – roughly

one catalyst molecule for every 10 to 20 molecules of the starting material. "That amount is still too high for industrial use and needs further improvement," says Duong.

His team now aims to expand the range of reactions that their catalyst can assist. "We are currently looking at exploiting the high reactivity of the copper catalyst toward carbon dioxide to prepare other valuable organic compounds under mild conditions," he says.

More information: Duong, H. A., Huleatt, P. B., Tan, Q.-W. & Shuying, E. L. Regioselective copper-catalyzed carboxylation of allylboronates with carbon dioxide. *Organic Letters* 15, 4034–4037, 2013. dx.doi.org/10.1021/ol4019375

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