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Synthesis of β,γ-Unsaturated Acids from Allenes and Carbon Dioxide

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β,γ-unsaturated carboxylic acids · allenes ·
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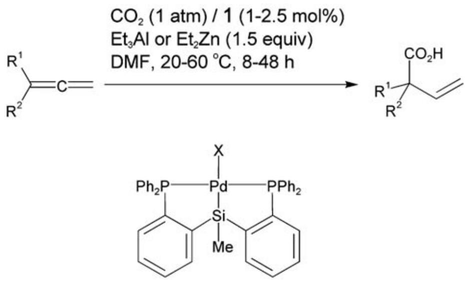
There is increasing interest in the use of carbon dioxide as a starting material for chemical reactions.[1] The main reason for this interest is the widespread acceptance that rising atmospheric levels of carbon dioxide are directly responsible for global warming and the associated climate changes.[2] If waste carbon dioxide produced by major fixed-site producers, such as fossil-fuel power stations, oil refineries, ammonia plants, and cement works, could be converted into feedstocks for the chemicals industry, this would not only reduce carbon dioxide emissions, but would also provide a new revenue stream for these industries. However, the raw material for almost all of the chemicals industry is currently provided by less than 10% of the output of an oil refinery,[3] the remaining output being used as fuel. Thus, even if the chemicals industry could utilize carbon dioxide as its only starting material, the maximum achievable reduction in carbon dioxide emissions would be of the order of 10–20% (taking into account that the chemicals industry currently uses both chemicals and energy produced from fossil fuels). This figure would, however, be considerably higher if carbon dioxide was to be converted into chemicals for use as fuels as well as building blocks for the chemicals industry.[4]

Irrespective of global-warming considerations, it is widely accepted[5] that the world-wide production of oil and gas will peak in the next 10–40 years (coal reserves could last another 200 years[6]), so there is an increasingly pressing need to find new and renewable raw materials for the chemicals industry, and carbon dioxide is an attractive, cheap, and readily available starting material. Unfortunately, carbon dioxide is a rather inert species. It reacts spontaneously only with reactive reagents, such as Grignard and organolithium reagents. However, transition-metal complexes are known[1,7] to catalyze the formation of carboxylic acids from carbon dioxide and less nucleophilic reagents, such as organoboronic esters,[8] organozinc compounds,[9] allyl stannanes,[10] alkynes,[11] conjugated dienes,[12] and allenes.[11,13,14] The most extensively studied catalytic systems involve the use of the Group 10 metals nickel[8b,9b,11,12,14] and palladium.[9b,10,13,15]

If carbon dioxide is to be used as a chemical starting material, then a number of requirements must be met. The transformation should occur at or near both ambient temperature and atmospheric pressure, otherwise the energy required to heat (or cool) and compress the carbon dioxide is liable to generate more carbon dioxide than is consumed by the chemical reaction. The reaction should occur catalytically, and all other components of the reaction should be readily available (preferably from renewable resources). Finally, there should be a real or potential, large-scale demand for the product. These requirements can be met, and carbon dioxide (though not necessarily waste carbon dioxide) is already used in a number of commercial processes,[1] including urea production, the synthesis of salicylic acids (for aspirin production), and the synthesis of cyclic carbonates and polycarbonates.

Takaya and Iwasawa clearly illustrated in a recent report[15] both what can be achieved by the use of carbon dioxide as a building block and what some of the problems are. They studied the reductive addition of carbon dioxide to allenes to give β,γ-unsaturated carboxylic acids (Scheme 1). Similar addition reactions with palladium-[13] and nickel-based[14] catalysts have been reported previously, but these reactions led to α,β-unsaturated carboxylic acid derivatives. The novel feature of the study by Takaya and Iwasawa was the use of a silyl-pincer palladium complex **1** to control the regioselectivity of the reaction and the reactivity of the reaction intermediates. Under the reaction conditions, complex **1** is converted into palladium hydride **2**; the hydride comes from the ethyl metal reagent through transmetalation and β elimination. The subsequent addition of complex **2** to



1: X=OTf
2: X=H

Scheme 1. Conversion of allenes into β,γ-unsaturated acids. DMF = *N*,*N*-dimethylformamide, Tf = trifluoromethanesulfonyl.

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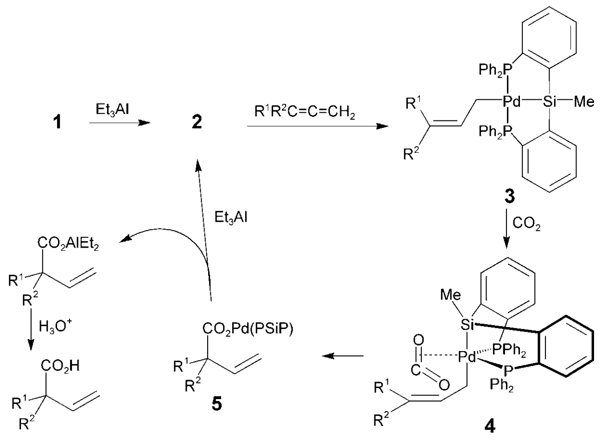

Scheme 2. Proposed catalytic cycle.

the less hindered double bond of the allene generates the σ-allyl complex **3** in which the palladium center is bound to the terminus of the allylic system (Scheme 2). The silyl pincer ligand ensures that complex **3** exists as a σ-allyl rather than a π-allyl complex, and the strained square-planar structure of complex **3**, along with the electron-donating nature of the silicon atom, enhances the nucleophilicity of the palladium center, and enables it to react with carbon dioxide to form complex **4** with a concomitant geometry change to trigonal bipyramidal. Subsequent insertion of carbon dioxide into the σ-allyl complex with allylic transposition generates palladium carboxylate **5**, which can undergo a second transmetalation and β elimination with the ethyl metal reagent to regenerate complex **2** and give the aluminum or zinc salt of the β,γ-unsaturated carboxylic acid. The free acid is liberated on acidic workup. The tridentate nature of the silyl pincer ligand also helps to avoid liberation of palladium(0) and thus prevents side reactions catalyzed by palladium(0) species.

Notable features of this chemistry are the use of carbon dioxide at atmospheric pressure at or near room temperature. Even when elevated temperatures are required, they are in the range ($< 60\,°C$) in which heat is considered unusable by most chemical and power plants. Waste heat streams could therefore be used as the heat source.[16] The transformation is also compatible with a range of functional groups, including ethers, esters, acetals, carbamates, and ketones. As well as 1,1-disubstituted allenes, monosubstituted and 1,3-disubstituted substrates can be employed, although in these cases small amounts ($< 10\,\%$ in total) of the regioisomeric β,γ-unsaturated acid and the α,β-unsaturated acid were obtained. The β,γ-unsaturated acids are useful bifunctional products, which could be transformed readily into a range of other chemicals.

From the point of view of carbon dioxide fixation, this approach does, however, have two major limitations. The first is the need for 1.5 equivalents of triethylaluminum or diethylzinc, which act as a hydride source. The use of an excess of these pyrophoric reagents is highly undesirable, especially on a large scale, and their synthesis requires significant amounts of chemicals and energy. It may be possible to replace these organometallic hydride donors with a secondary alcohol, such as 2-propanol, which acts as a hydride donor in the Meerwein–Ponndorf–Verley reduction.[17] The second limitation is the requirement for the large-scale availability of allenes. These compounds are generally prepared by multistep procedures, which again require large amounts of chemicals and energy.[18]

Overall, this transformation illustrates that it is possible to use carbon dioxide as a starting material for the synthesis of highly functionalized products under mild conditions. It should help to dispel the myth that carbon dioxide is too thermodynamically and kinetically inert to be a useful chemical feedstock.

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