RESNICK INSTITUTE
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RESEARCH HIGHLIGHTS

From the Resnick Sustainability Institute
Graduate Research Fellows at the
California Institute of Technology

Synthesis of Commodity Chemicals from Renewable Fatty Acids

Yiyang Liu

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Global Significance

Alpha olefins represent an important class of industrial chemicals with a wide range of applications. They are used as co-monomers for ethylene polymerization, drilling fluids, and precursors to plasticizers, lubricants and surfactants. As of 2013, global demand for alpha olefins is estimated to be 3.7 million metric tons per year. Currently, these olefins are mainly produced by oligomerization of ethylene, which is derived from petroleum.

With the world's oil reserves continually diminishing, there is a growing interest in producing alpha olefins from renewable feedstocks. Fatty acids are an ideal candidate because of their abundance, low cost, and inherent renewability. Decarboxylation of even-numbered natural fatty acids affords odd-numbered alpha olefins, which are not accessible from the ethylene oligomerization process and thus very expensive.

This project focuses on the development of a carboxylic acid decarboxylation process that produces alpha olefins of high value. By using fatty acids, which come from carbon dioxide via photosynthesis, our process will help keep atmospheric CO_2 in balance.

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Project Summary

We have developed a highly efficient palladium-catalyzed reaction that converts readily available carboxylic acids into alpha olefins in good yield and with high selectivity. Through extensive optimization of reaction parameters, we have identified a set of conditions that allow the reaction to proceed smoothly at moderately high temperature with low catalyst loading and no solvent. The reaction displays broad compatibility with a wide range of carboxylic acid substrates bearing various functional groups. We have also demonstrated the utility of our alpha olefin products by transforming one of them into insect pheromones, compounds that can be used as environmentally benign pesticides.

This project spans the areas of catalysis, synthetic organic chemistry, and green industrial processes.

- Optimized conditions greatly reduce material cost and energy input as compared with existing processes.
- The reaction provides access to various functionalized alpha olefins.
- While the ethylene oligomerization process generally produces a mixture of alpha olefins of various chain lengths, our decarboxylation process furnishes alpha olefins of a definite length.

Potential Impact

- The chemical industry's dependence on petroleum will be lightened by at least 3.7 million tons a year.
- Production of alpha olefins becomes an efficient and sustainable process.
- The cost of odd-numbered alpha olefins will be greatly reduced. (fatty acids: $7-16/kg; odd-numbered alpha olefins: $7,000-25,000/kg)

The reaction is carried out in a vacuum distillation apparatus. The volume is small since no solvent is needed.

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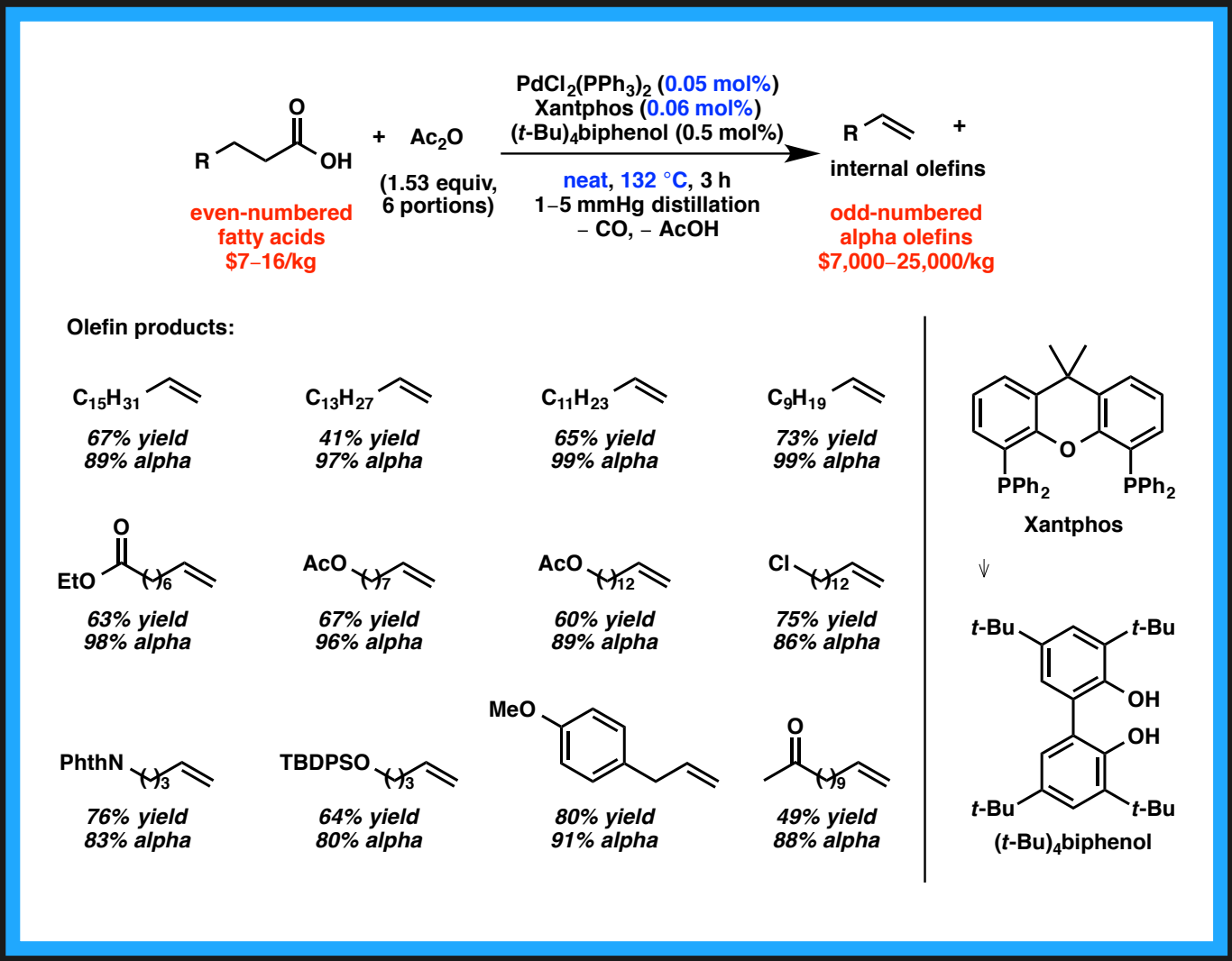
The Science

The conversion of fatty acids to alpha olefins has been pursued by a number of approaches. Radical decarboxylation is a classical reaction, but it suffers from low yields due to many side reactions. A more recent strategy entails transition metal-catalyzed decarbonylative dehydration of fatty acids. A variety of metals have been shown to catalyze the transformation, and among them, palladium is the most reactive. However, existing processes of palladium-catalyzed decarbonylative dehydration require either extremely high temperature (230-250 °C) or high catalyst loading (3 mol%) and an expensive solvent. In situ distillation of olefin product is often necessary to avoid double bond isomerization. These limitations make current processes unsuitable for large scale production. Therefore we set out to develop an improved process that overcome these hurdles by screening various reaction parameters.



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Key Results

We identify Xantphos as a unique ligand and tert-butylated biphenol as a protic additive. We also find that portionwise addition of acetic anhydride and subsequent distillation of acetic acid can effectively inhibit olefin isomerization. With acetic anhydride added in six portions, we are able to obtain olefin products in good yields and high selectivity without in situ distillation of the olefins. The reaction tolerates a wide range of functional groups and can be scaled to deliver multigram quantities of olefin products.

Future Steps

- Further reduction of catalyst loading
- Lowering reaction temperature
- Use of noncorrosive activators in place of acetic anhydride
- Development of a new process that furnishes even-numbered alpha olefins

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Publications

- **Palladium-Catalyzed Decarbonylative Dehydration of Fatty Acids for the Production of Linear Alpha Olefins.** Liu, Y.; Kim, K. E.; Herbert, M. B.; Fedorov, A.; Grubbs, R. H.*; Stoltz, B. M.* Adv. Synth. Catal. DOI: 10.1002/adsc.201301109