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# Olefins from biomass feedstocks: catalytic ester decarbonylation and tandem Heck-type coupling†

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**With the goal of avoiding the need for anhydride additives, the catalytic decarbonylation of *p*-nitrophenylesters of aliphatic carboxylic acids to their corresponding olefins, including commodity monomers like styrene and acrylates, has been developed. The reaction is catalyzed by palladium complexes in the absence of added ligands and is promoted by alkali/alkaline-earth metal halides. Combination of catalytic decarbonylation and Heck-type coupling with aryl esters in a single pot process demonstrates the viability of employing a carboxylic acid as a "masked olefin" in synthetic processes.**

Biomass, and chemicals derived therefrom, hold promise in transitioning to a more sustainable bio-based economy.[1] Carboxylic acids are an important class of biomass-derived molecules that can be used as starting materials for the synthesis of a variety of potentially useful compounds. For example, polymerizable olefins may be accessed through transition metal catalyzed dehydrative decarbonylation of aliphatic carboxylic acids (Fig. 1, top).[2–4] Such reactions often employ Pd,[3,4] Rh[2d] or Ir[5] catalysts and phosphine based ligands, with some recent attention to use of base metals like Fe[6] and Ni.[7] An indispensable ingredient in all of the processes reported thus far is a sacrificial stoichiometric anhydride, like acetic ($Ac_2O$) or pivalic anhydride ($Piv_2O$), which activates the carboxylic acid substrate by forming a mixed anhydride that can readily undergo oxidative addition to the metal center. A key goal of current research is to increase the efficiency of the reaction and avoid the use of such a stoichiometric (and wasteful) co-reagent. While some success in effecting decarbonylation of carboxylic acids directly at high temperatures (200–250 °C) using Ru catalysts has been reported,[8] attainment of high yields under mild conditions appears to require activation of the acid.

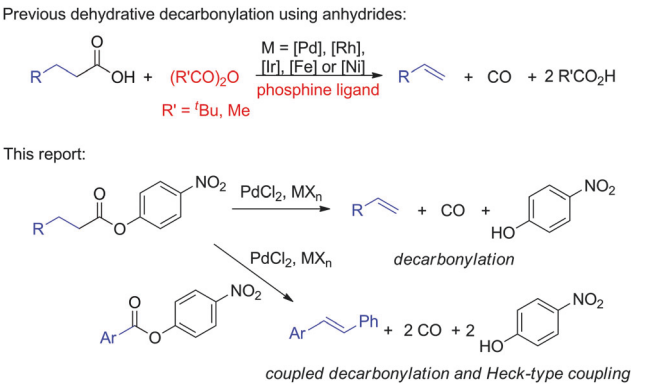


Fig. 1 Comparison of previous work to decarbonylation and *in situ* Heck-type coupling reactions reported herein.

Herein, we report (a) the development of a palladium-catalyzed decarbonylation of *p*-nitrophenylesters of aliphatic carboxylic acids to the corresponding olefins, and (b) demonstration of the viability of a one-pot tandem Heck-type coupling reaction starting from the *p*-nitrophenylesters of hydrocinnamic acid (a styrene precursor) and the *p*-nitrophenylesters of various aromatic carboxylic acids (Fig. 1, bottom). The catalytic decarbonylation of *p*-nitrophenylesters differs from the typical decarbonylation that involves intermediacy of a mixed anhydride. The tandem Heck-type process is particularly notable, especially in light of recent efforts to incorporate biomass derived chemicals in synthesis,[9] and because Heck-coupling is a powerful synthetic tool for coupling alkenes with aromatics.[10]

An early precedent for the use of esters as substrates includes the demonstration of a Ni(0)-mediated decarbonylation of phenyl propionates to yield ethylene using simple phosphine ligands like $PPh_3$ and $PCy_3$.[11] It was also noted in this work that (i) more than one turnover could be achieved with esters of electron-withdrawing phenols like *p*-cyanophenol and (ii) that simple alkyl esters did not participate in the reaction. We were also inspired by the report of a palladium-catalyzed decarbonylation of *p*-nitrophenylesters of aromatic carboxylic acids, which in the presence of alkenes resulted in a Heck-type coupling *via* a putative aryl–Pd intermediate.[12]

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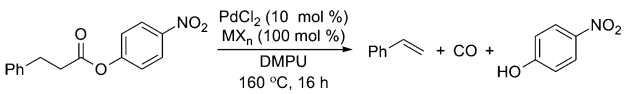
† Electronic supplementary information (ESI) available: Experimental procedures, characterization data and NMR spectra for compounds synthesized and isolated. See DOI: 10.1039/c4cc09003a

Table 1 Effect of metal halides on the decarbonylation reaction[a]




| Entry | $MX_n$ | Yield[b] (%) |
|---|---|---|
| 1 | — | 46 |
| 2 | NaCl | 51 |
| 3 | NaBr | 58 |
| 4 | KCl | 52 |
| 5 | $CH_3COONa$ | <5 |
| 6 | TBAB[c] | 62 |
| 7 | **$CaCl_2$** | **71** |
| **8** | **LiCl** | **78** |
| 9 | $MgCl_2$ | 53 |
| 10 | LiBr | 66 |

[a] Reaction conditions: *p*-nitrophenylhydrocinnamate (0.075 g, 0.28 mmol), $PdCl_2$ (0.004 g, 0.023 mmol, 10 mol%) and metal halide (0.26 mmol) in DMPU (*ca.* 0.5 mL) at 160 °C for 16 hours. [b] Determined by GC using 1,3,5-trimethoxybenzene as internal standard. [c] TBAB = tetra-*n*-butylammonium bromide.

Initial test reactions focused on screening the decarbonylation of the *p*-nitrophenylester of hydrocinnamic acid using various Ni and Pd catalysts (*e.g.* $NiI_2$, $Ni(COD)_2$, $PdCl_2$, $PdI_2$) in the presence of phosphine ligands (*e.g.* $PPh_3$, $PCy_3$, DPEPhos, dppe, dcype, dppb).[13] Irrespective of the conditions employed, the reactions yielded only ~5–10% styrene and almost quantitative ester hydrolysis was noted. Reasoning that the ligands could be acting as nucleophiles and promoting ester hydrolysis, we performed a reaction with $PdCl_2$ (10 mol%) in *N*,*N*′-dimethylpropyleneurea (DMPU) as solvent at 160 °C in the absence of any added ligands, and found that styrene was produced in 46% yield after 16 h. The reaction efficiency improved upon addition of stoichiometric amounts of alkali and alkaline-earth metal halides (Table 1). The nature of the halide as well as the metal were found to affect the observed reactivity, as styrene yield was 66% with LiBr while NaCl and KCl produced styrene in 51% and 52% yield, respectively. LiCl and $CaCl_2$ were found to increase styrene yield to 78% and 71%, respectively.

The amount of the LiCl promoter was found to be important as the yield dropped to 54% when its loading was reduced to 20 mol% (Table 2, entry 2). The reaction temperature also was found to have significant effect on the reaction efficiency (entries 4 and 5; 27% yield at 120 °C over 16 h *vs.* 67% yield at 140 °C in 3 h). Loadings of $PdCl_2$ of 2.5 mol% and 1 mol% resulted in only modest decreases in product yield (entries 3 and 7). Addition of N-donor ligands (pyridine, DMAP) had a detrimental effect (entry 6; styrene yield < 5%). Through these combined studies, optimal conditions were identified as $PdCl_2$ (2.5 mol%), LiCl (100 mol%) in DMPU (*ca.* 0.5 mL) at 160 °C for 3 h (Table 2, entry 3).

Table 2 Decarbonylation of *p*-nitrophenylhydrocinnamate[a]

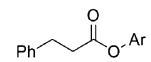
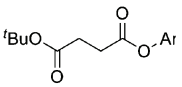
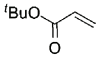
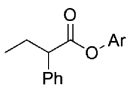
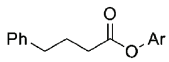
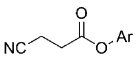
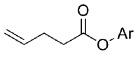
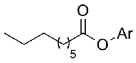
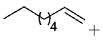
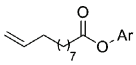
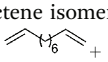
| Entry | Conversion (%) | *T* (°C) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1[c] | | 160 | 16 | 79 |
| 2[d] | | 160 | 16 | 54 |
| **3**[e] | | **160** | **3** | **75** |
| 4 | 65 | 120 | 16 | 27 |
| 5 | | 140 | 3 | 67 |
| 6[f] | 45 | 140 | 3 | <5 |
| 7[g] | 94 | 160 | 5 | 47 |

[a] Reaction conditions: *p*-nitrophenylhydrocinnamate (0.075 g, 0.28 mmol), $PdCl_2$ (0.004 g, 0.023 mmol, 5 mol%) and LiCl (0.010 g, 0.24 mmol, 100 mol%) in DMPU (*ca.* 0.5 mL). [b] Determined by GC using 1,3,5-trimethoxybenzene as internal standard. [c] $PdCl_2$ (5 mol%). [d] LiCl (20 mol%). [e] $PdCl_2$ (2.5 mol%). [f] Pyridine (50%). [g] $PdCl_2$ (1 mol%).

Using these optimized conditions, we explored the substrate scope of the reaction (Table 3).‡ The *p*-nitrophenylester of *tert*-butylsuccinate (which can be derived from bio-based succinic anhydride[3]) was readily converted to *tert*-butylacrylate in 46% yield (GC-MS; entry 2). Similarly, acrylonitrile was produced in 44% yield from 3-cyanopropanoic acid, which can be synthesized *via* oxidative decarboxylation[4b] of glutamic acid (entry 5). The substrates 4-phenylbutyric acid and 2-phenylbutyric acid (entries 3 and 4) gave identical product distributions with *trans*-β-methylstyrene as the major olefin product (*trans* : *cis* = 8 : 1); allylbenzene was also detected as a minor coproduct (10%). These results suggest that olefin isomerization occurs under the reaction conditions, probably *via* re-coordination and chain-walking of the π-allyl intermediate.[14] Decarbonylation of the fatty acids undecylenic acid and pelargonic acid (nonanoic acid; entries 7 and 8), also generated a mixture of the isomeric decadienes and octenes in 31% and 35% yields, respectively. Attempts to synthesize 1,3-butadiene by decarbonylation of 4-pentenoic acid resulted in <10% yield of the alkene, detected by trapping as tetrabromobutane using *in situ* bromination at −10 °C (entry 6).

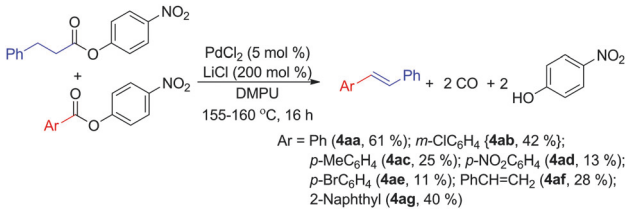
Having identified a system that would catalytically generate olefins from esters, we explored the possibility of coupling the decarbonylation

Table 3 Substrate scope for decarbonylation of *p*-nitrophenylesters[a]

| Entry | Acid | Olefin | Yield[b] (%) |
|---|---|---|---|
| 1 |  |  | 53 (79) |
| 2 |  |  | (46) |
| 3 |  |  | 52 |
| 4 |  |  | 59 |
| 5 |  |  | (44) |
| 6 |  |  | (<10) |
| 7[c] |  |  Octene isomers | 35 |
| 8[c] |  |  Decene isomers | 32 |

[a] Reaction conditions: *p*-nitrophenyl ester (0.26 mmol), $PdCl_2$ (0.004 g, 0.023 mmol, 5 mol%) and LiCl (0.010 g, 0.24 mmol, 100 mol%) in DMPU (*ca.* 0.5 mL) for 3 h. Ar = *p*-$NO_2C_6H_4$. [b] Determined by GC using 1,3,5-trimethoxybenzene as internal standard (in parenthesis); isolated yields were determined for reactions carried at 1 mmol scale and run for 5 h. [c] Reaction carried out for 16 h.




Scheme 1 Tandem double decarbonylative Heck-type coupling.

reaction with the decarbonylative Heck-type coupling of aromatic esters with olefins.[12] Reports on Heck-coupling have focused on alternate routes to incorporate the aromatic moiety in the cross-coupling reaction; we are unaware of any efforts that explore novel methods of introducing the olefin counterpart. Starting from equivalent amounts of *p*-nitrophenylbenzoate and *p*-nitrophenolhydrocinnamate, *trans*-stilbene was produced in 61% yield under our optimized reaction conditions. This first demonstration of the use of a carboxylic acid ester as a "masked olefin" in a Heck-coupling reaction has intriguing potential as a tool in synthesis. Monitoring of the progress of the tandem Heck-coupling reaction by GC-MS analysis showed initial build up of styrene and loss of the hydrocinnamic ester in the mixture prior to *trans*-stilbene generation accompanied by styrene and benzoate ester consumption (Fig. S1, ESI†). Substituted benzoic acid esters participated in the reaction to yield the respective asymmetric stilbenes, consistent with cross-coupling of components from the two different ester starting materials (Scheme 1). The cross-coupling efficiency decreased when activated aromatic esters (with electron withdrawing substituents) were used, as their decarbonylation to yield the corresponding parent arene *via* protonation of the Ar–Pd intermediate was competitive. When *p*-nitrophenol-4-bromobenzoate was employed as the coupling partner, a minor amount of *trans*-stilbene (<5%) was observed in the reaction mixture along with 4-bromostilbene, presumably arising from the coupling of styrene with bromobenzene.

In summary, we have identified a simple system for the catalytic decarbonylation of *p*-nitrophenylesters of aliphatic carboxylic acids that employs $PdCl_2$ as catalyst and is promoted by alkali/alkaline-earth metal halides like LiCl and $CaCl_2$. The reaction generates olefins, including commodity monomers like styrene, acrylates, acrylonitrile and octene(s), in moderate to good yields. We have also discovered that the olefins generated by the decarbonylative pathway can participate in a tandem decarbonylative Heck-type cross-coupling reaction. This reaction provides a new route to stilbenes, notable synthetic targets.[15] Ongoing efforts aim to further improve upon these processes by generating activated esters of bio-derived carboxylic acids *in situ* and, ultimately, rendering the process catalytic in phenol additive.

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## Notes and references

‡ *Representative procedure for decarbonylation reactions*. Inside a $N_2$ filled glove box, a Schlenk tube was charged with *p*-nitrophenylhydrocinnamate (0.075 g, 0.28 mmol, 1 equiv.), $PdCl_2$ (0.004 g, 0.026 mmol, 10 mol% or 0.002 g, 0.013 mmol, 5 mol%), LiCl (0.010 g, 0.24 mmol, 100 mol%) and DMPU (*ca.* 0.5 mL) followed by a Teflon-coated stir bar to yield a light yellow mixture. The Schlenk tube was sealed, brought outside the glove box and set in an oil bath pre-heated to 155–160 °C. The reaction mixture was allowed to stir at this temperature for the stipulated period of time during which it darkened to a final red-brown color. At the end of the reaction, the Schlenk tube was removed from the oil bath and allowed to cool to room temperature. (a) For GC-MS analysis: the reaction mixture was diluted with EtOAc (*ca.* 5 mL) and washed with 1 M HCl (*ca.* 5 mL × 2) and brine (*ca.* 5 mL). The organic layer was collected, dried over $MgSO_4$, and analyzed by GC-MS using 1,3,5-trimethoxybenzene as an internal standard. (b) For olefin isolation (reaction carried out at 1 mmol scale): the reaction mixture was diluted with 1 M HCl (*ca.* 10 mL) and extracted with pentane (*ca.* 5 mL × 3). The combined organic layers were washed with 1 M HCl (*ca.* 5 mL), the pentane extracts were dried with $MgSO_4$, and then they were concentrated under vacuum to remove solvent. Analysis of the residue by $^1$H NMR spectroscopy showed the olefin product in >90% purity.

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