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Catalytic decarbonylation of biomass-derived carboxylic acids as efficient route to commodity monomers†

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The palladium-catalyzed decarbonylation of bio-derived carboxylic acids to alkyl acrylates, styrene, and acrylonitrile is reported. The olefins were isolated by continuous distillation in yields up to 87% by heating a neat, equimolar mixture of pivalic anhydride with the appropriate carboxylic acid to 190 °C in the presence of a Pd-phosphine catalyst.

Introduction

Escalating demands for resources derived from diminishing fossil fuel reserves have made the quest for sustainable alternatives of paramount importance. With an annual global production of billions of metric tons per year,1 biomass (in the form of carbohydrates, oils, lignins, and terpenes) has emerged as a sustainable platform from which the generation of commodity chemicals, fuel, and energy can be realized.² As an example, the production of olefins via transition-metal-catalyzed decarbonylation is of considerable interest given the availability, low toxicity, and structural diversity of bio-derived carboxylic acids. Miller and coworkers were among the first to prepare terminal alkenes from long chain fatty acids by heating the latter to 250 °C (eqn (1)) neat with one equivalent of acetic anhydride, (Ac₂O), triphenylphosphine (PPh₃, 0.5 mol%), and 0.01 mol% of a Pd- or Rh-based catalyst.3 During this transformation, a mixed anhydride (generated in situ) is postulated to undergo oxidative addition onto a transition-metal species to yield an acyl complex (Scheme 1).4 Subsequent decarbonylation followed by β -hydride elimination affords the corresponding olefin along with an equivalent of carbon monoxide and two equivalents of acetic acid (in principle both the CO and acetic acid can be recycled to make syngas and acetic anhydride, respectively). Subsequent work by Gooßen and Rodríguez⁵ and Scott et al.⁶ showed that lower temperatures (ca. 110 °C) can be employed at the expense of using a solvent and higher palladium (ca. 3 mol%) and ligand (ca. 9 mol%) loadings; Maetani and coworkers have recently reported similar results using Ir-based catalysts in lieu of Pd.7



Scheme 1 Proposed decarbonylation mechanism.

Herein, we report a simple and facile method that converts bio-sourced mono-alkyl succinates into alkyl acrylates, monomers used extensively in the paint, coatings, adhesive, and textile industries.⁸ Moreover, we have extended the scope of this method to include the production of styrene and acrylonitrile from bio-derived hydrocinnamic acid⁹ and 3-cyanopropanoic acid,¹⁰ respectively. As is the case with alkyl acrylates, both

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styrene and acrylonitrile are high volume¹¹ petrochemically derived commodity chemicals, which are used in the production of many consumer items (*i.e.* toys, housings, computer components, furniture, disposable tableware),¹² fibers in the textile industry and molded components in the automobile and appliance industries.¹³ The bio-based synthesis of these monomers has been achieved in recent years using routes besides the decarbonylation of bio-based carboxylic acids. Most recently, engineered *E. coli* produced styrene biosynthetically from L-phenylalanine.¹⁴ The alkyl acrylates can be synthesized from glucose-derived α - or β -hydroxy acids *via* acrylic acid,¹⁵ and acrylonitrile can be synthesized renewably from glycerol.¹⁶

In addition to the novel substrates studied and practical application of the products, we also use lower catalyst and ligand loadings and shorter reaction times than reported by Goo β en, Scott and co-workers,^{5,6} as well as a solvent-free reaction and simple distillation procedure that avoids aqueous workup. In contrast to the method of Miller,³ we have chosen a high-boiling exogenous anhydride that avoids continuous addition to the reaction. Finally, we demonstrate the robustness of the reaction to air, water, and increased scale.

Experimental

Materials and physical methods

All experiments were carried out in an inert atmosphere unless otherwise noted. All organic reagents were purchased from Sigma Aldrich and used without further purification unless otherwise noted. Mono-methyl succinate¹⁷ and 3-cyanopropanoic acid¹⁰ were prepared according to literature procedures. While purchased from Sigma Aldrich, mono-tert-butyl succinate can be prepared by reacting succinic anhydride with tert-butanol.¹⁸ Palladium(II) chloride was purchased from Strem Chemicals and dried under vacuum for 24 h at 90 °C. Pivalic anhydride was dried over molecular sieves. Hydrocinnamic acid was recrystallized from dry pentane and sublimed prior to use. All phosphine ligands were dried under vacuum for 24 h at 90 °C. PPh₃, 1,3-bis(diphenylphosphino)propane (DPPP) and 1,2-bis(diphenylphosphino)ethane (DPPE) were recrystallized from ethanol prior to drying under vacuum. 4-tert-Butyl catechol was recrystallized from pentanes and dried under vacuum for 24 h at 120 °C. Triethylamine was allowed to stir over CaH₂ overnight prior to use. Ether and dichloromethane were passed through a purification column (Glass Contour, Laguna, CA) prior to use. All ¹H NMR spectra were collected on either a Varian VXR-500 or Varian VI-300 spectrometer and calibrated to the residual protonated solvent at δ 7.24 for deuterated chloroform (CDCl₃). All GC-MS experiments were conducted on an Agilent Technologies 7890A GC system and 5975C VL MSD. The GC column was a HP-5 ms with dimensions 30 m \times 0.25 mm. The standard method used for all runs involved an initial oven temperature of 50 °C (held for 2 min) followed by a 20 °C min⁻¹ ramp to 70 °C (held for 6 min), followed by a final 20 °C min⁻¹ ramp to 230 °C (held for 3 min).

Mono-n-butyl succinate

In a modified version of a reported procedure,¹⁹ to a 250 mL oven dried round bottom flask succinic anhydride (49.6 g,

49.2 mol) and n-butanol (44 mL, 48.1 mol) were added and a reflux condenser was attached. The mixture was heated to 120 °C and allowed to reflux for 3 h. After cooling overnight to room temperature, a white precipitate was observed. The unreacted succinic anhydride was removed by filtration, leaving crude mono-n-butyl succinate. A portion of the crude material (9.4 g) was chromatographed (column diameter = 7.6 cm, column height = 56 cm) on silica using dichloromethane as the eluent until the di-butyl succinate ester eluted. Ethyl acetate was then added to the column to remove the desired product, mono-n-butyl succinate. The product was dissolved in 50 mL of dry ether and dried over MgSO4, which was removed by filtration. The solvent was removed from the filtrate in vacuo to afford the product as a yellow oil (5.04 g, 54%). ¹H NMR (300 MHz, CDCl₃) δ 11.49 (1H, s, OH), 4.07 (2H, t, J = 6.6 Hz, OCH₂CH₂CH₂CH₂CH₃), 2.62 (4H, m, COCH₂CH₂CO), 1.58 (2H, quintet, J = 7.3 Hz, OCH₂CH₂CH₂CH₃), 1.34 (2H, sextet, J = 7.5 Hz, OCH₂CH₂CH₂CH₃), 0.89 (3H, t, J = 7.3 Hz, $OCH_2CH_2CH_2CH_3$) ppm.

Standard reaction protocol

In a dinitrogen atmosphere glovebox, hydrocinnamic acid (1 g, 6.7 mmol), palladium(II) chloride (3 mg, 0.25 mol%), pivalic anhydride (1.35 mL, 6.7 mmol), and phosphine ligand (2.2 mol% or 4.4 mol%) were loaded into an oven-dried 15 mL roundbottom flask equipped with a Teflon stir bar. Not all of the reagents were soluble at room temperature, resulting in a heterogeneous mixture. The round-bottom flask was attached to an oven-dried short-path distillation apparatus, removed from the glovebox and placed under an atmosphere of dinitrogen or argon gas. The reaction flask was lowered into a 160 to 170 °C oil bath and allowed to continue to heat until the oil bath reached 190 °C. In most cases, the reaction mixture became homogenous and yellow after heating. Once the reaction mixture reached about 185 °C, it began to bubble vigorously, indicating loss of carbon monoxide. The reaction was allowed to proceed for two hours, during which time a distillate was collected. After 2 h, heating was ceased and the reaction was exposed to air. Both the colorless distillate and yellow residual reaction mixture were analyzed using ¹H NMR spectroscopy, and the distillate was also analyzed using GC-MS.

Styrene separation protocol

A mixture comprised of styrene (3.13 g, 30.0 mmol), pivalic acid (6.35 g, 62.1 mmol), and pivalic anhydride (0.63 g, 3.4 mmol) was diluted with 35 mL of pentanes and washed with a 1.7 M aqueous NaOH solution (3×50 mL). The organic phase was diluted with an additional 15 mL of pentanes and dried over MgSO₄. After filtration, solvent was removed to afford a mixture of styrene and pivalic anhydride (as characterized by ¹H NMR spectroscopy) that was then chromatographed (column diameter = 5 cm, column height = 25 cm) on silica using pentane as the eluent to yield styrene (2.03 g, 65%).

N-Butyl pivalate ester²⁰

N-butanol (6.2 mL, 67.8 mmol), pivaloyl chloride (10.1 mL, 82.1 mmol), 4-dimethylaminopyridine (0.4196 g, 3.4 mmol)

and dry dichloromethane (140 mL) were added to an oven dried 250 mL round bottom flask equipped with a stir bar. To this, triethylamine was added (11.5 mL, 82.5 mmol). After an exothermic reaction, a white precipitate formed. The reaction was allowed to stir overnight, then 100 mL of dichloromethane was added. The organic layer was washed with 250 mL water twice, 250 mL of 1 M HCl, 250 mL of saturated aqueous Na₂CO₃, and 250 mL saturated aqueous NaCl. The organic layer was dried over MgSO₄, filtered, and the dichloromethane was removed from the filtrate *in vacuo*. A portion of the crude product (2.44 g) was chromatographed (column diameter = 5 cm, column height = 25 cm) using dichloromethane as the eluent (2.09 g, 86%). The ¹H NMR spectrum of the product matched data reported previously.²¹

Results and discussion

Mono-alkyl succinates were readily prepared according to eqn (2) by heating an alcohol (R = Me, t-Bu, n-Bu) with succinic anhydride, the dehydration product of succinic acid, a biorenewable resource produced from the fermentation of sugars.^{2b,22} In our variation of Miller's procedure,³ one equivalent of pivalic anhydride (Piv₂O, b.p. = 193 °C) was used in lieu of $Ac_2O(b.p. = 140 \degree C)$ at a reduced temperature of 190 °C to avoid continuous addition of anhydride during each experiment. To both compensate for the lower temperature and possibly increase reaction rates, palladium (*i.e.*, PdCl₂) and ligand loadings were initially increased to 0.25 mol% and 2.2 mol%, respectively, as compared to Miller's protocol. Using a standard short-path distillation head under a moderate flow of N_2 (or Ar), a clear solution was isolated by continuous distillation after 2 h of heating dry mono-succinate ester (1, 2 or 3), Piv₂O, PdCl₂, and ligand (eqn (3)).



Analysis of the distillate by both GC-MS and ¹H NMR spectroscopy confirmed the presence of the desired alkyl acrylate. Methyl acrylate (4) was prepared in 50% and 64% yield when using PPh₃ and bis[(2-diphenylphosphino)phenyl] ether (DPEPhos) as the ligands, respectively (entries 1 and 2, Table 1). Results for the production of *n*-butyl acrylate (5) were comparable, but the yields of *t*-butyl acrylate (6) from mono*t*-butyl succinate (3) were lower, 31% when using PPh₃ and 18% when using DPEphos (entries 5 and 6). Interestingly, minor amounts of alkyl pivalates (PivOR) were also produced during the course of these experiments, suggesting the presence of a competitive reaction. Indeed, in a control experiment, Piv₂O and 1 (or 3) were heated in an equimolar ratio to 190 °C for two hours. GC-MS analysis of the crude mixture (Figures S4,

Table 1Yields (%) for the catalytic decarbonylation of mono-alkylsuccinates $(eqn (3))^a$

Entry	Ligand	R	Acrylate ^b	PivOR ^b	PivOH ^c
1	PPh ₃	Me	50	3	71
2	DPEphos	Me	64	12	49
3	PPh ₃	<i>n</i> -Bu	62	8	62
4	DPEphos	<i>n</i> -Bu	45	21	60
5	PPh ₃	t-Bu	31	11	79
6	DPEphos	t-Bu	18	10	90

^{*a*} All experiments were carried out using dry reagents under an N₂ or Ar atmosphere unless otherwise noted. PdCl₂ loading: 0.25 mol%, ligand loading: 2.2 mol%, calculated based on succinic ester substrate. $T \approx 190$ °C. All results calculated from GC-MS data. Representative GC-MS traces can be found in the ESI, Figures S1–S3.† ^{*b*} Yields based on the succinic ester substrate. ^{*c*} Yields based on the stoichiometry of eqn (3) (2 moles PivOH per mole Piv₂O used).

S5, see ESI[†]) detected succinic anhydride, PivOH, and methyl pivalate (or *t*-butyl-pivalate). We hypothesize that the monoalkyl succinates undergo an intramolecular cyclization to reform succinic anhydride and alcohol, with the latter reacting with Piv_2O to form PivOH and PivOR (eqn (4)).



In an expansion of the scope to other bio-derived carboxylic acids, we examined the production of styrene from hydrocinnamic acid (eqn (5)). Both GC-MS and ¹H NMR analyses of the distillate (isolated under the aforementioned reaction conditions using PPh₃ as the ligand) revealed the formation of styrene in 74% (GC-MS) yield (entry 1, Table 2). Distillation began after approximately 30 min at 180–190 °C, and the reaction was allowed to continue for 2 h. Isolation of pure styrene was achieved by washing the diluted distillate with aqueous NaOH to remove the pivalic acid, followed by a short silica column to remove remaining pivalic anhydride.²³ In the previous study by Gooßen and Rodríguez, low yields (27%) were reported when PPh₃ was used as the ligand under their procedures.⁵

The nature of the ligand and its effect on the product yield were investigated by examining a number of bidentate phosphine ligands (Table 2). Styrene formation was inhibited when DPPE was used in lieu of PPh₃ (entries 2 and 7). In these cases, analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed only the presence of the mixed anhydride formed from hydrocinnamic acid and pivalic anhydride. In addition, palladium black formed instantly upon heating to 160 °C suggesting that the DPPE-palladium catalyst is not stable under these conditions. Using DPPP as the ligand afforded styrene, although lower yields and longer times for the onset of distillation (30–45 min) were observed (entries 3 and 8). DPEphos (known

Table 2 Yields (%) for the catalytic decarbonylation of hydrocinnamicacid $(eqn (5))^a$

Ligand mol%	^b Styrene ^c	PivOH ^e
2.2	74 (73)	65 (66)
2.2	0 (0)	0 (0)
2.2	55 (52)	52 (54)
os 2.2	81 (82)	83 (81)
os 2.2	80 (84)	85 (84)
4.4	65 (70)	81 (82)
4.4	0 (0)	0 (0)
4.4	48 (40)	60 (60)
os 4.4	84 (87)	85 (81)
os 4.4	87 (92)	86 (83)
os 0.5	68 (74)	88 (85)
os 2.2	72 (75)	73 (78)
os 2.2	78 (72)	84 (90)
2.2	71 (61)	66 (75)
0.5	57 (50)	60 (64)
os 0.25	54 (58)	70 (69)
	Ligand mol% 2.2 2.2 2.2 os 2.2 os 2.2 os 2.2 4.4 4.4 4.4 os 4.4 os 4.4 os 4.4 os 4.4 os 0.5 os 2.2 0s 2.2 0.5 os 0.25	Ligand mol%bStyrenec 2.2 $74 (73)$ 2.2 $0 (0)$ 2.2 $55 (52)$ $0s$ 2.2 2.2 $81 (82)$ $0s$ 2.2 $80 (84)$ 4.4 $65 (70)$ 4.4 $48 (40)$ $0s$ 4.4 44 $87 (92)$ $0s$ 0.5 $68 (74)$ $0s$ 2.2 $78 (72)$ 2.2 $71 (61)$ 0.5 $57 (50)$ $0s$ 0.25 $54 (58)$

^{*a*} All experiments were carried out using dry reagents under an N₂ or Ar atmosphere unless otherwise noted. PdCl₂ loading: 0.25 mol% and 1 g scale of hydrocinnamic acid unless otherwise noted. $T \approx 190$ °C ^{*b*} Calculated based on hydrocinnamic acid substrate. ^{*c*} Percent yield in distillate calculated from GC-MS (NMR) data. A representative GC-MS trace can be found in the ESI, Figure S6.†^{*a*} PdCl₂ loading: 0.01 mol% and 25 g scale of hydrocinnamic acid. ^{*e*} Air was used as carrier gas. Reagents were left open to the atmosphere for at least 24 h. ^{*s*} PdCl₂ loading: 0.005 mol% and 50 g scale of hydrocinnamic acid. Allowed to react for 31 h.

to be successful, vida supra) and 4.5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos), also were considered since both are strongly coordinating phosphine ligands that have been shown to improve product yields for hydrocyanation²⁴ and hydrocarbonylation²⁵ of styrene and the decarbonylation of phenylbutanoic acid to 3-phenylpropene.⁵ Consistent with trends reported by Gooßen and coworkers,5 Xantphos and DPEphos were determined to be the most effective phosphines in promoting decarbonylation, generating styrene in ca. 80% yield (entries 4,5,9-13,16). Unlike the more sluggish PPh₃ and DPPP systems, the onset of distillation proceeded quickly (ca. 5 min.), and rapid evolution of CO was observed once the reaction flask reached 190 °C. Increasing the ligand loading to 4.4 mol% (entries 6-10) and/or adding the stabilizer *t*-butyl catechol (data not shown) had a negligible effect on product yield. In contrast to the stark difference in yields reported by Gooßen and Rodríguez for the decarbonylation of phenylbutyric acid (27% for PPh₃ vs. 83-81% DPEphos),⁵ the improvements in yields for the more expensive chelating phosphines DPEphos and Xantphos relative to PPh₃ were negligible in our system. Scaling up the decarbonylation of hydrocinnamic acid was successful; using much lower PdCl₂ (0.01 mol%) and DPEphos (0.5 mol%) loadings on a *ca*. 25 g scale afforded styrene in ~ 70% yield (entry 11).

To test the robustness of the decarbonylation reaction, a series of experiments were performed using a combination of nondry/dry reagents and air instead of N₂ or Ar as the carrier gas. Performing the reactions using dry reagents (*i.e.*, PdCl₂, Piv₂O, DPEphos) and reagent-grade hydrocinnamic acid under a moderate flow of air afforded styrene in ~ 72% yield (entry 12, Table 2), only *ca.* 9% less when compared to using N₂ as a carrier gas and recrystallized, sublimed and dried hydrocinnamic acid (entry 4). Heating "wet" reagents²⁶ under a moderate flow of air (otherwise identical conditions) resulted in the formation of styrene in comparable yields to using dry reagents under air (entry 13). Using PPh₃ in lieu of DPEphos as a ligand gave rise to styrene in similar yields (entry 14). Reducing the wet²⁷ PdCl₂ and PPh₃ loadings to 0.01 mol% and 0.5 mol%, respectively, on a *ca.* 25 g scale of reagent-grade hydrocinnamic acid afforded styrene in ~ 57% (GC-MS) yield (entry 15). Thus, in contrast to previous studies that carried out decarbonylation reactions using dried reagents and under a flow of inert gas, we have demonstrated that this reaction is robust to both air and water; rigorously dried reagents and a flow of inert gas do not markedly improve yields or reduce reaction times. This obviously renders the overall transformation less energy, solvent and time intensive.

In an effort to further improve the reaction efficiency for the production of styrene, the Pd and ligand loadings were reduced to 0.005 mol% and 0.025 mol%, respectively (entry 16). The yield for this reaction is comparable to yields with higher loadings. However, the reaction is slower, requiring 31 h to complete the distillation, whereas reactions with double the Pd and ligand loadings (0.01 mol% Pd, 0.5 mol% ligand) required a maximum 3 h to complete the distillation.

Finally, we have applied our methodology to the synthesis of acrylonitrile from 3-cyanopropanoic acid. Using rather mild reagents (NaOCl, NaBr, water), 3-cyanopropanoic acid can be synthesized by the oxidative decarboxylation of glutamic acid, a biorenewable resource.¹⁰ Subsequent decarbonylation of 3-cyanopropanoic acid using our procedure (PdCl₂ 0.25 mol%, PPh₃ 2.2 mol%) resulted in isolation of distillate that contained acrylonitrile in 23% yield by GC-MS (see Figure S7 for representative GC-MS trace, ESI†). The distillate also contained PivOH and Piv₂O. The low yields are explained by the presence of polyacrylonitrile in the reaction mixture, as observed by ¹H NMR spectroscopy. Addition of *t*-butyl catechol to the reaction mixture as an inhibitor did not improve the yield of isolated acrylonitrile. Recently, similar results were obtained by Scott and coworkers¹⁰ using a modified version of Gooßen's procedure.

Conclusions

Using palladium-catalyzed decarbonylation of bio-derived carboxylic acids we prepared alkyl acrylates, styrene, and acrylonitrile in good yields. The developed procedure is applicable to a diverse set of carboxylic acid substrates, and involves continuous distillation of the desired products from the reaction mixture. In addition, catalyst loadings can be lowered to 0.005 mol% and the reaction scale increased to 50 grams with only a small reduction in product yield. We also performed a careful ligand screening using a variety of chelating phosphines, highlighting the importance of the ligand on reaction efficacy. Interestingly, PPh₃ was nearly as good a ligand at promoting the decarbonylation reaction as the strongly coordinating diphosphines DPEphos and Xantphos, demonstrating that a simple and inexpensive system can be realized for the decarbonylation of bio-derived carboxylic acids. Finally, we illustrated the robustness of this system. Using reagent-grade and wet starting materials under an air purge gives comparable yields to reactions using purified and dried reagents and an inert (N2 or Ar) gas purge. We plan to explore other bio-derived substrates²⁸ and perform detailed mechanistic studies on the decarbonylation reaction to optimize the identity of the catalyst such that lower temperatures (to prevent *in situ* polymerization of the product, have lower energy input and avoid deleterious side-reactions) and catalyst loadings (to minimize cost) can be achieved.

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