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Anhydride-Additive-Free Nickel-Catalyzed Deoxygenation of Carboxylic Acids to Olefins

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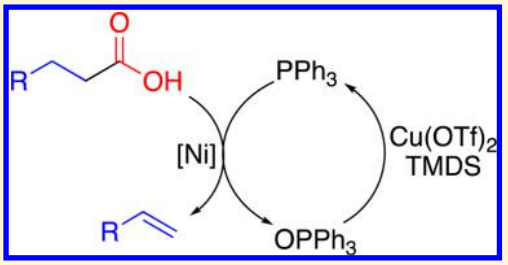
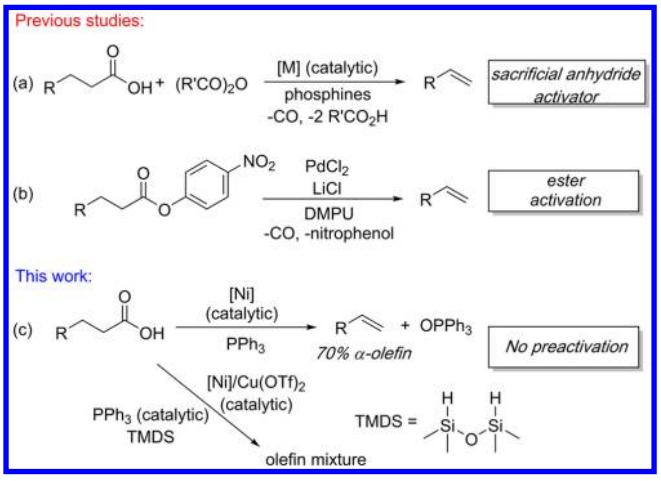
Supporting Information

ABSTRACT: A nickel-catalyzed route for direct, anhydride-additive-free deoxygenation of fatty acids to the corresponding olefins has been developed. The transformation is catalyzed by simple nickel salts of the type NiX_2 (X = halide, acetate, acetylacetonate), uses PPh_3 as a stoichiometric reductant, and exhibits selectivity for generation of linear α-olefin products. The reaction was rendered cocatalytic in PPh_3 using 1,1,3,3-tetramethyldisiloxane (TMDS) as terminal reductant for the in situ reduction of $OPPh_3$ and catalytic $Cu(OTf)_2$.



Olefins are the largest volume intermediates produced in the chemical industry and are almost exclusively obtained by steam cracking during petroleum and natural gas refining. Impetus to reduce our dependence on fossil fuels has led efforts to derive commodity chemicals such as olefins from renewable biomass.[1] Vegetable oils represent an abundant, renewable feedstock that can be converted to long-chain olefins, of which linear α-olefins (LAOs) are of particular interest, especially as polymerization feedstocks. The dehydrative decarbonylation reaction catalyzed by transition-metal reagents has been demonstrated to be effective and efficient at converting biomass-derived carboxylic acids to olefins.[2] A sacrificial anhydride is routinely employed to activate the carboxylic acid (Scheme 1a).[3] We recently demonstrated that *p*-nitrophenol esters of carboxylic acids are also decarbonylated under palladium catalysis (Scheme 1b).[4]

Scheme 1. Transition-Metal-Catalyzed Deoxygenation of Carboxylic Acids to Olefins



Direct decarboxylation/decarbonylation of carboxylic acids without an additive such as an anhydride is rare and is invariably effected at high temperature (≥350 °C) in the presence of supported catalysts under a reducing atmosphere of H_2.[5] However, these processes result in product mixtures comprising both saturated and unsaturated hydrocarbons, along with cracking products. In an effort to render the deoxygenation reaction more practical by using an earth-abundant catalyst, $Ni(OAc)_2$ was recently used for the deoxygenation of fatty acids in the absence of H_2 and solvent at 350 °C.[6] However, almost equimolar amounts of alkene and alkane products were obtained during the process. Enzymatic catalysis has also been recently shown to be efficient at carrying out the direct decarboxylation of fatty acids to the corresponding alkenes.[7] Our ultimate aim is to develop practical and efficient alternatives using base-metal catalysis.

Herein, we report on our findings on a nickel-catalyzed deoxygenation of carboxylic acids to olefins without the use of an activating additive, with PPh_3 serving as both a supporting ligand and terminal reductant. Use of $Ni(acac)_2$ or $Ni(OAc)_2$ as catalysts yields olefins in up to 82% yield with α-selectivity as high as 70%. Furthermore, we have demonstrated that the deoxygenation can be rendered catalytic in PPh_3 by using 1,1,3,3-tetramethyldisiloxane (TMDS) and a copper catalyst to effect in situ reduction of the generated $OPPh_3$ (Scheme 1c).

During our recent investigation of a NiI_2/PPh_3-catalyzed decarbonylation of nonanoic acid,[3k] we observed that octene(s) were generated even in the absence of the pivalic anhydride additive. Subsequent experiments showed that the yield of octene(s) under these conditions (NiI_2 (10 mol %)/PPh_3, 190 °C, under distillation conditions) scaled proportionately with the loading of PPh_3 (Table 1, entries 1−4). At 100 mol % of PPh_3 with respect to the acid, an 82% yield of octene(s) was

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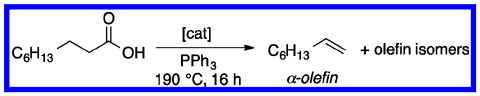
Table 1. Nickel-Catalyzed Deoxygenation of Nonanoic Acid[a]



entry	[cat.] (mol %)	PPh_3 (mol %)	yield (%)	α-olefin[b] (%)
1	NiI_2 (10)	25	27	15
2	NiI_2 (10)	40	33	9.5
3[c]	NiI_2 (10)	100	57	9.3
4	NiI_2 (10)	100	83	6.3
5	NiI_2 (6)	100	85	7.2
6	$NiCl_2$ (10)	100	86	14
7[d]	NiI_2 (10)	0	trace	
8	NiI_2 (0.1)	100	34	40
9	$Ni(PPh_3)_4$ (10)	40	31	66
10[e]	$(PPh_3)_2Ni(CO)_2$ (10)	40	25	70
11	$Ni(acac)_2$ (10)	100	73	55
12	$Ni(OAc)_2$ (10)	100	82	70
13	FeI_2 (10)	100	~5	76
14	$CoBr_2$ (10)	100	trace	

[a]Reaction conditions unless specified otherwise: nonanoic acid (1 equiv), PPh_3, and [catalyst] were heated in a distillation mode for 16 h at 190 °C. The distillate was analyzed by GC-MS and ^{1}H NMR spectroscopy. [b]Determined by GC-MS and confirmed by ^{1}H NMR spectroscopy (1-octene selectivity). Yield and α-olefin selectivity are an average of two to three runs. [c]Reaction stopped after 4 h. [d]Reaction carried out using $OPPh_3$ (100 mol %) instead of PPh_3. [e]Reaction carried out using P(Ph-*p*-OMe)$_3$.

obtained in the distillate (Table 1, entry 4). ^{31}P NMR analysis of the residue revealed that PPh_3 was quantitatively converted to $OPPh_3$, suggesting that PPh_3 served as a reductant in the reaction. A control experiment involving nonanoic acid and PPh_3 under similar conditions in the absence of nickel catalyst did not generate any octene(s) or $OPPh_3$. Similarly, octenes were not generated under nickel-catalyzed conditions when the reaction was carried out using $OPPh_3$ instead of PPh_3 (Table 1, entry 7). The reducing capability of PPh_3 has been employed by others, including recent reports on deoxydehydration reactions that convert biomass-derived glycols and polyols to olefins.[8] NiI_2 and $NiCl_2$ were found to be equally efficient. Transitioning to the Ni(0) catalyst precursor $Ni(PPh_3)_4$ resulted in a higher α selectivity but lower overall yield. Alternative Ni(II) precursors such as $Ni(acac)_2$ and $Ni(OAc)_2$ gave high yields while maintaining moderate α selectivity (55−70%) (Figure S1 in the Supporting Information). Other first-row transition-metal catalysts (Fe and Co) were found to be inefficient under similar conditions. A screen of various ligands using $Ni(acac)_2$ or $Ni(OAc)_2$ (10 mol %) did not uncover any marked improvements (Table S1 in the Supporting Information). The addition of KI to the reaction mixture was found to enhance yields; although the reason for this effect is unclear, we presume that iodide acts as a reductant (Table S1, entries 5 and 6).[7]

Using optimized conditions for deoxygenating nonanoic acid directly to 1-octene with good selectivity ($Ni(OAc)_2$ (10 mol %), PPh_3 (1 equiv) at 190 °C for 16 h), fatty acids with varying chain lengths (C_{11}−C_{16}) were examined (Table 2, 51−88% yield; Figures S2−S6 in the Supporting Information). For the heavier fatty acids the reactions had to be performed under reduced pressure (~500 mTorr) to assist distillation of the olefin from the reaction mixture. NiI_2 was consistently found to be more efficient than $Ni(OAc)_2$. The 2° cyclohexanecarboxylic acid was converted to cyclohexene in 80% yield (entry 8).

Table 2. Nickel-Catalyzed Deoxygenation of Fatty Acids[a]

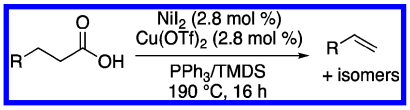
entry	fatty acid	olefin	[Ni]	yield[b]/α-olefin (%)
1	undecylenic (C_{11})	decadiene (C_{10})	NiI_2	85/nd
2			$Ni(OAc)_2$	65/71
3	lauric (C_{12})	undecene (C_{11})	$Ni(OAc)_2$	77/63
4[c]			$Ni(OAc)_2$	63/nd
5[d]	myristic (C_{14})	tridecene (C_{13})	NiI_2	88/17
6			$Ni(OAc)_2$	56/41
7[d]	palmitic (C_{16})	pentadecene (C_{15})	$Ni(OAc)_2$	51/38
8	cyclohexane (C_6)	cyclohexene	NiI_2	80

[a]Reaction conditions: Fatty acid (1 equiv), PPh_3 (100 mol %), and [Ni] (10 mol %) were heated in distillation mode for 16 h at 190 °C. The distillate was analyzed by GC-MS and ^{1}H NMR spectroscopy. Yield and α-olefin selectivity are an average of 2 to 3 runs. [b]From the distillate. [c]Using PPh_3 (40%) and KI (100%). [d]Reaction performed under weak vacuum (~500 mTorr). nd = not determined.

While PPh_3 has been used as terminal reductant in a variety of synthetically useful transformations,[9] separation of the $OPPh_3$ coproduct is problematic and could be avoided if $OPPh_3$ could be recycled. Among the known methods for efficient reduction of phosphine oxides to phosphine,[10] we focused on the use of 1,1,3,3-tetramethyldisiloxane (TMDS), which has been demonstrated to be effective under Cu or Ti catalysis.[10b,c,e,11]

When TMDS and $Cu(OTf)_2$ were incorporated into the NiI_2-catalyzed deoxygenation conditions with catalytic PPh_3, octene(s) were generated from nonanoic acid (94%, Table 3, entry 3).[12] In the absence of $Cu(OTf)_2$/TMDS only stoichiometric amounts of olefin corresponding to PPh_3 loadings were produced; no olefin was obtained in the absence of PPh_3. The reaction was equally efficient with $NiCl_2$ as the

Table 3. Ni/PPh_3-Catalyzed Deoxygenation using TMDS as Terminal Reductant[a]



entry	fatty acid	TMDS (mol %)	PPh_3 (mol %)	yield[b] (%)
1	nonanoic (C_9)		14	17
2	nonanoic (C_9)	40	14	53
3	nonanoic (C_9)	80	14	94
4	nonanoic (C_9)	80	7.5	50
5	nonanoic (C_9)	80	0	0
6[c]	nonanoic (C_9)	80	14	81
7[d]	nonanoic (C_9)	80	14	78
8[e]	nonanoic (C_9)	80	5	61
9	myristic (C_{14})	80	14	77
10	stearic (C_{18})	80	14	66

[a]Reaction conditions unless specified otherwise: fatty acid (2.84 mmol), TMDS, PPh_3, NiI_2 (2.8 mol %), and $Cu(OTf)_2$ (2.8 mol %), 16 h, 190 °C. Analysis by ^{1}H NMR spectroscopy. α-Olefin selectivities were <5% in all cases. [b]Versus 1,3,5-trimethoxybenzene internal standard. [c]Reaction stopped after 4 h. [d]$NiCl_2$ (2.8 mol %) used as catalyst. [e]Using NiI_2 (1 mol %) and $Cu(OTf)_2$ (1 mol %).

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catalyst. Finally, extending the conditions to longer chain fatty acids, myristic acid (C_{14}) and stearic acid (C_{18}), produced tridecene(s) and heptadecene(s) in 77% and 66% yields, respectively. Given the high volatility of TMDS relative to the other components of the mixture, these reactions were performed in a closed Schlenk tube and as a result gave relatively low α selectivity (<5%) since the olefin was not removed from the reaction mixture; isomerization to the more thermodynamically favored internal alkenes was implicated.

Analysis of the headspace volume in NiI_2/PPh_3 deoxygenation of nonanoic acid under standard reaction conditions tested positive for CO but not for CO_2, [15,13] suggesting that it follows a decarbonylation pathway.

In conclusion, we have identified a method for deoxygenating fatty acids to alkenes where PPh_3 serves as a terminal reductant and no exogenous acid-activating species is needed. The reaction is catalyzed by simple nickel salts under solvent-free conditions. Ni(II) precatalysts were found to be superior to Ni(0) counterparts, and by using $Ni(OAc)_2$ high yields (up to 82%) and α selectivity (up to 70%) could be achieved. The reaction can be run at a low loading of NiI_2 (0.1 mol %), achieving a high turnover number (TON) of 340. The deoxygenation reaction can be rendered catalytic in PPh_3 by using TMDS and $Cu(OTf)_2$, albeit to form a mixture of olefin products under the reaction conditions used.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00940.

Experimental details, including characterization data for the compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(12) On the basis of the results of GC-MS analysis, TMDS is converted to a mixture of cyclic silyl ethers.

(13) (a) CO_2 test: the headspace was analyzed by passing through a solution of $Ba(OH)_2$. No precipitation indicative of the formation of $BaCO_3$ was observed. (b) CO test: the gas in the headspace was

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transferred to a solution of $Ni(PPh_3)_4$ in dry toluene. When the mixture was stirred for 10 min, the solution changed from deep red-orange to light yellow. Analysis of the solution by ^{31}P NMR spectroscopy showed the formation of $(CO)_2Ni(PPh_3)_2$.

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