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A Highly Catalytic and Selective Conversion of Carboxylic Acids to 1-Alkenes of One Less Carbon Atom

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Summary: An equimolar mixture of a carboxylic acid and acetic anhydride produces a reagent combination that undergoes a highly efficient decarbonylation/dehydration at 250 °C using either Pd- or Rh-based catalyst systems, affording excellent yields of the corresponding 1-alkenes of one less carbon atom.

The stoichiometric and catalytic decarbonylation of aliphatic aldehydes and acid chlorides to alkanes and alkenes, respectively, by transition-metal complexes are well-known and synthetically useful transformations.[2,3a] Relatively little, however, has been reported concerning the analogous decarbonylation/dehydration of aliphatic carboxylic acids to olefins, with generally poor results achieved in terms of catalyst efficiency and selectivity toward terminal olefin formation in the product.[3] For example, the decarbonylation/dehydration of stearic acid to heptadecene using a Rh-based catalyst was reported to proceed with a maximum catalyst turnover number (TON; moles of olefin product formed per mole of catalyst used) of ca. 250, with selectivities toward 1-heptadecene formation typically below 50%.[3c] Interestingly, results were presented in this work which suggested that the decarbonylation of stearic acid proceeded via intermediate formation of stearic anhydride.[4] Use of a preformed, symmetrical anhydride is not desirable from an economic or synthetic viewpoint, particularly since its decarbonylation should result in the formation of equal amounts of olefin and carboxylic acid coproducts. We now report here that the use of a carboxylic acid substrate as an equimolar mixture with acetic anhydride (Ac_2O) produces a "mixed anhydride system"[5] which undergoes an extremely facile decarbonylation reaction to provide a general and highly selective route to the corresponding 1-alkenes of one less carbon atom (eq 1).

$$RCH_2CH_2CO_2H + Ac_2O \xrightarrow[250\ ^\circ C]{\text{Pd or Rh catalyst}} RCH{=}CH_2 + CO + 2AcOH \quad (1)$$

The following procedure for the conversion of decanoic acid into 1-nonene is representative. An equimolar mixture of decanoic acid and Ac_2O, together with $(Ph_3P)_2PdCl_2$ (1, 0.01 mol % based on the initial charge of decanoic acid) and Ph_3P (50 equiv relative to the Pd catalyst), was heated in an oil bath maintained at 250 °C under a moderate flow of N_2 in a round-bottomed flask fitted with a distillation head, and the distillate product formed was collected. The initial level of the reactor contents was maintained throughout the course of the entire reaction by continuously introducing a feed mixture composed of equimolar amounts of decanoic acid and Ac_2O. Decarbonylation initiated when the reaction temperature reached 180–190 °C, as evidenced by the rapid evolution of CO[6] from the reaction vessel. Distillation of the product subsided after about 45 min of reaction time. Analysis of the distillate by GC showed the presence of 1-nonene, formed with a selectivity of 97.3%[7] and a catalyst TON of 12 370. No nonane was produced in the reaction, and, other than recovered decanoic acid or related anhydrides, the only byproducts detected in the distillate product or remaining reaction mixture were trace amounts (≤0.5% combined yield relative to nonene product) of 2-undecanone and 10-nonadecanone. Thus, taking the minor amount of recovered starting material into consideration, the yield of 1-nonene product derived from this transformation is excellent. Significantly, this reaction has been carried out on a continuous basis with the catalyst and excess phosphine dissolved in the carboxylic acid/Ac_2O feed, thereby facilitating the rapid production of relatively large quantities of α-olefin product.[8]

As demonstrated by the data in Table I, the combination of carboxylic acid and Ac_2O results in substantially higher catalyst efficiency and terminal olefin product selectivity for both Pd- and Rh-catalyzed decarbonylation systems than that found by use of either the corresponding carboxylic acid alone or preformed symmetrical anhydride. For comparative purposes, analogous experiments utilizing the corresponding acid chloride and aldehyde were also carried out. It should be emphasized that heating an equimolar mixture of decanoic acid and Ac_2O without any

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[2] (a) Tsuji, J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. II, pp 595–654. (b) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978,** *100,* 7083. (c) Doughty, D. H.; Pignolet, L. H. In *Homogeneous Catalysis With Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 343–376 and references contained therein. (d) Belani, R. M.; James, B. R.; Dolphin, D.; Rettig, S. J. *Can. J. Chem.* **1988,** *66,* 2072. (e) Andrews, M. A.; Gould, G. L.; Klaeren, S. A. *J. Org. Chem.* **1989,** *54,* 5257. (f) Abu-Hasanayn, F.; Goldman, M. E.; Goldman, A. S. *J. Am. Chem. Soc.* **1992,** 114, 2520. (g) O'Connor, J. M.; Ma, J. *J. Org. Chem.* **1992,** *57,* 5075.

[3] (a) Prince, R. H.; Raspin, K. A. *J. Chem. Soc., Chem. Commun.* **1966,** 156. (b) Fenton, D. M. U.S. Patent 3,530,198, 1970. (c) Foglia, T. A.; Barr, P. A. *J. Am. Oil Chem. Soc.* **1976,** *53,* 737.

[4] The oxidative addition of anhydrides to Rh(I)–phosphine complexes, including the isolation and characterization of the resultant Rh(III) acyl derivatives, has recently been reported: Miller, J. A.; Nelson, J. A. *Organometallics* **1991,** *10,* 2958.

[5] The exact composition of the carboxylic acid/Ac_2O mixture clearly depends upon many factors, including temperature and volatilization of lower boiling components from the solution. For instance, an equimolar solution of decanoic acid/Ac_2O was determined by ^1H-NMR analysis to contain an 87:13:0 molar composition of n-$C_9H_{19}CO_2H$–n-$C_9H_{19}CO_2Ac$–$(n$-$C_9H_{19}CO)_2O$ after 30 min at 30 °C. Upon heating at 250 °C and allowing volatile materials to distill away, the ratio changed to 14:22:64 after ca. 1 min and 9:9:82 after 30 min.

[6] The presence of CO in the effluent gas was confirmed by FT-IR analysis.

[7] The remainder of the C_9-product mixture consisted of *trans*- and *cis*-2-nonene in a relative ratio of ca. 3:1.

[8] At the conclusion of the reaction, the spent Pd catalyst is present as an easily recoverable black powder. Due to the low concentration of Pd catalyst preferably employed in these carboxylic acid decarbonylation/dehydration reactions, carrying out the transformation in a continuous fashion also provides for the generation of larger and more conveniently recovered quantities of Pd. This recovered Pd has, in fact, been reconverted into 1[9] and utilized in subsequent runs.

[9] Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985.

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Table I. Comparison of Various Functional Groups and Substrates in Their Pd- or Rh-Catalyzed Decarbonylation/ Dehydration to Terminal Olefins[a]

	Pd catalyst[b]			Rh catalyst[c]		
substrate	C_{n-1} olefin α-selectivity (%)	TON	TON/h	C_{n-1} olefin α-selectivity (%)	TON	TON/h
n-$C_{11}H_{23}COCl$	76.0	50	100	27.7	1,330	400
n-$C_{11}H_{23}CHO$	*d*	20	40	*d*	240	75
n-$C_9H_{19}CO_2H$		*e*		97.9	190	11
n-$C_{11}H_{23}CO_2H$		*e*		78.6	60	6
$(n$-$C_9H_{19}CO)_2O$	91.6	4310	26 000	97.1	430	24
$(n$-$C_{11}H_{23}CO)_2O$	83.7	1260	7500	86.7	280	27
n-$C_9H_{19}CO_2H/Ac_2O$	97.3	12 370	16 500	97.2	710	110
n-$C_{11}H_{23}CO_2H/Ac_2O$	94.3	7350	17 600	96.9	700	130

[a] All reactions were carried out at 250 °C (oil bath temperature) under a slight flow of N_2, in a manner similar to that described in the text. Catalyst concentrations indicated below are relative to the initial amount of substrate present. Analyses were carried out by GC using n-decane as an internal standard. [b] Pd catalyst: $(Ph_3P)_2PdCl_2$ (0.01 mol %) and added Ph_3P (0.50 mol %). [c] Rh catalyst: $(Me_2PhP)_2Rh(CO)Cl$ (1.0 mol %). [d] The product consisted of a ≥95:5 ratio of undecane–1-undecene. [e] Little or no detectable reaction (TON < 5).

catalyst present at 250 °C for 8 h produced <0.1% 1-nonene.[10] It is readily apparent from Table I that superior terminal olefin selectivities and catalyst TONs were obtained for the C_{10}-substrates relative to the analogous C_{12}-derivatives. These observations reflect the shorter residence time of the more volatile olefin product in the reactor.[11] Notably, while $(Me_2PhP)_2Rh(CO)Cl$ **2**[12] promoted a faster rate of decarbonylation and led to a higher catalyst TON for lauroyl chloride than for the combination of lauric acid and Ac_2O, the selectivity toward terminal alkene with the former substrate was substantially lower (27.7% vs 96.9%).[14] This enhanced α-olefin selectivity marks a distinct advantage of the carboxylic acid/ Ac_2O decarbonylation system over the previous acid chloride-based methodology.

As noted above, efficient removal of the olefin product from the reaction solution is essential to ensure a high degree of terminal olefin selectivity. Therefore, upon extending this chemistry to substrates that liberate higher boiling alkene products, the reaction should be carried out under reduced pressure in order to allow the olefin to readily distill from the reactor upon formation. Using this approach, we have successfully converted stearic acid → 1-heptadecene (250 °C, 40 Torr) and myristic acid → 1-tridecene (250 °C, 150 Torr) by utilizing both **1** and **2** as catalyst, with TONs and α-olefin selectivities similar to that derived above for the decanoic acid → 1-nonene transformation. Furthermore, this chemistry can be remarkably chemoselective and is applicable to functionalized substrates. For example, decarbonylation/dehydration of adipic acid monomethyl ester/Ac_2O (1:1 molar ratio) using **2** cleanly produced methyl 4-pentenoate (97.9% α-olefin selectivity, TON = 220), signifying the stability of the ester functionality to these reaction conditions. Moreover, by means of simple adjustments in reaction conditions (such as the substrate/Ac_2O stoichiometry and the pressure at which the reaction is carried out), the decarbonylation/dehydration of an α,ω-dicarboxylic acid can be selectively accomplished in a stepwise- or complete manner. Thus, reaction of suberic acid/Ac_2O (1:1) with **2** at 250 °C under a slight vacuum (100 Torr) produced 6-heptenoic acid (>98% α-selectivity, TON = 370). Conversely, reaction of a 1:2 molar ratio of sebacic acid/Ac_2O with **2** at 250 °C and atmospheric pressure directly afforded 1,7-octadiene (92.8% α,ω-selectivity, TON = 470 based on conversion of acid groups).

The nature of the phosphine ligand has a moderate degree of influence with regard to both the catalyst lifetime and product α-olefin selectivity for the Rh-based catalyst systems. As an example, the decarbonylation/dehydration of decanoic acid/Ac_2O (1:1) with $P_2Rh(CO)Cl$ (1 mol % based on the decanoic acid charge; 250 °C) produced 1-nonene with α-olefin selectivities and catalyst TONs, respectively, varying from 97.2%/710 (P = Me_2PhP) to 92.0%/245 (P = Ph_3P) to 93.9%/790 (P = o-Tol_3P)[15] to 91.2%/225 [P = $(C_6H_{11})_2PhP$][16] using catalysts composed of the indicated phosphine ligands. On the other hand, variation of the phosphine group in the P_2PdCl_2-catalyzed decarbonylation/dehydration of carboxylic acids provided some deviation in catalyst lifetime, but virtually no change in α-olefin selectivity. Hence, conversion of decanoic acid/ Ac_2O (1:1) → 1-nonene (0.01 mol % P_2PdCl_2 and 0.50 mol % P with respect to the initial charge of decanoic acid; 250 °C) resulted in product terminal olefin selectivities and TONs of 97.3%/26 100 [P = $(C_6H_{11})_2PhP$],[17] 97.3%/12 370 (P = Ph_3P), 98.1%/9450 (P = o-Tol_3P),[18] and 97.9%/12 700 (P_2 = $Ph_2PCH_2CH_2PPh_2$).[19] The presence of excess phosphine ligand is very important to achieve high catalyst efficiency and product α-selectivity in the Pd-mediated decarbonylation/dehydration of carboxylic acid/Ac_2O

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(10) GC analysis of this reaction mixture also showed formation of the two ketone byproducts, 2-undecanone and 10-nonadecanone. Hence, these materials must not originate from catalyst-mediated transformations and are most likely produced via thermolysis of the corresponding mixed and symmetrical anhydrides (e.g., loss of CO_2).

(11) The notion that olefin isomerization is primarily due to a secondary interaction with the catalyst and related to the duration of the product in the reaction mixture is supported by the following experiment: An equimolar mixture of lauric acid/Ac_2O, containing **1** (0.01 mol %) and added Ph_3P (50 equiv per Pd), was heated at 250 °C and the olefin product distilled from the reactor. The feed mixture of lauric acid/Ac_2O that was continuously added to the reactor (in a rate approximately equal to that of product removal) also contained 10 mol % each (relative to lauric acid) of 1-nonene (≥99.8% purity) and 1-tridecene (≥99% purity). Analysis of the distillate product at the conclusion of the reaction showed the following α-olefin selectivities: 1-nonene (99.3%), 1-undecene (96.2%), and 1-tridecene (94.3%).

(12) An alternative procedure to that reported in the literature[13] was utilized for the preparation of **2**: A solution of $[RhCl(CO)_2]_2$ (1.00 g, 2.57 mmol) in toluene (15 mL) was treated at 25 °C under N_2 with Me_2PhP (1.61 mL, 11.3 mmol) and the solution stirred for 5 min. Hexane (15–20 mL) was then added in one portion and, after the reaction mixture was cooled to 0 °C, the resulting precipitate was collected. Recrystallization from toluene–hexane gave 1.71 g (75%) of **2** as small yellow needles, mp 106–110 °C dec; $IR_{(CO)}$ = 1977 cm^{-1} (KBr).

(13) Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1437.

(14) The lower 1-alkene selectivity obtained from decarbonylation of the acid chloride substrate may be due to isomerization of the initially formed terminal olefin product by the HCl coproduced in the reaction.

(15) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

(16) Prepared by a procedure similar to that described for **2**.[12] The crude material was recrystallized from chloroform–ethanol to provide the pure product as small yellow crystals: dec ≥260 °C; $IR_{(CO)}$ = 1966 cm^{-1} (KBr).

(17) Prepared from reaction of $(CH_3CN)_2PdCl_2$ with $(C_6H_{11})_2PhP$ (2.1 equiv) in benzene (reflux, 30 min). The product was precipitated from benzene–ethanol by addition of pentane (76% yield).

(18) Zhang, H. X.; Guibe, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

mixtures. Interestingly, while excess phosphine did not retard the rate of these Pd-catalyzed decarbonylation reactions, its presence did markedly slow the turnover frequency of the analogous Rh-catalyzed reactions. The existence of a constant low-level concentration of phosphine ligand in the reaction mixture (achieved by placing a small quantity of a relatively volatile phosphine in the carboxylic acid/Ac_2O feed) did, however, lead to a significantly increased lifetime for a Rh catalyst without adversely affecting the overall reaction rate. In this manner, the TON for the decarbonylation/dehydration of decanoic acid/Ac_2O catalyzed by **2** (1.0 mol % **2** relative to the initial amount of decanoic acid; 0.5 mol % Me_2PhP in the decanoic acid/Ac_2O feed mixture; 250 °C) was extended from 710 to 5910 and afforded >99% pure 1-nonene product.

The results described herein provide for an extraordinarily efficient and selective preparation of 1-alkenes via decarbonylation/dehydration of the corresponding carboxylic acids. It is noteworthy that the linear α-olefins commercially produced today are all composed of an *even* number of carbon atoms since they are manufactured by ethylene oligomerization processes. Hence, this new chemistry is complimentary in that naturally derived and readily available fatty acids, such as lauric, myristic, palmitic, stearic, etc., all afford linear α-olefin products composed of *odd* carbon chain lengths. The overall process may be viewed as one capable of producing a potentially important class of petrochemicals from renewable resources.

Supplementary Material Available: Complete experimental procedures for all of the carboxylic acid/Ac_2O → 1-alkene transformations reported, including the conversions of decanoic acid → 1-nonene and stearic acid → 1-heptadecene carried out in a continuous fashion (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(19) An interesting finding is that Pd(II) derivatives function much more efficiently as carboxylic acid decarbonylation catalysts than do the corresponding preformed Pd(0) compounds. For example, comparison of $(Ph_3P)_2PdCl_2$ with $(Ph_3P)_4Pd$ for the conversion of decanoic acid/Ac_2O → 1-nonene (using 50 equiv of added Ph_3P per Pd in each case) showed TONs of 12 370 and 1550, respectively, for the Pd(II) and Pd(0) catalysts. Selectivity toward 1-nonene formation was the same (97.3%) for both systems.