Tetrahedron Letters 51 (2010) 3712–3715

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Selective preparation of terminal alkenes from aliphatic carboxylic acids by a palladium-catalysed decarbonylation–elimination reaction

Jérôme Le Nôtre[a], Elinor L. Scott[a,*], Maurice C. R. Franssen[b], Johan P. M. Sanders[a]

[a] Valorisation of Plant Production Chains, Wageningen University and Research Centre, PO Box 17, 6700 AA Wageningen, The Netherlands
[b] Laboratory of Organic Chemistry, Wageningen University and Research Centre, Dreijenplein 8, 6703 HB Wageningen, The Netherlands

ARTICLE INFO

Article history:
Received 18 March 2010
Revised 21 April 2010
Accepted 7 May 2010
Available online 12 May 2010

Keywords:
Decarbonylation
Fatty acids
Palladium
Terminal alkenes

ABSTRACT

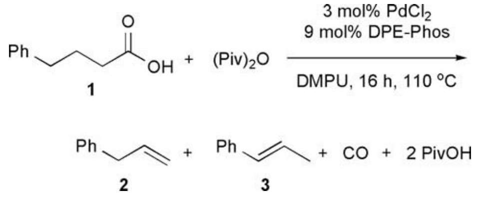
Trialkylamines were used as additives in the decarbonylation–elimination reaction catalysed by the combination of palladium(II) chloride and DPE-Phos. Aliphatic carboxylic acids were transformed at relatively low temperature into terminal alkenes in high yield and high selectivity, without the need for distillation, thereby avoiding isomerisation.

In recent years, biofuels have received significant interest due to the depletion of fossil feedstocks and the need for a reduction of carbon dioxide emission.[1] While bioethanol is the most important, fatty esters derived from renewable resources can also be used effectively as a transportation fuel. Fatty esters are easily prepared from vegetable oils by transesterification with alcohols.[2] However, a drawback is their reduced compatibility with conventional engines. Therefore, a more suitable approach consists of their transformation into high quality hydrocarbons.

Elimination of oxygen is required to convert fatty acids into hydrocarbons, for which several options are available. Catalytic deoxygenation reactions such as decarboxylation reactions can be performed using heterogeneous catalysts at high temperatures.[3–7] Conventional hydrotreating catalysts such as CoMo or NiMo,[4] as well as palladium on carbon,[5] platinum on alumina,[6] or zeolite[7] have been used to convert fatty acids or esters into alkanes. In addition, homogeneous catalysts based on palladium and rhodium can also be employed in deoxygenation reactions, following a different mechanistic pathway which allows the conversion of carboxylic acids into alkenes with the production of carbon monoxide and water.[8]

Decarbonylation/dehydration reactions have been scarcely studied, even though they would constitute a useful tool in organic synthesis. Performing the transformation selectively is a challenge in itself, since isomerisation into internal alkenes is thermodynamically favoured. High selectivity towards the 1-alkene is indeed difficult to achieve, especially with homogeneous catalysts, because of the high temperature needed for the reaction (200–280 °C).[8a,b] Heterogeneous catalysts also give modest selectivities (70–85%). In the latter case the alkene is distilled from the reaction mixture directly upon its formation, thereby reducing the risk of isomerisation.[8c] However, combining homogeneous catalysts such as palladium and rhodium salts with continuous distillation of the products during the reaction afforded selectivities above 95%.[8d] Alternatively, the reaction is stopped before completion. With a palladium-catalysed system (Scheme 1), high selectivity towards the 1-alkene **2** can only be achieved by stopping the reaction at a conversion of 85%; the product was isolated in a yield of 66%.[8e]

In our current research on converting biomass into bulk chemicals, we are concentrating our efforts on the transformation of amino acids, obtained from protein waste streams of biofuels production, into products for the chemical and plastics industries.[9] In particular, we focused our work on decarboxylation reactions, and showed for instance that glutamic acid, which can be obtained from the waste stream of bioethanol production, can be converted



Scheme 1. Decarbonylation/dehydration reaction of 4-phenylbutyric acid (**1**).

---

* Corresponding author. Tel./fax: +31 317 483011.
E-mail address: elinor.scott@wur.nl (E.L. Scott).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.05.018

enzymatically into 4-aminobutyric acid in an economically viable process.[9b]

Herein we report a catalytic method to fully convert aliphatic carboxylic acids into terminal alkenes in high yields and with high selectivities without the need for continuous distillation of the products. Trialkylamines are used as additives to stabilise the catalytic species and the reaction can proceed without isomerisation of the terminal double bond at relatively low temperatures (ca. 100 °C).

In the article of Gooßen and Rodriguez,[8e] palladium(II) chloride was used as the catalyst source with a bidentate phosphine ligand, bis(2-diphenylphosphinophenyl)ether (DPE-Phos) (Scheme 1). An excess of pivalic anhydride led to the in situ formation of a mixed anhydride with the substrate, which underwent a decarbonylation/dehydration reaction to form the corresponding alkene, carbon monoxide and pivalic acid. No distillation set-up was used, but the reaction had to be stopped before completion to avoid any isomerisation of the product (Table 1, entry 1). Indeed, when we repeated these experiments and allowed the reaction to reach complete conversion, the selectivity of 97:3 in favour of 1-alkene **2** decreased to 85:15 (Table 1, entry 2). In their research, Gooßen et al. tried to improve the selectivity by using different additives, but the addition of bases such as potassium carbonate and pyridine did not enhance the selectivity towards terminal alkenes (Table 1, entry 3).

It is known that alkylamines can have a positive effect on palladium-catalysed reactions.[10] They can play a role in reduction of the palladium(II) species and facilitate the formation of a palladium(0) active species.[11] In addition, they are suspected to play a role in the stabilisation of key palladium(II) intermediate species by coordination.[12] Therefore, we decided to use triethylamine as an additive in the catalytic system for the decarbonylation/dehydration reaction.[13] By using 1 equiv of triethylamine, full conversion was obtained after 18 h at 110 °C, the 1-alkene selectivity reached 99:1, and allylbenzene was isolated in 97% yield (Table 1, entry 4). The effect of trialkylamines on the catalytic system was then studied by changing the nature and the quantity of the base (Table 1, entries 5–11). In all the experiments the conversion was complete after 18 h at 110 °C. Triethylamine was used in excess compared to the substrate and it did not affect the 1-alkene:2-alkene selectivity, which remained above 95% (Table 1, entries 5 and 6). The use of a catalytic amount of base (9 mol % triethylamine) had the same positive effect as the use of 1 equiv and 98% selectivity was obtained (Table 1, entry 7). Thus, it appears that triethylamine only has an influence on the catalyst species, probably by activation and stabilisation, and is not involved in the catalytic cycle as a reactant. A variety of trialkylamines were tested as additives in catalytic amounts, and for all reactions, the selectivity towards the 1-alkene remained high, between 92% and 98% (Table 1, entries 8–11).

Table 1
Effect of base additive on the decarbonylation/dehydration reaction[a]

Entry	Base	Quantity	Conversion[b] (%)	Selectivity[b] **2/3**
1[c]	–	–	85	97:3
2	–	–	100	85:15
3[c]	Pyridine	1.0 mmol	80	70:30
4	Et_3N	1.0 mmol	100	99:1
5	Et_3N	2.0 mmol	100	98:2
6	Et_3N	3.0 mmol	100	99:1
7	Et_3N	9 mol %	100	99:1
8	nPr$_3$N	9 mol %	100	99:1
9	nBu$_3$N	9 mol %	100	96:4
10	TMEDA[d]	9 mol %	100	97:3
11	DBU[e]	9 mol %	100	99:1

[a] *Reactions conditions*: 1.0 mmol 4-phenylbutyric acid (**1**), 2.0 mmol pivalic anhydride, 3 mol % $PdCl_2$, 9 mol % DPE-Phos, DMPU, 110 °C, 18 h.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Literature result.[8e]
[d] *N,N,N′,N′*-Tetramethylethylenediamine.
[e] 1,8-Diazabicyclo[5.4.0]undec-7-ene.

A closer investigation of the catalytic system was then performed. A decrease in the palladium loading to 1 mol % had a dramatic effect on the reaction with a drop in conversion down to 35% after 18 h. In the same way, a decrease of the phosphine/palladium ratio had a similar consequence. Concerning the reaction conditions, the use of triethylamine also positively influenced the kinetics of the reaction. A conversion of 85% was obtained after 16 h reaction at 110 °C without additive (Table 1, entry 1), the presence of triethylamine gave the same level of conversion and selectivity after only 8 h at the same temperature (Table 2, entry 2). The reaction temperature could also be decreased to 90 °C without affecting the conversion and the selectivity (Table 2, entry 3), but a lower temperature appeared to be detrimental (Table 2, entry 4).

In their report, Gooßen and Rodriguez used pivalic anhydride as a reactant to form in situ mixed anhydride **4** (R′ = *t*-Bu) with the substrate.[8e] They explained that the new anhydride then adds oxidatively to the palladium(0) catalyst to form the less sterically demanding acyl complex **5**, which then undergoes a decarbonylation step in the catalytic cycle (Scheme 2, Pathway A).

However, acetic anhydride has been used previously in decarbonylation/dehydration reactions of carboxylic acids, and Miller et al. showed that it led to high yields and good selectivity at high temperature (250 °C).[8d] These results indicated that the steric effect of the mixed anhydride formed with the substrate (Scheme 2, Pathway A when R′ = Me) probably had no influence on the mechanistic pathway. These authors also explained that at high temperature, a new anhydride **6** could be formed by the substrate only. From this, one can conclude that oxidative addition to palladium(0) to obtain the acyl complex **5** is not determined by steric effects (Scheme 2, Pathway B). An additional advantage of using acetic anhydride is its ready availability and lower price compared to pivalic anhydride.

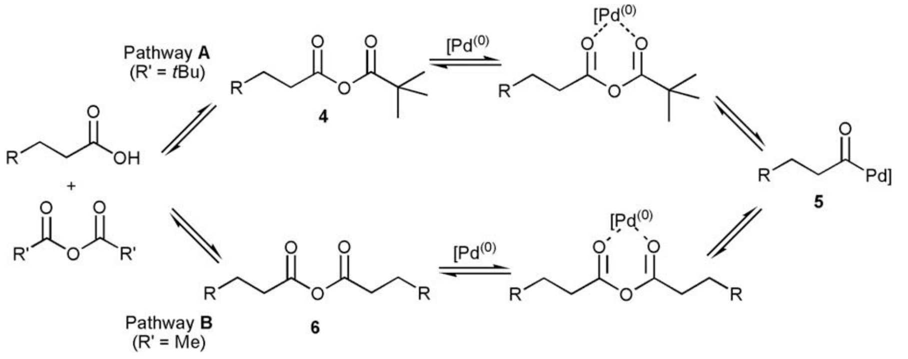
Hence, we decided to perform the reaction by substituting pivalic anhydride with acetic anhydride and we obtained comparable results as previously with full conversion and a selectivity of 97% for the 1-alkene **2** (Scheme 3). This result indeed proves that the presence of a bulky group on the anhydride reagent is not necessary.

According to Gooßen and Rodriguez,[8e] a highly polar solvent such as DMPU is needed to obtain the best turnovers and the highest selectivities. This was confirmed in our studies, since no solvent better than DMPU was found. Reactions using acetic anhydride as solvent only gave poor conversions. However, interesting results were obtained with acetonitrile. This solvent not only allowed a good conversion at reflux temperature but also provided a switch of selectivity, which reached 92% in favour of the 2-alkene **3**, and the configuration of the olefin was mainly (*E*) [(*E*)/(*Z*) = 92:8] (Scheme 4). It is possible that a highly efficient isomerisation catalyst, such as bis(acetonitrile)palladium(II) chloride, was formed to some extent in the reaction mixture.[14]

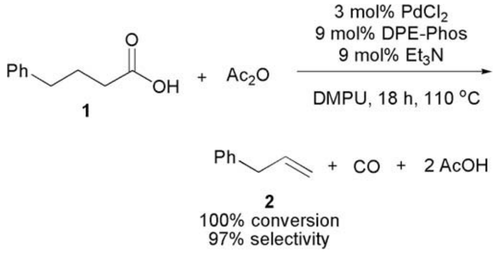
Table 2
Reaction conditions for the decarbonylation/dehydration reaction[a]

Entry	T (°C)	Time (h)	Conversion[b] (%)	Selectivity[b] **2/3**
1	110	6	74	98:2
2	110	8	81	96:4
3	90	18	100	95:5
4	70	18	20	99:1

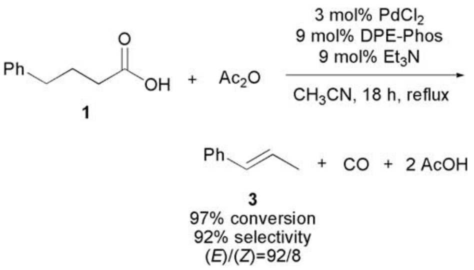
[a] *Reactions conditions*: 1.0 mmol 4-phenylbutyric acid (**1**), 2.0 mmol pivalic anhydride, 3 mol % $PdCl_2$, 9 mol % DPE-Phos, 9 mol % Et_3N, DMPU.
[b] Determined by ^{1}H NMR spectroscopy.



Scheme 2. Anhydride formation and insertion of palladium(0) in the first step of the two possible mechanisms.



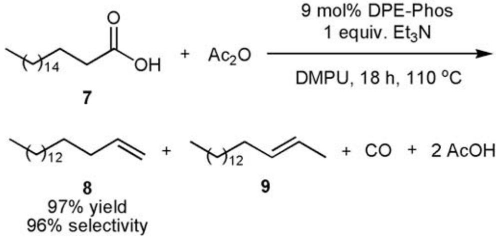
Scheme 3. Decarbonylation–elimination reaction using acetic anhydride.



Scheme 4. Decarbonylation–elimination reaction in acetonitrile.

We next focused our efforts on the application of the new catalytic system to the transformation of fatty acids. Using the optimum reaction conditions the transformation of stearic acid **7** was performed (Scheme 5). Full conversion was obtained with 1 equiv of triethylamine as an additive and the corresponding olefins **8** and **9** were isolated in 97% yield with a selectivity of 96% for 1-heptadecene **8**. The reaction was repeated in acetonitrile and an inversion of selectivity, albeit modest, was observed with a ratio 1-heptadecene/2-heptadecene of 41:59.

In conclusion, we have developed a palladium-catalysed reaction allowing the transformation of aliphatic carboxylic acids into terminal alkenes in high yield and high selectivity. The use of trialkylamines as additives had a drastic effect on the stability of the catalytic species avoiding olefin isomerisation during the reaction. We showed that the less expensive acetic anhydride can be use as a reactant for the decarbonylation–elimination reaction at relatively low temperature, and that the reaction can be applied to the deoxygenation of fatty acids into unsaturated hydrocarbons. Moreover, the side products of the reaction (carbon monoxide and acetic acid) can be eventually recycled, which shows the advantages of this approach compared to standard deoxygenation where carbon dioxide is produced. We are continuing to extend the scope of this reaction towards the conversion of biomass into bulk chemicals.



Scheme 5. Decarbonylation–elimination reaction of stearic acid (**7**).

Acknowledgement

We are grateful to the NWO-ACTS-ASPECT program for financial support.

References and notes

1. (a) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044; (b) Huber, G. W.; Corma, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7184.
2. (a) Ma, F.; Hanna, M. H. *Bioresour. Technol.* **1999**, *70*, 1; (b) Xie, W.; Peng, H.; Chen, L. *Appl. Catal., A* **2006**, *300*, 67; (c) Ramadhas, A. S.; Jayaraj, S.; Muraleedharan, C. *Fuel* **2005**, *84*, 335.
3. (a) Maier, W.; Roth, W.; Thies, I.; van Ragué Schleyer, P. *Chem. Ber.* **1982**, *115*, 808; (b) Snåre, M.; Kubickova, I.; Mäki-Arvela, P.; Eränen, K.; Murzin, D. Yu. *Ind. Eng. Chem. Res.* **2006**, *45*, 5708; (c) Kubickova, I.; Snåre, M.; Eränen, K.; Mäki-Arvela, P.; Murzin, D. Yu. *Catal. Today* **2005**, *106*, 197.
4. (a) Laurent, E.; Delmon, B. *Appl. Catal., A* **1994**, *109*, 77; (b) Kubička, D.; Šimáček, P.; Žilková, N. *Top. Catal.* **2009**, *52*, 161; (c) Liu, Y.; Sotelo-Boyás, R.; Murata, K.; Minowa, T.; Sakanishi, K. *Chem. Lett.* **2009**, *38*, 552.
5. (a) Lestari, S.; Mäki-Arvela, P.; Simakova, I.; Beltramini, J.; Lu Max, G. Q.; Murzin, D. Yu. *Catal. Lett.* **2009**, *130*, 48; (b) Mäki-Arvela, P.; Kubickova, I.; Snåre, M.; Eränen, K.; Murzin, D. Yu. *Energy Fuels* **2007**, *21*, 30; (c) Mäki-Arvela, P.; Snåre, M.; Eränen, K.; Myllyoja, J.; Murzin, D. Yu. *Fuel* **2008**, *87*, 3543.
6. Do, P. T.; Chiappero, M.; Lobban, L. L.; Resasco, D. E. *Catal. Lett.* **2009**, *130*, 9.
7. (a) Danuthai, T.; Jongpatiwut, S.; Rirksomboon, T.; Osuwan, S.; Resasco, D. E. *Appl. Catal., A* **2009**, *361*, 99; (b) Scheibel, J. J.; Reilman, R. T. PCT Int. Appl. WO2007136873, 2007; *Chem. Abstr.* **2008**, *148*, 35396.
8. (a) Fenton, D. M. U.S. Patent 3,530,198, 1970; *Chem. Abstr.* **1970**, *73*, 130601.; (b) Foglia, T. A.; Barr, P. A. *J. Am. Oil Chem. Soc.* **1976**, *53*, 737; (c) Stern, R.; Hillion, G. U.S. Patent 4,554,397, 1985; *Chem. Abstr.* **1985**, *103*, 70934.; (d) Miller, J. A.; Nelson, J. A.; Byrne, M. P. *J. Org. Chem.* **1993**, *58*, 18; (e) Gooßen, L. J.; Rodriguez, N. *Chem. Commun.* **2004**, 724.
9. (a) Könst, P. M.; Franssen, M. C. R.; Scott, E. L.; Sanders, J. P. M. *Green Chem.* **2009**, *11*, 1646; (b) Lammens, T. M.; De Biase, D.; Franssen, M. C. R.; Scott, E. L.; Sanders, J. P. M. *Green Chem.* **2009**, *11*, 1562.
10. Muzart, J. *J. Mol. Catal. A* **2009**, *308*, 15.
11. Vollmüller, F.; Mägerlein, W.; Klein, S.; Krause, J.; Beller, M. *Adv. Synth. Catal.* **2001**, *343*, 29.
12. Damez, C.; Estrine, B.; Bessmertnykh, A.; Bouquillon, S.; Hénin, F.; Muzart, J. *J. Mol. Catal. A* **2006**, *244*, 93.
13. *General procedure for the decarbonylation/elimination reaction of carboxylic acids in the presence of trialkylamines*: In a Schlenk tube under a nitrogen atmosphere were introduced palladium(II) chloride (3 mol %), bis(2-diphenylphosphinophenyl)ether (DPE-Phos, 9 mol %) and carboxylic acid (1 equiv). Anhydrous DMPU (4 mL) was then added followed by Ac$_2$O (2 equiv) and the trialkylamine (1 equiv or 9 mol %). The reaction mixture was heated at 110 °C for 18 h. After completion of the reaction, Et$_2$O (ca. 10 mL) was added and the organic layer

was washed with saturated $\mathrm{NH_4Cl}$ solution followed by $\mathrm{H_2O}$ and brine. Evaporation of the solvent afforded a crude mixture, which was analysed by ^{1}H NMR spectroscopy to determine the conversion. The crude was purified by filtration through a plug of silica gel using hexane as an eluent. After concentration to dryness the product was obtained as a colourless oil.

3-Phenyl-1-propene (**2**): Colourless oil; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.24–7.18 (m, 2H, aryl), 7.14–7.08 (m, 3H, aryl), 5.95–5.84 (m, 1H, $\mathrm{CH_2}\mathit{CH}{=}\mathrm{CH_2}$), 5.03–4.96 (m, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2$), 3.31 (d, 2H, *J* = 6.7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 140.0, 137.4, 128.5, 128.4, 126.0, 115.7, 40.2; MS (EI): *m*/*z* (%) = 118 (60) [M$^+$], 117 (100), 91 (60), 65 (52), 63 (45), 62 (14), 51 (64), 50 (39), 39 (90).

Trans-1-phenyl-1-propene (**3**): Colourless oil; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.34–7.24 (m, 4H, aryl), 7.22–7.14 (m, 1H, aryl), 6.45–6.36 (m, 1H, $\mathrm{PhC}\mathit{H}{=}\mathrm{CHCH_3}$), 6.22 (dq, 1H, *J* = 15.7 Hz, *J* = 6.5 Hz, $\mathrm{PhCH{=}C}\mathit{H}\mathrm{CH_3}$), 1.87 (dd, 3H, *J* = 6.5 Hz, *J* = 1.6 Hz, $\mathrm{PhCH{=}CHC}\mathit{H}_3$); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 137.2, 130.8, 128.1, 125.8, 125.6, 125.4, 18.1; MS (EI): *m*/*z* (%) = 118 (65) [M$^+$], 117 (100), 115 (35), 91 (34), 65 (12), 63 (15), 51 (34), 50 (26), 39 (36).

1-Heptadecene (**8**): Colourless oil; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 5.86–5.76 (m, 1H, $\mathrm{CH_2}\mathit{CH}{=}\mathrm{CH_2}$), 4.98 (br d, 1H, *J* = 17.1 Hz, *trans*-$\mathrm{CH_2CH{=}C}\mathit{H}_2$), 4.92 (br d, 1H, *J* = 10.2 Hz, *cis*-$\mathrm{CH_2CH{=}C}\mathit{H}_2$), 2.07–2.00 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 1.40–1.22 (m, 26H), 0.88 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 139.2, 114.1, 33.8, 32.0, 29.72, 29.70, 29.68, 29.65, 29.5, 29.4, 29.2, 29.0, 22.7, 14.1; MS (EI): *m*/*z* (%) = 238 (6) [M$^+$], 125 (10), 111 (18), 98 (10), 97 (38), 85 (12), 84 (22), 83 (50), 82 (20), 71 (31), 70 (42), 69 (58), 68 (16), 67 (15), 57 (81), 56 (57), 55 (89), 54 (22), 43 (100), 42 (34), 41 (92), 40 (15).

14. Yu, J.; Gaunt, M. J.; Spencer, J. B. *J. Org. Chem.* **2002**, *67*, 4627.