

## Catalytic properties of the Pd/C – triethylamine system

Yoann Coquerel\* and Jean Rodriguez\*

Aix-Marseille Université, Institut des Sciences Moléculaires de Marseille, ISM2 - UMR CNRS  
6263, Centre Saint Jérôme, Service 531, 13397 Marseille Cedex 20, France

E-mail: [yoann.coquerel@univ-cezanne.fr](mailto:yoann.coquerel@univ-cezanne.fr) and [jean.rodriguez@univ-cezanne.fr](mailto:jean.rodriguez@univ-cezanne.fr)

---

### Abstract

In the presence of Pd/C and a catalytic amount of triethylamine, allylic alcohols are isomerized into the corresponding carbonyl compounds. The isomerization is accompanied by Pd/C-catalyzed redox processes to give the saturated alcohol and the corresponding  $\alpha,\beta$ -unsaturated ketone. Pd/C also catalyses the conjugate reduction of activated double bonds, using triethylamine as the source of the two newly incorporated hydrogen atoms, probably via a hydrido complex. During the reaction, the triethylamine undergoes unexpected Pd/C-catalyzed oligomerization to produce elongated aliphatic tertiary amines and ethylamine, which, in the conjugate reduction of  $\alpha,\beta$ -unsaturated esters, resulted in the formation of the reduced ethylamides following a domino transamidation.

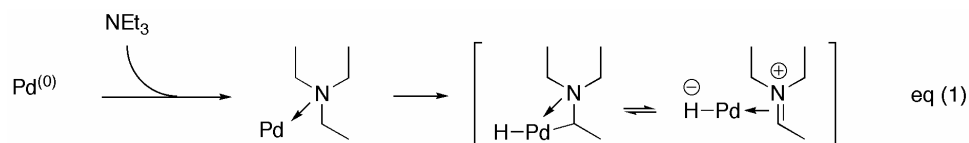
**Keywords:** Heterogeneous catalysis, palladium, triethylamine, isomerization, conjugate reduction, self-alkylation

---

### Introduction

When an alkyl amine is involved as a reactant, a reagent, or an additive in a palladium-catalyzed reaction, unexpected isomerizations and/or reductions are sometimes observed.<sup>1</sup> The formation of these side-products has been rationalized by invoking a hydrido-palladium iminium complex generated from the palladium catalyst and the alkyl amine. Although the chemical properties of the iminium moiety of the complex have been studied,<sup>2-6</sup> examples of the intentional exploitation of the hydrido moiety of the complex are scarce.<sup>7,8</sup> We reported recently that the suspected hydrido-palladium iminium complex generated from Pd/C and triethylamine (eq. 1) catalyses the isomerization of allylic alcohols into the corresponding carbonyl compounds, and that Pd/C catalyses the conjugate reduction of activated double bonds using triethylamine as the source of the two newly incorporated hydrogen atoms via the same complex.<sup>9</sup> A careful re-examination of these two reactions has revealed some Pd/C-catalyzed redox processes of allylic alcohols in the case of the isomerization reaction, and the *in situ* Pd/C-catalyzed production of ethylamine from

triethylamine. We now report our full detailed study on the catalytic properties of the Pd/C–NEt<sub>3</sub> system.



## Results and Discussion

### Isomerization of allylic alcohols

The isomerization of allylic alcohols into the corresponding carbonyl compounds is an important reaction.<sup>10</sup> This highly useful transformation is usually catalyzed by transition metal complexes, including, for the most generally used reagents, rhodium-, ruthenium-, and iron- compounds. For example, some elegant iron-catalyzed domino reactions have recently been reported for the synthesis of indanes and cyclopentenone derivatives.<sup>11</sup> However, a few examples of palladium catalyzed isomerization of allylic alcohols into carbonyl compounds have been reported,<sup>12</sup> and in close correlation with the present study, hydrogen pre-activated Pd/C was early recognized to be capable of isomerizing 4-penten-3-ol into 3-pentanone in the gas phase.<sup>13</sup> However, all attempts to isomerize allyl alcohols in the liquid-phase with Pd/C failed. We speculated that the suspected hydrido-palladium compound generated from Pd/C and triethylamine could effect the isomerization of allylic alcohols, and indeed 1-phenyl-2-propen-1-ol was mostly converted into propiophenone by heating at 70 °C in the presence of 5 mol.% of Pd/C and 10 mol.% of triethylamine for 22 hours (Table 1, entry 1). In this case, 8% of the reduced saturated product 1-phenylpropanol and 4% of the oxidized phenyl vinyl ketone were also formed. Nearly complete conversion and better selectivity were obtained on heating at 150 °C for 3 hours (entry 2). Similarly, 1-cyclohexyl-2-propen-1-ol was isomerized to the corresponding ketone (entry 3) with concomitant production of 17% of saturated product. Under the same conditions, 1-phenyl-2-methyl-2-propen-1-ol proved almost inert (entry 4), and 69% of the expected ketone was formed after 12 hours at 200 °C (entries 5), still with production of the redox products (9% and 13% for the reduced and unsaturated products, respectively). With 1-phenyl-3-buten-1-ol (a homoallylic alcohol), the expected ketone was formed in only 19% yield after 3 hours at 150 °C, together with 30% of the substituted allylic alcohol arising from the mono-isomerization (entry 6). Once again, quite a large proportion of the substrate was reduced to the saturated alcohol (9%) or oxidized to the *trans*-conjugated enone (18%). At higher temperature, 63% of the isomerized ketone was obtained, with 9% of the corresponding allylic alcohol, 19% of saturated alcohol, and 7% of conjugated enone (entry 7). A similar sharp decrease in the efficiency of the isomerization reaction with substituted allyl and homoallyl alcohols is observed with other, more commonly used, catalytic systems.<sup>10</sup> In the case of 4-phenyl-3-buten-2-ol, complete conversion could be obtained at slightly lower temperature and, as may now be expected, resulted in the formation of

the desired isomerized ketone, the saturated alcohol, and the corresponding enone, but this time the redox process was dominant, yielding a 1:1:1 mixture of the three products (entry 8). The prolonged heating of geraniol in the presence of a catalytic amount of Pd/C and triethylamine at 160 °C left the starting material totally unchanged (entry 9).

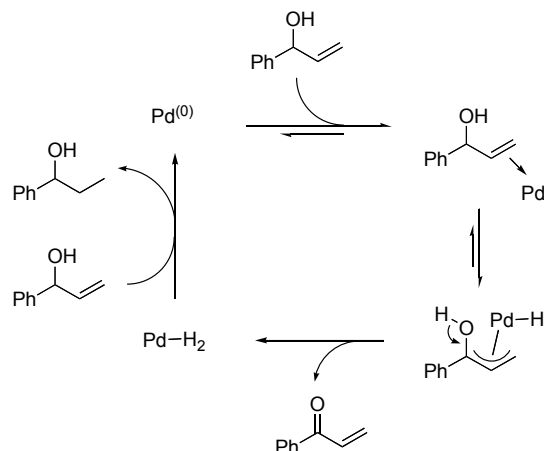
**Table 1.** Isomerization of allylic alcohols with Pd/C–NEt<sub>3</sub>

Entry	Substrate	Conditions <sup>a</sup>	Products	Yield (conversion) % <sup>b</sup>
1		70 °C, 22 h	+  +	67 + 8 + 4 (84)
2		150 °C, 3 h	+  +	91 + 5 + 1 (97)
3		150 °C, 3 h	+  +	72 + 17 + 1 (100)
4		150 °C, 3 h	+  +	3 + 1 + 1 (5)
5		200 °C, 12 h	+  +	69 + 9 + 13 (91)
6		150 °C, 3 h	+  +	19 + 30 + 9 + 18 (76)
7		200 °C, 12 h, 20 mol% NEt <sub>3</sub>	+  +  +	63 + 9 + 19 + 7 (98)
8		120 °C, 6 h, 20 mol% NEt <sub>3</sub>	+  +	34 + 34 + 32 (100)
9		160 °C, 72 h, 1 equiv. NEt <sub>3</sub>	-	0 (0)

<sup>a</sup>Unless stated otherwise, all reactions were conducted with 10% Pd/C (5 mol.% Pd) and 10 mol.% NEt<sub>3</sub> in 0.8-1.0 M dry toluene (sealed tube). <sup>b</sup>Yields and conversions were obtained by NMR analysis of the crude reaction mixture.

Similar redox properties of palladium species have previously been observed.<sup>14</sup> In order to determine the origin of the redox products, we carried out some control experiments. When propiophenone was treated with 5 mol.% of Pd/C at 150 °C for 12 h in *d*-8-toluene with 10 mol.% of triethylamine, or without triethylamine, no saturated alcohol or the  $\alpha,\beta$ -unsaturated ketone could be detected, and the substrate was recovered unchanged. This indicates that, under our conditions, the saturated alcohol co-product is not produced by reduction of the ketone product, and also that the enone co-product is similarly not the product of a Pd/C catalyzed

dehydrogenation of the ketone.<sup>15</sup> A second control reaction allowed us to rationalize our observations. When 1-phenyl-2-propen-1-ol was treated with 5 mol.% of Pd/C at 150 °C for 12 h in *d*-8-toluene without triethylamine, the resulting mixture was composed of 84% of the starting allylic alcohol, 9% of the corresponding  $\alpha,\beta$ -unsaturated enone, 7% of the saturated alcohol, and only a trace (<1%) of propiophenone. This last experiment clearly demonstrates that, in the conditions of our study, the redox products arise from a Pd/C-only catalyzed disproportionation of the allylic alcohol,<sup>14a</sup> and highlights the crucial role of triethylamine in the isomerization process. A plausible simplistic mechanism that accounts for the observed Pd/C-catalyzed disproportionation of allylic alcohols would involve a  $\pi$ -allyl hydrido-palladium complex (Scheme 1),<sup>16</sup> and the large amount of redox products obtained in the case of entry 8 might be explained by the facilitated formation of the  $\pi$ -allyl complex in this specific case. One should note that the analysis of by-products of the Pd/C-NEt<sub>3</sub> catalyzed isomerization of allylic alcohols presented herein has been rendered difficult by the propensity of the enone co-product to undergo Pd/C catalyzed conjugate reduction (see below).



**Scheme 1**

### Conjugate reduction of electro-deficient alkenes

Hydrido-palladium intermediates obtained by transmetalation of a metal hydride were reported to catalyze some conjugate reductions,<sup>17</sup> and more recently Sodeoka's group reported a palladium(II) catalyzed enantioselective conjugate reduction of enones using ethanol as hydride source.<sup>18</sup> To test the feasibility of conjugate reduction with the Pd/C-NEt<sub>3</sub> system, we initially examined the model reduction of *tert*-butyl acrylate and were pleased to find that reduction was achieved efficiently in the presence of 10 mol.% Pd/C and 1.2 equiv. of triethylamine at 140 °C (Table 2, entry 1). Benzylidene *tert*-butyl ketone could also be reduced efficiently, provided that an excess of triethylamine is used (entries 2-4). Benzylidene-acetone and cinnamionitrile were also reduced under these conditions (entries 5-7). The tricarbonyl(tropone)iron complex underwent the Pd/C catalyzed 1,4-conjugate reduction at 120 °C with moderate efficiency

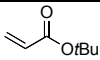

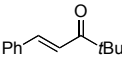
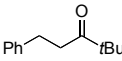
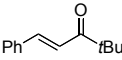
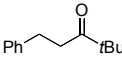
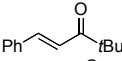
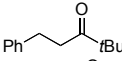
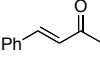

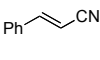

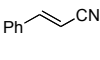

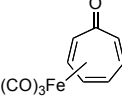
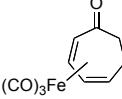
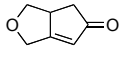
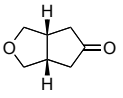
probably due to the competitive hydride addition to the carbonyl ligands (entry 8).<sup>19</sup> The trisubstituted double bond of a fused bicyclic cyclopentenone was also stereoselectively reduced (dr > 20:1) at 120 °C but still with concomitant degradation (entry 9). Some interesting observations arose from the reactions with an  $\alpha$ -chlorocyclopentenone and its acetal (entries 10 and 11, respectively). Indeed, in the case of entry 10, the conjugated reduction was followed by *in situ* dehydrohalogenation to restore the thermodynamically favored enone system. The reaction thus resulted in the net reduction of the  $\alpha$ -chlorocyclopentenone into a cyclopentenone,<sup>20</sup> and only a small amount of over-reduced product was observed, proving the chemoselective conjugate reduction of the  $\alpha$ -chloro-enone. The corresponding acetal was inert under the reaction conditions (entry 11), demonstrating that Pd/C neither catalyzes the dehydrogenation of triethylamine in the absence of a hydride acceptor,<sup>21</sup> nor the reduction of the vinylic chloride. We verified that Pd/C was not a catalyst for the reduction of electron-deficient alkenes using ethanol as the hydride source under the conditions of our study (entry 12). This result, compared to entry 1, clearly demonstrate that triethylamine is the source of the two newly incorporated hydrogen atoms during the reduction.

The case of *trans*-methyl cinnamate was particularly intriguing since the reaction resulted in the formation of a mixture of the expected reduced methyl ester (52%) and a non-negligible amount of the corresponding ethyl amide (11%) under the normalized conditions of the study (entry 13). Increasing the amount of triethylamine allowed higher conversion and better selectivity for the reduced ester (entry 14), while prolonged reaction times favored the amide product (entry 15). In order to optimize the formation of the amide product, reactions were performed at higher temperature (entry 16), and a prolonged reaction time combined with excess of triethylamine at 160 °C resulted in quantitative conversion of *trans*-methyl cinnamate into the reduced amide (entry 17). In the case of coumarin, the reduced lactone and the corresponding ring-opened phenol ethyl amide were obtained, albeit in low yields, at 140 °C for 16 h (entries 18 and 19). A reaction conducted at 200 °C with only 1.2 equiv. of triethylamine provided the expected phenol amide in relatively good yield (entry 20). With ethyl-3-coumarincarboxylate, the isolated product was ethyl-3-coumarincarboxamide (entry 21) probably resulting from a geometrically favored lactone reconstruction and competitive Pd/C-catalyzed dehydrogenation.

From the above results, we speculated that some ethylamine was generated *in situ* during the conjugate reduction reaction, and that the ethyl amide products (entries 13-21) would result from the efficient transamidation of the corresponding esters with ethylamine, as previously observed in the case of 2,3-dihydrocoumarin.<sup>22</sup> A control experiment was made as follows: heating a toluene solution of triethylamine in the presence of Pd/C at 140 °C for 16 h, then filtration and removal of all volatiles, allowed us to isolate a complex mixture which was analyzed by NMR and mass spectroscopy (MS). From the NMR data, we determined that the products of the mixture were essentially composed of aliphatic chains, and some CH<sub>2</sub>-N bonds were evidenced. The MS (and MS/MS) analysis showed that the products all contained a single nitrogen atom, and had molecular weights of general formula (101 + 28n) with n = 1-11. The products contained in the mixture were thus assigned the general formula

$N[(C_2H_4)_xH][(C_2H_4)_yH][(C_2H_4)_zH]$  with  $(x + y + z) = 4-14$ .<sup>23</sup> Thus, we believe that under the reaction conditions, triethylamine undergoes an unexpected self-alkylation to produce ethylamine and longer-chain alkyl amines with the above general formula, most probably, via the suspected hydrido-palladium iminium complex of eq. (1). In the specific cases of methyl cinnamate and coumarin substrates, triethylamine thus plays a dual role in the reaction: it is the source of the two newly incorporated hydrogen atoms, as in other cases of conjugate reduction, and also the precursor of ethylamine used for transamidation. In the context of atom-economy, this reaction is a nice example of a particularly attractive concept where, under heterogeneous catalytic conditions, the same “bifunctional” reactant is used in two chemically distinct steps of a domino process.<sup>24</sup> As the  $\alpha,\beta$ -unsaturated ethylamide was not detected in the product mixture, the reduction of the ester probably preceded the transamidation step, but a transamidation followed by reduction cannot be ruled out. Most probably, diethylamine, which has not been detected by itself or as a diethylamide derivative, is also formed in the reaction and then rapidly converted into ethylamine with concomitant transfer of ethylene to another amine (self-alkylation).

**Table 2.** Pd/C catalyzed conjugate reduction of activated double bonds with  $NEt_3$

Entry	Substrate	Product(s)	Conditions <sup>a</sup>	Yield (conversion) % <sup>b</sup>
1			$NEt_3$ (1.2 equiv.)	100 (100)
2			$NEt_3$ (1.2 equiv.)	50 (50)
3			$NEt_3$ (2.2 equiv.)	71 (71)
4			$NEt_3$ (4 equiv.)	86 (86)
5			$NEt_3$ (2.2 equiv.)	69 (69)
6			$NEt_3$ (1.2 equiv.)	37 (37)
7			$NEt_3$ (2.2 equiv.)	58 (58)
8			$NEt_3$ (1.2 equiv.), 20 mol% Pd, 120 °C, 4 h	46 (100)
9			$NEt_3$ (2.2 equiv.), 120 °C, 4 h	47 (91)

10		+	NEt <sub>3</sub> (2.2 equiv.)	61 + 6 (71)
11		-	NEt <sub>3</sub> (2.5 equiv.)	0 (0)
12		-	EtOH (10 equiv.)	0 (0)
13		+	NEt <sub>3</sub> (2.2 equiv.)	52 + 11 (63)
14		+	NEt <sub>3</sub> (4 equiv.)	85 + 2 (87)
15		+	NEt <sub>3</sub> (2.2 equiv.), 80 h	58 + 42 (100)
16		+	NEt <sub>3</sub> (1.2 equiv.), 200 °C <sup>[c]</sup>	82 + 18 (100)
17			NEt <sub>3</sub> (4 equiv.), 160 °C, 110 h	100 (100)
18		+	NEt <sub>3</sub> (1.2 equiv.)	9 + 17 (26)
19		+	NEt <sub>3</sub> (4 equiv.)	16 + 25 (41)
20		+	NEt <sub>3</sub> (1.2 equiv.), 200 °C <sup>[c]</sup>	5 + 72 (77)
21			NEt <sub>3</sub> (2.2 equiv.)	44 (100)

<sup>a</sup>Unless stated otherwise, reactions were conducted with 10% Pd/C (10 mol.% Pd) at 140 °C for 16 hours in 0.6-1.0 M dry toluene (sealed tube). <sup>b</sup>Yields and conversions determined by NMR analysis of the crude reaction mixture, except for entry 21 (isolated). <sup>c</sup>Reaction performed in xylenes.

Several other catalysts were tested in the conjugate reduction reaction. Almost no reduction (*ca.* <5%) of *tert*-butyl acrylate occurred with 10 mol.% of Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, Pd(allyl)<sub>2</sub>Cl<sub>2</sub>, when the reaction was conducted in degassed dry toluene in the presence of triethylamine (2.2 equiv.) at 140 °C for 16 h. If the same reactions were conducted in a dry but not degassed medium, palladium black precipitated and the reaction proceeded, though with much less efficiency than with Pd/C. Rh(PPh<sub>3</sub>)<sub>3</sub>Cl and rhodium on alumina were also tested under the same conditions and resulted in very low conversion (*ca.* 5%). Finally, some other

group VIII transition metals supported on charcoal were tested for the conjugated reduction and, quite ironically, they were all found superior to Pd/C. Indeed, the treatment of *tert*-butyl acrylate with 5 mol.% of Pd/C in the presence of 1.2 equiv. of triethylamine at 70 °C for 4 h gave 25% conversion and yield, while Pt/C, Ru/C and Rh/C gave, respectively, 37%, 50% and 60% conversion and yield under similar conditions. This points out that rhodium supported on charcoal (Rh/C) might be an efficient catalyst for the hydrogen transfer from triethylamine to conjugated electro-deficient alkenes under relatively mild conditions, yet to be studied. The good conversion obtained with Rh/C is in striking contrast to the poor result obtained with Rh/Al<sub>2</sub>O<sub>3</sub>, indicating the crucial importance of the metal support.

## Conclusions

We have discovered that the suspected hydrido-palladium iminium complex generated from Pd/C and triethylamine catalyses the isomerization of allylic alcohols into carbonyl compounds. The process is accompanied by Pd/C-catalyzed disproportionation of the substrate to give the saturated alcohol and the  $\alpha,\beta$ -unsaturated ketone. Also, Pd/C catalyses the conjugate reduction of activated double bonds, using triethylamine as the source of the two newly incorporated hydrogen atoms, probably via the same complex. During the conjugate reduction reaction, the triethylamine undergoes self-alkylation to produce elongated aliphatic tertiary amines and ethylamine which, in the reaction with methyl cinnamate and coumarin, resulted in the formation of the reduced ethyl amide following *in situ* domino transamidation. Although the Pd/C–NEt<sub>3</sub> system is clearly not the reagent of choice for both the isomerization and reduction reactions presented above, it might be a useful and cheap satisfactory alternative in some cases. In light of these results, unexpected isomerizations and/or reductions occurring in Pd-catalyzed reactions involving alkyl amines can now be rationalized.

## Experimental Section

**General Procedures.** All reactions were performed in oven-dried glassware under an argon atmosphere. All reagents were obtained from commercial sources and used as supplied. Toluene was dried by refluxing with CaH<sub>2</sub> and then distilled under argon. Triethylamine was dried over solid KOH and then distilled under argon. The reactions were monitored either by NMR, HPLC coupled with a Brüker Esquire 6000 mass spectrometer equipped with an electrospray ionization source and a ion-trap detector, or GC. NMR data were recorded on a Brüker Avance 300 spectrometer in CDCl<sub>3</sub> or *d*-8-toluene. HPLC was performed on a Hitachi LaChrom Elite system. GC was performed on a Varian 3900 system equipped with a capillary column (CP-S11-5-CB low bleed) and a flame ionization detector set at 240 °C. 1-Cyclohexyl-2-propen-1-ol was prepared by addition of cyclohexyl carboxaldehyde to a THF solution of vinylmagnesium



bromide.<sup>25</sup> 4-Phenyl-3-buten-2-ol was prepared by Luche reduction of the corresponding ketone.<sup>26</sup> The tricarbonyl(tropone)iron complex was prepared from tropone and  $\text{Fe}_2(\text{CO})_9$ .<sup>27</sup> The substrate for entry 9 (Table 2) was prepared from the corresponding 1,6-enyne by a Pauson-Khand reaction.<sup>28</sup> The  $\alpha$ -chlorocyclopentenone and its acetal were prepared through dichloroketene methodology.<sup>20</sup> All products are commercially available or were previously fully characterized and showed NMR and MS data in full agreement with their proposed structures (Table 1 entries 3<sup>29</sup> and 4,<sup>30</sup> Table 2 entries 2,<sup>31</sup> 8,<sup>19c</sup> 9,<sup>32</sup> 10,<sup>33</sup> and 18<sup>22</sup>). RT denotes room temperature.

**Isomerization of allylic alcohols with Pd/C-NEt<sub>3</sub>.** An 8 mL cylindrical tube with an outer Rodavis joint, equipped with a magnetic Teflon-coated stirring bar was charged at RT, under an argon atmosphere, in order, with the allylic alcohol substrate (1.2 mmol), 10% Pd/C (64 mg, 5 mol.% Pd), toluene or *d*<sub>8</sub>-toluene (1.5 mL), and triethylamine (17  $\mu\text{L}$ , 0.12 mmol), and was then sealed. The mixture was heated with an oil bath at the indicated temperature and time (see Table 1). The reaction vessel was allowed to cool to RT, and the reaction mixture was filtered through cotton and directly analyzed by NMR when the reaction was performed in *d*<sub>8</sub>-toluene, or filtered through a pad of Celite and concentrated to give the crude product which was analyzed by NMR and/or GC.

**Conjugate reduction with Pd/C-NEt<sub>3</sub>.** An 8 mL cylindrical tube with an outer Rodavis joint, equipped with a magnetic Teflon-coated stirring bar was charged under an argon atmosphere at RT, in order, with the unsaturated substrate (1 mmol), 10% Pd/C (106 mg, 10 mol.% Pd), toluene, *d*<sub>8</sub>-toluene or xylenes (1.4 mL), and triethylamine (1.2 to 4 equiv., see Table 2), and was then sealed. The mixture was heated with an oil bath at the indicated temperature and time (see Table 2). The vessel was allowed to cool to RT, and the reaction mixture was filtered through cotton and directly analyzed by NMR when the reaction was performed in *d*<sub>8</sub>-toluene, or filtered through a pad of Celite and concentrated to give the crude product which was analyzed by NMR and, in some cases, HPLC-MS or GC.

**Conjugate reduction with Rh/C-NEt<sub>3</sub>.** An 8 mL cylindrical tube with an outer Rodavis joint, equipped with a magnetic Teflon-coated stirring bar, was charged under an argon atmosphere at RT, in order, with the *tert*-butyl acrylate (180 mg, 1.40 mmol), 5% Rh/C (144 mg, 5 mol.% Rh), toluene (1.5 mL) and triethylamine (235  $\mu\text{L}$ , 1.68 mmol), and was then sealed. The mixture was heated with an oil bath at 70 °C for 4 hours, cooled to RT, and analyzed directly by GC, which showed a conversion of 60 % of the starting material and a yield of 60% of *tert*-butyl propionate.

## Acknowledgements

We thank A. Roulet and B. Lagrange (Université Paul Cézanne, Marseille) for technical assistance, P. Brémond (Université Paul Cézanne, Marseille) for early experiments, our friend Prof. J.-P. Deprés (Université Joseph Fourier, Grenoble) for a generous gift of  $\alpha$ -

chlorocyclopentenone, Dr. M. Feraud (Provence Technologies, Marseille) for generous gifts of Pt/C, Ru/C and Rh/C, Prof. L. Charles (Université Paul Cézanne, Marseille) for helpful assistance with mass spectroscopy, and Prof. F. Lamaty (Université de Montpellier) for his interest in our work. Financial support from the French research ministry, the CNRS, and the Université Paul Cézanne (UMR 6263) is gratefully acknowledged.

## References and Notes

1. See for example: (a) Stokker, G. E. *Tetrahedron Lett.* **1987**, 28, 3179. (b) Saá, J. M.; Dopico, M.; Martorell, G.; Garcia-Raso, A. *J. Org. Chem.* **1990**, 55, 991. (c) Cabri, W.; Candiani, I.; DeBernardinis, S.; Francalanci, F.; Penco, S. *J. Org. Chem.* **1991**, 56, 5796. (d) Brenda, M.; Knebelkamp, A.; Greiner, A.; Heitz, W. *Synlett* **1991**, 809. (e) Lau, S. Y. W.; Andersen, N. G.; Keay, B. A. *Org. Lett.* **2001**, 3, 181.
2. (a) McCrindle, R.; Ferguson, G.; Arsenault, G. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 571. (b) McCrindle, R.; Ferguson, G.; Arsenault, G. J.; McAlees, A. J.; Stephenson, D. K. *J. Chem. Res., Synop.* **1984**, 360.
3. Murahashi, S.-I.; Hirano, T.; Yano, T. *J. Am. Chem. Soc.* **1978**, 100, 348.
4. (a) Clark, F. R. S.; Norman, R. O. C.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 1* **1975** 121. (b) Murahashi, S.-I.; Watanabe, T. *J. Am. Chem. Soc.* **1979**, 101, 7429.
5. Murahashi, S.-I.; Yoshimura, N.; Tsumiyama, T.; Kojima, T. *J. Am. Chem. Soc.* **1983**, 105, 5002.
6. Miyazawa, A.; Tanaka, K.; Sakakura, T.; Tashiro, M.; Tashiro, H.; Surya Prakash, G. K.; Olah, G. A. *Chem. Commun.* **2005**, 2104.
7. Zawisza, A. M.; Muzart, J. *Tetrahedron Lett.* **2007**, 48, 6738.
8. Pletnev, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, 67, 9276.
9. Coquerel, Y.; Brémond, P.; Rodriguez, J. *J. Organomet. Chem.* **2007**, 692, 4805.
10. Uma, R.; Crévisy, C.; Grée, R. *Chem. Rev.* **2003**, 103, 27.
11. (a) Petriguet, J.; Roisnel, T.; Grée, R. *Chem. Eur. J.* **2007**, 13, 7374. (b) Petriguet, J.; Prathap, I.; Chandrasekhar, S.; Yadav, J. S.; Grée, R. *Angew. Chem. Int. Ed.* **2007**, 46, 6297.
12. See Section 2.2.3 of Muzart, J. *Tetrahedron* **2005**, 61, 9423. (b) See Section II.D.4 of ref. 10. (c) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, 40, 4089.
13. Delaby, R. *Compt. Rend.* **1926**, 182, 140. (b) Kraus, M. *Collect. Czech. Chem. Commun.* **1972**, 37, 460.
14. Rao, V. S.; Perlin, A. S. *J. Org. Chem.* **1982**, 47, 367. (b) Ganchegui, B.; Bouquillon, S.; Hénin, F.; Muzart, J. *J. Mol. Catal. A: Chem.* **2004**, 214, 65. (c) Esaki, H.; Ohtaki, R.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *J. Org. Chem.* **2007**, 72, 2143.
15. For palladium-promoted dehydrogenation of ketones, see: (a) Theissen, R. *J. Org. Chem.* **1971**, 36, 752. (b) Bierling, B.; Kirschke, K.; Oberender, H.; Schulz, J. *J. Prakt. Chem.* **1972**, 314, 170. (c) Muzart, J.; Pète, J.-P. *J. Mol. Catal.* **1982**, 15, 373. (d) Wenzel, T. T. *J.*

- Chem. Soc., Chem. Commun.* **1989**, 932. (e) Shvo, Y.; Arisha, A. H. I. *J. Org. Chem.* **1998**, *63*, 5640. (f) Tokunaga, M.; Harada, S.; Iwasawa, T.; Obora, Y.; Tsuji, Y. *Tetrahedron Lett.* **2007**, *48*, 6860.
16. For a mechanistic discussion, see: Muzart, J. *Tetrahedron* **2003**, *59*, 5789.
  17. Haskel, A.; Keinan, E. in: E. Negishi, Ed. *Handbook of Organopalladium Chemistry in Organic Synthesis*, John Wiley & Sons: New York, 2002; Vol. 2, Chap VII 2.3, pp 2767-2782.
  18. Tsuchiya, Y.; Hamashima, Y.; Sodeoka, M. *Org. Lett.* **2006**, *8*, 4851.
  19. (a) Coquerel, Y.; Deprés, J.-P. *Chem. Commun.* **2002**, 658. (b) Coquerel, Y.; Deprés, J.-P.; Greene, A. E.; Philouze, C. *J. Organomet. Chem.* **2002**, *659*, 176. (c) Coquerel, Y.; Deprés, J.-P.; Greene, A. E.; Cividino, P.; Court, J. *Synth. Commun.* **2001**, *31*, 1291.
  20. For reductions of  $\alpha$ -chlorocyclopentenones, see: Giannini, A.; Coquerel, Y.; Greene, A. E.; Deprés, J.-P. *Tetrahedron Lett.* **2004**, *45*, 6749.
  21. A pincer-ligated iridium complex catalyses the dehydrogenation of tertiary amines in the presence of a sacrificial hydrogen acceptor: Zhang, X.; Fried, A.; Knapp, S.; Goldman, A. S. *Chem. Commun.* **2003**, 2060. The Pd/C-NEt<sub>3</sub> system applied to an *E:Z* = 1:2.3 mixture of cyclododecene resulted only in the thermodynamically favored isomerization of the mixture to an *E:Z* = 1.9:1 mixture of cyclododecene (quantitative recovery). The Pd/C-NEt<sub>3</sub> system also left *O*-benzylated menthol unchanged under the reaction conditions.
  22. Kaupp, G.; Schmeyers, J.; Boy, J. *Tetrahedron* **2000**, *56*, 6899.
  23. Chao, K.-H. US Patent 4 845 295, 1989; *Chem. Abstr.* **1990**, 20669.
  24. *Domino Reactions in Organic Synthesis* Tietze, L. F.; Brasche, G.; Gericke, K. M. Wiley-VCH, Weinheim, 2006.
  25. Bergmeier, S. C.; Stanchina, D. M. *J. Org. Chem.* **1997**, *62*, 4449.
  26. Zhu, L.; Kedenburg, J. P.; Xian, M.; Wang, P. G. *Tetrahedron Lett.* **2005**, *46*, 811.
  27. Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316.
  28. Shambayani, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289.
  29. Trost, B. M.; Parquette, J. R. *J. Org. Chem.* **1993**, *58*, 1579.
  30. Suzuki, T.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1997**, *119*, 6774.
  31. Hattori, K.; Sajiki, H.; Hirota, K. *Tetrahedron* **2001**, *57*, 4817.
  32. Baraldi, P. G.; Pollini, G. P.; Simoni, D.; Barco, A.; Benetti, S. *Tetrahedron* **1984**, *40*, 761.
  33. Deprés, J.-P.; Greene, A. E. *J. Org. Chem.* **1980**, *45*, 2036.