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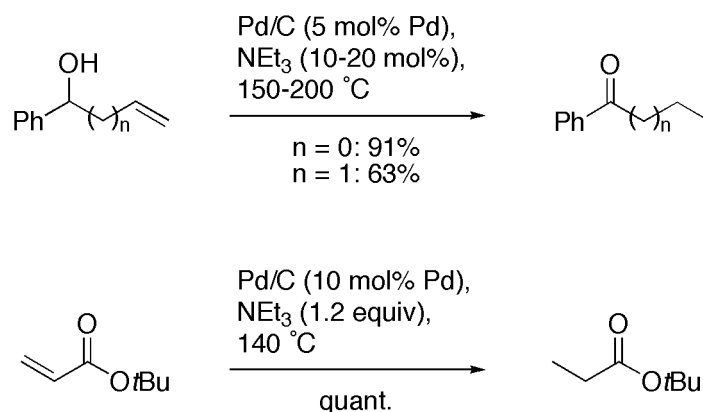
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Graphical Abstract



Abstract

The palladium hydride-iminium complex generated from Pd/C and triethylamine catalyses the isomerisation of allylic alcohols into carbonyl compounds, and 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.

Keywords

Catalysis, Palladium hydride, Triethylamine, Isomerisation, Conjugate Reduction

1. Introduction

Palladium based catalysts are involved in a number of highly useful synthetic transformations. In the cases where an amine bearing α and β hydrogen atoms is used as a co-reagent or co-catalyst in the reaction mixture, unexpected isomerisations and/or reductions are sometimes observed [1]. A rationale for this behaviour has been proposed which relies on the formation of a palladium hydride-iminium (or imine) complex, in equilibrium with the corresponding enamine complex. This palladium hydride-iminium complex, which has been otherwise characterized [2], has been found to be involved in the catalytic substituent exchange of trialkyl amines [3], and in the presence of water, the hydrolysis of the complex produces carbonyl compounds [4]. These reactions were also applied to primary and secondary amines, via an imine-palladium hydride complex [5], and a microwave-assisted version appeared recently [6]. So far, reactions of the complexes have concentrate on the imine or the iminium. Herein, we report a series of preliminary results on the implication of the hydride moiety of the complex generated from Pd/C and triethylamine for the catalytic isomerisation of allylic alcohols into carbonyl compounds, and the conjugate reduction of activated double bonds using triethylamine as the source of the two newly incorporated hydrogen atoms.


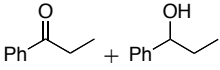

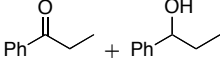

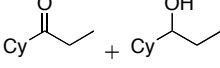

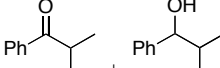

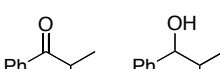

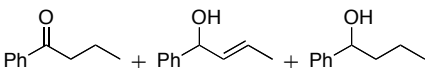

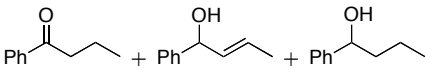
2. Discussion

2.1. Isomerisation of allylic alcohols

Examples of palladium catalysed isomerisation of allylic alcohols into carbonyl compounds are quite rare and are limited to Pd(II) catalysts [7], except for one example with hydrogen pre-activated Pd/C which was early recognized to be able of isomerising 4-penten-3-ol into 3-pentanone in the gas phase [8]. However, all attempts to isomerise allyl alcohols in the liquid-phase with Pd/C failed. We speculated that the palladium hydride generated from Pd/C and triethylamine could effect the isomerisation of allylic alcohols, and indeed 1-phenyl-2-propen-1-ol was partially converted to ethyl phenyl ketone on 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 that case, 8% of the saturated product 1-phenyl-propanol were also formed. Nearly complete conversion and better selectivity was obtained on heating at 150 °C for 3 hours (entry 2), still with production of a minor amount of 1-phenyl-propanol (5%). Similarly 1-cyclohexyl-2-propen-1-ol was isomerised to the corresponding ketone (entry 3) with production of 17% of saturated product. Under the same conditions, 1-phenyl-2-methyl-2-propen-1-ol proved almost inert, and 69% of the expected ketone were formed after 12 hours at 200 °C (entries 4

and 5, respectively). With 1-phenyl-3-buten-1-ol (homoallyl alcohol), the expected ketone was formed in only 19% yield, together with the substituted allylic alcohol raising from the mono-isomerisation as the major product (30%) after 3 hours at 150 °C (entry 6). At higher temperature, 63% of the isomeric ketone were obtained together with 9% of the corresponding allylic alcohol (entry 7) [9]. The decrease in the efficiency of the isomerisation with substituted allyl alcohols is also observed with other metal hydrides [7a].

Table 1: Isomerisation of allylic alcohols with Pd/C-NEt₃

entry	substrate	conditions ^a	products	yield (conversion) % ^b
1		70 °C, 22 h		67 + 8 (84)
2		150 °C, 3 h		91 + 5 (97)
3		150 °C, 3 h		72 + 17 (100)
4		150 °C, 3 h		3 + 1 (5)
5		200 °C, 12 h		69 + 9 (91)
6		150 °C, 3 h		19 + 30 + 9 (76)
7		200 °C, 12 h, 20 mol% NEt ₃		63 + 9 + 19 (98)

^aUnless stated otherwise, all reactions were conducted with 10% Pd/C (5 mol% Pd) and 10 mol% NEt₃ in 0.8-1.0 M dry toluene (sealed tube).

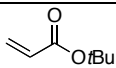
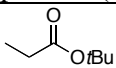
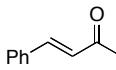
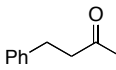
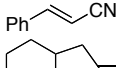
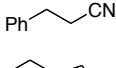
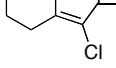
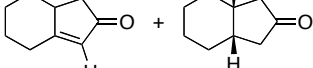
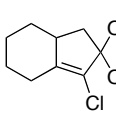
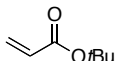
^bYields and conversions are obtained by NMR analysis of the crude reaction mixture.

2.2. Conjugate reduction of electro-deficient alkenes

The ability of the double bond of allyl alcohols to undergo hydro-palladation with the palladium hydride generated from triethylamine and Pd/C logically prompted us to examine the system for the reduction of electro-deficient alkenes. Hydrido-palladium compounds obtained by transmetalation of a metal hydride were reported to catalyse some conjugate reductions [10], and very recently, Sodeoka's group reported a palladium(II) catalysed enantioselective conjugate reduction of enones using ethanol as hydride source [11]. To test the feasibility of the conjugate reduction with the Pd/C-NEt₃ system, we first 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). Benzylideneacetone and cinnamitrile are also reduced under these conditions (entries 2 and 3, no attempt were made to optimize the yields). Some interesting observations emerged from the reactions with α -chlorocyclopentenones and its acetal (entries 4 and 5, respectively). Indeed, in the case of entry 4, the conjugated reduction is followed by in situ dehydrohalogenation to restore the thermodynamically favored enone system. The reaction thus results in the net reduction of the α -chlorocyclopentenone into a cyclopentenone, and a small amount of over-reduction product is observed. The corresponding acetal is inert under the reaction conditions (entry 5), thus demonstrating that Pd/C neither catalyses the deshydrogenation of triethylamine in the absence of an hydride acceptor, nor the reduction of the vinylic chlorine atom [12]. Since the report of Sodeoka's group [11] we verified that Pd/C was not a catalyst for the reduction of electro-deficient alkenes using ethanol as the hydride source under the conditions of the study (entry 6). Several other catalysts were tested in the reaction. No reduction of *tert*-butyl acrylate occurred with Pd(PPh₃)₄, PdCl₂, Pd(OAc)₂ and Pd(allyl)₂Cl₂ when the reaction was conducted in degazed dry toluene in the presence of triethylamine. If the same reactions were conducted in a dry but not degazed medium, palladium black precipitated and the reaction proceeded. Rhodium on alumina was also tested for the same reaction and resulted in very low conversion (ca. 5%) under the normalised conditions of the study.

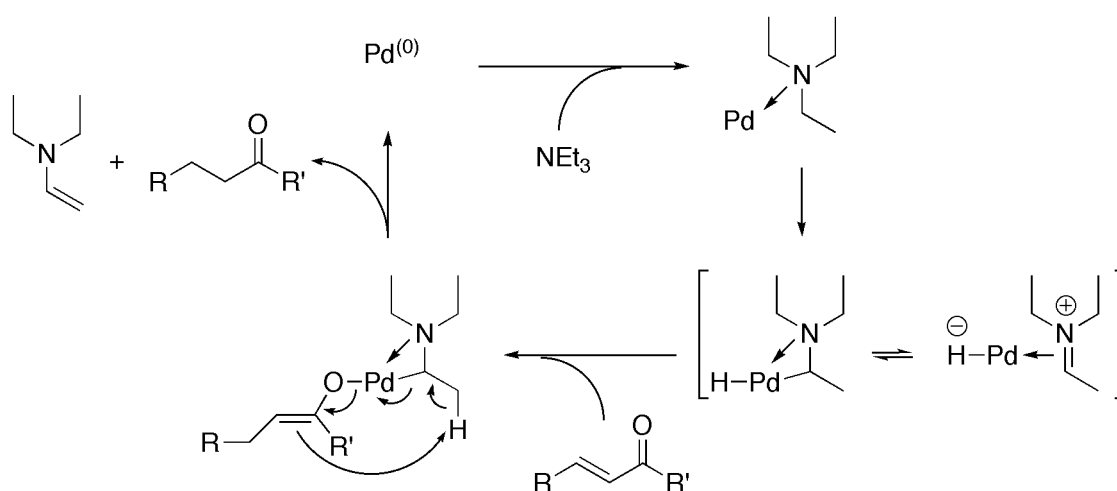
Table 2: Conjugate reduction of activated double bonds with Pd/C-NEt₃

entry	substrate	product(s)	Conditions ^a	yield (conversion) % ^b
1			NEt ₃ (1.2 equiv)	100 (100)
2			NEt ₃ (2.2 equiv)	69 (69)
3			NEt ₃ (2.2 equiv)	37 (37)
4			NEt ₃ (2.2 equiv)	61 + 6 (71)
5		-	NEt ₃ (2.5 equiv)	0 (0)
6		-	EtOH (10 equiv)	0 (0)

^aAll 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).

^bYields and conversions are unoptimized and were obtained by NMR analysis of the crude reaction mixture.

On a mechanistic point of view, the simplistic mechanism depicted on scheme 1 accounts for the observed reaction. The reaction would proceed via initial insertion of palladium into the carbon-hydrogen bond α to the nitrogen atom and subsequent formation of a trialkyliminium-palladium hydride complex, which would then undergo conjugate addition and enamine formation. Although, at this time, we can not provide a direct evidence for the formation of the vinyl(diethyl)amine as a product of the Pd/C-NEt₃ mediated reduction of electro-deficient alkenes [13], triethylamine is clearly the source of the two hydrogen atoms incorporated onto the double bond (compare entries 1 and 6 in Table 2).



Scheme 1 : Conjugate reduction with Pd/C-NEt₃

3. Conclusion

In summary, we have demonstrated that the palladium hydride generated from Pd/C and triethylamine can catalyse the isomerisation of allylic alcohols into carbonyl compounds, and that Pd/C catalyses the conjugate reduction of activated double bonds using triethylamine as the source of hydrogen atoms. It should be stressed here that the formation and the catalytic activity of the palladium hydride complex occurred at quite low temperature (70 °C), but only with unligated metallic palladium under the conditions of our study. Although the Pd/C-NEt₃ system is clearly not the reagent of choice for both the isomerisation and reduction reactions presented above, it might be a useful and cheap satisfactory alternative in some cases. In light of these results, unexpected isomerisations and/or reductions occurring in Pd catalysed reactions involving a tertiary amine can now be rationalized. Further studies on the synthetic

implications of the formation of the palladium hydride-iminium complex of triethylamine are currently underway.

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- [13] Enamines, and in particular vinyl(diethyl)amine, are highly unstable compounds. See reference 12 and references cited therein.