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Pd(0)/C catalyzed efficient Wacker oxidation of functionalized terminal olefins

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ABSTRACT

Wacker oxidation of terminal olefins was carried out at room temperature and atmospheric pressure by using Pd(0)/C in THF/H_2O (9:1). Palladium(0)/C was proven to be highly efficient catalyst for the Wacker oxidation of terminal olefins to the corresponding methyl ketones. The catalyst was reusable while maintaining its activity and selectivity to a high degree.

1. Introduction

Palladium catalyzed reactions such as Wacker oxidation, Heck reaction, Suzuki coupling reaction etc. have gained a lot of importance and popularity in the area of synthetic for organic chemistry over a period of time for its simplicity of operations in the preparation of useful synthetic intermediates. This is evident from the voluminous literature present in connection with these reactions. In all these reactions namely, Heck reaction[1,2], Suzuki reaction[3,4], and Sonogashira coupling reaction[5,6] palladium can be used as a catalyst either in the form of Pd(0)[7,10,11,3,13] or Pd(I/II) species.[8–10,12] However, in case of all of the Wacker oxidations[14,15] carried out so far, Pd was used in the form of Pd(II) ion. Palladium has never been used in the form of Pd(0) for any Wacker oxidation as there are no reports in the literature[16,17] to this effect.

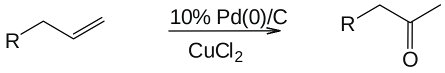
Further, conventional Wacker oxidation using homogeneous Pd(II) catalysts often leads to difficulties in isolation of the products, separation of the catalysts from the reaction mixture, and the difficulty about recycling the catalysts. Therefore, much effort has been devoted to the development of highly efficient Wacker oxidation by heterogeneous catalysts.[18,19] But these catalyst systems often have drawbacks such as low catalytic activity, low yield of product and severe dependence of success of the reaction on the substrate structure. We herein report the use of Pd(0) to effect Wacker oxidation of the terminal olefins.

Initially, the terminal olefin **1a** was heated with Pd(0)/C–Cu(0)/C catalyst[20] under the oxygen atmosphere. Unfortunately, no formation of methyl ketone was observed under these conditions even at elevated temperatures. To circumvent this problem, the olefin **1a** was treated with commercially available 10% Pd(0)/C and catalytic amount of $CuCl_2$ under oxygen atmosphere (Scheme 1). The reaction, at room temperature, was found to give methyl ketone in good yield. To test the generality of this method terminal olefins **1b**–**l** were subjected to Wacker oxidation under the above reaction conditions (Table 1). The results show that a variety of terminal olefins can be converted to methyl ketones quite efficiently in good yields.

2. General procedure for Wacker oxidation

To the solution of substituted, functionalized olefin (1 mmol), in aqueous THF (1:9, 10 ml), 10%Pd/C (0.1 mmol) and $CuCl_2$ (0.1 mmol) were added. This mixture was stirred and heated at reflux temperature under oxygen atmosphere. After the completion of reaction (TLC check), the reaction mixture was diluted with water and filtered through Whatman 40 filter paper. The greenish filtrate was extracted with ether. The combined ether layer was washed with water, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by column chromatography using appropriate solvent system.

It was further noticed that the recovered catalyst, after drying in the oven at 100 °C, could be reused as such, along with a fresh amount of $CuCl_2$, to carry out the Wacker oxidation of the new batch of the olefin. It was found that the reaction proceeds smoothly giving the same yield. So it is clear that the catalyst can be recycled without any problem. This finding makes present protocol of converting, terminal olefins into methyl ketone, a



1a - l

2a - l

Scheme 1.

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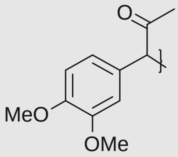
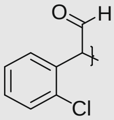
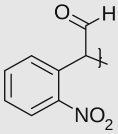
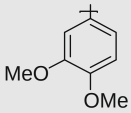
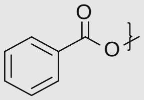
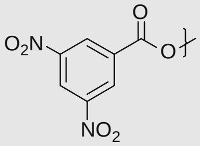
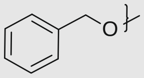
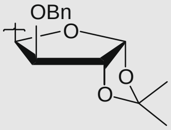
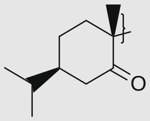
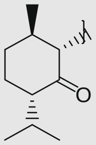
Table 1
Carbonyl compounds obtained by oxidation of terminal olefins as depicted in Scheme 1

	R	% Yield
a		78
b		80
c		74
d		72
e		65
f		68
g		71
h		57[a]
i		73
j		67
k	C_6H_{13}–	73
l	$C_{14}H_{27}CH(OH)CH_2$–	69

[a] Corresponding aldehyde was also obtained in 28% yield.

practical and cheap method with the potential application for large-scale preparation of methyl ketones.

From the above successful results it is clear that this type of Wacker oxidation carried out by using Pd(0) proved to be an efficient method for the preparation of methyl ketone from terminal olefin. Further, the yield of the products and the reusability of the catalyst while maintaining high activity and selectivity could facilitate the application of Wacker oxidation of terminal olefins, mediated by 10% Pd(0)/C, to multi-gram scale reactions and possibly in the industrial applications.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.173.

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