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Greening the Wacker process

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ABSTRACT

Wacker oxidation of various terminal olefins with Pd^0/C-$KBrO_3$, a nontoxic, environmentally benign, and easy to handle catalyst system, was achieved in high isolated yields. The described protocol offers an alternative to the traditional Wacker system which uses $CuCl_2$ as co-catalyst. The catalyst is reusable while maintaining high activity and selectivity.

Mature industrial chemical processes that are often based on technologies developed in the first half of the 20th century, like Wacker oxidation, are no longer acceptable in these environmentally conscious days, as these chemical processes lead to the production of enormous quantities of undesired and harmful substances.[1] These have an adverse effect on environment and have become the biggest challenge the chemistry has to face today. Conventional Wacker process is a palladium mediated reaction.[2] It is usually conducted with $PdCl_2$ cat./$CuCl_2$ cat./O_2 system.[3] It leads to the formation of substantial amounts of ecologically hazardous chlorinated by-products. Beside this, use of molecular oxygen as a final oxidant presents a significant safety issue.[4] In addition, use of $CuCl_2$, even in catalytic amount, resulted in the production of noxious copper waste which is potentially very toxic to aquatic life, both acutely and chronically, as the environmental impact of waste is not only determined by its amount but also by its nature.[1b]

Therefore, there is a definite need for an environmentally benign system for Wacker oxidation. This can be achieved by using a recyclable palladium catalyst with an environmentally acceptable co-oxidant. Several alternatives to this effect have been reported in the literature.[5] We have reported a very simple and inexpensive solution to the problems associated with use of $PdCl_2$ by using Pd^0/C–$CuCl_2$ as a heterogeneous recyclable catalyst system.[6] Elimination of $CuCl_2$ as co-catalyst would render the Wacker oxidation a completely green process. Potassium bromate ($KBrO_3$) is an inexpensive, readily available strong oxidizing agent. It has been used with different catalysts in various organic reactions as a co-oxidant in stoichiometric quantities.[7] Herein we report Wacker oxidation using Pd^0/C with $KBrO_3$ as terminal oxidant.

Wacker oxidation of terminal olefin was conducted using 10% Pd^0/C with potassium bromate as co-oxidant in aqueous THF at reflux temperature[8] and gave corresponding methyl ketone in good yield without any detectable amounts of side products (Table 1). Wacker oxidation of different terminal olefins having acid/base sensitive functional groups was converted smoothly and efficiently into the corresponding methyl ketones in excellent yields under established protocol (Table 1).

This finding makes present Wacker oxidation protocol, a practical, convenient, cheap, and environmentally benign method with the potential application for large-scale preparation of methyl ketones. Thus, Wacker oxidation smoothly gives the product in similar yields.

Various similar other co-oxidants were evaluated for the Wacker oxidation. Wacker oxidation of 1-octene with $NaIO_4$ gave corresponding methyl ketone in trace amount only (Table 2, entry 1). Reaction using NaOCl or $K_2S_2O_8$ gave the product again in very low yields (Table 2, entries 2 and 3). Wacker oxidation with $NaBrO_3$ leads to 2-octanone in moderate yield (Table 2, entry 5). Decomposition of 1-octene was observed with oxone® (Table 2, entry 6). This suggested that in Wacker oxidation, as compared to other oxidants $KBrO_3$ serves as the best oxidant with Pd^0/C.

In conclusion we have developed a practical, general, and a green method for Wacker oxidation, which uses an inexpensive oxidant, can tolerate different functional groups, and provides product selectively in high yields. This method is of particular interest for easy recoverability and recyclability of the catalyst without any decrease in the yield of expected methyl ketones.

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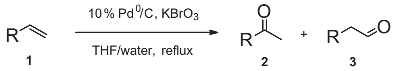
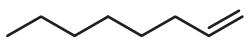
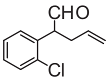
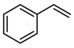
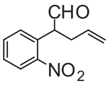
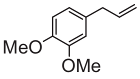
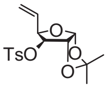
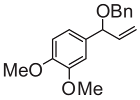
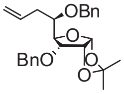
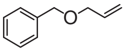
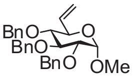
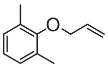
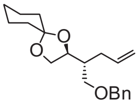
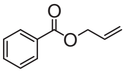
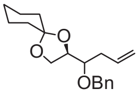
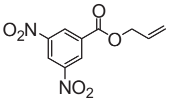
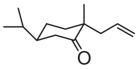
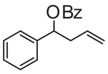
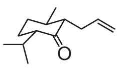
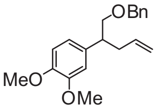
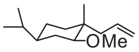
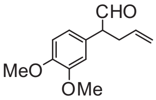
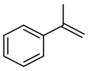
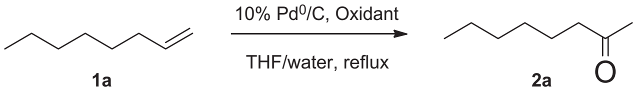
Table 1
Wacker oxidation of terminal olefins with 10% Pd^0/C-$KBrO_3$[a]



Sr. No.	Substrate	Product	Yield[b] (%)	Sr. No.	Substrate	Product	Yield[b] (%)
1		**2a**	84	12		**2l**	73
2		**2b**	86	13		**2m**	78
3		**2c**	73	14[c]		**3n**	76
4[c]		**3d**	76	15		**2o**	69
5		**2e**	77	16		**2p**	78
6		**2f**	86	17		**2q**	68
7		**2g**	65	18		**2r**	71
8		**2h**	71	19		**2s**	79
9		**2i**	68	20		**2t**	84
10		**2j**	81	21		**2u**	73
11		**2k**	80	22		—[d]	—

[a] All reactions were carried out with substrate (1 mmol), 10% Pd^0/C (0.05 mmol), $KBrO_3$ (3 mmol), THF/water (4:1, 15 mL), 65 °C.
[b] Isolated yields.
[c] α-Substituted olefin yielded corresponding aldehyde.[9]
[d] No reaction and all starting material was recovered.

Table 2
Screening of oxidant for Wacker oxidation of 1-octene with Pd^0/C[a]



Entry	Oxidant	Yield[b] (%)
1	$NaIO_4$	6
2	NaOCl	10
3	$K_2S_2O_8$	19
4	$KBrO_3$	84
5	$NaBrO_3$	62
6	Oxone®	—[c]

[a] All reactions were carried out with 1-octene (1 mmol), 10% Pd^0/C (0.05 mmol), oxidant (3 mmol), THF/water (4:1, 15 mL), 65 °C, 12 h.
[b] Isolated yields.
[c] Decomposition of 1-octene occurred.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.01.082.

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8. *General procedure for Wacker oxidation*: To the solution of olefin (1 mmol), in THF/water (4:1, 15 mL), 10% Pd/C (0.05 mmol) and $KBrO_3$ (3 mmol) were added. This mixture was heated at reflux temperature. After completion of the reaction (checked by TLC), the mixture was diluted with water and filtered through Whatman 40 filter paper. The filtrate was extracted with ethyl acetate. The combined organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (100–200 mesh) using pet ether/ethyl acetate (90:10) as eluent to get the product.
9. For a review on aldehyde formation through Wacker oxidation, see: (a) Muzart, J. *Tetrahedron* **2007**, *63*, 7505; (b) Weiner, B.; Baeza, A.; Jerphagnon, T.; Feringa, B. L. *J. Am. Chem. Soc.* **2009**, *131*, 9473.