

Pyridinium Chlorochromate Supported on Alumina as an Efficient Oxidizing Agent for Oxidation of Alcohols Under Solvent Free Conditions

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A rapid and convenient method is described for oxidizing alcohols into carbonyl compounds using pyridinium chlorochromate supported on alumina under solvent free conditions.

Key Words: Pyridinium chlorochromate, Oxidation, Solvent free, Alumina.

INTRODUCTION

Oxidation reactions are very important processes for biological systems and in organic chemistry. There are numerous oxidation reagents for organic compounds and new ones are added to this list almost every day¹. The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds has found considerable attention during recent years^{2,3} but introduction of new methods, inexpensive reagents and environment-friendly conditions for such functional groups transformation is still in demand.

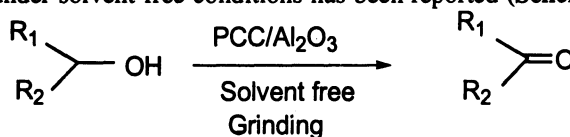
The use of high oxidation state transition metals⁴ such as chromium(VI) reagents for alcohol oxidation is well established. But the chromium residues are environmentally hazardous and have the potential danger (ignition or explosion) in terms of developing oxidizing methods using chromium trioxide along with solid supports.

Pyridinium chlorochromate (PCC) (Corey's reagent⁵) is well known as a versatile and very good oxidant for the conversion of primary alcohols into corresponding aldehydes. Pyridinium chlorochromate has shown a slightly acidic character and usually it does not react with simple olefinic C—C double bonds⁶. So, many modifications were done, for example, the chlorochromate anion has been supported on a polymeric matrix^{6–8}. Also, Cheng and co-workers reported⁹ that pyridinium chlorochromate adsorbed on alumina is a suitable reagent for the oxidation of alcohols to aldehydes and ketones. The reagent is mild, selective and remarkably effective, the yields being equal to or greater than those obtained with pyridinium chlorochromate. The reactions are very clean and the isolation of the products is simple. Thus, this methodology allows the elimination of the problems and the side reactions, sometime observed, due to the acidic character of pyridinium chlorochromate.

Application of heterogeneous systems especially by introduction of reagents on solid supports and under solvent-free conditions has circumvented some of

these problems and provided an attractive alternative in organic synthesis¹⁰. The advantage of these methods over conventional homogeneous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products and manipulative simplicity^{11, 12}.

Having the above facts in mind, a convenient method for oxidation of alcoholic groups into corresponding carbonyl compounds with PCC supported on Al_2O_3 as an oxidant under solvent-free conditions has been reported (Scheme-1).



Scheme-1

EXPERIMENTAL

All oxidation products are known compounds and are identified by comparison of their physical and spectral data with those of authentic samples. Pyridinium chlorochromate was prepared according to literature⁵. Alcohols and Al_2O_3 were purchased from Fluka and Merck. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

General procedure for the oxidation of alcohols using PCC/ Al_2O_3

A mortar was charged with Al_2O_3 (2 g) and pyridinium chlorochromate (0.43 g, 2 mmol); the mixture was ground with a pestle for 1 min. Then alcohols (1 mmol) and several drops of *t*-buOH were added to the mixture. The reaction mixture was ground for the time specified in Table-1. The progress of the reaction was monitored by TLC using ether- CCl_4 . Then the reaction mixture was poured into a mixture of ether (20 mL) and water (10 mL). The organic layer was passed through a small bed of silica gel and evaporated to dryness using a rotary evaporator to give the pure corresponding carbonyl compound (Table-1).

RESULTS AND DISCUSSION

Pyridinium chlorochromate supported on alumina was prepared by simply co-grinding Al_2O_3 with PCC in the ratio 5 : 1 (w/w) in an agate mortar. In this simple and efficient method the starting alcohols were oxidized to the corresponding carbonyl compounds in a mortar with grinding by a pestle in the presence of supported PCC on Al_2O_3 and little drops of *t*-buOH. The feasibility of the present oxidation of alcohol was first examined using benzyl alcohol as a model substrate. Thus, benzyl alcohol was thoroughly mixed with 2 equivalents of PCC/ Al_2O_3 and small amount of *t*-buOH in a mortar with a pestle and in an ambient air environment at room temperature and benzaldehyde was obtained in 94% yield within 10 min. It is noteworthy that the oxidation did not proceed to completion even after prolonged hours of reaction when less than 2 equivalents of the oxidant were used.

With the first successful result in hand, oxidations of other alcohols with PCC/ Al_2O_3 were carried out under similar reaction conditions. The results obtained are presented in Table-1.

TABLE-1
CONVERSION OF ALCOHOLS TO CARBONYL COMPOUNDS
USING PCC SUPPORTED ON $Al_2O_3^a$

| Compd. No. | Substrate | Product | Time (min) | Yield ^{b, c} % |
|------------|----------------------|-------------------|------------|-------------------------|
| 1 | | | 10 | 94 |
| 2 | $CH_3(CH_2)_4CH_2OH$ | $CH_3(CH_2)_4CHO$ | 8 | 87 |
| 3 | $CH_3(CH_2)_6CH_2OH$ | $CH_3(CH_2)_6CHO$ | 8 | 89 |
| 4 | | | 10 | 92 |
| 5 | | | 10 | 75 |
| 6 | | | 10 | 86 |
| 7 | | | 10 | 89 |
| 8 | | | 10 | 87 |
| 9 | | | 10 | 85 |
| 10 | $HC\equiv CCH_2OH$ | $HC\equiv CCHO$ | 10 | 89 |
| 11 | | | 10 | 88 |
| 12 | | | 10 | 89 |
| 13 | | | 10 | 87 |
| 14 | | | 10 | 87 |

^aMolar ratio of reagent to substrate was 2 : 1.

^bYields refer to isolated products.

^cProducts were characterized by comparison of their physical data, IR, NMR spectra with known samples.

As shown in Table-1, primary and secondary saturated aliphatic, benzylic and heterocyclic alcohols were oxidized to the corresponding carbonyl compounds in very good to excellent isolated yields with very short times (8–10 min). 4-Phenyl-but-3-en-2-ol and propargyl alcohol as α , β -unsaturated alcohols were easily converted to corresponding carbonyl compounds in 88 and 89% isolated yields, respectively. Furfuryl alcohol was converted to furfural in 85% yield.

The rapid and selective formation of oxidation products demonstrates the efficiency of this new method. The structures of all the products were established from their analytical and spectral (IR, ^1H NMR) data and by direct comparison with authentic samples.

In conclusion, oxidation of primary and secondary alcohols with PCC/ Al_2O_3 under solvent free conditions is a rapid, manipulatively simple, selective and environment-friendly protocol when compared to the conventional solution phase or heterogeneous condition and should have utility in contemporary organic synthesis.

REFERENCES

1. S. Servi and A. Acar, *Molecules*, **7**, 104 (2002) and references therein.
2. (a) R.C. Larock, *Comprehensive Organic Transformations*, VCH, Weinheim (1989); (b) M. Hudlicky, *Oxidation in Organic Chemistry*; ACS Monograph 86, American Chemical Society, Washington DC (1990).
3. A.R. Kiasat, F. Kazemi and K. Nourbakhsh, *Phosphorus, Sulfur & Silicon*, **179**, 457 (2004).
4. E. Eisenbraun, *J. Org. Synth. Coll.*, **5**, 310 (1973).
5. E.J. Corey and J.W. Suggs, *Tetrahedron Lett.*, **16**, 2647 (1975).
6. G. Piancatelli, A. Scetteri and M. D' Auria, *Synthesis*, 245 (1982).
7. J.M.J. Frechet, H. Warnock and H.J. Farrall, *J. Org. Chem.*, **43**, 2618 (1978).
8. G. Cainelli, G. Cardillo, M. Orma, and S. Sandri, *J. Am. Chem. Soc.*, **98**, 6737 (1976).
9. Y.S. Cheng, W.L. Liu and S.H. Chen, *Synthesis*, 223 (1980).
10. D. Laszlo, *Preparative Chemistry Using Supported Reagents*, Academic Press, San Diego (1987).
11. M. Balogh and P. Laszlo, *Organic Chemistry Using Clays*, Springer-Verlag, Berlin (1993).
12. M.M. Heravi, N. Farhagi, Y.S. Beheshtiha, K. Assadolah, M. Ghassemzadeh and K. Tabarhydar, *Phosphorus, Sulfur & Silicon*, **177**, 2843 (2002) and references therein.

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