Short Communication

A Mild and Efficient Oxidation of Benzylic Alcohols Without Solvent Using Iodic Acid Supported on Wet Montmorillonite K10 or Silica Gel Under Microwave Irradiation

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Abstract

Iodic acid supported on wet silica gel and K10 clay are used for the efficient oxidation of benzylic alcohols under microwave irradiation and solvent free condition.

Key words: Oxidation, Ionic acid, Benzyl alcohols, Microwave irradiation

Introduction

Recently the combination of supported reagents and microwave irradiation were used to carry out a wide range of reactions in short times, with high conversion, selectivity and without solvent.[1–2] Owing to environmental concerns, there is increasing need and interest in developing processes that minimize production of toxic waste. Therefore the discovery of new methods for oxidation using supported reagents without solvent is of prime importance in synthetic organic chemistry.

The oxidation of alcohols to carbonyl compounds is a fundamental transformation of organic chemistry which is attracting much current interests.[3] For example a great number of oxidizing agents have been reported for the oxidation of benzyl alcohols.[4–9]

However some of the reported reagents and catalysts suffer from disadvantages such as availability of the reagent, difficult work-up, long reaction time, toxicity or high cost of the reagents. Thus milder and more selective reagents are still in demand.

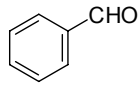
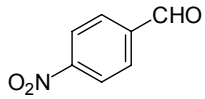
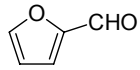
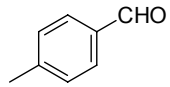
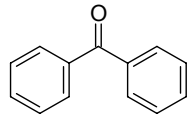
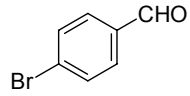
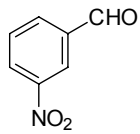
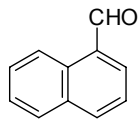
Iodic acid is a rather mild inorganic acid (pKa 0.80) of moderate oxidizing power in aqueous acid and of low toxicity to humans as it has been used in medicine.[10]

Results and discussion

In continuation of our studies on the application of iodic acid[11–13] we were interested in using this reagent for the oxidation of benzyl alcohols to corresponding aldehydes and ketones.

Iodic acid was supported on wet montmorillonite K10 and silica gel and used for the oxidation of benzyl

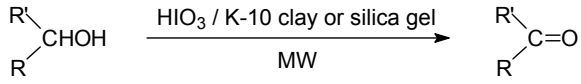
Table 1. Oxidation of benzyl alcohols by iodic acid supported on silica gel and montmorillonite K10.

Entry	Time (s)	Product	Yield (%)[a]	
			K10 clay	Silica gel
1	60.0		92	85
2	120.0		87	70
3	50.0		94	83
4	60.0		91	87
5	90.0		88	82
6	60.0		92	87
7	90.0		89	78
8	50.0		92	89

[a] The yield of isolated products.

alcohols under microwave irradiation without solvent. This method offers some advantages in term of simplicity of performance, solvent-free condition, no side product formation, very low reaction time and a wide range of benzyl alcohols can be converted to their corresponding aromatic aldehydes and ketones. In addition to the montmorillonite K10, silica gel can also be recycled after activation. The results for oxidations of variety of benzyl alcohols are summarized in Table 1.

Some experiments have been performed to check the efficiency of microwave irradiation in our synthesis. When this reaction was done in toluene under reflux conditions, after 10 hour only starting materials were observed on the TLC plate. In the absence of the surface yields are much lower after longer time.



R, R' = H, Aryl, Heteroaryl

Scheme 1

Conclusions

In summary we have extended successfully the application of montmorillonite K10 and silica gel supported iodic acid under microwave irradiation and without solvent. Meanwhile this method offers some advantages in term of simplicity of performance, solvent free condition, no side product formation and very low reaction time.

Experimental

All of aldehydes and ketones have been described previously in literature and were identified by their IR and ^{1}H-NMR spectra and melting point of 2,4-dinitrophenylhydrazones. The progress of the reaction was monitored by TLC.

Typical procedure for the oxidation of benzyl alcohol to benzaldehyde:

Wet montmorillonite K10 or silica gel was prepared by addition of 50 mL distilled water into 450 g of dry montmorillonite K10 (surface 200 m^2/g, fluka) or silica gel followed by mixing for 30 minutes. The wet montmorillonite K10 or silica gel must be stored in a well-closed container.

Benzyl alcohol (0.54 g, 5 mmol), iodic acid (1.76 g, 10 mmol) and wet montmorillonite K 10 or silica gel (5 g) were taken in a microwave oven (Butane household apparatus) and irradiated (1000 W) for 1 min. The progress of the reaction was monitored by thin layer chromatography (10% ethyl acetate in petroleum ether). After completion of the reaction, the product was extracted into dichloromethane (3×15 mL) and after decolourisation with activated charcoal at 45 °C, was filtered after 5 minutes and then was dried over sodium sulphate. Evaporation of the solvent followed by distillation of the residue gave 0.5g (92% yield) of benzaldehyde, which was identified by its boiling point, IR and ^{1}HNMR spectroscopic properties.

References

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Povzetek

Vodikov jodid na vlažnem silikagelu in K10 je bil uporabljen za oksidacijo benzilnih alkoholov. Reakcije so potekale v odsotnosti topila, s pomočjo mikrovalov.