

Facile Synthesis of 1,1-Diacetates Catalyzed by MCM-41-SO₃H Under solvent free condition

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Abstract

Acylals can be prepared very fast and in excellent yields by the direct condensation of aldehydes with acetic anhydride under solvent-free condition by employing of MCM-41-SO₃H as heterogeneous catalyst at room temperature.

Introduction

Acylals are important protective group for carbonyl compounds because they are stable to neutral and basic condition [1]. 1, 1-Diacetates are synthetically useful precursors for the synthesis of dienes for Diels- Alder cycloaddition reactions.

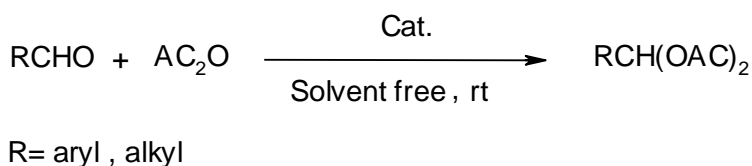
Usually gem-diacetate are synthesized from condensation of aldehydes and acetic anhydride in the presence of both protonic and Lewis acids such as sulphuric acid [3,4], phosphoric acid and methane sulphonic acid [5], NH₂SO₃H [6], and Lewis acids, such as Bi(NO₃)₃·5H₂O [7], ZrCl₄ [8], FeCl₃ [9], anhydrous FeSO₄ [10], Bi(OTf)₃ [11], PCl₃ [12], and LiBr [13].

Although in many case the gem-diacetate are obtained in good yield but many of these method suffer from some of the following disadvantages: Long reaction time, tedious work-up, use of homogenies catalyst, reflux condition and use of harmful solvents.

We herein wish to report an efficient procedure for the synthesis of acylals from various aldehydes with acetic anhydride by employing of MCM-41-SO₃H as heterogenic catalyst under solvent free condition.

Result and Discussion

In a typical experiment, a mixture of aldehyde (1 mmol), Ac₂O (5 mmol) and MCM-41-SO₃H (10 mg), was stirred magnetically at ambient temperature for an appropriate time (Scheme 1).



Scheme 1. Preparation of acylals from aldehyde and acetic anhydride

The reaction progress was monitored by TLC or GC. After completion of the reaction, the mixture was diluted with CH₂Cl₂ and filtered. The organic layer was washed with 10% NaHCO₃ solution and water, dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the solid crude product was recrystallized from petroleum ether yielding each of the pure acylals (Table 1).

Table 1: Preparation of imines catalyzed by MCM-SO₃H

| Entry | Substrate | Time (min) | Yield (%) | Mp (°C) |
|-------|-----------------------|------------|-----------|---------|
| 1 | Propionaldehyde | 5 | 91 | oil |
| 2 | Benzaldehyde | 3 | 95 | 43–45 |
| 3 | 4-Chlorobenzaldehyde | 3 | 99 | 82–83 |
| 4 | 2-Hydroxybenzaldehyde | 4 | 95 | 101–103 |
| 5 | 4-Methoxybenzaldehyde | 5 | 85 | 65–66 |

Conclusion

Herein we report a mild and efficient catalyst for the preparation of 1,1-diacetates from aldehydes and acetic anhydride under solvent-free conditions at room temperature. We found that both aromatic and aliphatic aldehydes gave high yields and the reaction time was shorter than that of previous methods. This method is selective for the preparation of 1,1-diacetates from aldehydes in the presence of ketones.

Experimental

Typical experimental procedure for the preparation of MCM-41-SO₃H:

MCM-41(1g) was poured into a 100 mL round bottom flask equipped with a gas inlet tube and a dropping funnel containing chlorosulfonic acid (2 ml) and dichloromethane (15ml). Then chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction mixture was conducted via the gas inlet tube over a NaOH solution. After the completion of the reaction, solvent was evaporated under reduced pressure and the white solid (MCM-41-SO₃H) was collected.

Typical experimental procedure for the preparation of acylals:

In the typical experiment, a mixture of aldehyde (1mmol), Ac₂O (5 mmol) and MCM-41-SO₃H (10 mg), was stirred magnetically at ambient temperature for an appropriate time. The reaction progress was monitored by TLC or GC. After completion of the reaction, the mixture was diluted with CH₂CL₂ and filtered. The organic layer was washed with 10% NaHCO₃ solution and water, dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the

solid crude product was recrystallized from n-hexane and ethanol yielding each of the pure acylals

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