

A Rapid and Practical Method for Deprotection of 1,1-Diacetates Catalyzed by Zirconium Sulfate Tetrahydrate-Silica Gel

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Abstract

A simple and efficient procedure for converting a variety of 1,1-diacetates into the corresponding aldehydes was developed. The methodology has been done with zirconium sulfate tetrahydrate-silica gel as catalyst. The temperature plays an important role in these reactions. The phenolic acetate function can selectively be deprotected into phenol.

Keywords: Deprotection; 1,1-Diacetates; Zirconium sulfate tetrahydrate

Introduction

Selective protection and deprotection of carbonyl groups are very important in synthetic organic chemistry. In recent years, 1,1-diacetates have been recognized as important agents for protecting carbonyl groups since they are very stable against oxidation [1,2], readily prepared [3-8] and show straightforward conversion into corresponding aldehydes. At the same time, they are also important precursors for the synthesis of valuable intermediates compounds for Diels-Alder cycloaddition reaction and Wittig reactions. In addition 1,1-diacetates are used as substrates in nucleophilic substitution reaction [9].

There are a huge number of reports on methods for conversion of 1,1-diacetates to corresponding aldehydes [1-3,10-15]. While each of these methods has own merit, some have drawbacks such as employing strong mineral acids [1-2], long reaction time [3], low yield (<60%) [11], needing expensive and rare catalysts [10] and so on. More recently, expansive graphite [16], aluminum chloride [17], $\text{TiO}_2/\text{SO}_4^{2-}$ solid super acid

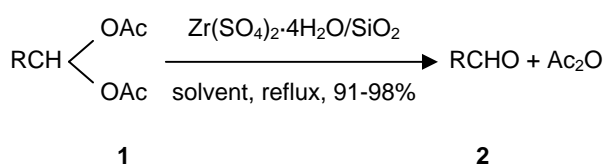
[18], anhydrous ferrous sulfate [19] and β -cyclodextrin [20] have been applied as catalysts to obtain relatively better results.

Although a number of catalysts have been reported for deprotection of 1,1-diacetates, there is still a great demand to solid acid catalysts for deprotection of 1,1-diacetates. Zirconium sulfate tetrahydrate has been used as a catalyst for organic reactions [21-23]. Recently we have developed an efficient and convenient procedure for preparation of 1,1-diacetates from aldehydes in the presence of $\text{NH}_2\text{SO}_3\text{H}$ [8]. We report herein a rapid method for the deprotection of 1,1-diacetates to aldehydes catalyzed by zirconium sulfate tetrahydrate-silica gel in high yields (**Scheme 1**).

Experimental Section

1,1-Diacetates (**1**) were synthesized as described previously [8]. The products were characterized by ^1H NMR spectra and comparison of their melting or boiling points with authentic samples [19].

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Scheme 1

Preparation of Catalyst

A mixture of $\text{Zr(SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (5 g), ether (20 mL), silica gel (5 g) was stirred at room temperature for 30 min. After the solvent was evaporated under reduced pressure, the residue was dried at 100°C for 2 h and stored in a desiccator until use.

General Procedure

A mixture of 1,1-diacetate (**1**) (1.00 mmol), dichloromethane, benzene or toluene (5 mL), and zirconium sulfate tetrahydrate-silica gel (0.14 mmol) was stirred under refluxing conditions for the time being indicated in Table. The reaction was monitored by TLC. After disappearance of the starting material, the mixture was cooled and zirconium sulfate tetrahydrate-silica gel was filtered off. The catalyst was washed with Et_2O and then

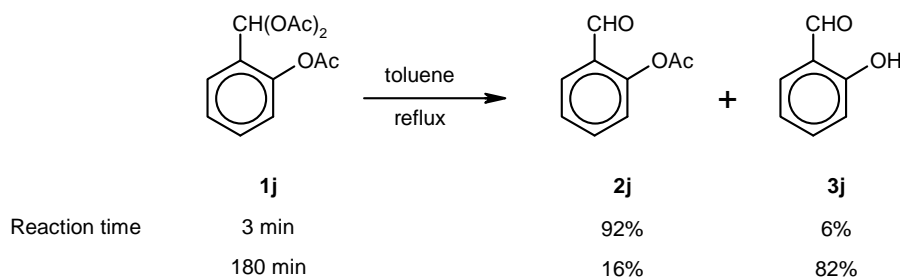
the organic layer was washed with brine two times (2×15 mL) and dried with anhydrous MgSO_4 . The solvent was evaporated under reduced pressure and the crude product was chromatographed on silica gel with petroleum-ether(8:1) as eluent to give the pure product (**2**).

Results and Discussion

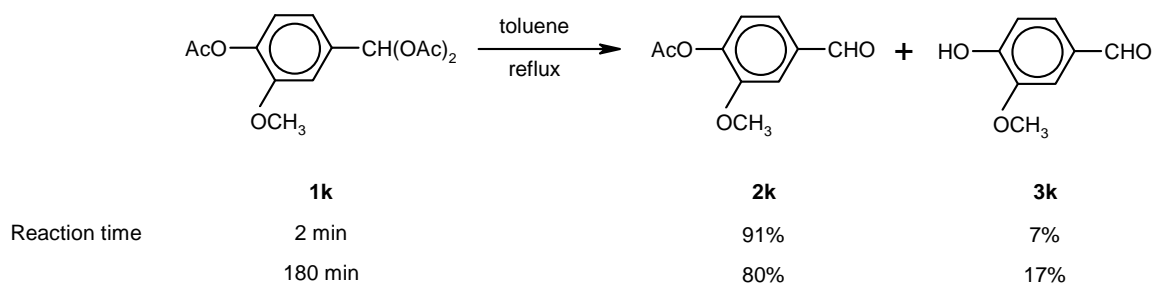
When 1,1-diacetates (**1**) are heated in refluxing dichloromethane, benzene or toluene in the presence of zirconium sulfate tetrahydrate-silica gel, the corresponding aldehydes (**2**) were obtained in excellent yields. The results are summarised in Table 1.

The results showed that these reactions are not proceed in the absence of zirconium sulfate tetrahydrate-silica gel. The reaction rate is markedly dependent on temperature. We found that nitro derivatives (**1g**, **1h** and **1i**) gave lower yields (<60%) in refluxing benzene for 2 h whereas in refluxing toluene were 98% yield for 4-15 min. This may be due to the strongly electron-withdrawing nitro substituent, which requires a high refluxing temperature.

It should be noticed that the phenolic acetate function (**1j**) can be converted to phenol in a longer reaction time (**Scheme 2**), while the phenolic acetate (**1k**) was only deprotected in small amount (**Scheme 3**).

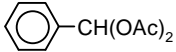
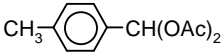
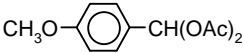
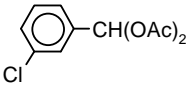
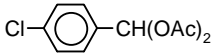
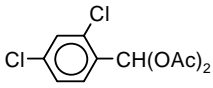
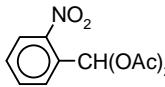
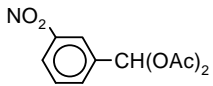
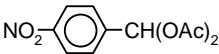
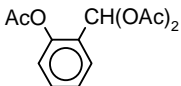
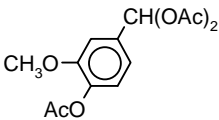
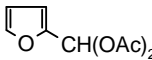
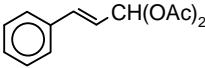
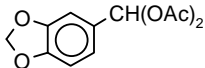


Scheme 2



Scheme 3

Table 1. Deprotection of 1,1-diacetates catalyzed by zirconium sulfate tetrahydrate-silica gel

Entry	Substrate	Solvent	Time (min)	Yield (%) ^a	Bp/torr or Mp (°C)		
					Found	Reported	
1		1a	CH ₂ Cl ₂	2	97	72-74/20	60-62/10 [19]
2		1b	CH ₂ Cl ₂	2	98	104-105/10	104-106/10 [19]
3		1c	CH ₂ Cl ₂	2	96	140-142/20	130-133/10 [19]
4		1d	Benzene	2	98	100-102/20	95-97/10 [19]
5		1e	Benzene	4	98	45-46	46-47 [19]
6		1f	Toluene	3	97	72-73	74.5 [24]
7		1g	Toluene	4	98	42-43	43-44 [24]
8		1h	Toluene	4	98	56-57	57-58 [19]
9		1i	Toluene	15	98	105-106	105-107 [19]
10		1j	Toluene	3	92	38-39	38-39 [24]
11		1k	Toluene	2	91	101-102	102-103 [25]
12		1l	Toluene	2	98	65-67/20	53-55/10 [19]
13		1m	Toluene	2	98	130-132/20	128-130/20 [19]
14		1n	Toluene	5	98	37-38	36-37 [19]

^aYields refer to isolated products.

We also found that the 1,1-diacetates (**1b** and **1c**) with electron-donating groups converted to the corresponding aldehydes in shorter reaction time (20 min) in dichloromethane at room temperature while the 1,1-diacetates (**1g**, **1h** and **1i**) with electron-withdrawing group need longer reaction time (8 h). This indicates that electron-donating groups benefit to the deprotection while electron-withdrawing groups not.

The catalyst can be reused six times in this method without significant losing of its activity.

Conclusion

We have developed a rapid and efficient procedure for deprotection of 1,1-diacetates. The advantages of this procedure are being straightforward, short reaction time, high yield, inexpensive and reusable catalyst, no corrosiveness and performing without an aqueous workup. The method is superior to the previous methods regarding the reaction time, yield, workup, being environment-friendly and reusable catalyst [7].

Acknowledgments

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