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Potassium Ferrate Supported on Montmorillonite K-10: A Mild and Efficient Reagent for Oxidative Deprotection of Acetals and Ketals

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Summary. A variety of acetals and ketals were oxidatively deprotected to their parent compounds using potassium ferrate(VI) supported on montmorillonite K-10 under non-aqueous conditions.

Keywords. Oxidative deprotection; Potassium ferrate; Clay; Acetals; Ketals.

Introduction

The protection and deprotection of functional groups constitutes an important feature in the synthesis of polyfunctional molecules, including the total synthesis of natural products. The shielding of carbonyl groups from nucleophilic attack or other kinds of unwanted reactions is common practice in multistage organic synthesis.

Although the protection of carbonyls can be achieved by a variety of protecting groups; protection as cyclic or acyclic acetals have proved to be most promising [2]. Hence, the deprotection of acetals and ketals to their carbonyl compounds is of practical significance. The general methods employed for the deprotection of acetals and ketals involve aqueous conditions using mineral acids [3]. Other methods employ silica gel [4], phosphorus triiodide [5], titanium(IV) chloride [6], boron-trifloride iodide [7], cerium(III) chloride [8], and silver and sodium bromate in the presence of AlCl₃ [9]. Recently, a repertoire concerning rapid and selective methods for the cleavage of acetals using supported ammonium nitrate under microwave irradiation has been reported [10]. Potassium ferrate (K_2FeO_4), a hexavalent iron compound, has been introduced recently by *P. Laszlo et al.* as a novel oxidizing reagent [11]. The use of a mineral support has attracted much attention because of improved selectivity, reactivity, and associated ease of manipulation [12, 13].

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Herein we wish to report that potassium ferrate(VI) supported on montmorillonite K-10 can efficiently deprotect cyclic acetals and ketals to the corresponding carbonyl compounds in high to excellent yields.

Results and Discussion

Potassium ferrate(VI) (K_2FeO_4) can be prepared easily by oxidizing ferric nitrate with sodium hypochlorite and subsequent treatment with potassium hydroxide [14]. The synthesis of the above reagent has been improved, and it has been claimed to be a law polluting oxidizer [11]. Prompted by stringent environmental protection laws in recent years, there has been increasing emphasis on the use and design of ecofriendly supported reagents to reduce the amount of toxic waste and byproducts arising from chemical processes [15].

Our approach to a clean and selective deprotection of acetals and ketals is to make use of potassium ferrate(VI) supported on montmorillonite K-10. Combination of ferric nitrate with zeolite had been pioneered in our laboratory, resulting in the design of zeofen as a versatile oxidizing agent [13b, 16]. Armed with this experience we reasoned that using an iron salt as less toxic transition metal salt [17] along with clay instead of *Brønsted* (H₂SO₄, HNO₃, *etc.*) and *Lewis* acids (AlCl₃, TiCl₄, *etc.*) would help to maintain a non-polluted environment.



Scheme 1

Substrate ^a	Product ^b	<i>t</i> /min	Yield/% ^c	M.p./°C or b.p./°C	
				Found	Reported [18]
1a	2a	10	95	177-178 (760 torr)	178–179 (760 torr)
1b	2b	10	85	247 (760 torr)	248 (760 torr)
1c	2c	15	90	235-236 (760 torr)	238 (760 torr)
1d	2d	15	92	56–57	57–59
1e	2e	15	91	151-153 (760 torr)	153 (760 torr)
1f	2f	10	90	120 (10 torr)	121 (10 torr)
1g	2g	10	93	201-202 (760 torr)	202 (760 torr)
1h	2h	15	92	116–118	116-118
1i	2i	15	88	76–77	75–77
1j	2j	15	82	77–79	78-80
1k	2k	15	88	111-112 (6 torr)	113-116 (6 torr)

Table 1. Oxidative cleavage of acetals and ketals using K₂FeO₄ supported on montmorillonite K-10

^a All substrates were synthesized according to known procedures; ^b all Products were characterized by comparison of their physical and spectroscopic data with those of authentic samples; ^c yield are based on isolated products

The reaction between potassium ferrate(VI) supported on montmorillonite K-10 and the acetal proceeded smoothly and afforded the corresponding carbonyl compound in high yield. It is noteworthy to mention that the reaction remained incomplete when the solid support was not used even with a higher ratio of reagent (2:8) as well as at a higher temperatures (refluxing in acetonitrile) and longer reaction times (5 h). Overoxidation was also not observed.

The acetal of cinnamaldehyde was transferred to the parent aldehyde by this method, showing that the carbon-carbon double bond is not prone to cleavage by the reagent. To assess the generality of the method, a variety of acetals and ketals were deprotected in high to excellent yields (Scheme 1, Table 1).

In conclusion, we have developed a selective, simple, inexpensive, efficient, and environmentally benign protocol for oxidative deprotection of acetals and ketals.

Experimental

All starting materials and products were known; their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Acetals and ketals were synthesized following a reported procedure [17]. The reagent (K_2FeO_4) was prepared according to the literature [11] and impregnated on montmorillonite K-10.

Oxidative deprotection of acetals and ketals with potassium ferrate(VI) supported on montmorillonite K-10; general procedure

In a round-bottomed flask (50 cm³) equipped with a magnetic stirrer and a condenser, a solution of 2 mmol acetal or ketal in (20 cm³) CH₂Cl₂ was prepared. Potassium ferrate (4 mmol) was mixed intimately with 1 g montmorillonite K-10 and added to this solution. The reaction mixture was refluxed and magnetically stirred for 10–15 min. The progress of the reaction was monitored by TLC (eluent: petrol ether:ethyl acetate = 8:2). The reaction mixture was filtered and washed with CH₂Cl₂.

The combined filtrate was evaporated to dryness. The crude residue was passed through a silica pad using a suitable solvent to regenerate the corresponding carbonyl compounds.

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