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Zeofen: A User-Friendly Catalyst for Oxidative Cleavage of Tetrahydropyranyl Ethers Under Non-Aqueous Conditions

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Summary. Primary and secondary tetrahydropyranyl ethers are efficiently converted to carbonyl compounds in excellent yields by zeofen under non-aqueous conditions.

Keywords. *THP* ethers; Zeofen; Oxidative deprotection; Carbonyl compounds.

Introduction

The tetrahydropyranyl group is one of the most widely employed protecting groups in organic synthesis [1]. Because of the remarkable stability of tetrahydropyranyl ethers towards a variety of conditions such as strongly basic media, reactions involving *Grignard* reagents and lithium alkyls, reduction with hydride, oxidation, oxidative alkylation, and acylation reactions, tetrahydropyranylation is one of the methods of choice to protect a hydroxy group in a multi-step organic synthesis [2]. Many catalysts have been reported for the tetrahydropyranylation of alcohols and the cleavage of tetrahydropyranyl ethers to the parent alcohols [3]. Direct oxidation of tetrahydropyranyl ethers to the corresponding carbonyl compounds has been relatively less considered. Although a number of reagents are known for such a transformation [4], there is still a need either to improve the existing oxidative deprotection methods or to introduce new reagents to permit better selectivity and, most importantly, to be environmentally benign. Most of the reagents used for oxidative dehydropyranylation are based on chromium [4]. Chromium compounds are toxic, corrosive, and they are irritants for the skin and for sensitive parts of body such as eyes [5]. Chromium(VI) compounds are suspected to be carcinogens [6].

In this communication we report that zeofen can efficiently oxidatively deprotect tetrahydropyranyl ethers to yield the corresponding carbonyl compounds.

Results and Discussion

Zeofen (zeolite HZSM-5 and ferric nitrate) has been used for the oxidation of alcohols to the corresponding carbonyl compounds by classical heating and micro-

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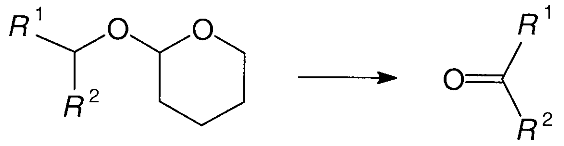
Table 1. Oxidative cleavage of *THP* ethers with zeofen in CH_2Cl_2 at reflux temperature



Substrate	*t*/h	Product	Yield/%	m.p./°C or b.p./°C(torr)	
				Found	Ref. [11]
PhCH$_2$O*THP*	6	PhCHO	91	177–178(760)	178–179(760)
4-MeC$_6$H$_4$CH$_2$O*THP*	6	4-MeC$_6$H$_4$CHO	98	58–59	59–61
2-NO$_2$-5-MeC$_6$H$_3$O*THP*	10	2-NO$_2$-5-MeCH$_3$CHO	80	66–67	66–67
PhCH(Me)O*THP*	6	PhCOMe	85	201–202(760)	202(760)
Ph$_2$CHO*THP*	8	PhCOPh	88	46–47	49–59
PhCH=CHCH$_2$O*THP*	10	PhCH=CHCHO	78	247–248(760)	248(760)
Cyclohexyl-*THP*	12	Cyclohexanone	82	156–157(760)	155(760)
Me-Cyclohexyl-*THP*	10	2-Me-Cyclohexanone	85	163–164(760)	165(760)
(−)-Menthyl-*THP*	10	(−)-Menthone	88	207–208(760)	200–210(760)

wave irradiation [7]. The association of ferric salts with clay had been pioneered in the 1980s, leading to the design of clayfen [8] as a versatile reagent [9] including the oxidative cleavage of tetrahydropyranyl ethers to carbonyl compounds.

A variety of tetrahydropyranyl ethers were treated with catalytic amounts of zeofen [7]. The corresponding aldelydes and ketones were obtained in high to excellent yields. The results are summarized in Table 1. To prepare zeofen, $Fe(NO_3)_3 \cdot 9H_2O$ and a weight equivalent of HZSM-5 zeolite were crushed together to form an intimate mixture. In a typical procedure, 1–1.2 equivalents of zeofen were refluxed with a tetrahydropyranyl ether in dichloromethane.

In conclusion, zeofen represents a convenient reagent for the one-pot oxidative deprotection of tetrahydropyranyl ethers to the corresponding carbonyl compounds. The notable advantages of this methodology are use of non-toxic ferric nitrate, mild conditions, and high to excellent yields.

Experimental

Zeofen was prepared by a reported method [7]. Yields refer to isolated products which were identified by comparison of their physical and spectroscopic data with those of authentic samples [11]. *THP* ethers were prepared according to Ref. [3b].

Oxidative deprotection of tetrahydropyranyl ethers; general procedure

In a round-bottomed flask (5 cm^3) equipped with stirrer and condenser, 1 mmol *THP* ether was dissolved in 15 cm^3 CH_2Cl_2 was prepared. Zeofen (equivalent to 1.2 mmol ferric nitrate) was added to this solution and refluxed for the time indicated. The progress of the reaction was monitored by TLC (eluent: petroleum ether:ethyl = acetate 8:2). After completion of the reaction the mixture was filtered, and the solid material was washed with CH_2Cl_2. The filtrate was combined and evaporated to dryness. The crude residue was subjected to column chromatography using petroleum ether:ethyl acetate = 8:2 as eluent to afford the corresponding carbonyl compounds (Table 1).

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