



An efficient iron catalyzed regioselective acylative cleavage of ethers: scope and mechanism



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ABSTRACT

A method involving iron catalyzed acylative cleavage of cyclic and acyclic ethers with acyl/aroyl chlorides has been studied to produce chloroesters and esters respectively. Examination of the scope revealed that less electron rich alkyl group in unsymmetric, acyclic ether was acylated while the chloride derived from the counterpart moiety was volatile and difficult to isolate. In contrast, α -branched cyclic ethers were converted to the corresponding primary ester and secondary chloride. Steric hindrance of ether also plays an important role in acylative C–O bond cleavage. The mechanism of ether cleavage is proposed to involve a single electron initiated S_N1 dissociative pathway.

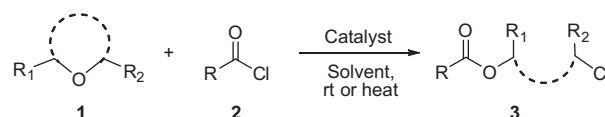
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The cleavage of ethers is a venerable reaction in organic synthesis and has been often utilized in simplifying the synthesis of complex bio-active molecules by producing various key intermediates.¹ At the same time, the synthesis of chloroesters from various organic substrates including cyclic ethers is also of great interest because they produce important intermediates for the synthesis of natural products.² Due to the high chemical stability of ethers, their cleavage is normally only possible under strongly acidic or extremely basic conditions. An important alternative strategy for the cleavage of ethers (**1**) exploits acid chlorides (**2**) resulting in esters or chloroesters (**3**). Often, these cleavages are mediated by homogeneous or heterogeneous catalyst systems based on Lewis acids,³ group V, VI, and VII transition metal complexes,⁴ and metals and their derivatives (Zn,⁵ Al,^{6a} Pt,^{6b} Pd,^{6c} and iodine⁷) as well as non-metals like graphite⁸ as shown in Scheme 1. A recent report by Enthaler and Weidauer describes the ZnCl₂ mediated ring opening of cyclic ethers with acid chlorides and subsequent functionalization into cyano-esters.^{3r} Some methods using acid chlorides have not been applied to acyclic ethers^{3l,n} while some are limited to cyclic ethers, yet failed to cleave acyclic aliphatic ethers.^{6b} Pasha and Myint used ultrasound and zinc dust to cleave

tetrahydrofuran (THF), but required excess equivalents.^{5b} Lewis acids like ZnCl₂,^{3a,b} FeCl₃,^{3c} [emim]Al₂Cl₇,^{3k} and FeCl₂,^{3s} etc., usually require extended reaction times, whereas TiCl₄^{3e} and BCl₃^{3m} are air sensitive; others result in mixtures of regioisomers.

In addition, toxic catalysts like Hg⁶ and expensive reagents such as Cp₂YCl,⁹ SmI₂,^{3l} M(CO)₆ [M = Cr, Mo and W],^{4a–d} WCl₆, NbCl₅,^{4e} etc., have also been employed, but are not attractive for large scale reactions and/or due to environmental restrictions. Some heterogeneous catalysts have also been studied for the cleavage of ethers,^{5,8} but the identification and validation of more environmentally acceptable and expedient catalysts continues.

Hence, development of simple, convenient, and efficient procedures for the cleavage of ethers resulting in useful synthetic intermediates remains an interesting topic. A catalytic/pre-catalytic system would be better alternative to the previous catalysts, so



R = alkyl or aryl; R₁, R₂ = H, alkyl or aryl;

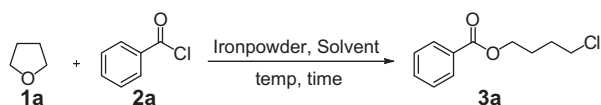
Catalyst = Lewis acids, Non-metals, Metals and Metal complexes etc.

Scheme 1. Cleavage of ethers with acid chlorides in presence of a catalyst.

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Table 1
Solvent screening in the acylative cleavage of **1a** with **2a** using iron



Entry	Equiv of THF (1a)	Equiv of iron	Solvent	Reaction conditions	Yield 3a ^a (%)
1	—	1.0	THF	66 °C, 3 h	23
2	1.1	2.5	CH ₃ CN	80 °C, 3 h	9
3	1.1	2.5	DCM	45 °C, 3 h	11
4	1.2	1.0	DCE	80 °C, 3 h	65
5	1.1	0.2	DCE	80 °C, 3 h	51
6	1.1	0.2	DCE	80 °C, 8 h	78

^a Isolated yield after column chromatography.

Table 2
Acylative cleavage of **1a-1** with **2a**

Entry	Ether ^a	Equiv of iron powder	Temp (°C) and time (h)	Product ^b	Yield ^c (%)
1		0.2	70, 7		94
2		1.0	55, 7	—	—
3		0.2	80, 7		99
4		0.2	80, 7		90
5		0.2	45, 8	3d	76 ^d
6		1.0	84, 7	—	—
7		0.2 0 0.2	70, 8 70, 0.5 70, 0.5		91 72 ^e 69 ^e
8		2.0	84, 3		97
9		1.0	84, 7	—	—
10		0.2	80, 7		95 ^f
11		1.0	80, 7	—	—

^a 1.1 equiv of ether was used in DCE.

^b All products were characterized by using NMR spectrometry and GC–MS analysis.

^c Isolated yields based on benzoyl chloride.

^d 2 equiv of ether was used.

^e When treated in presence of 0.2 equiv of FeCl₃.

^f Products ratio was calculated by ¹H NMR.

that it can be easily separable from the reaction mixture with negligible amounts of catalyst loss. Since iron satisfies many of the desired criteria including ease of handling, minimal toxicity, relatively low costs, and commercial availability in various forms, it has been in demand for years in the area of transition metal catalysis.¹⁰ Iron is not only a green catalyst when compared to its expensive metal competitors, but also offers a wide range of organic transformations. Chloride salts of iron were used to cleave ethers with perilous solvent acetic anhydride^{3c} and to depolymerize polyethers but for longer hours (24 h) at high temperatures (>100 °C),^{3r} demonstrate limited scope even with respect to their cost and quantity. However, there have been no reports to date on elemental iron as a pre-catalyst/initiator for the cleavage of ethers by acid chlorides at moderate temperatures with excellent yields.

In continuation of our interest in the applications of elemental iron,¹¹ we herein report a mild and efficient method affording

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