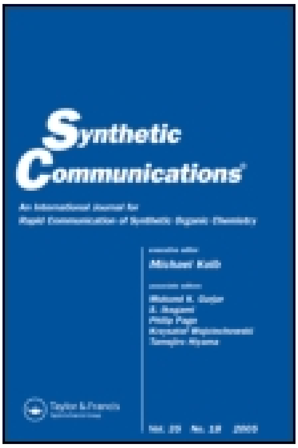


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Use of Magnesium (Turnings) as a Powerful Catalyst for the O-Acylative Cleavage of Tetrahydrofuran

M. A. Pasha [a] & Krishnappa Manjula [a]

[a] Department of Studies in Chemistry, Bangalore University, Bangalore, India

Version of record first published: 25 May 2011.

To cite this article: M. A. Pasha & Krishnappa Manjula (2011): Use of Magnesium (Turnings) as a Powerful Catalyst for the O-Acylative Cleavage of Tetrahydrofuran, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:15, 2309-2314

To link to this article: http://dx.doi.org/10.1080/00397911.2010.502992

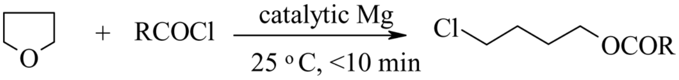
Synthetic Communications®, 41: 2309–2314, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.502992

USE OF MAGNESIUM (TURNINGS) AS A POWERFUL CATALYST FOR THE *O*-ACYLATIVE CLEAVAGE OF TETRAHYDROFURAN

M. A. Pasha and Krishnappa Manjula
Department of Studies in Chemistry, Bangalore University, Bangalore, India

GRAPHICAL ABSTRACT



Abstract *In a short reaction time, acyl chlorides and dry tetrahydrofuran react in the presence of a catalytic amount of magnesium turnings (Mg) at 25 °C to give 4-chlorobutyl esters in excellent yields.*

Keywords Acyl chlorides; 4-chlorobutylesters; magnesium turnings; tetrahydrofuran

INTRODUCTION

The cleavage of tetrahydrofuran (THF) with acyl chlorides to give 4-chlorobutyl esters is a useful reaction, particularly in the synthesis of natural products and polyfunctional molecules where a four-carbon chain is required to be added.[1] Syntheses of 4-chlorobutyl esters from THF and acid chloride in the presence of $ZnCl_2$,[2] $FeCl_3$,[3] $Mo(CO)_6$,[4] $MoCl_5$,[5] SmI_2,[6] $PdCl_2(PPh_3)_2$,[7] $CoCl_2$,[8] NaI,[9] lanthanide salts,[10] graphite,[11] aluminum complexes,[12] $InBr_3$,[13] and $La(NO_3)_3 \cdot 6H_2O$,[14] have been reported.

Many of these procedures suffer from one or other limitations such as use of expensive reagents, longer reaction times, and high temperatures. In some cases, the yields are poor to moderate, environmentally toxic catalysts are used, and cumbersome methodologies are employed. Therefore, there is a need for versatile, simple, and environmentally friendly processes for the synthesis of 4-chlorbutyl esters.

Studies on the use of the nontoxic and inexpensive environmentally benign metal magnesium have greatly expanded all around the world, and a search for application of magnesium and magnesium compounds has pulled up numerous records.[15] Cleavage of the THF ring by triphenylmethylmagnesium bromide to give 5,5,5-triphenylpentan-1-ol,[16] the use of magnesium bromide for the acylation of

Received February 19, 2010.

Address correspondence to M. A. Pasha, Department of Studies in Chemistry, Central College Campus, Bangalore University, Bangalore 560 001, India. E-mail: m_af_pasha@ymail.com

alcohols,[17] and the use of magnesium alkoxides in the synthesis of benzoheterocyclic compounds[18] have been investigated recently.

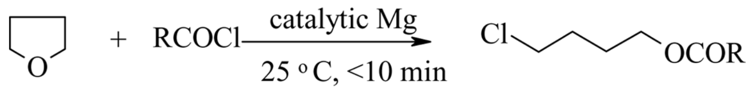
In this paper, we describe our successful use of magnesium as a catalyst for the *O*-acylative cleavage of THF in the presence of acyl chlorides at 25 °C to get 4-chlorobutyl esters.

RESULTS AND DISCUSSION

Earlier reports from our laboratory described the synthesis of 4-chlorobutyl esters from THF and acyl chlorides in the presence of zinc dust under sonication.[19a] To avoid the use of sonication, we studied the reaction under normal condition with a catalytic amount of molecular iodine to get 4-chlorobutyl esters.[9b] In continuation with our work on the synthesis of 4-chlorobutyl esters using simpler reagents and catalysts, we are reporting a simple and efficient method of synthesis of 4-chlorobutyl esters from THF and acyl chlorides using a catalytic amount of magnesium turnings in the absence of any additional solvent at 25 °C (Scheme 1) in less than 10 min with excellent yields.

To standardize the reaction conditions, different amounts of magnesium turnings were used to get 4-chlorobutyl benzoate from THF and benzoyl chloride; the results are summarized in Table 1. From Table 1 it is clear that the reaction can be carried out in the presence of a catalytic amount of magnesium turnings, and the yield of the product is maximum (94% with 0.024 g). It is not possible without magnesium turnings (entries 5 and 6).

To extend the reaction of THF with different acyl chlorides in the presence of catalytic magnesium, the reactions of THF with alkyl, aryl, and allyl, substituted acyl chlorides were taken up. The reactions were carried out under normal condition, and the results are summarized in Table 2. From this table, it is clear that aroyl



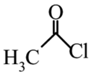
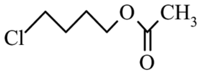
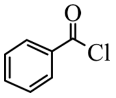
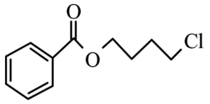
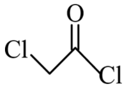
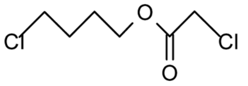
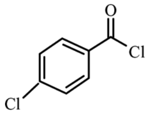
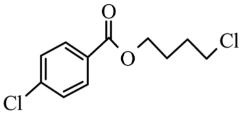
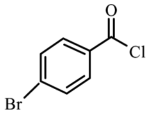
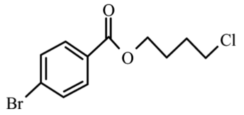
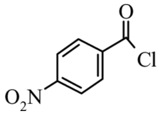
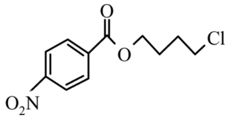
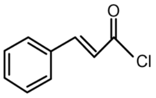
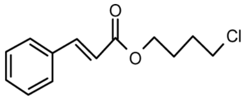
R = CH_3-, C_6H_5-, $ClCH_2$-, *p*-Cl C_6H_5-, *p*-BrC_6H_4-, *p*-$NO_2C_6H_4$-, $C_6H_5CH{=}CH$-

Scheme 1. Mg metal-catalyzed *O*-acylative cleavage of tetrahydrofuran.

Table 1. Reaction of THF and benzoyl chloride in the presence/absence of Mg turnings at 25 °C

Entry	Amount of Mg (g)	Time (min)	Yield (%)
1	0.24	30	78
2	0.18	30	80
3	0.12	30	80
4	0.06	30	87
5	0.024	05	94
6	Nil	24 (hours)	No reaction

Table 2. Reaction of acyl chlorides with THF in presence of magnesium turnings[a] at 25 °C

Entry	Acid chloride (**2**)	Product[b] (**3**)	Time (min)	Yield (%)
a			03	95
b			05	94
c			05	92
d			05	90
e			05	94
f			06	90
g			08	92

[a] 0.024 g of Mg.

[b] Products are characterized by IR, ^{1}H NMR, and LC–mass spectral analysis.

chlorides containing both electron-withdrawing and electron-donating groups react equally efficiently to give 4-chlorobutylesters in excellent yield in less than 10 min.

EXPERIMENTAL

Different acyl chlorides were prepared by standard procedures[20] and purified before use. All reagents were commercial products, solids were used without further purification, and liquids were distilled before use. Reactions were monitored on TLC by comparison with the samples prepared by known methods.[19a,b] Yields refer to the isolated yields of the products and are based on 10 mmol of starting acid chloride. A Nicolet 400D Fourier transform–infrared (FT-IR) spectrophotometer was used for IR spectral analysis. ^{1}H NMR spectra were recorded on a 400-MHz Bruker instrument and liquid chromatography (LC)–mass analysis was performed on an Agilent Technologies 1200 series instrument.

General Experimental Procedure for the Preparation of 4-Chlorobutyl Esters

Acyl chloride (10 mmol) and THF (10 ml) were taken in a 25-ml round-bottomed flask. To this, magnesium turnings (0.024 g) were added and stirred at 25 °C. The progress of the reaction was monitored by thin-layer chromatography (TLC); after completion of the reaction, the contents were filtered and washed with ether (25 ml), and the organic layer was washed successively with saturated $NaHCO_3$(10 ml), followed by water (3 × 10 ml), dried over anhydrous Na_2SO_4, concentrated, and purified by silica-gel column chromatography (5% ethyl acetate–petroleum ether) to afford pure 4-chlorobutyl esters. The IR, ^{1}H NMR, and LC-MS spectral data of 4-chlorobutyl esters prepared by this procedure are presented.

Spectroscopic Data of the Products

$CH_3CO_2(CH_2)_4Cl$ (3a). IR (neat) $\nu = 1739$, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.78–1.87 (m, 4H), 2.04 (s, 3H), 3.55–3.58 (t, 2H, $J = 6$ Hz), 4.06–4.11 (t, 2H, $J = 6$ Hz); MS: $m/z = 151.0$ (M^+).

$C_6H_5CO_2(CH_2)_4Cl$ (3b). IR (neat) $\nu = 1716$, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.97 (m, 4H), 3.59 (t, 2H, $J = 4$ Hz), 4.35 (t, 2H, $J = 4$ Hz), 7.44 (d, 2H, $J = 8$ Hz), 7.61 (t, 1H, $J = 8$ Hz), 8.01 (d, 2H, $J = 8$ Hz); MS: $m/z = 212$ (M^+).

$ClCH_2CO_2(CH_2)_4Cl$ (3c). IR (neat) $\nu = 1751$, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.65–1.93 (m, 4H), 2.07 (s, 2H), 3.61 (t, 2H, $J = 6$ Hz), 4.15 (t, 2H, $J = 6$ Hz); MS: $m/z = 184$ (M^+).

$ClC_6H_4CO_2(CH_2)_4Cl$ (3d). IR (neat) $\nu = 1720$, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93 (m, 4H), 3.65 (m, 2H), 4.38 (m, 2H), 7.67 (d, 2H, $J = 8$ Hz) 7.89 (d, 2H, $J = 8$ Hz); MS: $m/z = 246$ (M^+).

$BrC_6H_4CO_2(CH_2)_4Cl$ (3e). IR (neat) $\nu = 1725$, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93 (m, 4H), 3.55 (m, 2H), 4.38 (m, 2H), 7.63 (d, 2H, $J = 8.4$ Hz), 7.88 (d, 2H, $J = 8.5$ Hz); MS: $m/z = 292$ (M^+).

$NO_2C_6H_4CO_2(CH_2)_4Cl$ (3f). IR (neat) $\nu = 1745$, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (m, 4H), 3.65 (m, 2H), 4.36 (m, 2H), 7.52 (d, 2H, $J = 8$ Hz), 7.96 (d, 2H, $J = 8$ Hz); MS: $m/z = 257$ (M^+).

$C_6H_5CH{=}CHCO_2(CH_2)_4Cl$ (3g). IR (neat) $\nu = 1768$, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93 (m, 4H), 3.65 (m, 2H), 4.38 (m, 2H), 6.42 (d, 1H, $J = 16$ Hz), 7.74 (d, 1H, $J = 16$ Hz), 7.50 (d, 2H, $J = 8$ Hz), 7.49 (t, 1H, $J = 8$ Hz), 7.61 (d, 2H, $J = 8$ Hz); MS: $m/z = 238$ (M^+).

CONCLUSION

In conclusion, we have presented a simple, efficient, economically viable, and solvent-free protocol for the preparation of 4-chlorobutyl esters from THF and acyl chlorides in the presence of catalytic amounts of nontoxic, readily available, and inexpensive magnesium turnings. The advantageous of our method include a simple reaction setup not requiring specialized equipment, room temperature conditions, excellent product yields, short time, and elimination of solvents. The present method is as efficient as our previous methods of synthesis of 4-chlorobutyl esters.[19a,b]

ACKNOWLEDGMENT

Krishnappa Manjula is thankful to V. P. Jayashankara for his timely help and encouragement.

REFERENCES

1. (a) Bhatt, M. V.; Kulkarni, S. U. Cleavage of ethers. *Synthesis* **1983**, 249–282; (b) Maercker, A. Ether cleavage with organo-alkali-metal compounds and alkali metals. *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 972–989; (c) Zhang, C.; Price, L. M.; Daly, W. H. Synthesis and characterization of a trifunctional aminoamide cellulose derivative. *Biomacromolecules* **2006**, *7*, 139–145.
2. Cloke, J. B.; Pilgrim, F. J. The reaction of tetrahydrofuran and 2,5-dimethyltetrahydrofuran with acyl halides. *J. Am. Chem. Soc.* **1939**, *61*, 2667–2669.
3. Ganem, B.; Small, Jr. V. R. Ferric chloride in acetic anhydide: Mild and versatile reagent for the cleavage of ethers. *J. Org. Chem.* **1974**, *39*, 3728–3730.
4. Alper, H.; Huang, C. C. Group VI metal carbonyl–catalyzed reaction of ethers and acid halides. *J. Org. Chem.* **1973**, *38*, 64–71.
5. Guo, Q.; Miyaji, T.; Gao, G.; Hara, R.; Takahashi, T. Catalytic C–O bond cleavage of ethers using group 5 or 6 metal halide/acid chloride systems. *J. Chem. Soc., Chem. Commun.* **2001**, 1018–1019.
6. Kwon, D. W.; Kim, Y. H. Highly regioselective cleavages and iodinations of cyclic ethers utilizing SmI_2. *J. Org. Chem.* **2002**, *67*, 9488–9491.
7. Pri-Bar, I.; Stille, J. K. Acylative cleavage of ethers catalyzed by triorganotin halides and palladium(II) complexes. *J. Org. Chem.* **1982**, *47*, 1215–1220.
8. Iqbal, J.; Srivastava, R. R. A practical synthesis of D-malate esters from L-tartrate esters. *Tetrahedron* **1991**, *47*, 3155–3158.
9. (a) Oku, A.; Harada, T.; Kita, K. Selective cleavage of ethers by sodium iodide–acyl chloride. *Tetrahedron Lett.* **1982**, *23*, 681–684; (b) Mimero, P.; Saluzzo, C.; Amouroux, R. Regiocontrolled ring opening of 2-methyltetrahydrofuran with acid chlorides and iodides. *Tetrahedron Lett.* **1994**, *35*, 1553–1556.
10. Taniguchi, Y.; Tanaka, S.; Kitamura, T.; Fujivara, Y. Lanthanoid-catalyzed ring-opening reaction of epoxides with acyl halides. *Tetrahedron Lett.* **1998**, *39*, 4559–4560.
11. Suzuki, Y.; Matsushima, M.; Kodomari, M. Graphite-catalyzed acylative cleavage of ethers with acyl halides. *Chem. Lett.* **1998**, 319–320.
12. Green, L.; Hemeon, L.; Singer, R. D. 1-Ethyl-3-methylimidazolium halogenoaluminate ionic liquids as reaction media for the acylative cleavage of ethers. *Tetrahedron Lett.* **2000**, *41*, 1343–1346.
13. Yadav, J. S.; Reddy, B. W. S.; Reddy, M. K.; Desh, U.; Guptha, M. K. Indium(III) bromide–catalyzed cleavage of cyclic and acyclic ethers: An efficient and practical ring opening reaction. *J. Mol. Cat., Sec. A* **2007**, *271*, 266–269.
14. Suresh, V.; Suryakiran, N.; Rajesh, K.; Selvam, J. J. P.; Srinivasulu, M.; Venkateswarlu, Y. Synthesis of chloroesters by the cleavage of cyclic and acyclic ethers using $La(NO_3)_3 \cdot 6H_2O$ as a mild and efficient catalyst under solvent-free conditions. *Synth. Commun.* **2008**, *38* (1), 92–99.

15. Ke, W.; Han, E. H.; Han, Y. F.; Kainer, K.; Luo, A. A. Magnesium—Science, technology, and applications. *Materials Science Forum* **2005**, *488–489*, 975.
16. (a) Jensean, F. K.; Bedard, R. Cleavage of tetrahydrofuran by triphenylmethylmagnesium bromide. *J. Org. Chem.* **1959**, *24*, 874–875.
17. Pansare, S. V.; Malusare, M. G.; Rai, A. N. Magnesium bromide–catalysed acylation of alcohols. *Synth. Commun.* **2000**, *30*, 2587–2592.
18. Svoboda, J.; Nic, M.; Palecek, J. Application of magnesium alkoxides to syntheses of benzoheterocyclic compounds. *Coll. of Czechoslovak Chem. Commun.* **1993**, *58*, 592–599.
19. (a) Pasha, M. A.; Myint, Y. Y. Ultrasound-assisted synthesis of δ-chloroesters from tetrahydrofuran and acyl chlorides in the presence of catalytic zinc dust. *Ultrason. Sonochem.* **2005**, *13*, 175–179; (b) Pasha, M. A.; Manjula, K. Simple and efficient method for the synthesis of δ-chloroesters from tetrahydrofuran and acyl chlorides in the presence of catalytic iodine. *Synth. Commun.* **2007**, *37*, 927–932.
20. Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed; ELBS: London, 1975.