Chemical Papers
https://doi.org/10.1007/s11696-020-01267-2

ORIGINAL PAPER

Synthesis of chloroesters by the reaction of ethers with acyl chlorides catalyzed by ZnO

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Received: 16 February 2020 / Accepted: 23 June 2020

Abstract
An efficient method for the synthesis of chloroesters by the reaction of ethers with acyl chlorides catalyzed by nano-ZnO under solvent-free condition at room temperature was described. The method is compatible with a range of ethers including tricyclic ethers, tetracyclic ethers, pentacyclic ethers and hexacyclic ethers and have afforded the products with moderate to good yields. The ZnO could be reused up to three times and the product yield after three cycles is 87%.

Keywords Chloroesters · Cyclic and acyclic ethers · Zinc oxide · Solvent-free

Introduction

The synthesis of chloroesters is a versatile organic transformation by the reaction of ethers with acyl chlorides. Ether cleavage synthesis of chloroesters was frequently utilized to simplify the synthesis of complex bio-active molecules by producing various key intermediates (Burwell 1954; Schelhaas and Waldmann 1996). Catalysts for cracking cyclic ethers to form chloroesters using Lewis acids had been reported, such as $ZnCl_2$ (Cloke and Pilgrim 1939), $Mo(CO)_6$ (Alper and Huang 1973), $FeCl_3$ (Ganem and Small 1974), $TiCl_4$ (Delaney et al. 1986), NaI (Oku et al. 1982) (Mimero et al. 1994), $PdCl_2(PPh_3)_2$ (Pri-Bar and Stille 1982), $CoCl_2$ (Iqbal and Srivastava 1991), WCl_6 (Guo et al. 2001), $MoCl_5$ (Guo et al. 2002), BCl_3 (Malladi and Kabalka 2002), SmI_2 (Kwon and Kim 2002), $Bi(NO_3)_3{\cdot}5H_2O$ (Suresh et al. 2007), InBr (Yadav et al. 2007), $La(NO_3)_3{\cdot}6H_2O$ (Suresh et al. 2008), $FeCl_2$ (Enthaler and Weidauer 2012a) etc. However, these methods displayed some disadvantages, such as using toxic, expensive and non-recyclable catalysts, long reaction time and low product yields. Thus, it is necessary to develop a novel method to synthesize chloroesters.

ZnO as a non-toxic, inexpensive, non-hygroscopic Lewis acid catalyst has been widely used in many organic transformations. For example, Zhang et al. (2013) described solvent-free synthesis of 2-acylpyrroles and its derivatives; Javadi and Tayebee (2016) and Tayebee et al. (2012, 2013a) proposed synthesis of 2-aminothiophenes via the Gewald reaction; Tayebee et al. (2010, 2013b) reported the one-pot synthesis of 2,4,6-trisubstituted-1,3,5-trioxanes and as an efficient and environmentally benign catalyst for homogeneous benzoylation of hydroxyl functional groups. Bahrami et al. (2009) reported the highly efficient solvent-free synthesis of dihydropyrimidinones; Hosseini-Sarvari and Sharghi (2007) reported a novel method for the synthesis of *N*-sulfonylaldimines; Sarvari and Sharghi (2004) proposed an efficient Friedel–Crafts acylation reaction. At present, there is no report about the synthesis of chloroesters by the cleavage of cyclic and acyclic ethers catalyzed by ZnO.

In our study (Scheme 1), nano-ZnO powder was utilized as the catalyst to decompose cyclic ether and acyclic ether with acyl chlorides to form chloroesters under solvent-free condition. The method has the advantages of high yields, environmental friendliness, simple operation and mild reaction condition.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11696-020-01267-2) contains supplementary material, which is available to authorized users.

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Published online: 07 July 2020

Experimental

Materials and instruments

The reagents utilized in the experiment were purchased from commercial channels and could be used directly without further purification. ZnO nanoparticles with the average particle size of about 30 nm. All reactions were monitored by thin-layer chromatography (TLC) on GF-254 silica gel plates and viewed under UV light at 254 nm. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance DPX-300 MHz/500 MHz instrument in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard and the chemical shifts (δ) were given in parts per million (ppm).

Typical experimental procedure for the synthesis of chloroesters by the cleavage of cyclic and acyclic ethers

In the mixture of cyclic/acyclic ether (11 mmol) and acid chloride (10 mmol), nano-ZnO (5 mol%) was added at 0–5 °C and stirred at room temperature for an appropriate time. After the TLC monitoring reaction, the ZnO was removed by filtration and washed repeatedly with dichloromethane and water. It was then dried at 60 °C for 3 h and used for the next catalytic cycle. The solution was extracted three times with dichloromethane and water, and dried on anhydrous Na_2SO_4. The product was purified on a silica gel column chromatography using a mixture of petroleum ether/ethyl acetate (150:1, v/v). The product is obtained by vacuum distillation to remove the solvent. The compounds were characterized by ^{1}H NMR and ^{13}C NMR.

Characterization of compound

1,3-Dichloropropan-2-yl benzoate (Table 2, entry 1): ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 7.99–7.95 (m, 2H), 7.69–7.64 (m, 1H), 7.55–7.49 (m, 2H), 5.43–5.38 (m, 1H), 4.06–3.89 (m, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 164.7, 133.8, 133.6, 129.3, 128.8, 72.3, 43.5 (Bodduri et al. 2015).

2,3-Dichloropropyl benzoate: ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 7.98–7.29 (m, 2H), 7.66–7.59 (m, 1H), 7.54–7.48 (m, 2H), 3.94–3.80 (m, 3H), 3.76–3.69 (m, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 165.4, 133.6, 133.4, 129.2, 128.7, 75.9, 64.1, 44.1 (Bodduri et al. 2015).

3-Chloropropyl benzoate (Table 2, entry 2): ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 7.95 (d, J = 6 Hz, 2H), 7.65–7.60 (m, 1H), 7.49 (t, J = 7.5 Hz, 2H), 4.35 (t, J = 6 Hz, 2H), 3.76 (t, J = 6 Hz, 2H), 2.18–2.10 (m, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 165.6, 134.3, 133.3, 129.1, 128.7, 61.7, 41.9, 31.1 (Guo et al. 2002).

4-Chlorobutyl benzoate (Table 2, entry 3): ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 8.00 (d, J = 10 Hz, 2H), 7.70–7.67 (m, 1H), 7.56 (t, J = 7.5 Hz, 2H), 4.34 (t, J = 5 Hz, 2H), 3.74 (t, J = 7.5 Hz, 2H), 1.92–1.86 (m, 4H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ: 166.1, 133.7, 130.3, 129.5, 129.2, 64.4, 45.5, 29.3, 26.2 (Bodduri et al. 2015).

4-Chloropentyl benzoate (Table 2, entry 4): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.93 (d, J = 10 Hz, 2H), 7.65–7.60 (m, 1H), 7.49 (t, J = 12.5 Hz, 2H), 4.28–4.24 (m, 2H), 4.22–4.16 (m, 1H), 1.90–1.72 (m, 4H), 1.45 (d, J = 10 Hz, 3H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ: 165.7, 133.2, 129.8, 129.0, 128.7, 64.1, 59.1, 36.2, 25.5, 25.1 (Guo et al. 2002).

5-Chloropentyl benzoate (Table 2, entry 5): ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 8.00 (d, J = 5 Hz, 2H), 7.70–7.67 (m, 1H), 7.56 (t, J = 7.5 Hz, 2H), 4.31 (t, J = 5 Hz, 2H), 3.68 (t, J = 5 Hz, 2H), 1.84–1.74 (m, 4H), 1.58–1.52 (m, 2H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ 166.2, 133.7, 130.3, 129.5, 129.2, 64.9, 45.6, 32.1, 27.9, 23.4 (Bodduri et al. 2015).

4-Chlorobutyl acetate (Table 3, entry 2): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 4.06 (t, J = 7.5 Hz, 2H), 3.69 (t, J = 5 Hz, 2H), 2.03 (s, 3H), 1.83–1.78 (m, 2H), 1.75–1.69 (m, 2H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ 170.8, 63.6, 45.4, 29.2, 26.1, 21.1 (Bodduri et al. 2015).

4-Chlorobutyl 2-chlorobenzoate (Table 3, entry 3): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.83 (d, J = 5 Hz, 1H), 7.62–7.58 (m, 2H), 7.52–7.47 (m, 1H), 4.35 (t, J = 5 Hz, 2H), 3.73 (*t*, J = 7.5 Hz, 2H), 1.93–1.84 (m, 4H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ 165.6, 133.5, 132.1, 131.4, 131.2, 130.8, 127.8, 65.1, 45.41, 29.3, 26.1 (Yadav et al. 2007).

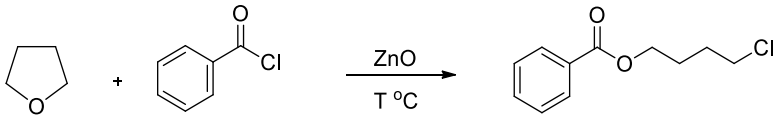
4-Chlorobutyl 3-chlorobenzoate (Table 3, entry 4): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.89–7.87 (m, 2H), 7.71–7.68 (m, 1H), 7.56–7.50 (m, 1H), 4.28 (t, J = 6 Hz, 2H), 3.67 (t, J = 6 Hz, 2H), 1.88–1.77 (m, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 185.5, 164.5, 133.0, 131.8, 130.7, 128.6, 127.7, 64.5, 44.9, 28.8, 25.6 (Chen et al. 2014).

4-Chlorobutyl 4-chlorobenzoate (Table 3, entry 5): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.92 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 4.27 (t, J = 5.8 Hz, 2H), 3.67 (t, J = 6.0 Hz, 2H), 1.89–1.74 (m, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 164.8, 138.2, 130.9, 128.9, 128.6, 64.2, 44.9, 28.8, 25.6 (Enthaler and Weidauer 2012b).

4-Chlorobutyl 4-methylbenzoate (Table 3, entry 6): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.34 (t, J = 5.8 Hz, 2H), 3.61 (t, J = 6.0 Hz, 2H), 2.40 (s, 3H), 1.95 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.1, 143.1, 129.1, 128.6, 127.0, 63.4, 44.0, 28.8, 25.7, 21.1 (Bodduri et al. 2015).

4-Chlorobutyl 4-fluorobenzoate (Table 3, entry 7): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.07–8.02 (m, 2H), 7.13–7.08 (m, 2H), 4.34 (d, J = 5.0 Hz, 2H), 3.62–3.59 (m, J = 5.4 Hz, 2H), 1.99–1.89 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ

Table 1 Optimization of the reaction conditions



Entry	ZnO (mol%)	T (°C)	Time	Yield [a](%)
1	-	RT	8h	N.R.
2	1	RT	25min	49
3	2	RT	25min	67
4	5	RT	25min	95
5	7	RT	25min	95
6	10	RT	25min	89
7	12	RT	25min	85
8	5	-10	8h	N.R.
9	5	0	25min	38
10	5	10	25min	79
11	5	50	25min	94

Reaction condition: THF (11 mmol) and benzoyl chloride (10 mmol) were used

N.R. no reaction

[a]Isolated yield

167.0, 165.1 (d, $J = 109.5$ Hz), 131.6 (d, $J = 9.3$ Hz), 126.0 (d, $J = 3$ Hz), 115.2 (d, $J = 22.5$ Hz), 63.7, 43.9, 28.8, 25.7 (Bodduri et al. 2015).

4-Chlorobutyl 4-methoxybenzoate (Table 3, entry 8): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (d, $J = 8.9$ Hz, 2H), 7.01 (d, $J = 8.9$ Hz, 2H), 4.23 (t, $J = 5.9$ Hz, 2H), 3.80 (s, 3H), 3.67 (t, $J = 6.1$ Hz, 2H), 1.87–1.75 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.3, 163.1, 131.1, 122.1, 114.0, 63.6, 55.5, 44.9, 28.9, 25.8 (Bodduri et al. 2015).

4-Chlorobutyl 2-chloronicotinate (Table 3, entry 9): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84–7.76 (m, 1H), 7.55 (d, $J = 4.9$ Hz, 1H), 7.15–7.07 (m, 1H), 4.33 (t, $J = 5.8$ Hz, 2H), 3.63–3.57 (m, 2H), 1.94–1.86 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 185.5, 161.7, 133.3, 132.9, 131.9, 127.3, 63.8, 43.9, 28.7, 25.7 (Suresh et al. 2007).

4-Chloropentyl 4-chlorobenzoate (Table 4, entry 2): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.92 (d, $J = 8.6$ Hz, 2H), 7.56 (d, $J = 8.6$ Hz, 2H), 4.28–4.16 (m, 3H), 1.90–1.71 (m, 4H), 1.45 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 164.8, 138.2, 130.9, 128.9, 128.6, 64.4, 59.1, 36.2, 25.4, 25.1 (Bodduri et al. 2015).

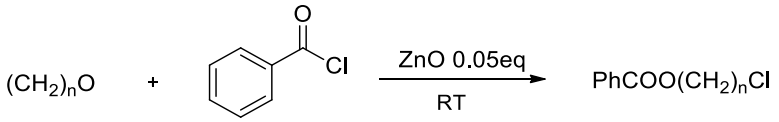
4-Chloropentyl 4-fluorobenzoate (Table 4, entry 3): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.01–7.96 (m, 2H), 7.34–7.28 (m, 2H), 4.27–4.16 (m, 3H), 1.89–1.72 (m, 4H), 1.45 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 166.7, 164.7 (d, $J = 99.8$ Hz), 132.0 (d, $J = 9.8$ Hz), 126.4 (d, $J = 3$ Hz), 116.0 (d, $J = 22.5$ Hz), 64.3, 59.1, 36.2, 25.5, 25.1 (Bodduri et al. 2015).

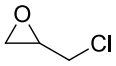
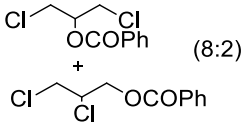
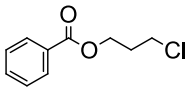
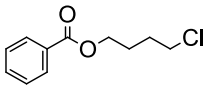
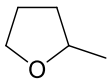
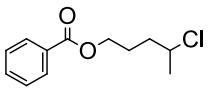
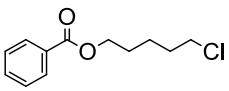
4-Chloropentyl 4-methoxybenzoate (Table 4, entry 4): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.89–7.85 (m, 2H), 7.02–6.99 (m, 2H), 4.27–4.18 (m, 3H), 3.79 (s, 3H), 1.88–1.71 (m, 4H), 1.45 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 165.3, 163.1, 131.1, 122.0, 114.0, 63.7, 59.1, 55.5, 36.2, 25.6, 25.1 (Bodduri et al. 2015).

5-Chloropentyl 2-chlorobenzoate (Table 4, entry 6): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (dd, $J = 7.6$, 1.1 Hz, 1H), 7.45–7.36 (m, 2H), 7.32–7.26 (m, 1H), 4.34 (t, $J = 6.4$ Hz, 2H), 3.54 (t, $J = 6.6$ Hz, 2H), 1.88–1.75 (m, 4H), 1.65–1.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.6, 133.5, 132.1, 131.3, 131.2, 130.9, 127.8, 65.5, 45.6, 32.0, 27.8, 23.3 (Suresh et al. 2007).

Benzyl benzoate (Table 4, entry 7): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.97 (d, $J = 7.2$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.52–7.31 (m, 7H), 5.32 (s, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 165.5, 136.1, 133.3, 129.6, 129.1, 128.7, 128.5, 128.0, 127.9, 127.4, 66.1 (Shen et al. 2020).

Table 2 Cleavage of different cyclic ethers using catalyst nano-ZnO



Entry	Ether	Product	Time (h)	Yield[a] (%)
1		 (8:2)	1	79 18
2			0.5	93
3			0.5	95
4			3	94
5			4	81

[a]Isolated yield

Prop-2-yn-1-yl benzoate (Table 4, entry 8): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.95–7.92 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 4.92 (d, J = 2.4 Hz, 2H), 3.56 (t, J = 2.4 Hz, 1H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ 164.9, 133.6, 129.2, 129.0, 128.8, 78.3,77.9, 52.4 (Yadav et al. 2007).

Results and discussion

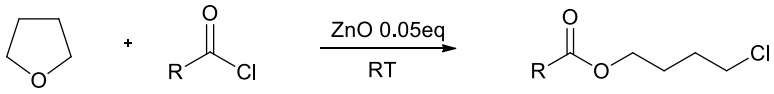
In our initial study, the reaction of benzoyl chloride (10 mmol) with tetrahydrofuran (11 mmol) was chosen as a model to optimize the reaction conditions (Table 1).

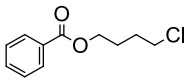
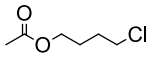
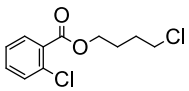
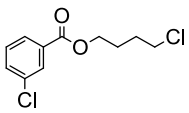
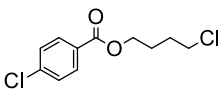
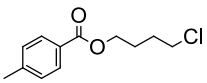
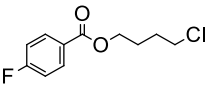
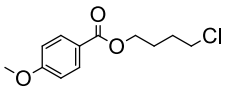
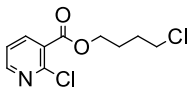
As shown in Table 1, the reaction of benzoyl chloride and tetrahydrofuran without the addition of zinc oxide catalyst at room temperature for 8 h and product had not been found, which was consistent with our expectation (Table 1, entry 1). The reaction was conducted in the presence of 1%, 2%, 5%, 7%, 10% and 12% of ZnO and the product 4-chlorobutyl benzoate was isolated in 49%, 67%, 95%, 95%, 89% and 85% yield, respectively (Table 1, entry 2–7). The results showed that the yield reached the maximum when the catalyst was increased to 5 mol%. Thereafter, the amount of catalyst continued to increase, and the efficiency of the catalytic system gradually decreased. This phenomenon can be explained by the fact that with the increase of the amount of catalyst, the number of active sites increases, leading to a decrease in the concentration of reactants at the active sites and diminishing yield. To investigate the optimum temperature for the reaction, no products were formed at − 10 °C for 12 h (Table 1, entry 8). The yield of the reaction at 0 °C for 25 min was 38%, and the yield did not increase when the reaction time was prolonged. The yield was 79% at 10 °C for 25 min and 94% at 50 °C for 25 min (Table 1, entry 9–11). Therefore, room temperature is the optimal reaction temperature.

To study the range and limitation of cracking ring ethers in this catalytic system, ring opening experiments were carried out on benzoyl chloride and a series of ring ethers, and the corresponding benzoates were obtained (Table 2).

Epichlorohydrin reacted violently with benzoyl chloride and the ratio of symmetric to asymmetric dichlorobenzoates was 8:2, and the yield was 79% and 18%, respectively (Table 2, entry 1). It was found that cyclic ethers

Table 3 Cleavage of THF by a series of acyl chlorides



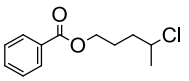
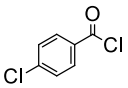
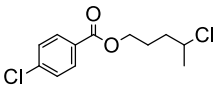
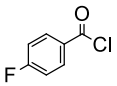
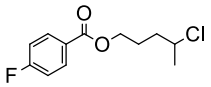
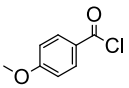
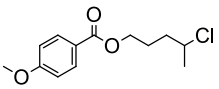
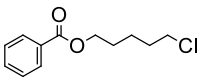
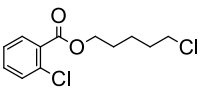
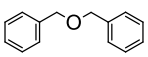
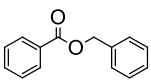
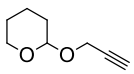
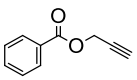
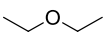
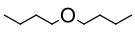
Entry	R	Product	Time	Yield[a] (%)
1	C_6H_5-		25min	95
2	H-		15min	73
3	2-(Cl)C_6H_4-		30min	93
4	3-(Cl)C_6H_4-		30min	85
5	4-(Cl)C_6H_4-		30min	82
6	4-(CH_3)C_6H_4-		40min	76
7	4-(F)C_6H_4-		35min	90
8	4-(CH_3O)C_6H_4-		40min	69
9	2-chloropyridine-		30min	92
10	Thiophene-	-	8h	N.R.
11	C_2H_5OOC-	-	8h	N.R.

N.R. no reaction

[a]Isolated yield

with substituents, such as 2-methyltetrahydrofuran could form C–O bonds with excellent selectivity, and the yield of 4-chloropentyl benzoate was 94% at room temperature (Table 2, entry 4). The cracking rate of tetrahydropyran ring was much slower than that of tetrahydrofuran. The reaction of tetrahydropyran was completed in 4 h and the yield was 81% (Table 2, entry 5). This can be explained as the ring tension of tetrahydrofuran is larger than that of tetrahydropyran, and the ring stability is lower; therefore, C–O bond is more prone to fracture. The low regioselectivity of products formed from epichlorohydrin may be due to the steric effect of chlorine atoms. The ring stability of tricyclic ether, tetracyclic ether and pentacyclic ether is lower than that of hexacyclic ether, the chemical reaction is more vigorous, the reaction time with benzoyl chloride is relatively short, and the yield is high. The results showed that benzoyl chloride can react with a series

Table 4 Nano-ZnO catalyzed cleavage of other cyclic ethers and acyclic ethers by acyl chloride

Entry	Ether	Acyl chloride	Product	Time (h)	Yield[a] (%)
1				2	94
2				2	89
3				2	92
4				2.5	95
5				4	81
6				0.5	91
7				2.5	98
8				3	65
9			-	24	N.R.
10			-	24	N.R.

N.R. no reaction

[a]Isolated yield

Table 5 Synthesis of chloroesters using ZnO as an efficient and reusable catalyst

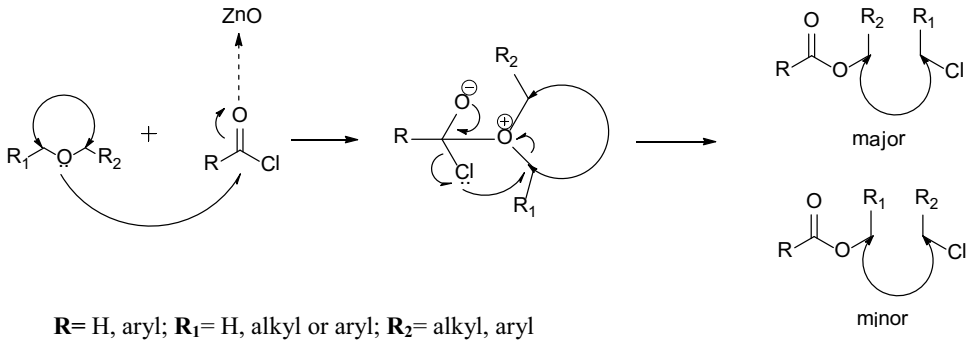
Entry	Cycle	Time (min)	Yield (%)[a]
1	Cycle 1	25	95
2	Cycle 2	25	92
3	Cycle 3	25	87

[a]Isolated yield

of cyclic ethers and the product yields were medium to good (Table 2).

To study the effect of substituents on the reactivity and product distribution of acid chloride, the reaction of THF with different aryl chlorides was studied. We first investigated the solvent-free reaction of tetrahydrofuran with acetyl chloride at room temperature and obtained the corresponding 73% yield (Table 3, entry 2). The yield of the same substituted aromatic chloride with electron-withdrawing group is significantly higher than that of the electron-donating group (Table 3, entry 5–8). The position of electron-withdrawing also has great influence on the yield (Table 3, entry 3–5). The higher the electron-withdrawing capacity of the substituent, the higher the yield (Table 3, entry 5, 7). The reaction of 4-methylbenzoyl chloride and 4-methoxybenzoyl chloride with THF demonstrates that the higher the electron supply, the lower the yield (Table 3, entry 6, 8).

Scheme 1 The mechanism of ZnO catalyst for synthesis of chloroesters by the cleavage of cyclic and acyclic ethers



R= H, aryl; **R**$_1$= H, alkyl or aryl; **R**$_2$= alkyl, aryl

To investigate the selectivity of the reaction, acylation and cleavage reactions of 2-methyltetrahydrofuran and tetrahydropyran and other cyclic ethers, as well as a range of symmetric acyclic ethers including benzyl ether, diethyl ether, dibutyl ether and asymmetric cyclic ethers such as tetrahydro-2-(2-propynyloxy)-2*H*-pyran were studied (Table 4). With the observation of the regioselectivities of 2-methyltetrahydrofuran products, we can also see that the yield of aryl chloride with electron-donating groups is slightly higher than that of aryl chloride with electron-withdrawing groups (Table 4, entry 2–4). Other acyclic ethers, such as benzyl ether, can be smoothly cleaved and the yield of benzyl benzoate can reach 98% (Table 4, entry 7). For the reaction of the unsymmetric ethers, such as tetrahydro-2-(2-propynyloxy)-2*H*-pyran, it is interesting to note that the C-O bond of the ethers was selectively cleaved (Table 4, entry 8). Ethyl ether and dibutyl ether react with benzoyl chloride (Table 4, entry 9, 10), but no product was produced even at room temperature for 24 h. We hypothesized that this may be due to the absence of orbital approach onto the sp^2-hybridized aromatic carbons and the lower boiling point of ethers. On the whole, the yield of aryl chloride is better; while, aryl chloride has more stable benzoyl radicals or acylium ions.

The reusability of ZnO was studied under optimized reaction conditions. After the reaction, ZnO was removed by filtration. After repeated washing with distilled water and dichloromethane, ZnO was dried at 60 °C for 3 h for the next catalytic cycle, and more than 80% of ZnO can be recovered from the reaction mixture. The ideal product was obtained by concentrating the organic layer under reduced pressure, and the desired product was obtained in 95% (Table 5, entry 1), 92% (Table 5, entry 2), and 87% (Table 5, entry 3) yields after one to three runs, respectively.

Conclusion

The acylation cleavage of cyclic and acyclic ethers catalyzed by nano-ZnO powder under solvent-free conditions was developed. The method has the following advantages: reusable catalysts, high yields, environmental friendliness and simple operation, and essential process for the synthesis of chloroesters. Hence, it is an essential complement to existing methodologies. We anticipate that our cost-effective nano-zinc oxide catalyzed for acylative ether cleavage will find broad utility.

Acknowledgements This work was partially supported by the Fundamental Research Funds for the Central Universities (No. 2242014R30019).

Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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