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Indium(III) bromide catalyzed cleavage of cyclic and acyclic ethers: An efficient and practical ring opening reaction

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Abstract

Ethers undergo smooth cleavage with acyl chloride in the presence of catalytic amount of indium(III) bromide under mild conditions to give the corresponding halo esters. This new procedure offers significant advantages, such as high conversions, short reaction times and enhanced selectivity together with mild reaction conditions.

Keywords: Ethers; Acyl chloride; Indium tribromide; Halo ester

The cleavage of ethers is a versatile reaction in organic synthesis, mainly in degradation or transformation of complex molecules especially in biologically active natural products, such as carbohydrates and macrolide antibiotics. Particularly, aliphatic, benzylic and allylic ethers are frequently used as protecting groups for hydroxyl functions [1] and subsequent cleavage is a very interesting route to polyfuntional molecules useful in organic synthesis [2]. As a result, the cleavage of ethers with acyl chloride has been reported using Lewis acids, such as SmI_2 [3], $ZnCl_2$ [4], $FeCl_3$ [5], $Mo(CO)_6$ [6], $MoCl_5$ [7], $PdCl_2(PPh_3)_2$ [8], $CoCl_2$ [1], NaI [9], lanthanide salts [10], Zn [11], graphite [12], aluminum complexes [13] and others [14]. However, many of these methods often involve the use of toxic or expensive reagents and the formation of mixture of products resulting in low yields. Therefore, the development of simple, convenient and practical procedures for the cleavage of cyclic and acyclic ethers continues to be a challenging endeavor in synthetic organic chemistry. Recently, there have been considerable interest on the catalytic use of indium(III) halides [15] in organic synthesis. Due to their unique catalytic properties, indium(III) bromide have been widely used for a variety of organic transformations [16]. Particularly, indium tribromide is found to be a more effective catalyst than conventional Lewis acids in promoting various transformations, including glycosidation, thioacetalization, cyanation of ketones and conjugate addition reactions. However, there have been no reports on the use of indium(III) halides for the cleavage of cyclic and acyclic ethers with acyl chloride under solvent-free conditions.

In continuation of our interest on the catalytic application of indium halides [17], we disclose herein a mild, efficient and practical methodology for the cleavage of cyclic and acyclic ethers with acyl chloride using indium(III) bromide as the novel catalyst under solvent-free conditions. Initially, we attempted the cleavage of tetrahydrofuran (**1**) with acetyl chloride (**2**) in the presence of indium(III) bromide. The reaction went to completion within 2.5 h and the product (**3a**) was obtained in 89% yield (Scheme 1).

Encouraged by the results obtained with tetrahydrofuran and acetyl chloride, we turned our attention to various acyl chlorides. Interestingly, several acyl chlorides, such as benzoyl chloride, 3-methyl-, 2-chloro-benzoylchloride and the acid chloride derived from cyhalothrin involved in the cleavage of tetrahydrofuran to afford the corresponding halo esters in excellent to good yields (entries **b–d**, Table 1). Like tetrahydrofuran, several other cyclic and acyclic ethers are cleaved by a range of acyl chlorides to afford the corresponding halo esters in good yields (entries **f–l**, Scheme 2, Table 1).

The probable mechanism seems to be the activation of carbonyl group of acyl chloride, by indium tribromide and a subsequent attack of furan onto activated carbonyl group. This

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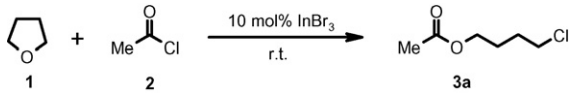
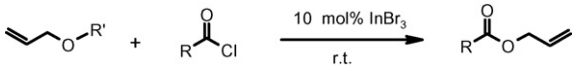


Scheme 1.



Scheme 2.

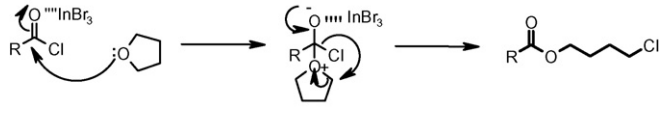
facilitates an intramolecular attack of leaving chloride ions onto the electronically deficient carbon of tetrahydrofuran moiety which would result in the required product (Scheme 3).

In all cases, the reactions proceeded rapidly at room temperature with high efficiency. In the absence of catalyst, no cleavage was observed between ethers and acyl chloride. Among various indium(III) salts such as $InCl_3$, $In(ClO_4)_3$ and $In(OTf)_3$ tested, $InBr_3$ was found to be the most effective for this cleavage in the terms of reaction rates and yields. The scope and generality of this process is illustrated with respect to various cyclic and acyclic ethers and acyl chlorides and the results are presented in Table 1.

In summary, we have described a simple, convenient, efficient and practical method for the cleavage of cyclic and acyclic ethers with acyl chloride using indium(III) bromide as the novel catalyst under solvent-free conditions. This method offers several significant advantages, such as high conversions, easy handling and high catalytic nature of indium compounds, solvent-free conditions, cleaner reaction profiles and short reaction times which makes it a useful and attractive process for the rapid cleavage of cyclic and acyclic ethers in a single-step operation.

Column chromatography was performed using silica gel 60–120 mesh. All solvents were dried and distilled prior to use. IR spectra were recorded on a Perkin-Elmer Infrared spectrophotometer as KBr wafers, neat or in $CHCl_3$, as a thin film. ^1H NMR were recorded on a Varian Gemini 200 or Bruker Avance 300 or Varian Unity 400 instrument using TMS as an internal standard. Mass spectra were recorded on micromass Quatro LC triple quadrupole mass spectrometer for ESI analysis.

General procedure for cleavage of THF, ethers and epoxides: a mixture of 0.5 g (6.90 mmol) of tetrahydrofuran and 0.229 g (0.69 mmol) of cyhalothrin acid chloride was taken in a round bottom flask, catalytic amount of $InBr_3$ (10 mol%) was added. The reaction mixture was stirred at room temperature under nitrogen atmosphere for an appropriate time (Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was quenched with saturated sodium bicarbonate (15 ml) and extracted with ethyl acetate (2 × 15 ml). Evaporation of the solvent followed by purification on silica gel chromatography (Merck, 60–120 mesh ethyl acetate-hexane, 0.5–9.5) afforded



Scheme 3.

pure ester derivative. The products were characterized by IR, ^1H NMR spectroscopy and physical constants. All the products (**3a–l**) were prepared by the same procedure.

(**3a**) 4-Chlorobutyl acetate—liquid, IR (KBr): υ_{max} 2924, 2853, 1724, 1632, 1459, 1379, 1272, 1114, 711 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.08 (t, J = 6.0 Hz, 2H), 3.54 (t, J = 6.0 Hz, 2H), 2.03 (s, 3H), 1.90–1.74 (m, 4H). ESI/MS: m/z 173 $[M + Na]^+$, 160.9, 151, 141, 135, 129.1, 103, 63.2.

(**3b**) 4-Chlorobutyl benzoate—liquid, IR (KBr): υ_{max} 3065, 2958, 1719, 1601, 1584, 1491, 1451, 1386, 1314, 1275, 1176, 1115, 1070, 1026, 712, 651 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.02–7.99 (m, 2H), 7.56–7.50 (m, 1H), 7.41 (t, J = 7.5 Hz, 2H), 4.35 (t, J = 6.0 Hz, 2H), 3.59 (t, J = 6.0 Hz, 2H), 1.99–1.90 (m, 4H). ESI/MS: m/z 235 $[M + Na]^+$, 220.9, 181, 173, 103, 79, 63.2.

(**3c**) 4-Chlorobutyl 3-methylbenzoate—IR (KBr): υ_{max} 3019, 2930, 2160, 1728, 1630, 1440, 1360, 1280, 1050, 930 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.80 (m, 2H), 7.20–7.40 (m, 2H), 4.35 (t, 2H, J = 2.8 Hz), 3.6 (t, 2H, J = 2.8 Hz), 2.40 (s, 3H), 1.90–2.10 (m, 4H). ESI/MS: m/z 226 (M^+), 191, 136, 119, 91, 65.

(**3d**) 4-Chlorobutyl-3-[(E)-2-chloro-3,3,3-trifluoro-1-propenyl]-2,2-dimethyl-1-cyclopropanecarboxylate—liquid, IR (KBr): υ_{max} 3079, 2961, 1727, 1654, 1453, 1416, 1275, 1201, 1140, 1087, 955, 772 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.90 (d, J = 9.4 Hz, 1H), 4.10 (t, J = 5.8 Hz, 2H), 3.55 (t, J = 5.8 Hz, 2H), 2.14 (t, J = 9.4 Hz, 1H), 1.95–1.82 (m, 5H), 1.30 (d, J = 3.6 Hz, 6H). ESI/MS: m/z 334 (M + 1), 301, 279, 205, 149, 116, 107, 69, 57.

(**3e**) Allyl-2-chlorobenzoate—liquid, IR (KBr): υ_{max} 2926, 1732, 1648, 1592, 1508, 1470, 1436, 1360, 1291, 1248, 1120, 1048, 966, 932, 748, 647 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.85–7.81 (m, 1H), 7.46–7.22 (m, 3H), 6.12–5.93 (m, 1H), 5.48–5.27 (m, 2H), 4.82 (d, J = 5.1 Hz, 2H). ESI/MS: m/z 218.9 $[M + Na]^+$, 181, 139, 63.2.

(**3f**) Allyl benzoate—liquid, IR (KBr): υ_{max} 3068, 2926, 1722, 1646, 1602, 1450, 1360, 1270, 1174, 1112, 1069, 1024, 971, 932, 711 cm^{-1}. ^1H NMR ($CDCl_3$ 300 MHz): δ 8.06–8.02 (m, 2H), 7.52 (tt, J = 1.3, 7.3, 14.7 Hz, 1H), 7.40 (tt, J = 1.3, 7.5, 14.9 Hz, 2H), 6.08–5.95 (m, 1H), 5.40 (qd, J = 1.7, 3.2, 17.1 Hz, 1H), 5.20 (dq, J = 1.3, 2.6, 10.3 Hz, 1H), 4.79 (td, J = 1.3, 2.8, 5.6 Hz, 2H). ESI/MS: m/z 185.1 $[M + Na]^+$, 142.9, 103.0, 63.2.

(**3g**) 3-Phenylpropyl benzoate—liquid, IR (KBr): υ_{max} 3063, 2925, 1718, 1602, 1495, 1452, 1387, 1313, 1273, 1175, 1114, 1069, 1025, 748, 709 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.04–8.0 (m, 2H), 7.59–7.38 (m, 3H), 7.30–7.39 (m, 5H), 4.34 (t, J = 7.0 Hz, 2H), 2.80 (t, J = 7.0 Hz, 2H), 2.11 (quin, J = 7.8, 14.8 Hz, 2H). ESI/MS: m/z 263 $[M + Na]^+$, 241, 220.9, 181, 63.2.

(**3h**) 3-Phenylpropyl-2-chlorobenzoate—liquid, IR (KBr): υ_{max} 3063, 2925, 1729, 1593, 1495, 1436, 1384, 1291, 1250, 1124, 1047, 960, 911, 747, 698, 649 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.82–7.77 (m, 1H), 7.48–7.12 (m, 8H), 4.35 (t, J = 6.2 Hz, 2H), 2.81 (t, J = 7.0 Hz, 2H), 2.18–2.04 (m, 2H). ESI/MS: m/z 297 $[M + Na]^+$, 274.9, 220.9, 181, 141, 63.2.

(**3i**) 2-Propynyl benzoate—liquid, IR (KBr): υ_{max} 3298, 3066, 2925, 2854, 1724, 1602, 1451, 1370, 1314, 1269, 1176, 1105, 1070, 1024, 981, 928, 759, 711, 677, 639, 566 cm^{-1}. ^1H NMR ($CDCl_3$ 300 MHz): δ 8.07–8.03 (m, 2H), 7.54 (tt, J = 1.5,