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$AlCl_3 \cdot 6H_2O/KI/CH_3CN/H_2O$: An Efficient and Versatile System for Chemoselective C-O Bond Cleavage and Formation of Halides and Carbonyl Compounds from Alcohols in Hydrated Media

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$AlCl_3 \cdot 6H_2O/KI/CH_3CN/H_2O$: An Efficient and Versatile System for Chemoselective C–O Bond Cleavage and Formation of Halides and Carbonyl Compounds from Alcohols in Hydrated Media

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Abstract: $AlCl_3 \cdot 6H_2O/KI/CH_3CN/H_2O$, an efficient and versatile system, cleaves the C–O bonds of esters, acetals, ethers, and oxathiolanes to the corresponding acids, alcohols, and carbonyl compounds chemoselectively at 80 °C in hydrated media with good yields. This system also converts the alcohols (primary/secondary) to halides and oxidizes the alcohols (primary/secondary) to the corresponding carbonyl compounds in the presence of DMSO.

Keywords: $AlCl_3 \cdot 6H_2O/KI/CH_3CN$, chemoselective, cleavage of C–O bonds, halide formation and oxidation, hydrated media, system

The protection–deprotection of functional groups serves a fundamental role in organic chemistry.[1] A number of efficient reagents are reported for the cleavage of C–O bonds under heterogeneous and homogeneous conditions. The heterogeneous reagents[2] include Al_2O_3,[3] mont. K10,[4]

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$K_5CoW_{12}O_{40}3H_2O$,[5] (P)-DCKA,[6] SiO_2/CAN,[7] Pd/C,[8] sulfated SnO_2,[9] and Dowex 50WX8.[10] The homogeneous reagents used for the cleavage of C–O bonds include mineral acids,[11] Me_3SiI,[12] BF_3 etherate-I,[13] $TiCl_4 \cdot LiI$,[14] pyridinium tosylate,[15] $Hg(OAc)_2 \cdot KSCN$,[16] $Me_3SiSiMe_3 \cdot I_2$,[17] and NaSePh.[18] This transformation could also be achieved by using enzymatic methods.[19]

In a previous communication, we reported that $AlCl_3 \cdot 6H_2O/KI/CH_3CN$ is an efficient system for dehydration[20] of oximes and amides to nitriles, the Beckmann rearrangement, and the Bischler–Napieraliski reaction in hydrated media. The system could smoothly deoxygenate organic *N*-oxides to the corresponding imines in hydrated media.[21] Here, we first demonstrate the efficiency of $AlCl_3 \cdot 6H_2O/KI/CH_3CN/H_2O$ for chemoselective C–O bond cleavage of esters, ethers, and acetates and formation of halides and carbonyl compounds from alcohols in hydrated media.

The reagent system cleaved the C–O bonds of esters, (Table 1 entries **1**–**4**) and acetates (entries **5**–**11**) to the corresponding acids and phenols respectively. The acetate groups were chemoselectively cleaved when both the acetate and ester groups were present within the same molecules (entries **8** and **9**). The ester/acetate groups preferentially cleaved when one of these functionalities were present with ether functionality within the substrate (entries **10** and **11**). The oxathiolanes were cleaved to the corresponding carbonyl compounds (entries **13**–**18**), and the system chemoselectively cleaved the oxathiolanes when both the acyclic acetals/ketals and oxathiolanes were present within the substrates (entries **15**–**18**). In all the cases, the optimum ratio of water and acetonitrile was 1:10. The system converted the primary alcohols (entries **19**–**22**) to the corresponding halides in very good yields. The cleavage of C–O bonds of these substrates with HI proceeded with lower yields and required more time.

The system in the presence of DMSO oxidized selectively both the primary (entries **23**–**26**) and the secondary (entry **27**) alcohols to the corresponding carbonyl compounds (Table 2).

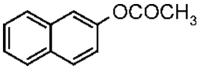
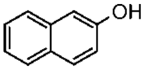
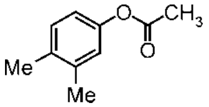
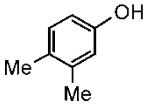
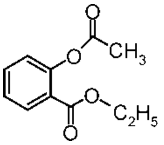
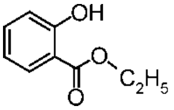
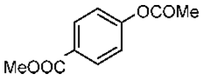
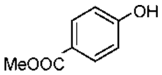
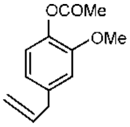
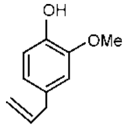
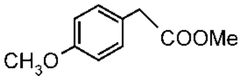
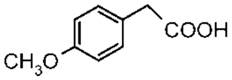
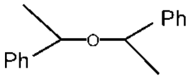
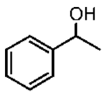
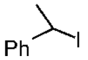
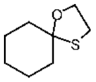
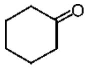
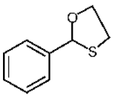
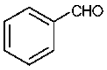
Regarding the mechanism of the reactions, it may be proposed that $AlCl_3 \cdot 6H_2O$ is in reality[20–22] $[Al(H_2O)_6]Cl_3$, which reacts with KI to form $[Al(H_2O)_6]I_3$, which can exist as $[Al(H_2O)_5(OH)]^{2+}$ H^+ $3I^-$ [A] or $[Al(H_2O)_4(OH)_2]^+$ $2H^+$ $3I^-$ [B] and so forth in solution. The liberated proton forms HI and in the presence of aluminium cleaves C–O bonds of esters to the corresponding acids as shown below (Scheme 1).

In summary the utility of $AlCl_3 \cdot 6H_2O/KI/CH_3CN/H_2O$ for various transformations has been successfully demonstrated.

EXPERIMENTAL

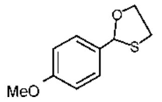
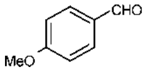
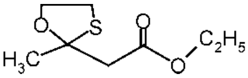
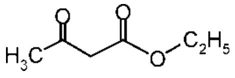
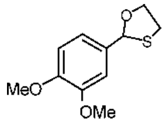
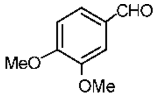
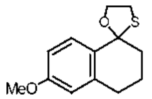
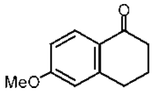
^1H NMR spectra were recorded at 60 MHz. Chemical shifts are expressed in δ units relative to tetramethylsilane (TMS) signal as internal reference in

Table 1. Cleavage of C–O bonds and formation of halides using $AlCl_3\cdot 6H_2O/KI/CH_3CN/H_2O$ system

Sl. No.	Substrate	Time (h)	Yield (%)	Product[a,b,c,d]
1	$CH_2(COOEt)_2$	17	65	$CH_2(COOH)_2$
2	Ph–COOEt	13	75	Ph–COOH
3	Ph–CH=CH–COO-Me	14	65	Ph–CH=CH–COOH
4	Ph–O–CO–Ph	9	80 78	Ph–OH + Ph–COOH
5	Ph–OCOMe	4	92	Ph–OH
6		10	90	
7		5	95	
8		4	80	
9		4	85	
10		4	83	
11		12	76	
12		5	89	 +
			90	
13		6	85	
14		6	89	

(*continued*)

Table 1. Continued

Sl. No.	Substrate	Time (h)	Yield (%)	Product[a,b,c,d]
15		6	90	
16		6	84	
17		6	90	
18		6	77	
19	$C_6H_5{-}CH_2{-}OH$	3	91	$C_6H_5{-}CH_2{-}I$
20	*p*-$HO{-}C_6H_4{-}CH_2{-}OH$	3	90	*p*-$HO{-}C_6H_4{-}CH_2{-}I$
21	*p*-$MeO{-}C_6H_4{-}CH_2{-}OH$	3	92	*p*-$MeO{-}C_6H_4{-}CH_2{-}I$
22	*p*-$Cl{-}C_6H_4{-}CH_2{-}OH$	4	88	*p*-$Cl{-}C_6H_4{-}CH_2{-}I$

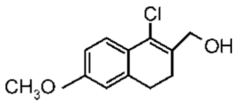
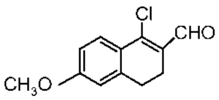
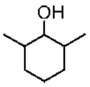
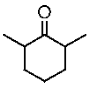
[a] Isolated yield.

[b] The ratio of water and acetonitrile 1:10.

[c] Melting points were compared with authentic samples.

[d] All the compounds gave satisfactory IR, NMR, and elemental analyses.

Table 2. Oxidation of alcohols to aldehydes and ketones using $AlCl_3 \cdot 6H_2O/KI/CH_3CN/H_2O$ in the presence of DMSO

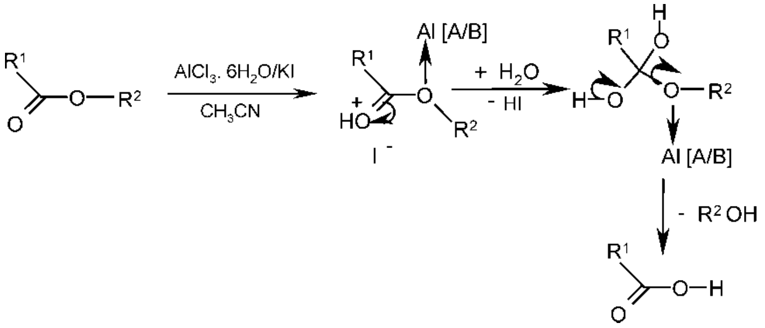
Sl. No.	Substrate	Time (h)	Yield (%)	Product[a,b,c,d]
1	$C_6H_5{-}CH_2{-}OH$	5	70	$C_6H_5{-}CHO$
2	*p*-$NO_2{-}C_6H_4{-}CH_2{-}OH$	5	69	*p*-$NO_2{-}C_6H_4{-}CHO$
3		5.5	65	
4	$CH_3O{-}C_6H_4{-}CH_2OH$	4	71	$CH_3O{-}C_6H_4{-}CHO$
5		7	54	

[a] Isolated yield.

[b] The ratio of water and acetonitrile 1:10.

[c] Mp and bp were compared with authentic samples.

[d] All the compounds gave satisfactory IR, NMR, mass, and elemental analyses.



Scheme 1.

$CDCl_3$. FTIR spectra were recorded in $CHCl_3$ or on KBr pellets. Commercially available $AlCl_3 \cdot 6H_2O$ and potassium iodide (KI) were used directly. Column chromatography was performed on silica gel (60–120 mesh) using ethyl acetate and hexane as eluent.

General Procedure for Chemoselective C–O Bond Cleavage

$AlCl_3 \cdot 6H_2O$ (0.240 g, 1 mmol) and KI (0.249 g, 1.5 mmol) were stirred in acetonitrile and water (15 ml, 10:1) at room temperature for 30 min, and ester (1 mmol) was added to it. The reaction mixture was refluxed at 80 °C for the stipulated time (Table 1), and the progress of the reaction was monitored by TLC. The solvent was distilled under reduced pressure, and the residue was diluted with water (25 ml) and extracted with DCM. The organic layer was washed with 5% sodium thiosulphate solution (25 ml) and with water (2 × 50 ml) and dried over anhydrous sodium sulphate. The solvent was evaporated and after preparative TLC gave the desired product.

General Procedure for Oxidation of Alcohols

$AlCl_3 \cdot 6H_2O$ (0.240 g, 1 mmol) and KI (0.249 g, 1.5 mmol) were stirred in acetonitrile and water (15 ml, 10:1) at room temperature for 30 min. To this mixture, alcohol (1 mmol) and DMSO (390 mg, 5 mmol) were added and refluxed at 80 °C under nitrogen for the stipulated time (Table 1, entries **23–26**). The solvent was distilled off to half of its volume under reduced pressure and poured into water (2 × 100 ml) and extracted with diethyl ether (2 × 25 ml). The organic layer was washed with 5% sodium thiosulphate solution (20 ml) and then with water (4 × 50 ml) and dried over anhydrous Na_2SO_4. The residue was purified by preparative TLC to get analytically pure aldehyde/ketones. All the products were commercially available and identified by comparison of the isolated products with authentic samples.

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