Ytterbium(III) Triflate as a Recyclable Catalyst for the Selective Atom Economic Oxidation of Benzyl Alcohols to Benzaldehydes

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Abstract: Ytterbium(III) triflate (10mol%) was found to catalyse the selective oxidation of a range of simple benzyl alcohols to benzaldehydes in good to excellent yield using a stoichiometric quantity of 69% nitric acid as the oxidant, and where the only by-products were water and oxides of nitrogen. The catalyst can be readily recovered and recycled by a simple evaporative process.

Keywords: alcohols, aldehydes, catalysis, lanthanides, oxidations

The selective oxidation of benzylic alcohols to benzaldehydes is a transformation of considerable importance in organic synthesis. Whilst numerous reagents have been developed to effect this process in excellent yield, many of them employ greater than stoichiometric quantities of toxic heavy metals or co-oxidants which severely handicap their applicability to large scale industrial processes.^{1,2} We have instigated a research program in the area of clean technology whereby we seek to develop atom-economic transformations in which little or no waste is generated, and have recently reported the use of lanthanide(III) salts as recyclable catalysts for the nitration of simple arenes, affording water as the only sideproduct.^{3,4} During our attempts to apply this nitration methodology to benzyl alcohol, we noticed a rapid evolution of brown gas as the reaction mixture approached reflux temperature. Within a very short space of time the starting alcohol had undergone almost complete conversion to a less polar product, which upon isolation and analysis proved to benzaldehyde. Whilst oxidation of benzyl alcohols to benzaldehydes using nitric acid has been described previously, the procedure demanded the use of at least 3 equivalents of nitric acid and a resultant neutralization step at the end of the reaction.5

Optimization of the reaction conditions revealed that simply refluxing a solution of benzyl alcohol (1 equivalent), 69% w/w nitric acid (1 equivalent) and ytterbium triflate (10 mole%) in 1,2-dichloroethane effected the formation of benzaldehyde in 91% isolated yield within 0.5h. In the absence of ytterbium triflate, the reaction proceeded to only 17% conversion in 6h. Further studies showed that this oxidation protocol can be applied to a wide range of benzyl alcohols (Table 1).

Although the reaction becomes slower as electron withdrawing substituents are added to the ring, the advantages of the catalyst are still clear, with 3,5-dinitrobenzyl alcohol giving a 70% conversion to the aldehyde over 24h, as **Table 1.** HNO₃ oxidation of benzylic alcohols to benzaldehydes catalyzed by $Yb(OTf)_3$.^a

Ar	ArC	НО			
(CH ₂ Cl) ₂ , Reflux					
Entry	Ar	Yb(OTf) ₃ / mole %	t/h	Yield/%⁵	
1 0	<u>с н</u>	10	0.5	91	
	$\cup_6 \square_5$	-	6	17	
2	2-CI-C ₆ H₄	10	0.5	86	
3	2-Br-C ₆ H ₄	10	0.5	84	
4°	4-Br-C ₆ H₄	10	0.5	88	
5	2-I-C ₆ H₄	10	0.5	95	
6	2-Me-C ₆ H₄	10	0.5	92	
7	4-Me-C ₆ H ₄	10	0.5	94	
8	2,4-F-C ₆ H ₃	10	2	80	
9	3-CF₃-C₅H₄	10	1	87	
10	4-MeO ₂ C-C ₆ H ₄	10	2	82	
11	3-C₅H₄N	10	24	33	
12	4-NO ₂ -C ₆ H ₄	10	12	82	
13	3,5-NO ₂ -C ₆ H ₃	10	24	70	
		-	24	0	

^a To a 1,2-dichloroethane solution (50 mL) of ArCH₂OH (20 mmol) was added Yb(OTf)₃ (2 mmol) and HNO₃ (69%w/w, sp. g. = 1.42, 20 mmol) at 20°C. The solution was warmed to reflux (gas evolution) and stirred for the appropriate time period. The reaction mixture was allowed to cool and diluted with water (20 mL) before being extracted (CH₂Cl₂, 2 x 20mL). The combined organic components were dried (MgSO₄), and concentrated *in vacuo*. The residue was purified by flash chromatography to afford the desired aldehyde. ^b Isolated yield. ^c Performed on a 3 mmol scale.

opposed to the uncatalyzed case, which failed to give any conversion whatsoever. The reaction was unsuccessful for electron rich arenes, which presumably suffered complications due to competing nitration of the aromatic ring.

A distinct advantage of the present method is the ease with which the ytterbium triflate can be recycled without detriment to the yields of aldehyde. Simple evaporation of the aqueous phase allows almost quantitative recovery of the catalyst. In the case of 4-bromobenzyl alcohol, 3 consecutive oxidations with the same batch of catalyst effected conversion to the aldehyde in similar timescales and yields (Table 2).

In conclusion, we have shown that ytterbium triflate is a suitable catalyst in a novel procedure employing 69% nitric acid for the highly selective and fast conversion of

Table 2. Recycling of ytterbium(III) triflate in the
oxidation of 4-bromobenzyl alcohol. ^a

Dup No	t/h	Yield of	Recovery of
Hull NO.		aldehyde/%	Catalyst/% ^b
1	0.5	88	100
2	0.5	85	92
3	0.5	84	100
4	0.5	86	98
1 2 3 4	0.5 0.5 0.5 0.5	88 85 84 86	100 92 100 98

^a Initial oxidation performed on a 3 mmol scale. ^b The catalyst was recovered by extracting the reaction mixture with water and evaporating the combined aqueous components.

benzyl alcohols to benzaldehydes. Further applications of ytterbium triflate and related catalysts in organic chemistry are being investigated.⁶

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