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Catalytic and Efficient Cleavage of Allylic and Tertiary Benzylic Ethers and Esters with Ce(IV)

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Abstract: The reaction of cerium(IV) as ceric ammonium nitrate (CAN) with a variety of allylic and tertiary benzylic ethers and esters has been examined in different alcohols and acetic acid under catalytic and mild conditions. Experiments have been conducted to elucidate the scope of this ether-to-ether, ether-to-acetate and acetate-to-ether transformations.

Introduction

In a previous paper[1] we reported that catalytic amounts of Ce(IV) as ceric ammonium nitrate can bring about the conversion of allylic and tertiary benzylic alcohols to their corresponding ethers. In this study we extended the synthetic utility of this catalyst for carbon-oxygen bond cleavage in allylic and tertiary benzylic ethers and esters to bring about an ether-to-ether, ether-to-acetate and acetate-to-ether transformation.

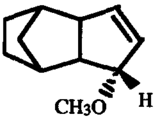
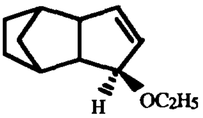
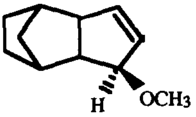
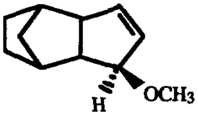
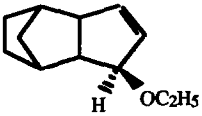
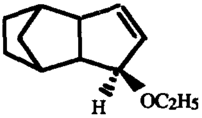
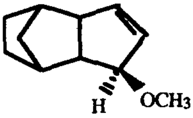
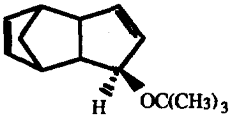
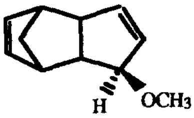
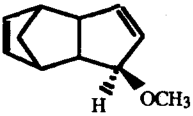
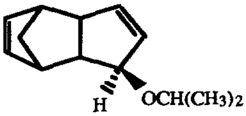
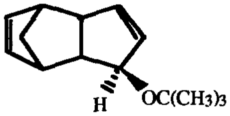
By this efficient and catalytic method, readily transetherification of allylic and tertiary benzylic ethers can be performed in 1°, 2° and also 3° alcohols. Ether-to-acetate and acetate-to-ether conversion can also be achieved in excellent yields.

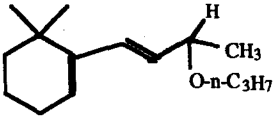
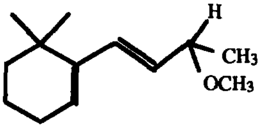
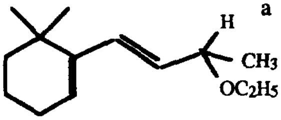
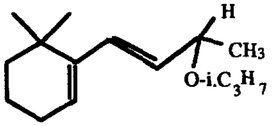
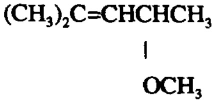
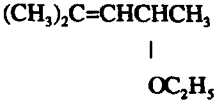
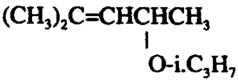
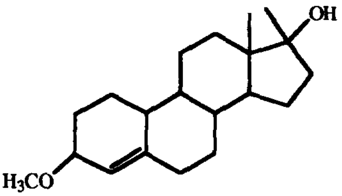
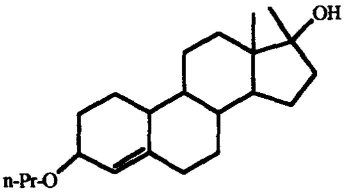
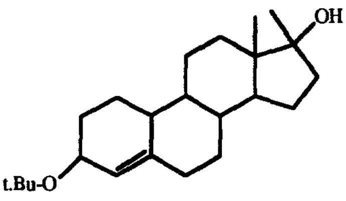
Although there are versatile methods for the conversion of alcohols to ethers[2], methods for carbon-oxygen bond cleavage in ethers and esters are scarce[3-10] and in most cases suffer from unsuitable reaction conditions and low reaction yields. Therefore, there is still a great demand in devising suitable methods for high yield carbon-oxygen bond cleavage.

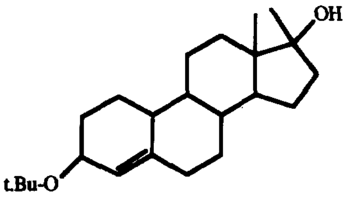
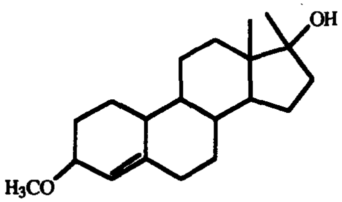
Results and Discussion

Alcoholysis of different classes of allylic, cinnamylic and tertiary benzylic ethers was performed in the presence of 0.2 molar equivalents of Ce(IV) as ceric ammonium nitrate (CAN) in 1°, 2° and 3° alcohols under refluxing conditions. Ether-to-ether conversion occurred efficiently. The results which are obtained from transetherification of allylic ethers are tabulated in Table 1.

Table 1. Transetherification of Allylic Ethers by Ce(IV)(0.2 mole%) Under Refluxing Conditions.

Entry	substrate	solvent	yield/Time(h)	product
1		C_2H_5OH	$89/(^{3}/_{4})$	
2	"	CH_3OH	$92/(^{1}/_{2})$	
3		C_2H_5OH	$92/(^{1}/_{2})$	
4		CH_3OH	$95/(^{3}/_{4})$	
5		"	$97/(^{1}/_{10})$	
6		$(CH_3)_2CHOH$	95/(2)	
7	"	$(CH_3)_3COH$	89/(3)	

8		CH_3OH	93/($1^{1}/_{4}$)	
9	 [a]	$i.C_3H_7OH$	90/(2)	
10	 $(CH_3)_2C{=}CH\underset{\underset{OCH_3}{\mid}}{C}HCH_3$	C_2H_5OH	93/($^{1}/_{3}$)	 $(CH_3)_2C{=}CH\underset{\underset{OC_2H_5}{\mid}}{C}HCH_3$
11	"	$i.C_3H_7OH$[b]	92/($^{1}/_{2}$)	 $(CH_3)_2C{=}CH\underset{\underset{O\text{-}i.C_3H_7}{\mid}}{C}HCH_3$
12		$n\text{-}C_3H_7OH$	97/($^{1}/_{2}$)	
13	"	$(CH_3)_3COH$[b]	88/(1)	

14		CH_3OH	$98(^1/_{10})$	

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a) The reaction was performed with 0.6 molar equivalent of CAN.

b) 0.4 molar equivalents of CAN was used.

Alcoholysis of cinnamylic and tertiary benzylic ethers also occurred efficiently. The results are shown in Table 2.

Table 2. Transetherification of Cinnamylic and Tertiary Benzylic Ethers with 0.2 mole% of CAN under Refluxing Condition.

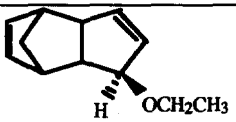
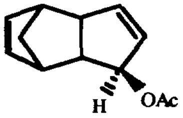
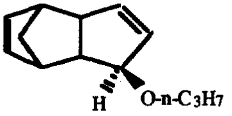
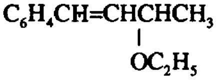
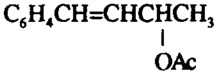
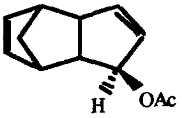
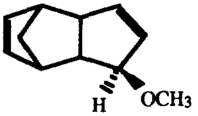
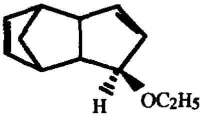
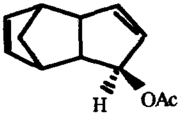
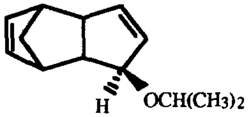
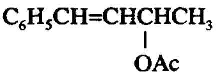
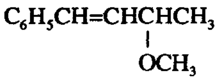
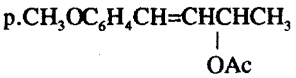
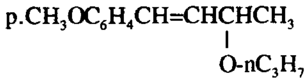
Entry	substrate	solvent	yield/Time(h)	product
1	$p.CH_3OC_6H_4CH{=}CH\underset{OCH_3}{\underset{\vert}{C}}HCH_3$	C_2H_5OH	$97/(^3/_4)$	$p.CH_3OC_6H_4CH{=}CH\underset{OC_2H_5}{\underset{\vert}{C}}HCH_3$
2	"	$(CH_3)_3COH$	55/(1)	$p.CH_3OC_6H_4CH{=}CH\underset{OC(CH_3)_3}{\underset{\vert}{C}}HCH_3$
3	"	$(CH_3)_2CHOH$	96/(1)	$p.CH_3OC_6H_4CH{=}CH\underset{OCH(CH_3)_2}{\underset{\vert}{C}}HCH_3$
4	$p.CH_3OC_6H_4CH{=}CH\underset{OC_2H_5}{\underset{\vert}{C}}HCH_3$	CH_3OH	$98/(^1/_{10})$	$p.CH_3OC_6H_4CH{=}CH\underset{OCH_3}{\underset{\vert}{C}}HCH_3$
5	$C_6H_5CH{=}CH\underset{OCH_3}{\underset{\vert}{C}}HCH_3$	$n.C_3H_7OH^a$	$97/(^3/_4)$	$C_6H_5CH{=}CH\underset{OC_3H_7}{\underset{\vert}{C}}HCH_3$
6	$C_6H_5CH{=}CH\underset{O\text{-}n.C_3H_7}{\underset{\vert}{C}}HCH_3$	$(CH_3)_2CHOH^a$	$75/(^3/_4)$	$C_6H_5CH{=}CH\underset{OCH(CH_3)_2}{\underset{\vert}{C}}HCH_3$

7	$C_6H_5CH{=}CH\underset{OCH(CH_3)_2}{\underset{\vert}{C}}HCH_3$	CH_3OH	$95/(^1/_2)$	$C_6H_5CH{=}CH\underset{OCH_3}{\underset{\vert}{C}}HCH_3$
8	Ph_3COCH_3	C_2H_5OH	$96/(^1/_4)$	$Ph_3COC_2H_5$
9	"	$n\text{-}C_3H_7OH$	95/(14)	$Ph_3CO\text{-}n\text{-}C_3H_7$
10	"	$(CH_3)_3COH$	$80/(1^1/_2)$	$Ph_3COCH(CH_3)_2$
11	$PhCO\text{-}n\text{-}C_3H_7$	CH_3OH	$97/(^1/_3)$	Ph_3COCH_3
12	"	$(CH_3)_2CHOH$	60/(1)	$Ph_3COCH(CH_3)_2$
13	$Ph\underset{OCH_3}{\underset{\vert}{C}}(CH_3)C_2H_5$	C_2H_5OH	$65/(1^1/_3)$	$Ph\underset{OC_2H_5}{\underset{\vert}{C}}(CH_3)C_2H_5$
14	$Ph\underset{O\text{-}n\text{-}C_3H_7}{\underset{\vert}{C}}(CH_3)C_2H_5$	CH_3OH	$82/(1^1/_3)$	$Ph\underset{OCH_3}{\underset{\vert}{C}}(CH_3)C_2H_5$
15	$Ph\underset{OCH(CH_3)_2}{\underset{\vert}{C}}(CH_3)C_2H_5$	C_2H_5OH	$90/1^1/_3)$	$Ph\underset{OC_2H_5}{\underset{\vert}{C}}(CH_3)C_2H_5$

a. 0.4 molar equivalent of CAN was used.

We examined the utility of Ce(IV) for ether-to-acetate conversion. Our results showed that conversion of the above mentioned ethers to their corresponding acetate esters can be achieved catalytically and in excellent yields (Table 3). We also found that the conversion of allylic and tertiary benzylic acetate esters to their corresponding ethers can be performed under similar conditions. The results of acetate ester-to-ether conversion are shown in Table 3.

Table 3. Interconversion of Allylic and Cinnamylic Ethers and Esters with 0.2 mole % of Ce(IV) Under Refluxing Conditions.

entry	Substrate	Solvent	Yield/Time(h)	Product
1		HOAc	$93/(^1/_4)$	
2		"	$91/(^1/_4)$	"
3	 $C_6H_4CH=CH\underset{\substack{\vert \\ OC_2H_5}}{C}HCH_3$	"	$96/(^1/_4)$	 $C_6H_4CH=CH\underset{\substack{\vert \\ OAc}}{C}HCH_3$
4		CH_3OH	95/(1)	
5	"	C_2H_5OH	95/(1)	
6		$(CH_3)_2CHOH$	90/(2)	
7	 $C_6H_5CH=CH\underset{\substack{\vert \\ OAc}}{C}HCH_3$	CH_3OH	$94/(^1/_4)$	 $C_6H_5CH=CH\underset{\substack{\vert \\ OCH_3}}{C}HCH_3$
8	 $p.CH_3OC_6H_4CH=CH\underset{\substack{\vert \\ OAc}}{C}HCH_3$	$n\text{-}C_3H_7OH$	$97/(^1/_4)$	 $p.CH_3OC_6H_4CH=CHCH\underset{\substack{\vert \\ O\text{-}nC_3H_7}}{C}H_3$

As it is shown in the previous paper[1], Ce(IV) can act as a one-electron transfer agent for C-O bond cleavage. This is in consistent with our previous observation concerning one-electron transfer ability of Ce(IV) in ring opening reactions of epoxides[11-13] and thiiranes[14]. Here, also the assumption of formation of a radical cation ( , R=alkyl, acyl) followed by C-O bond cleavage and the formation of a carbonium ion as intermediate could account for the above features of the reactions. The intermediacy of a carbonium ion in these reactions can be shown by the formation of exo-ethers from the endo- ethers (Table 1, entries 1,2). Regeneration of Ce(IV) can occur through the reaction of Ce(III) with $RO^{\bullet}$ or $RCO_2^{\bullet}$ similar to that reported for the reaction of $HO^{\bullet}$ [15,16]. This could account for the catalytic nature of the above reactions.

Due to the catalytic nature of the reagent, efficiency, mildness and neutrality of reaction conditions, availability and safety of the reagent, high yield and ease of work up, the present method could be a useful addition to the available methods of C-O bond cleavage in organic synthesis.

Experimental

Products were isolated and their physical, i.r, nmr and mass spectral data were compared with those of known samples.[1] All yields refer to the isolated products.

General Procedure for the Alcoholysis of Ethers and Esters: A solution of ether or ester (1 mmole) in the appropriate alcohol (5 ml) was treated with 0.2 molar equivalents of CAN and refluxed for 6-180 min (tables 1,2,3). The progress of the reaction was monitored by g.l.c and t.l.c. After evaporation of the solvent, the residue was washed with ether. Evaporation of solvent followed by chromatography on a short column of silica-gel afforded the pure product (55-97%). The product was identified by comparison with known sample.

General Procedure for the Acetolysis of Ethers: A mixture of ether (1 mmole) and 0.2 molar equivalents of CAN in acetic acid (10 ml) was refluxed for 15-60 min. The reaction was followed by g.l.c and t.l.c. After completion of the reaction, the solvent was evaporated. The residue was dissolved in ether and washed with 5% sodium bicarbonate solution and then water and was dried. Evaporation of solvent followed by chromatography on a short column of silica-gel gave the corresponding acetate in 91-96% yield.

References and Footnotes

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16. The reactions of allyl ethers (Table 1, entries 1,2) with Ce(IV) in methanol were performed in the presence of excess acrylamide. A large amounts of polyacrylamide was formed with considerable decrease in the reaction rate.

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