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Cerium(IV), as a Selective and Efficient Catalyst For Alcoholyses of Allylic and Tertiary Benzylic Alcohols

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Abstract: *An efficient and selective method is described for the catalytic conversion of allylic, and tertiary benzylic alcohols into their corresponding ethers in the presence of Ce(IV) under solvolytic and non-solvolytic conditions.*

INTRODUCTION

The hydroxyl group and its alkylated derivatives are very valuable and tremendously versatile and important functional groups in organic synthesis. The common methods for conversion of alcohols to ethers are based on the reaction of metal salts of alcohols with different alkylating agents[1-5] with or without phase transfer catalysts. Condensation of alcohols or their salts with aldehydes[6,7], olefines[8], alkyl oxides[9] and dialkyl phosphites[10] under basic or acidic conditions, are also reported to be useful methods for this transformation. However, in most cases these methodologies are described only for reactions with primary substrates and suffer from highly basic or acidic conditions.

Recently we have reported the use of Ce(IV) as an efficient catalyst for ring opening of epoxides and thiiranes in alcohols, acetic acid and water[11-13]. In this study, the use of Ce(IV) is reported as a mild and efficient catalyst for C - O cleavage in allylic and tertiary benzylic alcohols under solvolytic and non-solvolytic conditions. Selective alcoholysis of these alcohols is achieved in the presence of 1^{o},$2^{o}$and 3^{o}

alcohols and some other hyroxy compounds in high yields using Ce(IV) as ceric ammonium nitrate (CAN).

RESULTS AND DISCUSSION

Alcoholyses of different types of allylic and tertiary benzylic alcohols were performed in 1°, 2° and 3° alcohols as solvent and in the presence of catalytic amounts of Ce(IV) as CAN in good to excellent yields. The method described here is simple, mild,efficient and selective. Allylic alcohols are smoothly converted, not only to their corresponding 1° and 2° ethers, but also to their 3° ethers in high to excellent yields. The results are shown in Table 1.

Table 1. CAN (0.2 Molar equivalent) Promoted Alcoholyses of Allylic Alcohols

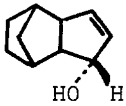
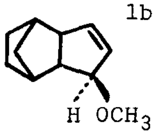
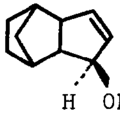
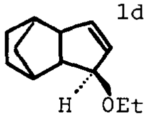
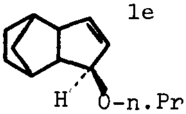
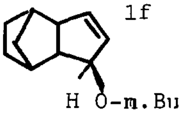
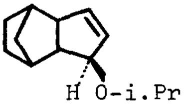
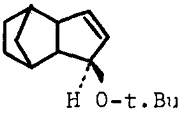
Entry	Subestrate	Solvent	Yield/ Time(h) Room Temp.	Yield/Time(min) Refluxing Temp.	Product
1	 1a	CH_3OH	85(½)	82(10)	 1b
2	 1c	CH_3OH	90(¼)	-	"
3	"	EtOH	94(¼)	-	 1d
4	"	n-PrOH	90(½)	93(10)	 1e
5	"	n-BuOH	92(1¼)	-	 1f
6	"	i-PrOH	85(5)	90(30)	
7	"	t-BuOH	80(24)	92(30)	

Table 1. Continued

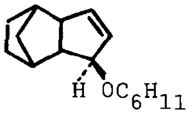
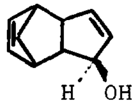
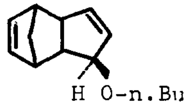
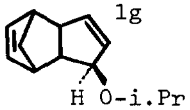
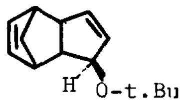
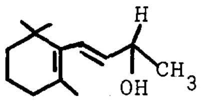
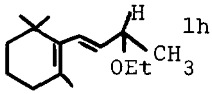
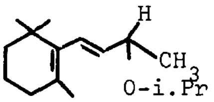
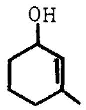
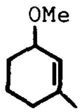
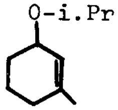
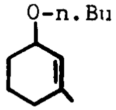
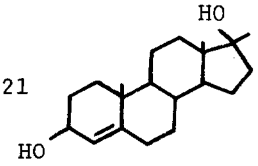
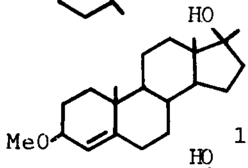
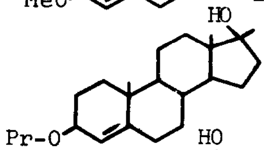
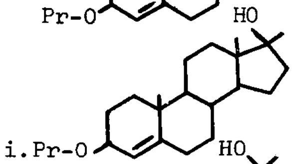
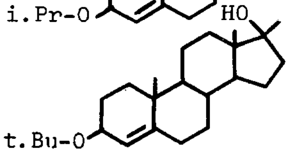
8	"	Cyclohexanol	90(¼)	-	
9		n-BuOH	95(½)	-	
10	"	i-PrOH	95(24)	97(30)	 1g
11	"	t-BuOH	75(24)	95(15)	
12		EtOH[1]	70(1½)	-	 1h
13	"	i.PrOH[1]	60(1½)	-	
14	$(CH_3)_2C{=}CHCH(OH)CH_3$	EtOH	95(6½)	95(15)	$(CH_3)_2C{=}CHCH(OET)CH_3$ 1i
15	"	i-PrOH	95(8)	91(15)	$(CH_3)_2C{=}CHCH(O\text{-i.Pr})CH_3$
16	$CH_2{=}CH\text{-}C(CH_3)(OH)\text{-}C_2H_5$	EtOH	-	89(60)	$C_2H_5C(CH_3) = CHCH_2OEt$
17	"	t-BuOH	-	70(150)	$C_2H_5C(CH_3) = CHCH_2O\text{-t.Bu}$
18		MeOH	93(¼)	-	 ij

Table 1 Continued

19	"	i-PrOH	96(½)	-	
20	"	n-BuOH	95(½)	-	
21		MeOH	98(2)	-	 1k
22	"	PrOH	96(3)	98(15)	
23	"	i-PrOH	95(2.5)	-	
24	"	t-BuOH	93(3.5)	-	

I. Three portions of 0.2 molar equivalents of CAN were used.

II. Two portions of 0.2 molar equivalents of CAN were used.

Formation of the isomerized product (exo-isomer)from the endo-substrate (entry 1) and also formation of thermodynamically more stable products from the substrate with less substituted double bond (entries 16,17) are diagnostic of the formation of carbonium ion intermediates in these reactions. Selective alcoholyses of allylic hydroxyl groups in the presence of tertiary groups are shown in the reaction of the steroidal alcohol with 1°, 2° and 3° alcohols (entries 21-24).

Alcoholyses of cinnamylic and tertiary benzylic alcohols were also performed efficiently at both room temperature and under refluxing conditions. The corresponding ethers were also separated and identified by comparison with authentic samples or by their mass and spectral data. The results are summerized in Table 2.

Table 2. CAN(0.2 Mole%) Promoted Alcoholyses of Cinnamylic and Tertiary Benzylic Alcohols

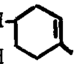
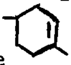
Entry	Substrate	Solvent	Yield/Time(h) Room Temp.	Yield/Time(min) Refluxing Temp.	Product
1	$C_6H_5CH{=}CHCH(OH)CH_3$	MeOH	65(24)	-	$C_6H_5CH{=}CHCH(OMe)CH_3$ 2a
2	"	PrOH	-	97(60)	$C_6H_5CH{=}CHCH(OPr)CH_3$
3	"	i-PrOH	-	96(60)	$C_6H_5CH{=}CHCH(O\text{-}i.Pr)CH_3$ 2b
4	$PCH_3OC_6H_4CH{=}CHCH(OH)CH_3$	MeOH	95(2)	-	$P.CH_3OC_6H_4CH{=}CHCH(OMe)CH_3$
5	"	PrOH	97(3)	95(30)	$P.CH_3OC_6H_4CH{=}CHCH(OPr)CH_3$
6	"	i-PrOH	96(5)	92(30)	$CH_3OC_6H_4CH{=}CHCH(O\text{-}i.Pr)CH_3$
7	"	t-BuOH	96(7½)	93(60)	$CH_3OC_6H_4CH{=}CHCH(O\text{-}t.Bu)CH_3$
8	$P.ClC_6H_4CH{=}CHCH(OH)\text{-}$ 	MeOH	-	97(45)	$P.ClC_6H_4CH{=}CHCH(OMe)\text{-}$  2c
9	"	EtOH	-	96(90)	$P.ClC_6H_4CH{=}CHCH(OEt)\text{-}$ 

Table 2. Continued

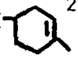
10	"	i-PrOH	-	92(120)	$P.ClC_6H_4CH{=}CHCH$– O i.Pr [2d]
11	$C_6H_5C(CH_3)C_2H_5$ OH	MeOH	75(48)	65(75)	$C_6H_5C(CH_3)C_2H_5$ OMe [2e]
12	$C_6H_5C(CH_3)C_2H_5$ OH	EtOH	73(48)	75(75)	$C_6H_5C(CH_3)C_2H_5$ OEt
13	"	PrOH	36(48)	90(75)	$C_6H_5C(CH_3)C_2H_5$ OPr
14	"	i-PrOH	14(48)	21(75)	$C_6H_5C(CH_3)C_2H_5$ O-i.Pr
15	"	t-BuOH	0(48)	0(240)	-
16	Ph_3COH	MeOH	97(4½)	98(15)	Ph_3COMe [2f]
17	"	EtOH	97(6½)	96(30)	Ph_3COEt [2g]
18	"	BuOH	-	98(30)	Ph_3COBu
19	"	i.PrOH	0(24)	0(60)	Ph_3CO-i.Pr

Table 2. Continued

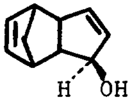
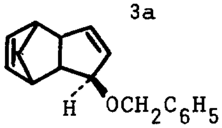
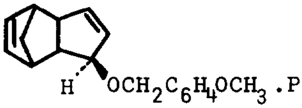
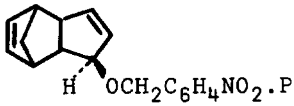
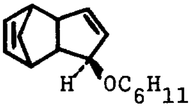
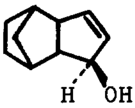
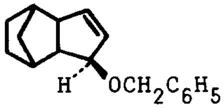
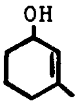
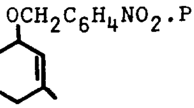
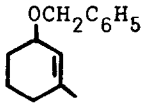
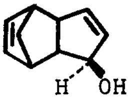
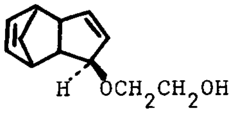
20	Ph_3COH	allyl alcohol	-	62(30)	$Ph_3COCH_2CH{=}CH_2$	2h
21	$Ph_2\underset{OH}{C}CH_3$ [I]	MeOH	97(24)	93(30) [II]	$Ph_2\underset{OMe}{C}CH_3$	
22	"	EtOH	94(24)	95(30) [II]	$Ph_2\underset{OEt}{C}CH_3$	
23	"	PrOH	97(30)	94(90) [II]	$Ph_2\underset{OPr}{C}CH_3$	
24	"	i-PrOH	45(48)	-	$Ph_2\underset{O\text{-}i.Pr}{C}CH_3$	
25	"	t-BuOH	48(48)	-	$Ph_2C{=}CH_2$	

I. The reaction was performed with two portions of CAN at room temperature.

II. The reaction was performed at 70-75^{o}C. The elimination product is the major product under refluxing condition.

The applicability of this method under non-solvolytic conditions was also demonstrated by performing the reactions in acetone using hydroxy compounds as nucleophile. The results are shown in Table 3.

Table 3. CAN(0.2 Molar equivalent) Promoted Alcoholyses of Alcohols Using Other Hydroxy Compounds as Nucleophile in Acetone.

Entry	Substrate	Nucleophile (3 equimolar)	Yield/Time(h)	Product
1		$C_6H_5CH_2OH$	90(2)	3a 
2	"	$P.CH_3OC_6H_4CH_2OH$	92(1½)	
3	"	$P.NO_2C_6H_4CH_2OH$	38(4)	
4	"	Cyclohexanol	94(1)	
5		$C_6H_5CH_2OH$	93(2)	
6		$P.NO_2C_6H_4CH_2OH$	35(2)	 3b
7	"	$C_6H_5CH_2OH$	98(1)	 3c
8		$HOCH_2CH_2OH$ [I]	95(2)	3d 
9	Ph_3COH	$CH_2=CH-CH_2OH$ [II]	67(2)	$Ph_3COCH_2CH=CH_2$ 2h

I. The reaction was performed under solvolytic condition and at room temperature.
II. The reaction was performed under refluxing condition.

The precise mechanism of the reaction is not clear but, on the basis of the results obtained from this study (entries 16,17,21-24) which show the formation of a carbonium ion as an intermediate, the use of acrylamide as a radical traping agent[14] and also our previous observations with epoxides[11,13] and thiiranes[12], the assumption of the formation of a radical cation() followed by C - O cleavage may account for the above features of the reaction. The catalytic nature of the reaction could be due to the regeneration of Ce(IV) from the reaction of $\dot{O}H$ and Ce(III) ($K = 7.2 \times 10^{7}\ M^{-1}\ Sec^{-1}$)[15].

EXPERIMENTAL

Products were characterized by comparison with authentic samples or with their mass and spectral data. Reactions were monitored by thin layer or gas chromatography. All yields refer to the isolated products.

General Procedure for the Alcoholysės of Alcohols. A solution of the substrate (3 mmole) and the approperiate alcohol (40 cm^3) was treated with (0.2-0.6) molar equivalents of ceric ammonium nitrate (CAN) at room temperature or under refluxing condition. (Table 1,2). The progress of the reaction was monitored by t.l.c. using n-hexane/ether (5:1) as eluent or with gas chromatography. The solvent was evaporated and water (10 cm^3) was added. Extraction with ether, followed by chromatography on a short column of silica gel gave the pure product. Physical, mass and spectral data of some of the starting materials and products are shown below. (1a) M.P. 108-111(Lit[16]. 109-112^o); Found C, 79.7 H, 9.6% . Calc. for $C_{10}H_{14}O$: C, 80.0; H, 9.4%. (1b) B.b. 46^o/0.05 mm. n_D^{25}= 1.4930; Found C, 80.3; H, 9.5% Calc. For C, 80.4; H, 9.8%. ν_{max}(CCl_4)=3040(m), 2940(v.s.) 2910(m), 2865(s), 2810(m), 1445(m), 1365(s), 1312(m), 1180(m), 1110(s), 1088(v.s.), 960(s), 920(m) and 882(m) Cm^{-1}. N.m.r. ($CDCl_3$) δ(ppm) 5.8(2H,complex) 4.17(1H, unresolved singlet), 3.16(3H,s) 2.3(3H,complex), 1.2-1.5(7H, complex). (1c) M.P. 49-50^o (Lit[17] m.p. Ca. 30^o). Found: C, 79.7; H, 9.2%. Calc. for $C_{10}H_{14}O$: C, 80.0; H, 9.4%. (1d) n_D^{25}= 1.4990(b.p 210^o)[18], Found= C, 80.7; H, 10.0%. $C_{12}H_{18}O$ requires C, 80.9; H, 10.1%. ν_{max}(CCl_4)3050(m), 2960(s), 2930(m), 2865(s), 2780(m), 1370(m), 1360(m), 1315(m), 1110(s), 1080(s), 1040(m), 930(m) and 890(m) Cm^{-1}. N.m.r. (CCl_4) δ(ppm) 5.8(2H, b.s), 4.25(1H, unresolved, s) 3.38(2H.q, J=7Hz), 2.3(3H, unresolved), 1.2-1.6 (7H, complex). (1e) n_D^{25}= 1.5011 (b.p. 61^o/0.1 mm), Found: C, 81.5; H, 10.3%. $C_{13}H_{20}O$ requires C, 81.25; H, 10.42%. ν_{max} (CCl_4) = 3040(m), 2960(s), 2925(s), 2880(s), 1450(m) 1365(m), 1320(m), 1300(m), 1110(s), 1085(vs) 1050(s) and 1025(m). N.m.r. ($CDCl_3$) δ(ppm): 5.78(2H,broad singlet), 4.22(1H, broad s) 3.25(2H, t, J=7Hz), 2.3(3H, unresolved), 1.1-1.5(9H, complex), 0.9(3H, t, J=7Hz), (1f) n_D^{25}= 1.5195, M^+(204), ν_{max} (neat) 3060(m), 2960(s), 2930(s), 2870(s), 1465(m), 1455(m), 1365(s), 1340(s), 1125(m), 1110(m), 1085(s) and 910(m) Cm^{-1}. N.m.r. δ 5.8(2H,b.s), 4.16(1H, b.s), 3.25(2H, t, J=7Hz), 2.2-2.5(3H, unresolved), 1.2-1.6(11H, complex), 0.6(3H, t, J=7Hz). (1g) n_D^{25}= 1.5191, M^+(190), N.m.r. (CCl_4) δ (ppm) 5.60(4H, complex), 3.8(1H, multiplet), 2.5-1.0(6H, d, J=6Hz+7H, complex). (1h) n_D^{25}= 1.4850, M^+(222), ν_{max}(neat): 2930(s), 2880(s), 1450(m), 1370(m), 1100(s), 975(m)and 860(m) Cm^{-1}. N.m.r. (CCl_4) δ(ppm) 5.9(1H,d, J=16Hz), 5.2(1H, dd, J=16, 8Hz), 3.1-4.0(3H, t, J=7Hz+1H, m), 0.9-2.2 (21H, complex). (1i) n_D^{25}= 1.4181, M^+(128), N.m.r. ($CDCl_3$) δ (ppm) 4.9(1H, d, J=9Hz), 3.9(1H, m), 3.25(2H, t, J=7Hz), 1.70(3H,s), 1.60(3H,s),0.8-1.10 (6H, complex). (1j)n_D^{25}= 1.4462, M^+(126), ν_{max}(neat) 3045(m), 2980(m), 2930(s), 2880(m), 2820(m), 1450(m), 1380(m), 1190(s), 1090(s), 925(m), 785(s) and 710(s) Cm^{-1}. N.m.r. (CCl_4) δ (ppm)5.4(1H, b,s), 3.5(1H,s), 1.3-2.1(3H, s+6H,m), (2a) n_D^{25}= 1.5490, M^+(162), N.m.r. (CCl_4) δ (ppm) 5H(Ph), 1H(d, J=16Hz), 6.0(1H,dd, J=16,8Hz), 3.8(1H, quintet, J=8Hz), 3.3(3H, s), 1.3(3H, d, J=6Hz). (2b) n_D^{25}= 1.5145, M^+(190), N.m.r.(CCl_4) δ (ppm) 7.1(5H, Ph), 6.3(1H, d, J=16Hz), 5.8(1H, dd, J=16,7Hz), 3.9(1H, quintet J=8Hz), 3.5(1H, septet, J=7Hz), 1.3(3H, d, J=8Hz), 1.0(6H, d, J=7Hz). (2c) M^+(270) ν_{max} (neat) 3030(m), 2980(m), 2920(s), 2831(m), 1493(m), 1092(s), 972(m) and 805(m) Cm^{-1}. N.m.r.($CDCl_3$) δ (ppm) 7.2(4H,Ph) 6.4(1H, d, J=16Hz), 6.0(1H, dd, J=16,7Hz), 5.2(1H, unresolved singlet), 3.3(1H, m), 3.2(3H, s), 1.0-2.3(10H, complex). (2d) M^+ (304), ν_{max}(neat) 3030(m), 2960(s), 2916(s), 2830(m), 1495(s), 1370(m), 1122(s), 1092(s), 970(m) and 800(m) Cm^{-1}. N.m.r. ($CDCl_3$) δ (ppm) 7.2(4H, Ph), 6.9(1H, d, J=16 Hz), 6.0(1H, dd, J=16,7Hz), 5.2(1H, unresolved singlet), 3.3(1H,m), 3.2-3.7(2H, m), 1.2-2.2(10H, complex), 1.0(6H, d, J=7Hz). (2e) n_D^{25}=1.5590, M^+(212) ν_{max}(neat) 3030(m), 3060(m), 2980(s), 2930(s), 2845(m), 1600(m), 1446(s), 1100(s), 1090(s), 768(m), and 702(s) Cm^{-1}. N.m.r. ($CDCl_3$)δ (ppm) 7.2(10H, 2Ph), 3.1(3H, s), 1.8(3H, s). (2f) M.P. 83-84° (Lit[19]. m.p. 83). (2g) M.P. 82.4-83°(Lit[20]. m.p. 82.5-83°). (2h) m.p. 69-71° (Lit[21] 73-75°). (3a) n_D^{25} = 1.5620 M^+ (238), N.m.r. ($CDCl_3$, (ppm) 7.3(5H, s), 5.8(4H, complex), 4.5(2H,s), 3.9(1H, unresolved singlet), 2.5-3.6(4H, complex), 1.2-1.8 (2H, m). (3b) n_D^{25}= 1.5290, M^+ (248), N.m.r. ($CDCl_3$) δ (ppm) 7.2-8.2 (4H, Ph), 5.4(1H, unresolved singlet), 4.5(2H,s), 3.9(1H, unresolved, m), 1.3-2.0(9H, m). (3c) n_D^{25}= 1.5223, M^+(202), N.m.r. ($CDCl_3$) δ(ppm) 7.1(5H,s), 5.35(1H, b,s), 4.3(2H, s), 3.65(1H,m), 1.2-2.0(9H, complex). (3d) n_D^{25}= 1.5185, M^+(193), ν(OH) neat, 3400(b), N.m.r. ($CDCl_3$) δ (ppm) 5.7(4H AA'BB'), 3.75(1H b,s), 2.4-3.7(9H,complex) 1.2-1.8(2H,m).

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References and Notes:

1. White, W.N. and Norcross, B.E., J. Am. Chem. Soc., **1961**, 83, 3268.
2. Olson, W.T.; J. Am. Chem. Soc. **1947**, 69, 2451.
3. Marks, E.M.; J. Am. Chem. Soc. **1973**, 59, 946.
4. Organic Functional Group Preparation; Sandler, S.R.; Academic Press, **1986**, Vol. 1, pp 139.
5. Dubios, R.A.; Diss Abstr. Int. B. **1976**, 37(1), 223.
6. Shomaker, B.H.; Board, C.E.; J. Am. Chem. Soc., **1931**, 53, 1505.
7. Torli, S.; Takagishi, S.; Inokuchi, T., Bull. Chem. Soc., Jpn, **1987**, 60, 775.
8. Nenitzescu, C.D.; Przemetzki, V.; Chem. Ber.; **1936**, 69, 2706.
9. Chitmood, H.C.; Freure, B.T.; J. Am. Chem. Soc.; **1946**, 68, 680.
10. Kashman, Y., J. Org. Chem., **1972**, 37(6), 912.
11. Iranpoor, N.; Mohamadpour.B.I.; Synthetic Commun. **1990**, 20(18),2789.
12. Iranpoor, N.; Owji, J.; Tetrahedron, **1991**, 47(1), 149.
13. Iranpoor, N.; Mohamadpour, B.I.; Shirini, Z.F.; Tetrahedron, **1991**, 47(47), 9861.
14. The reaction of allylic alcohols (Table 1, entries 1,2,9) with Ce(IV) in alcohols was performed in the presence of excess acrylamide. A large amounts of polyacrylamide was formed with considerable decrease in the reaction rate.
15. Schwartz, H.H; J. Phys. Chem.; **1962**, 66, 255.
16. Dilling, W.L.; Plepy, R.A. J. Org. Chem. **1970**, 35, 2971.
17. Alder, K.; Stein, G.; Annalen, **1933**, 504, 205.

18. Iranpoor, N.; Ph.D. Thesis, Birmingham University, **1980**. Birmingham, England.
19. Withig, G.; Heintzeler, M.; Ann., **1947**, 557, 201.
20. Smith, S.A., Smith, R.J., J. Am. Chem. Soc., **1948**, 70, 2400.
21. "Shell" Research Ltd, Chem. Abs., **1965**, 62, p 4010 c.

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