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Ceric Ammonium Nitrate: a Mild and Efficient Reagent for Conversion of Epoxides to β-Nitrato Alcohols

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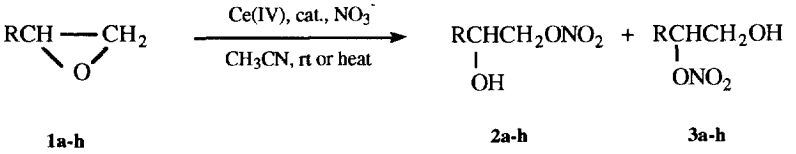
Abstract: Catalytic amount of Ce(IV) as ceric ammonium nitrate (CAN) alone or in the presence of excess nitrate ion reacts smoothly and efficiently with epoxides under mild conditions to produce the corresponding β-nitrato alcohols in good to excellent yields.

Organic nitrato compounds are often synthesized by nitration of alcohols[1,2] or nucleophilic attack by nitrate ion[3]. Both methods suffer from disadvantages such as highly acidic conditions and low yield of reactions.Very recently nitration of alcohols with nitrate ion has been reported to occur in the presence of Boron trifluoride hydrate [4]. Alkyl nitrates have a variety of applications . They are useful reagents for preparation of important class of nitro compounds[5] through their reaction with carbanions. They can also be used for aliphatic and aromatic nitration.[5] β-Nitrato alcohols as functionalized alkyl nitrates have been prepared in low yields through the reaction of epoxides in concentrated nitric acid[6] or by nitration of halohydrines[7] with silver nitrate. However both methods are not attractive due to highly acidic condition of the first method and the use of expensive silver nitrate in the second one. Ring opening reactions of epoxides with a large number of nucleophiles have been extensively studied[8]. As far as we know there is no report in the literature concerning this reaction by nitrate ion as nucleophile.

CAN is a versatile reagent in oxidation reactions[9] and has also been used for transfer of nitrate ion to some organic molecules[10-12]. Recently we have reported the ability of this reagent to catalyze ring opening reaction of epoxides and thiiranes in the presence of several nucleophiles[13,14] and also carbon-oxygen bond cleavage in some classes of alcohols[15] and ethers possibly through a radical type reaction.

In the course of our studies of the reaction of epoxides with CAN, we found that this reagent alone or in the presence of excess nitrate ion as its ammonium or tetra-n-butyl ammonium salts can act as a smooth and efficient nitrate transfer agent to convert epoxides to their corresponding vicinal nitrato alcohols in high to excellent yields (Scheme and Table).

Scheme



1a-h **2a-h** **3a-h**

R or epoxide: **(a)** $ClCH_2$- **(b)** $PhOCH_2$- **(C)** $CH_2=CHCH_2OCH_2$- **(d)** $(CH_3)_2CHOCH_2$- **(e)** CH_3- **(f)** $CH_3(CH_2)_3$- **(g)** Ph- **(h)** cyclohexene oxide

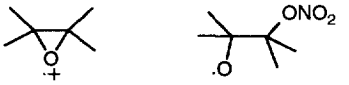
Table: Conversion of epoxides to β-nitrato alcohols with CAN.

Entry	Epoxide	Method[I]	CAN/Epoxide Molar Ratio	Reaction Time(h) and Temperature °C	Product	Yield%[II]
1	a	A	0.3	1.0(80 °C)	2a	80
2	a	B	0.4	6.0(80 °C)	2a	98
3	a	C	0.4	2.0(80 °C)	2a	85
4	b	A	0.6	2.0(80 °C)	2b	98
5	b	B	0.8	6.0(80 °C)	2b	98
6	b	C	0.8	3.5(80 °C)	2b	85
7	c	A	0.65	2.0(80 °C)	2c	88
8	c	B	0.7	4.0(80 °C)	2c	93
9	c	C	0.8	2.5(80 °C)	2c	80
10	d	A	0.6	2.0(80 °C)	2d	88
11	d	B	0.6	3.0(80 °C)	2d	92
12	d	C	0.6	2.5(80 °C)	2d	88
13	e	A	0.3	3.0(r.t)	2e+3e	25+50
14	e	B	0.3	3.0(r.t)	2e+3e	30+65
15	e	C	0.4	3.0(80 °C)	2e+3e	28+60
16	f	A	0.6	2.0(80 °C)	2f+3f	42+45
17	f	B	0.6	2.0(80 °C)	2f+3f	40+46
18	f	C	0.6	1.5(80 °C)	2f+3f	40+45
19	g	A	0.25	0.2(r.t.)	3g+diol	40+35
20	g	B	0.4	2.0(80 °C)	3g+diol	85+10
21	g	C	1.0	1.5(80 °C)	3g+PhCHO	10+65
22	h	A	0.4	0.25(r.t.)	trans-2-nitrato-	80
23	h	B	0.35	6.0(r.t.)	cyclohexanol	97
24	h	C	0.4	1.5(r.t.)		82

[I]A: CAN and NH_4NO_3 were used in acetonitrile-water (6:1) [I]B: CAN and tetra-n-butyl ammonium nitrate were used in dry acetonitrile. [I]C: CAN was used alone in dry acetonitrile..[II]Yield refers to isolated product.

Reaction of different epoxides carrying activating or deactivating groups with ceric ammonium nitrate (CAN) alone or in the presence of some nitrate ion as either its ammonium or tetra n- butyl ammonium salts were performed in dry or aqueous acetonitrile under refluxing conditions or at room temperature depending on the reaction conditions. High regioselectivity was observed in most cases except for (1f) in which electronic and steric effects counterbalance each other. Reaction of styrene oxide with CAN without addition of nitrate ion was accompanied by carbon-carbon bond cleavage and benzaldehyde was obtained as the major product. However this reaction in the presence of n- Bu_4NNO_3 produce the corresponding nitrato alcohol in good yield.

Our results show that CAN is an efficient reagent for one pot synthesis of vicinal nitrato alcohols from epoxides. The reaction probably occurs through a one-electron transfer process with the formation of an epoxonium radical cation (i) followed by attack of ONO_2^- ion as nucleophile to produce the corresponding alkoxy radical (ii). Regeneration of Ce(IV) may occur through the reaction of Ce(III) with radical (ii). This latter reaction has been shown to be very fast between Ce(III) and hydroxy radical[7].



(i) (ii)

The intermediacy of a radical in these reactions can be shown by performing the reaction in the presence of a radical trapping agent[18]. Good regioselectivity, high yield and mildness of the reaction conditions, ease of work up and availability of the reagent make this new method an efficient and useful methodology for preparation of β-nitrato alcohohs in organic synthesis.

Experimental

Products were isolated and identified by their physical, i.r.,n.m.r. and mass spectral data or comparison with known samples which were prepared according to the literature procedures[6,7].

General Procedure: (method A); Ceric ammonium nitrate (0.3-0.6 mmole) was added gradually to a mixture of epoxide (1.0 mmole) and NH_4NO_3 (3.0 mmole) in acetonitrile -water (6:1) (4 ml). (method B); Ceric ammonium nitrate (0.3-0.8 mmole), epoxide (1.0 mmole) and Bu_4NNO_3 (3.0 mmole) were mixed in dry acetonitrile (4 ml). (method C); Ceric ammoniun nitrate (0.4-1.0 mmole) and epoxide (1.0 mmole) were mixed in dry acetonitrile. the mixture obtained from each method was then stirred for the specified time and in appropriate temperature according to the table. The progress of reaction was monitored by t.l.c. and g.c. The solvent was evaporated, water (15 ml) was added and extracted with ether (3x20 ml). Evaporation of the solvent followed by vacuum distillation or column chromatography on a short column of silica-gel afforded the corresponding product in 25-98% yield.Physical constants of some selected products are shown 2a: N.M.R.($CDCl_3$) δ: 3.1(1H, s), 3.65(2H, d, J = 5.0Hz), 4.15(1H, quint., J = 5.5Hz) , 4.6(2H, d, J = 5.5Hz). I.R.(neat) v: 3400(s), 2985(m), 2905(m), 1640(s),1435(m), 1375(m),1280(s), 1110(m), 1070(m), 1000(m), 850(s), 705(m) cm^{-1} MS(20ev) m/z: 154(M-1), 93(M-ONO2). B.p(°C) /torr=70/4, Lit.[7](75/7). 2c: N.M.R.($CDCl_3$) δ: 3.15(1H, S), 3.45 (2H, d, J=6.0 Hz), 3.6(1H, quint., J = 5.5 Hz), 3.95 (2H, d, J = 6.0Hz), 4.5 (2H, d, 5.7 Hz), 5.1(1H, dd, j =17.0, 4.5 H), 5.3 (1H, dd, J = 9.0, 4.5 Hz), 5.5 (1H, complex). I.R.(neat) v: 3400(s), 3090(m), 2990(m), 2900(s), 2885(s), 1650(s), 1640(s), 1570(m), 1430(m), 1350(m), 1280(s), 1100(s), 1000(s), 980(s), 850(s) 760(m). MS(20ev) m/z = 176 (M-1), 115 (M-ONO2). B.p(°C)/torr = 85/2 Lit[7]. 80/1.

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(18) (a)The reaction of cyclohexene oxide with CAN was performed in the presence of excess acrylamide. A large amount of polyacrylamide was formed with considerable decrease in the reaction rate. (b) A considerable increase in the reaction rate was also observed when the reaction was performed in deareated solvent and under nitrogen atmosphere.

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