

Brief Communications

Oxidation of primary and secondary alkanols with the $\text{Ce}^{\text{III}}\text{—LiBr—H}_2\text{O}_2$ system*

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Action of a novel oxidation system, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (cat.)— LiBr (cat.)— H_2O_2 (stoichiometric oxidant) on primary aliphatic $\text{C}_6\text{—C}_9$ alcohols gives selectively esters, whereas secondary aliphatic $\text{C}_5\text{—C}_9$ alcohols are converted into ketones. Selectivity of these transformations is provided by slow addition of H_2O_2 to the other reactants.

Key words: primary and secondary alcohols, esters, ketones, hydrogen peroxide, lithium bromide, oxidation, cerium(III) nitrate.

Among the cerium compounds, ammonium cerium(IV) nitrate (CAN) is the most widely used in the organic chemistry due to its ability to act in diverse chemical transformations not only as the oxidant, but also as the catalyst and the radical initiator.

In 1969, the first application of CAN for the oxidation of alkanols, namely cyclization of pentan-1-ol into 2-methyltetrahydrofuran, was documented.¹ Analogously, 4-phenylbutan-1-ol and 5-phenylpentan-1-ol gave 2-phenyl- and 2-benzyltetrahydrofurans,² respectively; cyclopropylmethanol³ and benzylic alcohols⁴ provided the corresponding aldehydes. Depending on the structure, secondary alcohols either oxidized into ketones or gave aldehydes due to the $\text{C—C}(\text{OH})$ bond cleavage.⁵ Secondary cyclic

$\text{C}_5\text{—C}_8$ alcohols furnished ketones.⁶ Cyclopropanol and cyclobutanol in the presence of CAN afforded aliphatic aldehydes.⁷ Norbornanol (either *exo*- or *endo*-isomer) underwent oxidative cleavage to give three main products, 3- and 4-cyclopenteneacetaldehydes and 3-nitroxycyclopentaneacetaldehyde.⁸

In contrast to CAN, oxidation of primary alcohols with a CAN—LiBr system proceeded by a different mechanism: participation in this reaction of generated from LiBr bromine led to the predominant formation of esters.⁹ Depending on the alkanol : CAN : LiBr molar ratio, secondary alkanols converted selectively to ketones, α -bromoketones or α,α' -dibromoketones.¹⁰ Tertiary cyclic alcohols, 1-alkyl and 1-arylcyclopropanols in the presence of a CAN—MX system ($\text{M} = \text{Na}, \text{K}, \text{NH}_4$; $\text{X} = \text{Br}, \text{I}, \text{N}_3, \text{SCN}$) gave β -X-substituted aliphatic ketones.¹¹

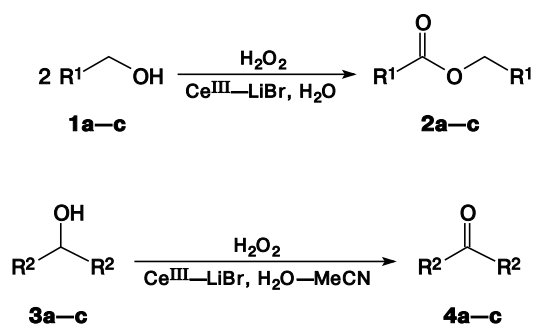
* Dedicated to Academician L. I. Eremenko on the occasion of his 60th birthday.

Ammonium cerium(IV) nitrate is a convenient and efficient compound for the oxidation of small amounts of substrate. Application of this oxidant in large scale is limited by a high molecular weight and, consequently, by large amounts required. For this reason, long time ago it was intended to use CAN as mediator (redox catalyst $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$) in the combination with more simple and inexpensive stoichiometric oxidant, *e.g.*, sodium bromate. Primary and secondary benzylic alcohols oxidized readily with a CAN--NaBrO_3 system in the ratio of 0.01 : 1 giving the corresponding aldehydes and ketones.¹² These conditions were extended on the oxidation of secondary alkanols,¹³ hydroquinones,¹⁴ sulfides,¹⁵ and alkyl and silyl esters.¹⁶ The double mediator system including 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and CAN was tested in oxidation of benzylic alcohols to carbonyl compounds with oxygen.¹⁷

In recent years, new approaches for the application of the cerium salts as oxidants, which based on the replacement of Ce^{IV} on Ce^{III} species, hardly started to develop. To date, hydroxylation of β -dicarbonyl compounds with molecular oxygen in the presence of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ¹⁸ and allylic chlorination of olefins with a $\text{Ce}^{\text{III}}\text{--NaClO}$ system¹⁹ were only studied.

The present work was focused on the application of Ce^{III} instead of Ce^{IV} for the oxidation of primary and secondary alkanols to esters and ketones using the $\text{Ce}^{\text{III}}\text{--LiBr--H}_2\text{O}_2$ system (Scheme 1) (for the preliminary communication see Ref. 20).

Scheme 1



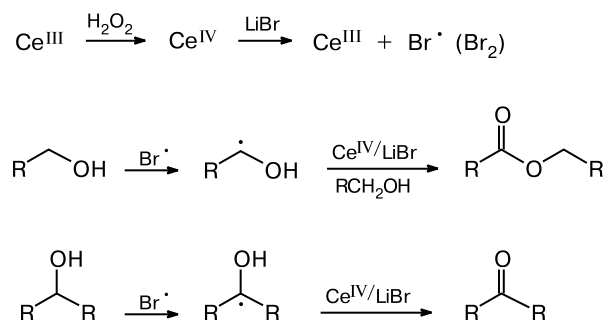
1, 2: $\text{R}^1 = \text{C}_5\text{H}_{11}$ (**a**), C_6H_{13} (**b**), C_8H_{17} (**c**)

3, 4: $\text{R}^2 = \text{Et}$ (**a**), Bu^n (**b**), Pr^i (**c**)

In the reaction under study, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and LiBr were used as mediators and hydrogen peroxide was applied as a stoichiometric oxidant. Our task was to convert the Ce^{III} species to Ce^{IV} in the presence of H_2O_2 , generate bromine from LiBr involving Ce^{IV} as an oxidant, and employ the generated bromine in the combination with Ce^{IV} for the oxidation of alkanols using the procedures similar to that suggested previously for the CAN--LiBr ⁹ and

$\text{CAN--Ce}(\text{SO}_4)_2\text{--LiBr}$ systems.²¹ However, extension of these procedures on the reactions under study encountered certain difficulties because Ce^{IV} oxidized not only the bromine anions, but also hydrogen peroxide; this side reaction decreased the contribution of H_2O_2 and the Ce^{IV} formed into oxidation of alcohols. The high yields of esters and ketones were achieved by maintaining the very low concentration of H_2O_2 and higher concentration of LiBr relative to the Ce^{III} concentration in the reaction mixture. For this purpose, hydrogen peroxide was added to the reaction mixture slowly in small portions. Immediately after addition of hydrogen peroxide, yellow color of the reaction mixture characteristic of Ce^{IV} was observed. The next portion of H_2O_2 was added only after virtually disappearance of the color. In competition with hydrogen peroxide, the bromine anions can capture part of the forming Ce^{IV} ions, and thereby initiate oxidation of alcohols with generated atomic (Scheme 2) or/and molecular bromine.

Scheme 2



Oxidation initiated by molecular bromine proceeds by the mechanism different from the one shown above, probably, *via* hemi-acetals as intermediates, which then are converted into the final products. This possibility relates mainly to primary alkanols.

The high steady-state concentration of Ce^{III} relative to the Ce^{IV} concentration allows decreasing the amount of H_2O_2 , which decomposed in the reaction with Ce^{IV} , however, it was not possible to avoid decomposition of H_2O_2 completely. Therefore, the amount of H_2O_2 exceeding the stoichiometric ratio is required. The conditions for the oxidation of primary alcohols were studied on the example of heptan-1-ol (**1b**) (Table 1).

It should be noted that no oxidation of alcohol **1b** with hydrogen peroxide in the absence of one of the mediators, $\text{Ce}(\text{NO}_3)_3$ or LiBr, occurred (see Table 1, entries 1 and 2). Good results were obtained at molar reactant ratio **1b** : Ce^{III} : LiBr : H_2O_2 equal to 1 : 0.5 : 5 : 10; in this case, the conversion of **1b** was 90% and the selectivity of the formation of **2b** was 98%. The increase in the amount of Ce^{III} (upto 1.0 mol) does not affect the conversion of **1b** and the yield of **2b**, while its decrease resulted in the de-

Table 1. Oxidation of heptan-1-ol (**1b**) with the $\text{Ce}(\text{NO}_3)_3\text{--LiBr--H}_2\text{O}_2$ system^a

| Entry | Molar ratio 1b : $\text{Ce}(\text{NO}_3)_3$: LiBr : H_2O_2 | Conversion of 1b (%) | Product | Yield ^b (%) |
|-----------------|---|--------------------------------|-----------|------------------------|
| 1 | 1 : 0 : 5 : 10 | — | — | — |
| 2 | 1 : 0.5 : 0 : 10 | — | — | — |
| 3 | 1 : 0.2 : 5 : 10 | 45 | 2b | 43/96 |
| 4 | 1 : 0.3 : 5 : 10 | 60 | 2b | 58/97 |
| 5 | 1 : 0.5 : 5 : 10 | 86 | 2b | 84/98 |
| 6 | 1 : 1 : 5 : 10 | 95 | 2b | 93/98 |
| 7 | 1 : 0.5 : 1 : 10 | 10 | 2b | 9/90 |
| 8 | 1 : 0.5 : 3 : 10 | 48 | 2b | 46/96 |
| 9 | 1 : 0.5 : 5 : 5 | 55 | 2b | 53/96 |
| 10 ^c | 1 : 0.5 : 5 : 10 | 43 | 2b | 42/98 |
| 11 ^d | 1 : 0.5 : 5 : 10 | 33 | 2b | 31/94 |

^a **1b** (1.0 mmol); solvent, H_2O (20 mL); reaction temperature, 65–70 °C; reaction time, 4–4.5 h.^b Based on starting/converted **1b**.^c Reaction temperature, 50–55 °C; reaction time, 6.5 h.^d Reaction temperature, 85–90 °C; reaction time, 1.5 h.

crease in their values (see Table 1, entries 3–9). These results reflect complex competing process of the Ce^{III} and Ce^{IV} species in the reaction with H_2O_2 and simultaneous reaction of Ce^{IV} with LiBr. All reactions were carried out in water; in aqueous MeCN, oxidation of **1b** proceeded nonselectively to give mainly heptanoic acid. Depending on the H_2O : MeCN volume ratio, ester **2b** formed in 10–12% yield relative to the acid. When NaBr or KBr were used instead of LiBr under the same reaction conditions, the decrease in the conversion of **1b** and insignificant decrease in the selectivity of the formation of **2b** were observed (Table 2, entries 3 and 4). The use of Ce^{III} acetate or chloride instead of $\text{Ce}(\text{NO}_3)_3$ affected also negatively the conversion of alkanol **1b** and the selectivity of its conversion into ester **2b** (see Table 2, entries 2, 5 and 6).

Under similar conditions, the close homologs of alcohol **1b**, hexan-1-ol (**1a**) and nonan-1-ol (**1c**), were oxidized with hydrogen peroxide in the presence of $\text{Ce}(\text{NO}_3)_3$ and LiBr as mediators to give the corresponding esters **2a**

and **2c**; the yields of esters **2a–c** were almost identical (see Table 2, entries 1, 2 and 7).

Thus, in the case of primary $\text{C}_6\text{--C}_9$ alkanols the reaction under consideration is general and in some cases can be used for the synthesis of "symmetrical" esters.

Oxidation of secondary alkanols proceeds more readily as compared with primary ones. This reaction requires lesser amounts of all mediators involved; however, similar to primary alkanols, larger amount of LiBr requires as compared with $\text{Ce}(\text{NO}_3)_3$ (Table 3, entries 3–6). All reactions were carried out in aqueous MeCN. When water was used as a solvent, lower conversion and lower yields of the ketones were observed (see Table 3, entry 7). It was shown with pentan-3-ol (**3a**) as an example, that molar ratio **3a** : Ce^{III} : LiBr : H_2O_2 equal to 1 : 0.1 : 0.4 : 10 was sufficient for the synthesis of pentan-3-one (**4a**) in nearly quantitative yield (see Table 3, entry 6). Similar result for primary alkanol **1b** was obtained with the molar reactant ratio equal to 1 : 0.5 : 5 : 10, *i.e.* when the greater excess of

Table 2. Oxidation of primary alkanols **1a–c** with the $\text{Ce}^{\text{III}}\text{--MBr--H}_2\text{O}_2$ system^a

| Entry | Alcohol 1a–c | Ce^{III} | MBr | Conversion of 1a–c (%) | Product | Yield ^b (%) |
|-------|------------------------|----------------------------|------|----------------------------------|-----------|------------------------|
| 1 | 1a | $\text{Ce}(\text{NO}_3)_3$ | LiBr | 85 | 2a | 84/99 |
| 2 | 1b | $\text{Ce}(\text{NO}_3)_3$ | LiBr | 86 | 2b | 84/98 |
| 3 | 1b | $\text{Ce}(\text{NO}_3)_3$ | NaBr | 71 | 2b | 69/97 |
| 4 | 1b | $\text{Ce}(\text{NO}_3)_3$ | KBr | 80 | 2b | 78/98 |
| 5 | 1b | $\text{Ce}(\text{OAc})_3$ | LiBr | 54 | 2b | 51/94 |
| 6 | 1b | CeCl_3 | LiBr | 24 | 2b | 21/88 |
| 7 | 1c | $\text{Ce}(\text{NO}_3)_3$ | LiBr | 88 | 2c | 87/99 |

^a **1** (1.0 mmol), molar ratio, **1** : Ce^{III} : MBr : H_2O_2 = 1 : 0.5 : 5 : 10; solvent, H_2O (20 mL); reaction temperature, 65–70 °C; reaction time, 4–4.5 h.^b Based on starting/converted **1a–c**.

Table 3. Oxidation of secondary alkanols **3a—c** with the $\text{Ce}(\text{NO}_3)_3\text{—LiBr—H}_2\text{O}_2$ system^a

| Entry | Alcohol 3a—c | Molar ratio 3 : Ce(NO₃)₃ : LiBr : H₂O₂ | <i>t</i> /h | Conversion of 3a—c (%) | Product | Yield ^b (%) | |
|----------------|------------------------|--|-------------|----------------------------------|----------------|------------------------|----------|
| | | | | | | 4 | 5 |
| 1 | 3a | 1 : 0 : 0.1 : 10 | 6 | — | — | — | — |
| 2 | 3a | 1 : 0.1 : 0 : 10 | 6 | — | — | — | — |
| 3 | 3a | 1 : 0.1 : 0.1 : 10 | 6 | 10 | 4a | 9/90 | — |
| 4 | 3a | 1 : 0.1 : 0.2 : 10 | 6 | 65 | 4a | 63/96 | — |
| 5 | 3a | 1 : 0.1 : 0.3 : 10 | 6 | 75 | 4a | 72/96 | — |
| 6 | 3a | 1 : 0.1 : 0.4 : 10 | 6 | 100 | 4a | 98/98 | — |
| 7 ^c | 3a | 1 : 0.1 : 0.4 : 10 | 6 | 40 | 4a | 39/98 | — |
| 8 | 3a | 1 : 0.1 : 0.4 : 5 | 6 | 66 | 4a | 64/97 | — |
| 9 | 3a | 1 : 0.2 : 1 : 10 | 6 | 100 | 4a | 98/98 | — |
| 10 | 3a | 1 : 0.2 : 1 : 10 | 9 | 100 | 4a | 98/98 | — |
| 11 | 3a | 1 : 0.5 : 1 : 10 | 9 | 100 | 4a + 5a | 30/30 | 65/65 |
| 12 | 3a | 1 : 0.5 : 2 : 10 | 9 | 100 | 4a + 5a | 24/24 | 72/72 |
| 13 | 3a | 1 : 0.5 : 4 : 10 | 9 | 100 | 4a + 5a | 13/13 | 79/79 |
| 14 | 3b | 1 : 0.1 : 0.4 : 10 | 6 | 100 | 4b + 5b | 95/95 | 4/4 |
| 15 | 3b | 1 : 0.2 : 0.2 : 10 | 6 | 100 | 4b + 5b | 97/97 | 3/3 |
| 16 | 3b | 1 : 0.5 : 2 : 10 | 9 | 100 | 4b + 5b | 66/66 | 32/32 |
| 17 | 3b | 1 : 0.5 : 4 : 10 | 9 | 100 | 4b + 5b | 57/57 | 41/41 |
| 18 | 3c | 1 : 0.1 : 0.4 : 10 | 6 | 100 | 4c + 5c | 79/79 | 20/20 |
| 19 | 3c | 1 : 0.2 : 0.2 : 10 | 6 | 64 | 4c | 63/98 | — |
| 20 | 3c | 1 : 0.2 : 0.3 : 10 | 6 | 100 | 4c + 5c | 90/90 | 9/9 |
| 21 | 3c | 1 : 0.5 : 4 : 10 | 9 | 100 | 4c + 5c | 30/30 | 65/65 |

^a **3** (1.0 mmol); solvent, 80% aqueous MeCN (20 mL); reaction temperature, 65—70 °C.^b On starting/converted **3a—c**.^c Solvent, H₂O (20 mL).

LiBr was used. Low consumption of LiBr in the oxidation of alcohol **3a** is due to the first step of the process. Generated from LiBr bromine reacts with secondary alkanol with high rates as compared with primary one. In addition, one cannot exclude that in water solution small amount of bromine can give bromic acid, which then converted into hydrobromic acid with oxygen evolution. In the case of oxidation of secondary alkanols, bromine is involved in this side reaction in a lesser extent. Oxidation of secondary alkanols could be used not only for the synthesis of ketones, but directed also toward α -bromoketones. Thus, the increase in the amount of LiBr in 2.5, 5, and 10 times with respect to alcohol **3a** (see Table 3, entries 11—13) favored the formation of 2-bromopentan-3-one (**5a**) in the yield of 65, 72, and 77%, respectively. However, even under conditions with complete conversion, the reaction is not highly selective. No complete conversion of ketone **4a** into bromoketone **5a** was observed, as it was documented for the oxidation of secondary alkanols with the CAN—LiBr system¹⁰.

Results of oxidation of the other secondary alkanols are given in Table 3. Oxidation of nonan-5-ol (**3b**) using the same reactant ratio as for alkanol **3a** resulted in nonan-5-one (**4b**) as a major product and 4-bromononan-5-one (**5b**) as a minor product (95% and 4%, respectively). 2,4-Dimethylpentan-3-ol (**3c**) with complete conversion

furnished 2,4-dimethylpentan-3-one (**4c**) in 90% yield. Along with **4c**, small amount of 2-bromo-2,4-dimethylpentan-3-one (**5c**) formed, which grew the major product, when the amount of LiBr was raised (see Table 3, entries 20, 21).

Structures of compounds **2a—c**, **4a—c**, and **5a—c** were established by ¹H and ¹³C spectroscopy, GC-MS technique, IR spectroscopy, and by comparison with the authentic samples.^{10,21}

In summary, in the present work the Ce^{III} salts in the combination with stoichiometric oxidant, hydrogen peroxide, were used for the first time as mediators (redox catalysts) for the oxidation of the organic compounds. Under the action of a pair of mediators Ce^{III}—LiBr, primary aliphatic alcohols are oxidized with hydrogen peroxide to esters, while secondary aliphatic alcohols afforded ketones.

Experimental

GC analysis was performed on a Chrom-5 chromatograph with the flame-ionization detector and 3×3000 mm analytical glass columns with 5% SE-30 and 5% FFAP on Chromaton N-AW-HMDS (0.16—0.20 mm). The product yields were determined by an internal standard method with the empirical correlation coefficients. The IR spectra (Nujol) were recorded on

a Perkin—Elmer 577 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument in CDCl_3 . The GC-MS analysis was performed on a Finigan MAT ITD-700 spectrometer (EI, 70 eV, the source of ion—ionic trap system temperature was 220 °C) connected with Carlo Erba 4200 chromatograph with a 0.2×2500 mm Ultra-1 column (Hewlett—Packerd), the stationary phase (polymethylsiloxane) thickness 0.33 μm , helium was used as a carrier gas. The reaction products were isolated by column chromatography (silica gel, L 40×100 μm , eluent — heptane—ethyl acetate). The starting primary alcohols (hexan-1-ol (**1a**), heptan-1-ol (**1b**), nonan-1-ol (**1c**)) and secondary alcohols (pentan-3-ol (**3a**), nonan-5-ol (**3b**), 2,4-dimethylpentan-3-ol (**3c**)) (Acros) were distilled prior to use. Cerium(III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) of 99.5% purity (Acros) was used as purchased. Lithium bromide, sodium bromide, and potassium bromide were dried in the oven prior to use. Acetonitrile (pure grade, Acros) was distilled before use.

Oxidation of primary alkanols with a $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ — LiBr — H_2O_2 system (general procedure). A solution of hydrogen peroxide (35% solution) in water (10 mL) was added portionwise (20—25 portions of 0.4—0.5 mL) at 65—70 °C to a vigorously stirred solution of primary alkanol **1a—c** (1 mmol), Ce^{III} nitrate and LiBr in water (10 mL) (ratio of reagents are given in Tables 1 and 2). After addition of the first portion of hydrogen peroxide solution, a yellow color of the reaction mixture characteristic of Ce^{IV} salts was observed, next portion of the hydrogen peroxide solution was added only after the color completely disappeared. Then the reaction mixture was cooled, extracted with diethyl ether (3×15 mL), the combined organic phase was washed with water, and dried with MgSO_4 . After removal of the solvent *in vacuo*, the yield of products **2a—c** and conversion of alkanols **1a—c** were determined by GC using internal standard. The products were isolated by column chromatography on silica gel.

Oxidation of secondary alkanols with a $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ — LiBr — H_2O_2 system (general procedure). A solution of hydrogen peroxide (35% solution) in water (10 mL) was added portionwise (20—25 portions of 0.4—0.5 mL) at 65—70 °C to a vigorously stirred solution of secondary alkanol **3a—c** (1 mmol), Ce^{III} nitrate and LiBr in 80% aqueous MeCN (10 mL) (ratio of reagents are given in Table 3). The products were isolated as described above.

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