Bromination of alkenols with the H_2O_2—LiBr—Ce^{III} and H_2O_2—LiBr—Ce^{IV} systems

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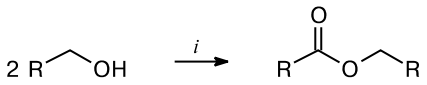
Reactions of alkenols with H_2O_2—LiBr—$Ce(NO_3)_3 \cdot 6H_2O$ or H_2O_2—LiBr—$Ce(NH_4)_2(NO_3)_6$ system led to bromination of the double bond to yield vicinal dibromoalkanols. The reaction proceeded highly selectively, no oxidation of the hydroxyl group virtually occurred.

Key words: alkenols, hydrogen peroxide, cerium(IV) ammonium nitrate, cerium(III) nitrate.

Among oxidants used in the organic chemistry, hydrogen peroxide is highly attractive since it is of low molecular weight, low cost, rather high oxidation potential, easy for handling (aqueous solution), and environmentally friendly. Hydrogen peroxide oxidizes primary alcohols to carboxylic acids in the presence of phase transfer catalysts,[1] complexes of tungsten[2,3] and cobalt.[4] In the case of platinum group metal catalysts, oxidation of primary alcohols results predominantly in carboxylic acids or aldehydes depending on the promoter used;[5] oxalate complexes of platinum diacetate lead selectively to aldehydes.[6] In the presence of platinum black, allylic alcohols are selectively oxidized to aldehydes;[7] in the presence of arylselenenic and arylseleninic acids, they give oxiranes;[8] in the reaction catalyzed by Ti-silicate molecular sieves, allylic alcohols are oxidized to oxiranes and aldehydes with various selectivity.[9]

Alcohols are oxidized to "symmetrical" esters in a two-phase system (water—organic solvent) in the presence of catalytic amounts of Br_2 or HBr.[10] Esters are obtained in the quantitative yields with a system containing more convenient in some cases alkali bromides MBr (M = Li, Na, K) and HCl instead of Br_2 or HBr.[11] In the reaction with an oxidizing system H_2O_2—LiBr—Ce^{III} (Ce^{III} and LiBr are redox catalysts), alcohols give also esters.[12] Similar results were obtained[13] with a cerium(IV) ammonium nitrate (CAN)—LiBr system (Scheme 1).

Scheme 1



i. H_2O_2, LiBr, Ce^{III} or LiBr, Ce^{IV}.

Irrespective the protocol used, the first step of the reaction is generation of bromine from LiBr under the action of Ce^{IV}. The resulted bromine (atomic and/or molecular) selectively brominates the geminal CH_2 group of the primary alcohol with its subsequent transformations into the carbonyl one. Hydrogen bromide formed upon bromination reacts in a new cycle of the oxidation.

Reaction of alkenols with a CAN—LiBr system follows another pattern. Bromine generated from LiBr adds at the double bond to yield vicinal dibromoalkanes.[14] Formation of methyl 2,3-dibromo-3-phenylpropionate from methyl cinnamate proceeds by the same mechanism. Cinnamic acid on treatment with CAN—LiBr system gives β-bromostyrene, at the same time, no addition product at the double bond was detected.[15] Solid-phase reaction of β-acrylic acids with the CAN—LiBr system also resulted only in β-bromostyrenes.[16]

In the present work, we studied the reactions of alkenols **1a—h** with suggested by us novel oxidizing systems, H_2O_2—LiBr—$Ce(NO_3)_3 \cdot 6H_2O$ (**A**) and H_2O_2—LiBr—$Ce(NH_4)_2(NO_3)_6$ (**B**) (the Ce^{III} and Ce^{IV} salts are redox catalysts, LiBr is stoichiometric reagent). The aim was to study how the oxidation of primary and secondary alcohols proceeds: are the corresponding esters and ketones formed as in the case of saturated alcohols or the formation of dibromoalkanes as in the case of alkenes occurred. Moreover, the third direction of the reaction, oxidation to aldehydes and carboxylic acids, cannot be neglected. In fact, treatment of allylic alcohols **1a**,**d**,**e**,**g**,**h** and other olefinic alcohols with more remote position of the double bond **1b**,**c**,**f** with the oxidizing systems **A** and **B** led exclusively to vicinal dibromoalkanols **2a—h** (Scheme 2).

No formation of esters, even from alkenols **1a**,**d**,**e** bearing readily oxidized activated α-CH_2 group, was ob-

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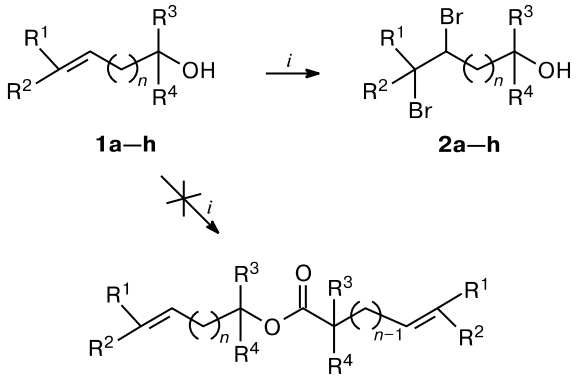
Scheme 2



i. H_2O_2, Ce^{III} or Ce^{IV}, LiBr, H_2O.

Compound **1**, **2**	R^1	R^2	R^3	R^4	*n*
a	H	H	H	H	0
b	H	H	H	H	3
c	Et	H	H	H	1
d	Pr	H	H	H	0
e	Me	Me	H	H	0
f	H	H	H	H	1
g	H	H	Me	H	0
h	H	H	Me	Me	0

Ce^{III} is $Ce(NO_3)_3$; Ce^{IV} is $Ce(NH_4)_2(NO_3)_6$

served. Effect of the reagent ratios on the completeness of the reaction is evaluated on an example of the parent allyl alcohol **1a** (Table 1). At molar ratio **1a** : Ce^{III}/Ce^{IV} : LiBr : H_2O_2 of 1 : 0.3 : 3 : 10, conversion of **1a** was approximately 100%, the yield of 2,3-dibromopropan-1-ol (**2a**) is nearly quantitative (see Table 1, entries *7* and *8*). These results were achieved performing the reaction with the system **A** at 65—70 °C for 5 h, and with the system **B** for 10 h. Lowering the amount of any components of the oxidizing system, Ce^{III} or Ce^{IV} to 0.2 mol, or LiBr to 2.2 mol, or H_2O_2 to 5 mol, results in the drop of the conversion of **1a** by 10—20%, while the yield of **2a** calculated on the converted **1a** remained high (see Table 1, entries *1—6*, *11*, *12*). This reaction can be carried out employing the same reagents but without H_2O_2 using stoichiometric (not catalytic) amount of CAN (entries *9—10*). In the absence of H_2O_2 and LiBr, CAN oxidizes alkenol **1a** to acrylic acid (entry *15*). Cerium ammonium nitrate and cerium(III) nitrate do not catalyze oxidation of alkenol **1a** with hydrogen peroxide without LiBr (entries *13—14*).

Bromination of alkenols **1b—h** with the systems **A** and **B** is performed under conditions optimized for **1a** (**1a** : Ce^{III}/Ce^{IV} : LiBr : H_2O_2 = 1 : 0.3 : 3 : 10) (Table 2). According to the data obtained, conversion of alkenols with the system **A** is 86—95% and with the system **B** is 91—100%, the yields of the bromination products **2b—c** are the same for both systems (86—94%). In the case of alkenols **1c** and **1d**, the products of bromination **2c** and **2d** are the approximately equal mixtures of two diastereomers (~1 : 1 ratio, see Table 2, entries *6—13*).

In principle, bromination of but-3-en-1-ol (**1f**) can afford two products. After 5 h, 3-bromotetrahydrofuran (**3**)

Table 1. Oxidation of allylic alcohol **1a** with the H_2O_2—LiBr—Ce^{III}/Ce^{IV} system[a]

Entry	Molar ratio **1a** : Ce : LiBr : H_2O_2	Ce^{III}/Ce^{IV}	Conversion of **1a** (%)	Yield[b] of **2a** (%)
1	1 : 0.2 : 3 : 5	Ce^{IV}	88	85
2	1 : 0.2 : 3 : 5	Ce^{III}	83	80
3	1 : 0.2 : 3 : 10	Ce^{IV}	95	92
4	1 : 0.2 : 3 : 10	Ce^{III}	91	89
5	1 : 0.3 : 3 : 5	Ce^{IV}	96	94
6	1 : 0.3 : 3 : 5	Ce^{III}	93	91
7	1 : 0.3 : 3 : 10	Ce^{IV}	100	>99
8	1 : 0.3 : 3 : 10	Ce^{III}	100	>99
9[c]	1 : 2 : 3 : 0	Ce^{IV}	65	55
10[c]	1 : 2.5 : 3 : 0	Ce^{IV}	70	62
11	1 : 0.3 : 2.2 : 10	Ce^{IV}	91	88
12	1 : 0.3 : 2.2 : 10	Ce^{III}	80	76
13[d]	1 : 0.3 : 0 : 5	Ce^{IV}	10	(9)
14	1 : 0.3 : 0 : 5	Ce^{III}	—	—
15[d]	1 : 4.4 : 0 : 0	Ce^{IV}	85	(84)
16[c,d]	1 : 4.4 : 2.2 : 0	Ce^{IV}	93	68 (21)
17[d]	1 : 4.4 : 2.2 : 0	Ce^{IV}	96	60 (33)

[a] **1a** (1 mmol), H_2O (20 mL), 65—70 °C, 10 h (for Ce^{III}), 5 h (for Ce^{IV}), Ce^{III} is $Ce(NO_3)_3 \cdot 6H_2O$, Ce^{IV} is $Ce(NH_4)_2(NO_3)_6$. [b] Based on the starting **1a**. Yields of **2a** based on the converted **1a** are 95—98% (see entries *1—6* and *11*, *12)*. Yield of acrylic acid is given in parenthesis. [c] Reaction temperature, 20 °C. [d] Acrylic acid is formed.

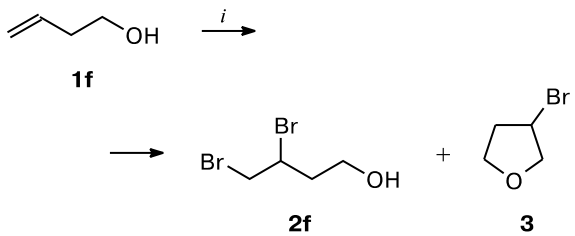
Table 2. Oxidation of unsaturated alcohols **1a—h** with the H_2O_2—LiBr—Ce^{III}/Ce^{IV} system[a]

Entry	Starting alkenols	Ce^{III}/Ce^{IV}	Conversion of **1a—h** (%)	Product (yield[b] (%))
1	**1a**	Ce^{IV}	100	**2a** (>99)
2	**1a**	Ce^{III}	100	**2a** (>99)
3	**1b**	Ce^{IV}	97	**2b** (94)
4	**1b**	Ce^{III}	90	**2b** (86)
5	**1b**	Ce^{III}	95[d]	**2b** (92)
6	**1c**	Ce^{IV}	91	**2c**[c] (89)
7	**1c**	Ce^{IV}	95[d]	**2c**[c] (92)
8	**1c**	Ce^{III}	86	**2c**[c] (86)
9	**1c**	Ce^{III}	92[d]	**2c**[c] (90)
10	**1d**	Ce^{IV}	93	**2d**[c] (90)
11	**1d**	Ce^{IV}	98[d]	**2d**[c] (97)
12	**1d**	Ce^{III}	90	**2d**[c] (87)
13	**1d**	Ce^{III}	97[d]	**2d**[c] (96)
14	**1e**	Ce^{IV}	100	**2e** (95)
15	**1e**	Ce^{III}	95	**2e** (91)
16	**1e**	Ce^{III}	100[d]	**2e** (98)
17	**1f**	Ce^{IV}	95	**2f** (13); **3** (79)
18	**1f**	Ce^{IV}	97[d]	**2f** (10); **3** (85)
19	**1f**	Ce^{IV}	98[e]	**3** (97)
20	**1f**	Ce^{III}	80	**2f** (33); **3** (45)
21	**1f**	Ce^{III}	87[d]	**2f** (36); **3** (50)
22	**1g**	Ce^{IV}	100	**2g** (98)
23	**1g**	Ce^{III}	85	**2g** (83)
24	**1g**	Ce^{III}	93	**2g** (91)
25	**1h**	Ce^{IV}	96	**2h** (93); **4** (1)
26	**1h**	Ce^{III}	86	**2h** (76); **4** (6)
27	**1h**	Ce^{III}	91	**2h** (83); **4** (4)

[a] **1a—h** (1 mmol), **1** : Ce : LiBr : H_2O_2 = 1 : 0.3 : 3 : 10, H_2O (20 mL), 65—70 °C, 10 h (for Ce^{III}), 5 h (for Ce^{IV}), Ce^{III} is $Ce(NO_3)_3 \cdot 6H_2O$, Ce^{IV} is $Ce(NH_4)_2(NO_3)_6$. [b] Based on the starting **1a—h**. [c] Ratio of diastereomers *meso : rac* = 1 : 1. [d] **1** : Ce : LiBr : H_2O_2 = 1 : 0.3 : 4 : 10. [e] Reaction time, 15 h.

is major product and 3,4-dibromobutan-1-ol (**2f**) is minor one (Scheme 3). Additional heating of the reaction mixture for 10 h favors complete conversion of **2f** into **3**, the latter being the only product.

Scheme 3



i. H_2O_2, Ce^{III} or Ce^{IV}, LiBr, H_2O.

Similar results were obtained during bromination of pent-4-en-1-ol with the $ArSeO_2H$: NaBr : H_2O_2 system; this reaction yielded 4,5-dibromopentan-1-ol and 2-bromomethyltetrahydrofuran.[17]

Likewise to primary alkenols **1a**,**d**,**e**, secondary alkenol, but-3-en-2-ol (**1g**), in the reaction with the systems **A** and **B** also adds bromine (see Table 2, entries *22—24*). Reaction proceeds selectively, no oxidation of the resulting 3,4-dibromobutan-2-ol (**2g**) and the starting alkenol **1g** takes place (formation of ketones could be expected since under described conditions the secondary hydroxy groups oxidize more readily than the primary one[12]).

Tertiary alkenol **1h** gives 3,4-dibromo-2-methylbutan-2-ol (**2h**), the small amount of the latter (~1—5%) oxidizes with the C—C bond cleavage to form methyl vinyl ketone (**4**) which was identified in the reaction mixture by GLC, IR spectroscopy, and ^1H NMR spectroscopy.

In summary, in contrast to saturated alcohols, no oxidation of unsaturated primary and secondary alcohols with the H_2O_2—LiBr—Ce^{III} and H_2O_2—LiBr—Ce^{IV} systems to esters and ketons, respectively, occurs; these compounds undergo bromination at the double bonds to give vicinal dibromoalkanols. In this reaction, the cerium salts are redox catalysts in the repeating stages of generation of

bromine from LiBr under the action of Ce^{IV} and oxidation of Ce^{III} with hydrogen peroxide to Ce^{IV}.

Experimental

GLC analysis was performed on a LKhM-80 chromatograph with the flame-ionization detector and 2000×3 mm analytical metal 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. ^{1}H and ^{13}C NMR spectra were run on Bruker AC-200 and Bruker AM-300 instruments in $CDCl_3$. The GC-MS analysis was carried out on a Finnigan 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 25 m×0.2 mm Ultra-1 column (Hewlett—Packard), 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, elution with heptane—ethyl acetate). The starting alkenols (prop-2-en-1-ol (**1a**), hex-5-en-1-ol (**1b**), hex-3-en-1-ol (**1c**), hex-2-en-1-ol (**1d**), 3-methylbut-2-en-1-ol (**1e**), but-3-en-1-ol (**1f**), but-3-en-2-ol (**2g**), 2-methylbut-3-en-2-ol (**2h**) (Acros)) were distilled prior to use. Lithium bromide, cerium ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$), cerium(III) nitrate ($Ce(NO_3)_3 \cdot 6H_2O$), hydrogen peroxide (35% aqueous solution) (Acros) were used as purchased.

Bromination of alkenols with the H_2O_2—LiBr—Ce^{III}/Ce^{IV} system (general procedure). To a vigorously stirred solution of alcohol **1a—h** (1 mmol), LiBr, and the Ce^{III} or Ce^{IV} salts in water (10 mL), a solution of 35% H_2O_2 in water (10 mL) was added by portions of 0.5—0.7 mL within ~4—5 h at 65—70 °C (reagent ratios are given in Tables 1 and 2). After addition of the first portion of the H_2O_2 solution, the reaction mixture turns pale yellow, the color disappeared after 20—30 min. The reaction mixture was cooled, extracted with diethyl ether (3×15 mL), the combined organic layers were washed with water, and dried with $MgSO_4$. The solvent was removed *in vacuo*, the yields of the products **2a—h**, **3**, **4** and the conversion of alcohol **1a—h** were determined by GLC with the internal standard. The products were isolated by column chromatography.

The structures of the synthesized compounds were evaluated from ^{1}H and ^{13}C NMR spectra, GC-MS data, and IR spectroscopic data.

2,3-Dibromopropan-1-ol (2a) (see Ref. 18). ^{1}H NMR ($CDCl_3$), δ: 3.78 (m, 2 H, CH_2Br); 3.95 (d, 2 H, CH_2OH, J = 8.7 Hz); 4.35 (m, 1 H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 31.57, 53.36, 64.04. MS, m/z: 217 $[M]^+$ (^{79}Br); 219 $[M]^+$ (^{81}Br).

5,6-Dibromohexan-1-ol (2b) (see Ref. 19). ^{1}H NMR ($CDCl_3$), δ: 1.62 (m, 4 H, C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$OH); 1.84 (m, 2 H, CHBr—C<u>H</u>$_2$CH$_2$CH$_2$CH$_2$OH); 3.61 (t, 2 H, CH_2OH, J = 6.6 Hz); 3.89 (m, 2 H, CH_2Br); 4.28 (m, 1 H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 23.29, 29.41, 35.91, 36.26, 52.56, 62.69.

3,4-Dibromohexan-1-ol (2c) (see Ref. 20). ^{1}H NMR ($CDCl_3$), δ: 1.02 (m, 3 H, CH_3, J = 7.2 Hz); 1.87 (m, 2 H, CH_3C<u>H</u>$_2$); 2.16 (m, 2 H, C<u>H</u>$_2$CH$_2$OH); 3.76 (t, 2 H, CH_2OH, J = = 6.1 Hz); 3.92 (m, 1 H, BrC<u>H</u>CH$_2$CH$_2$OH); 4.08 (m, 1 H, CH$_3$CH$_2$C<u>H</u>Br). ^{13}C NMR ($CDCl_3$), δ: 10.42, 26.53, 36.86, 49.45, 60.09, 65.90.

2,3-Dibromohexan-1-ol (2d) (see Ref. 21). ^{1}H NMR ($CDCl_3$), δ: 0.95 (t, 3 H, CH_3, J = 7.5 Hz); 1.47 (m, 2 H, CH_3C<u>H</u>$_2$); 1.62 (m, 2 H, CH$_3$CH$_2$C<u>H</u>$_2$); 3.93 (m, 2 H, CH_2OH); 4.08 (m, 1 H, BrC<u>H</u>CH$_2$OH); 4.13 (m, 1 H, CH$_3$CH$_2$CH$_2$C<u>H</u>Br). ^{13}C NMR ($CDCl_3$), δ: 13.94, 18.92, 36.66, 54.82, 60.87, 64.58.

2,3-Dibromo-3-methylbutan-1-ol (2e) (see Ref. 22). ^{1}H NMR ($CDCl_3$), δ: 1.42 (s, 3 H, CH_3); 1.44 (s, 3 H, CH_3); 3.65 (d, 1 H, CHBr, J = 8.7 Hz); 4.04 (m, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$), δ: 27.00, 27.16, 34.32, 67.05, 73.08.

3,4-Dibromobutan-1-ol (2f) (see Ref. 23). ^{1}H NMR ($CDCl_3$), δ: 2.31 (m, 2 H, C<u>H</u>$_2$CH$_2$OH); 3.98 (m, 2 H, CH_2OH); 4.02 (m, 2 H, CH_2Br); 4.45 (m, 1 H, CHBr). ^{13}C ($CDCl_3$), δ: 37.22, 37.76, 49.45, 60.21.

3,4-Dibromobutan-2-ol (2g) (see Ref. 24). ^{1}H NMR ($CDCl_3$), δ: 1.38 (d, 3 H, CH_3, J = 7.0 Hz); 3.77 (m, 2 H, CH_2Br); 4.02 (m, 1 H, CHBr); 4.48 (m, 1 H, C<u>H</u>OH). ^{13}C NMR ($CDCl_3$), δ: 22.56, 32.77, 60.81, 65.75.

3,4-Dibromo-2-methylbutan-2-ol (2h) (see Ref. 19). ^{1}H NMR ($CDCl_3$), δ: 1.40 (s, 3 H, CH_3); 1.42 (s, 3 H, CH_3); 3.99 (m, 2 H, CH_2Br); 4.20 (d, 1 H, CHBr, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.13, 27.32, 34.30, 67.13, 73.06.

3-Bromotetrahydrofuran (3) (see Ref. 25). ^{1}H NMR ($CDCl_3$), δ: 2.08 (m, 2 H, CH$_2$C<u>H</u>$_2$CHBr); 3.71 (m, 2 H, C<u>H</u>$_2$CHBrCH$_2$); 3.99 (m, 2 H, CH$_2$C<u>H</u>$_2$CHBr); 4.18 (m, 1 H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 38.75, 46.56, 66.97, 76.37.

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