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Letters to the Editor

Oxidation of alkanols with a Ce^{III}—LiBr— H_2O_2 system

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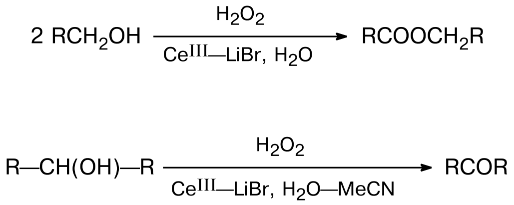
Among cerium compounds, only cerium(IV) ammonium nitrate (CAN) has found wide application mainly as a stoichiometric oxidant and as a catalyst for reactions of different nature. Unlike Ce^{IV}, Ce^{III} compounds are virtually not used in oxidation processes of organic synthesis. Hydroxylation of β-dicarbonyl compounds under the action of $CeCl_3 \cdot 7H_2O$ in combination with molecular oxygen[1] and allylic chlorination of olefins with a $CeCl_3 \cdot 7H_2O$–NaClO system[2] are known. Separate examples of the application of Ce^{III} in the oxidation of secondary alkanols[3] and ethers[4] to ketones, sulfides to sulfoxides[5] with a CAN–$NaBrO_3$ system are documented. In these reactions, sodium bromate, the stoichiometric reagent, generates Ce^{IV} from produced Ce^{III}.

In the present paper we give the results that can attract additional attention to Ce^{III} compounds and give a new impetus to the development of studies on their application in organic chemistry.

An oxidative system $Ce(NO_3)_3 \cdot 6H_2O$–LiBr–H_2O_2 was first proposed and assayed. Using this system, the oxidation of primary and secondary alkanols to esters and ketones, respectively, was accomplished (Scheme 1). In this reaction, hydrogen peroxide is a stoichiometric oxidant, Ce^{III} and LiBr serve as mediators (redox catalysts).

Scheme 1



$$2\ RCH_2OH \xrightarrow[Ce^{III}\text{—LiBr, } H_2O]{H_2O_2} RCOOCH_2R$$

$$R\text{—}CH(OH)\text{—}R \xrightarrow[Ce^{III}\text{—LiBr, } H_2O\text{—MeCN}]{H_2O_2} RCOR$$

The aim was to convert Ce^{III} to Ce^{IV} with H_2O_2 and to use Ce^{IV} as an oxidant to generate bromine from LiBr, and bromine, in turn, as an oxidant of alkanols according to the previously proposed[6] scheme (Scheme 2).

The success of the reaction was not obvious *a priori* because of the ability of Ce^{IV} to competitively oxidize both the bromide anion in LiBr and hydrogen peroxide. Positive results were achieved by maintaining very low H_2O_2 concentration in the reaction mixture relative to the concentration of Ce^{III}. These experimental conditions became determinant for the transformation of alkanols into the reaction products. However, even under these conditions, part of H_2O_2 was oxidized, therefore its excess relative to alkanols was required.

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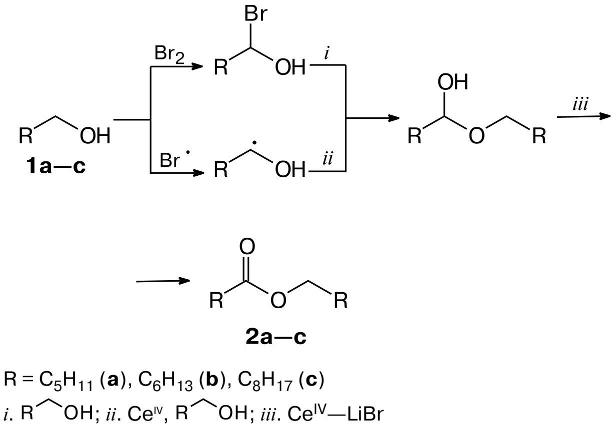
Scheme 2



By the example of the oxidation of heptan-1-ol (**1b**) in water, it was established that no reaction occurs in the absence of one of mediators. At slow uniform addition of H_2O_2 to the mixture in 4 h at 65—70 °C at a molar ratio of reactants **1b** : Ce^{III} : LiBr : H_2O_2 equal to 1 : 0.5 : 5 : 10 the conversion of alkanol **1b** was 81 %, the selectivity of its transformation to heptyl heptanoate (**2b**) was 98%. With doubled amounts of Ce^{III} and LiBr, these characteristics were almost unchanged, while with halved amounts the conversion of alkanol **1b** noticeably decreased. Substitution of NaBr and KBr for LiBr decreases the conversion as well, but the selectivity remained unchanged.

Like compound **1b**, hexan-1-ol (**1a**) and nonan-1-ol (**1c**) oxidize to form esters $C_5H_{11}COOC_6H_{13}$ (**2a**) and $C_8H_{17}COOC_9H_{19}$ (**2c**), respectively, with the same yield and selectivity.

Secondary alkanols oxidize more readily than primary ones. Pentan-3-ol (**3**) is converted to pentan-3-one (**4**) in a qualitative yield in 80% aqueous acetonitrile at a molar ratio **3** : Ce^{III} : LiBr : H_2O_2 equal to 1 : 0.1: 0.4 : 10. With a decreased amount of LiBr, the yield of ketone **4** and conversion of alkanol **3** decrease: these are 75, 65, and 10% in the case of 0.3, 0.2, and 0.1 mol. equiv. of LiBr, respectively. The selectivity is about 100 %. In the absence of LiBr or Ce^{III}, no ketone is formed.

In the Ce^{III}—H_2O_2—alkanol (primary and secondary) system, only H_2O_2 undergoes decomposition in the recurring cycle Ce^{III}—Ce^{IV}—Ce^{III}. In the presence of LiBr, the bromide anions succeed to intercept a part of produced Ce^{IV} ions, which prevents their reduction with H_2O_2, and initiates thereby a process of oxidation of alkanol with bromine that is generated.

In the case of primary alkanols, an excess of LiBr is required, which probably is caused by solvation of the bromide anions with water molecules, and therefore deceleration of their oxidation by Ce^{IV}. The excess of LiBr compensates this effect. In the oxidation of secondary alkanols to alkanones, a catalytic amount of LiBr suffices; stoichiometric amount of LiBr leads to α-bromo ketones. At a molar ratio **3** : Ce^{III} : LiBr : H_2O_2 equal to 1 : 2 : 1 : 10, 2-bromopentan-3-one is formed in a yield of 77 %.

Oxidation of alkanols with a $Ce(NO_3)_3 \cdot 6H_2O$—LiBr—H_2O_2 system (general procedure). To an aqueous solution of an alkanol (1 mmol), $Ce(NO_3)_3$, and LiBr (10 mL), portions (0.5—0.6 mL) of 35% H_2O_2 (overall. 10 mL, the reactant ratio is given above) were added at 65—70 °C and vigorous stirring. After addition of the first portion, yellow coloration typical of Ce^{IV} salts appeared, only after complete discoloration of the reaction mixture the next portion of H_2O_2 was added. Next, the reaction mixture was cooled, extracted with ether (3×15 mL), washed with aqueous $NaHCO_3$ solution and water, and dried with $MgSO_4$. The yields of the reaction products and conversion were determined by GLC with authentic samples of the internal standards. For the preparative isolation of the products, column chromatography on silica gel was used.

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