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Highly Efficient Halogenation of Organic Compounds with Halides Catalyzed by Cerium(III) Chloride Heptahydrate Using Hydrogen Peroxide as the Terminal Oxidant in Water

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Abstract: In this article a new environmentally friendly catalytic method is described for the efficient monoiodination and bromination of arenes and also iodoetherification and iodolactonization of olefins using hydrogen peroxide as the terminal oxidant. The method is based on using sodium iodide or sodium bromide, hydrogen peroxide (35%) and cerium(III) chloride as an effective catalyst in water at room temperature or under reflux conditions. By this protocol, iodination of anilines proceeded with high regioselectivity at the *para* position with the formation of small amounts of the *ortho* isomers. However, bromination of anilines proceeded with absolute regioselectivity to give the *para* isomers as the sole products in high yields. Iodinations and brominations of *m*-xylene, toluene, chloro- and bromobenzenes were proceeded with excellent regioselectivity to produce the *para* isomers as the sole products. Benzene was also halogenated by this catalytic system to give the monohalogenated benzene in good yields. Iodoetherification and iodolactonization of olefins also proceeded easily in high yields at room temperature. However, the bromination of olefins by this protocol failed and the starting materials were detected intact.

Keywords: aromatic compounds; bromination; cerium(III) chloride; hydrogen peroxide; iodination; water

Introduction

Environmentally sustainable chemical processes involving clean organic reactions in the absence of harmful organic solvents are highly encouraged from economical and social concerns. For these reasons, in response, industry has started adopting green chemistry practices including waste prevention rather than its treatment. Disposal of organic solvents in the pharmaceutical industries is nowadays a major problem and constitutes around 80% of their wastes.[1,2] Replacement of expensive, toxic, flammable, not recyclable organic solvents with water is a challenge and in great demand from academia and chemical industries.[3–7] The use of water as the reaction medium has several benefits; water is a cheap and abundant, nontoxic, non-flammable and relatively green solvent. However, the heat capacity of water is not favorable and isolation and drying of the products sometimes creates problems, especially when large-scale operation is concerned. On the other hand, water with its chemical and physical properties imposes selectivity and reactivity in reactions conducted in aqueous media which cannot be attained using organic solvents.[8–10] In addition, in water, phase separation is easier because most organic compounds are not soluble in water and can be easily separated from the aqueous phase.

Using water as the reaction mediunm has been a topic of our interest in recent years. Along this line, we have introduced the Michael addition of amines and thiols to α,ß-unsaturated ketones,[11] regioselective iodination of aromatic compounds,[12] ring opening of epoxides with varieties of nucleophiles,[13] oxidation of sulfides to their sulfoxides with H_2O_2,[14] Michael addition of indoles and pyrroles to α,ß-unsaturated electron-deficient compounds[15] and the conver-

sion of epoxides to thiiranes and amino alcohols in aqueous media.[16]

The aromatic halogenation reaction is an important electrophilic substitution reaction and haloarenes are useful synthetic intermediates in the pharmaceuticals, pesticides and agrochemical industries.[17,18] They are also useful and important substrates for various cross-coupling reactions.[19–22] Halogenation of organic substrates consists of using chlorine, bromine, or iodine. However, halogenation reactions are associated with serious environmental hazards with respect to the handling, transportation and storage of chlorine, bromine and iodine.[23] Handling halide salts is safer and easier and they can be easily oxidized to the corresponding positive halogens or hypohalous acids by a variety of methods.[24] One method for this purpose is to use H_2O_2 as an environmentally friendly and strong oxidant.[25] However, the rate of oxidation of halides with H_2O_2 is slow and not a practical process.[26] At lower pH, the rate enhancement for halogenation occurs by the *in situ* generation of hypohalous acids. However, acid-sensitive functional groups do not tolerate these reaction conditions.[27,28]

Due to the potential utility of aryl bromides in the synthesis of aryl esters, arylolefins and other useful compounds, bromination of aromatic compounds has been the subject of numerous studies.[29–32]

Because of the low electrophilicity of molecular iodine, compared to those of molecular bromine and chlorine, the direct iodination of aromatic compounds with iodine is difficult. Recently, methodologies intensively developed for the preparation of iodoarenes are based on a wide range of iodinating agents[33] such as I_2-Ag_2SO_4,[34] I_2-HgO,[35] NIS in ionic liquids,[36] ICl/$In(OTf)_3$ in MeCN-$CHCl_3$,[37] $I_2/O_2/H_5PV_2Mo_{10}O_{40}$ in MeCN,[38] $I_2/Fe(NO_3)_3/H_3PW_{12}O_{40}$ in CH_2Cl_2,[39] I_2 or NaI/$Fe(NO_3)\cdot 1.5\,N_2O_4$/charcoal,[40] NIS/$ZrCl_4$ in CH_2Cl_2,[41] $I_2/Bi(NO_3)_3/BiCl_3$/air in CH_3CN or CH_2Cl_2,[42] I_2/silfen in CH_2Cl_2,[43] and I_2/*ortho*-periodic acid in EtOH (95%) under microwave irradiation or by conventional heating.[44] Some disadvantages of these methods are: a) use of large amounts of the oxidants, b) some of the oxidants are hazardous and toxic compounds, c) usually high reaction temperatures and long reaction times are needed and, in addition, the reactions are conducted in organic solvents.

However, a number of articles describing the application of peroxo compounds for the oxidative iodination and bromination of arenes has been recently appeared in the literature; $Ce(OH)_3OH$/SDS-H_2O,[12] NH_4I/oxone/MeOH,[45] KI/oxone/MeOH,[46] KI/benzyltriphenylphosphonium peroxomonosulfate/MeCN,[47] KI/H_2O_2(30%)/H_2SO_4/MeOH,[48] KI or I_2/PVP supported $H_2O_2/H_3PW_{12}O_{40}$ in CH_2Cl_2,[49] I_2 or KI/$(Na_2CO_3\cdot 3\,H_2O_2)$,[50] $I_2/(Bu_4N)_4(S_2O_8)$/MeCN or CH_2Cl_2,[51] $I_2/(MePPh_3)_2(S_2O_8)$/MeCN,[52] NaS_2O_8/MeCN[53] and NaI/H_2O_2/organotelluride catalyst at pH 6 buffer in Et_2O-H_2O,[54] KBr/benzyltriphenylphosphonium peroxodisulfate/MeCN,[55] Br_2 or LiBr/tetrabutylammonium peroxydisulfate/MeCN or CH_2Cl_2[56] and I_2/poly(4-vinylpyridine)-supported peroxodisulfate/MeCN.[57]

All the above-mentioned reactions proceed in organic solvents except for one in which $Ce(OH)_3OOH$ is used in SDS micellar solution.[12]

Iodoetherification and iodolactonization are significant and fundamental transformations in organic synthesis from different points of view. These reactions are also of importance for structural elucidation of organic molecules.[58,59] Examples consist of Corey's prostaglandin synthesis,[60] total synthesis of tumor inhibitors, for example, vernolepin and vernomenin[61] and in vitamin D_2 and D_3 synthesis.[62] In this study, we have also paid attention to the application of this catalytic system for haloetherification and halolactonization reactions.

Literature surveys show that easy, inexpensive and environmentally friendly catalytic methods for the halogenation of arenes, especially those conducted in water in the absence of any organic co-solvents, are scarce in the literature and are of interest and in demand from different points of view.

Now in this article we introduce a new and a novel catalytic method using $CeCl_3\cdot 7\,H_2O$ as an efficient catalyst for the iodination and bromination of arenes by NaI or NaBr to their monosubstituted halides using H_2O_2 (35%) as the terminal oxidant in neat water. In addition, the syntheses of iodinated cyclic ethers and the iodinated lactones from their corresponding unsaturated alcohols and carboxylic acids in the presence of this catalytic system in water are presented.

Results and Discussion

To optimize the reaction conditions, we first studied the iodination of anisole as a model compound using the H_2O_2 (35%)/NaI system in the presence of a catalytic amount of $CeCl_3\cdot 7\,H_2O$ in H_2O at room temperature. We observed that the reaction of anisole (1.0 mmol) with 1 mL of H_2O_2 (35%), 1 mmol of NaI and 0.5 mmol of $CeCl_3\cdot 7\,H_2O$ in 2 mL of H_2O proceeded to completion within 3 h (GC analysis). Work-up of the reaction mixture resulted in the corresponding 4-iodoanisole with excellent regioselectivity and in excellent isolated yield (93%).

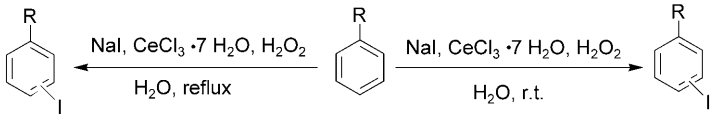
Then similar reaction conditions were applied for the mono-iodination of benzene, bromo- and chlorobenzenes and activated aromatic compounds. As is evident from the results indicated in the tables, iodination and bromination substitution reactions all proceeded well at room temperature with this catalytic system in water. The reaction of 1,3-dimethoxybenzene was completed after 45 min to produce the

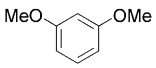
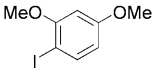
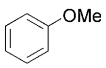
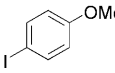
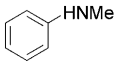
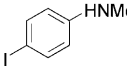
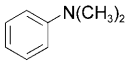
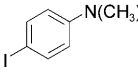
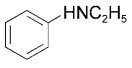
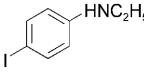
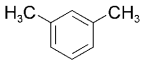
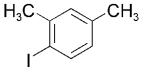
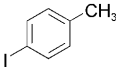
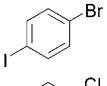
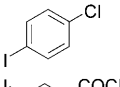
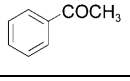
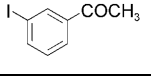
mono-iodinated compound in 95% isolate yield. The reaction of anisole took longer and was completed within 3 h to give 4-iodoanisole as the sole product of the reaction. Iodinations of *N*-methylaniline, *N,N*-dimethylaniline and *N*-ethylaniline were also completed in a short reaction time (30 min) and the mono-iodinated *para* isomers were obtained in 80–82% isolated yields plus their corresponding *ortho* isomers, which were isolated in 5–15% yields. The iodination of toluene produced 4-iodotoluene in 79% isolated yield as the sole product after 15 h together with unreacted starting material. 1,3-Dimethylbenzene also was iodinated within 8 h to give the mono-iodinated product in 89% isolated yield as the sole product of the reaction.

Iodinations of benzene, bromobenzene and chlorobenzene as less reactive arenes were also studied. Progress of the reactions was monitored by GC analysis whereby, after 24 h, 65, 60 and 63% conversions at room temperature were observed, respectively. Isolation of iodobenzene in 60%, *p*-iodobromobenzene in 55% and 4-iodochlorobenzene in 59% from the reaction mixtures as the sole products of the reaction indicates the high regioselectivity of the method. The iodination of acetophenone under similar reaction conditions failed and the stating material was isolated intact after 48 h. The results of this study are summarized in Table 1. We have also studied the iodination reactions under reflux conditions in which the reactions proceeded faster with higher yields (Table 1).

Iodoetherification and iodolactonization are important and crucial reactions in organic synthesis and for structural elucidation of organic molecules.[63] Examples include Corey's prostaglandin synthesis,[64] total syntheses of tumor inhibitors. for example, vernolepin and vernomenin[65] and in vitamin D_2 and D_3 syntheses.[66]

Table 1. Monoiodination of aromatic compounds using NaI/H_2O_2 catalyzed by $CeCl_3 \cdot 7H_2O$.



Entry	Substrate	Product	Time (r.t./reflux)	Conversion [%] (GC)	Isolated yield [%]
1			45 min/10 min (7 h)[a]	100/100 (62)[a]	95/97
2			3 h/25 min (5 h)[a]	100/100 (53)[a]	93/95
3			30 min/5 min (24 h)[a]	100/100 (66)[a]	82/85
4			30 min/5 min (24 h)[a]	100/100 (70)[a]	81/83
5			30 min/5 min (24 h)[a]	100/100 (70)[a]	80/87
6			8 h/3 h	95/100[b]	89/91[b]
7			15 h/4 h	85/100[b]	79/87[b]
8			24 h/6 h	65/93[b]	60/83[b]
9			24 h/12 h	60/90[b]	55/86[b]
10			24 h/12 h	63/90[b]	59/83[b]
11			48 h/48 h	0/30	–

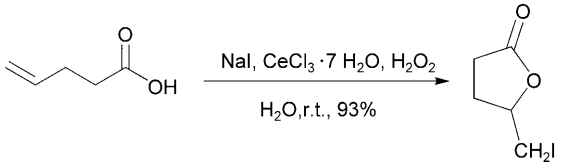
[a] The data in parentheses refer to aromatic compound (1 mmol), NaI (1 mmol), $CeCl_3 \cdot 7H_2O$ (0.1 mmol), H_2O_2 (2 mL) and H_2O (3 mL) under reflux conditions.

[b] Only *para*-isomers were detected and isolated

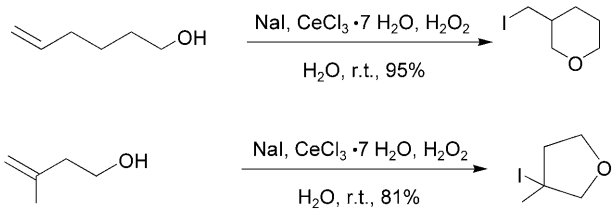
However, we have studied the reaction of iodination followed by ring-closure of unsaturated alcohols and carboxylic acids by this method. For this purpose, the lactonization of 4-pentene-1-carboxylic acid as a model reaction was studied. The carboxylic acid (1.0 mmol) with 1 mL of H_2O_2 (35%), 1.0 mmol of NaI and 0.5 mmol of $CeCl_3{\cdot}7\,H_2O$, in 2 mL of H_2O proceeded to completion immediately and the desired iodolactone was isolated as the sole product in 93% yield (Scheme 1).

Then we applied these optimized conditions to unsaturated alcohols (Scheme 2). The reactions proceeded well and produced the iodo-cyclic ethers in excellent yields within short reaction times.

The bromination of aromatic nuclei with NaBr in the presence of H_2O_2 (35%) and a catalytic amount of $CeCl_3{\cdot}7\,H_2O$ in water also was studied. We found the molar ratios used in iodination reactions work well for bromination also. Then a broad spectrum of aromatic compounds was subjected to the conditions of 1 mmol of arene, 1 mL of H_2O_2, 0.5 mmol of $CeCl_3{\cdot}7\,H_2O$ in 2 mL of H_2O_2 at room temperature. The highly regioselective bromination of activated aromatic nuclei proceeded well in short reaction times with excellent yields at room temperature. The brominations of toluene, 1, 3-dimethylbenzene, benzene, chloro- and bromobenzenes proceeded also smoothly with high yields in longer reaction times. The results of this study are presented in Table 2. By this method bromoetherification and bromolactonization failed

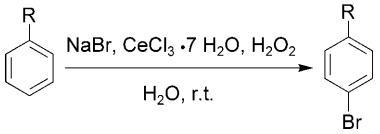


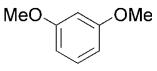
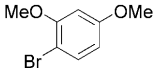
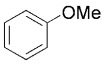
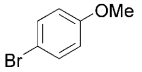
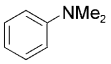
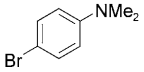
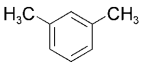
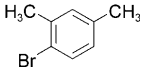
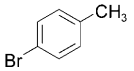
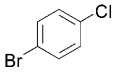
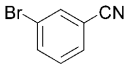
Scheme 1.



Scheme 2.

Table 2. Bromination of aromatic compounds using $NaBr/H_2O_2$ catalyzed by $CeCl_3{\cdot}7\,H_2O$.



Entry	Substrate	Product	Time	Conversion [%] (GC)	Isolated yield [%]
1			30 min (2.5 h)[a]	100 (68)[a]	95
2			1 h (5 h)[a]	100 (71)[a]	93
3			25 min (3 h)[a]	100 (76)[a]	92
4			2 h	100	90
5			3 h	100	87[b]
6			4.5 h	95	82[b]
7			6 h	89	81[b]
8			12 h	–	–

[a] The data in parentheses refer to aromatic compound (1 mmol), NaBr (1 mmol), $CeCl_3{\cdot}7\,H_2O$ (0.1 mmol), H_2O_2 (2 mL) and H_2O (3 mL) under reflux conditions.

[b] Only *para*-isomers were detected and isolated

Table 3. Comparison of the results obtained for direct catalytic iodination of benzene with $NaI/H_2O_2/CeCl_3{\cdot}7H_2O$ system and some of those using non-catalytic methods.

Methods	System	Time (Temperature)	Isolated Yield [%]
Catalytic method	$H_2O_2/CeCl_3{\cdot}7H_2O$ (cat.)	24 h (r.t.)	60
		6 h (reflux)	83
	$Fe(NO_3)_3{\cdot}1.5N_2O_4$/charcoal[40]	24 h (r.t.)	74
Non-catalytic methods using oxidizing reagents	Ag_2SO_4[67]	74 h (r.t.)	74
	$NaIO_3$[68]	4 h (r.t.)	65
	Na_2WO_4	10 h (100 °C)	–[a]

[a] Our observations.

and the starting materials remained intact after the appropriate reaction time.

Both iodination and bromination of arenes were also investigated in the presence of lower amounts of $CeCl_3{\cdot}7H_2O$ (0.1 mmol). The results showed that the reactions were sluggish and proceeded only for activated arenes under reflux conditions in moderate yields. The results are shown in Table 1 (entries 1–5) and Table 2 (entries 1–3).

In order to show the merit of this method, we have compared our results with some other protocols using different oxidizing agents for the direct iodination of benzene (Table 3).

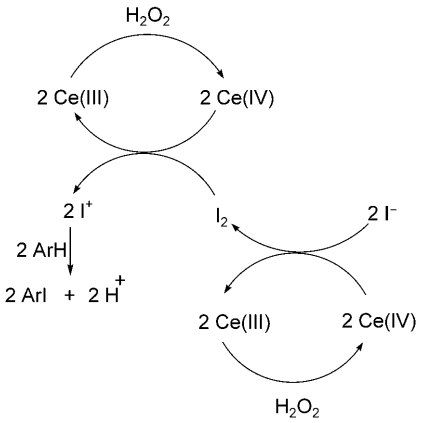
The role of cerium(III) chloride as a Lewis acid catalyst in organic reactions is well documented.[69,70,71] However, as we have observed in this study, $CeCl_3{\cdot}7H_2O$ does not act as an ordinary Lewis acid for the activation of H_2O_2. In order to show this difference, we have studied the iodination of 1, 3-dimethoxybenzene (1 mmol) using H_2O_2 (1 mmol) and NaI (1 mmol) in the presence of a catalytic amount of various Lewis acids (0.5 mmol) at room temperature for 1 h. Analysis of the reaction mixtures showed the formation of the mono-iodinated product from a trace to a maximum of 20% plus unreacted starting materials (Table 4, entries 2–11). The drastic rate enhancement and the yield of the reaction catalyzed by $CeCl_3{\cdot}7H_2O$ (Table 4, entry 1, 45 min, and 95%) in comparison with other Lewis acid catalysts suggests that the reactions conducted in the presence of $CeCl_3{\cdot}7H_2O$ should not be a simple Lewis acid catalysis and there may be an electron-transfer process operating plus Lewis acid catalysis in these reactions. The suggested mechanism *via* an electron-transfer process is shown in Scheme 3.

Therefore, to obtain more evidence in support of the proposed mechanism, we conducted the following experiments. First, 0.5 mmol of $CeCl_3{\cdot}7H_2O$ was added to an equivalent amount of H_2O_2 (35%) in acetonitrile. The colorless solution of Ce(III) was immediately changed to a yellowish colored solution of Ce(IV) the UV-visible spectrum of which showed a strong absorption band at 600 nm. This is very strong evidence for the *in situ* generation of Ce(IV) species in the mixture. Then addition of I_2 (0.7 mmol) to this solution, followed by work-up with $Na_2S_2O_4$ solution (5%) produces a colorless solution of which the UV-visible spectrum did not show any absorption at 600 nm. This is an indication for the formation of Ce(III) in the mixture. Addition of H_2O_2 to this colorless solution, changed the color to yellow which is an indication of the *in situ* generation of Ce(IV) species.

Table 4. Comparison of the experimental results obtained for the mono-iodination of 1,3-dimethoxybenzene using NaI/H_2O_2 in the presence of 0.5 molar ratio of $CeCl_3{\cdot}7H_2O$ and other Lewis acid catalysts at room temperature.

Entry	Lewis acid catalysts	Time [h][a]	Yield [%][a]
1	$CeCl_3{\cdot}7H_2O$	45 min	95
2	$AlCl_3$	1	20
3	$AlPW_{12}O_4$[72]	1	20
4	$ZnCl_2$	1	15
5	$CdCl_2$	1	15
6	$BF_3{\cdot}Et_2O$	1	17
7	$CoCl_2$	1	trace
8	$CrCl_3$	1	trace
9	$CuCl_2$	1	trace
10	$MnCl_2$	1	trace
11	$NiCl_2$	1	trace

[a] Even after longer reaction times (10 h) the yield of the product was not altered within the range of the experimental error.



Scheme 3.

Conclusions

In this article a new, novel and environmentally friendly catalytic protocol for highly regioselective mono-iodination and bromination of arenes is report-

ed using safe NaI or NaBr, catalytic amounts of Ce(III), and H_2O_2 (35%) as the terminal oxidant in neat aqueous medium at room temperature and under reflux conditions. The high regioselective iodination and bromination of activated aromatic nuclei as well as unreactive ones, in excellent yields, are regarded as advantages of this catalytic system. Also, by this method, the immediate iodination followed by ring closure of unsaturated alcohols and an unsaturated carboxylic acid to the corresponding iodinated cyclic ethers and iodinated lactone were achieved in high yields at room temperature. Comparison of the catalytic activity of $CeCl_3{\cdot}7\,H_2O$ with several other Lewis acids and the drastic rate enhancement and the yield of the reaction in the presence of $CeCl_3{\cdot}7\,H_2O$ suggests that a simple Lewis acid catalysis is not working in this reaction and an electron-transfer process may be involved in the halogenation process using H_2O_2 as the terminal oxidant in the presence of this catalyst.

Experimental Section

Typical Procedure for Mono-Iodination of Anisole with NaI/$CeCl_3{\cdot}7\,H_2O$/H_2O_2 System in H_2O under Reflux Conditions

To a mixture of anisole (0.108 g, 1 mmol), NaI (0.149 g, 1 mmol) and $CeCl_3{\cdot}7\,H_2O$ (0.186 g, 0.5 mmol) in water (3 mL), H_2O_2 (1 mL) was added and the mixture was refluxed for 25 min. The progress of the reaction was monitored by GC or TLC. The resulting reaction mixture was treated with $Na_2S_2O_4$ solution (10 mol%, 10 mL) and extracted with diethyl ether (2×10 mL). The ethereal solution was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent resulted in the desired crude product which was further purified by a plate chromatography technique to give the pure compound in 95% yield (Table 1, entry 2). Then similar reaction conditions were applied for the iodination at room temperature.

Typical Procedure for Bromination of Anisole with NaBr/$CeCl_3{\cdot}7\,H_2O$/H_2O_2 System in H_2O at Room Temperature

To a mixture of anisole (0.108 g, 1 mmol), NaBr (0.103 g, 1 mmol) and $CeCl_3{\cdot}7\,H_2O$ (0.186 g, 0.5 mmol) in water (3 mL), H_2O_2 (1 mL) was added at room temperature. The progress of the reaction was monitored by GC or TLC. The resulting reaction mixture was treated with $Na_2S_2O_4$ solution (10 mol%, 10 mL) and extracted with diethyl ether (2× 10 mL). The ethereal solution dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent resulted in the desired crude product which was further purified by a plate chromatography technique to give the pure compound in 93% yield (Table 2, entry 2).

Typical Procedure for Iodoetherification of 5-Hexene-1-ol with NaI/$CeCl_3{\cdot}7\,H_2O$/H_2O_2 System in H_2O at Room Temperature

To a mixture of 5-hexene-1-ol (0.1 g, 1 mmol), NaI (0.149 g, 1 mmol) and $CeCl_3{\cdot}7\,H_2O$ (0.186 g, 0.5 mmol) in water (3 mL), H_2O_2 (1 mL) was added. The progress of the reaction was monitored by GC or TLC. The resulting reaction mixture was treated with $Na_2S_2O_4$ solution (10 mol%, 10 mL) and extracted with diethyl ether (2×10 mL). The ethereal solution was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent resulted in the desired crude product which was further purified by plate chromatography technique to give the pure compound in 95% yield (Scheme 2).

Typical Procedure for Iodolactonization of 4-Penten-1-oic Acid with NaI/$CeCl_3{\cdot}7\,H_2O$/H_2O_2 System in H_2O at Room Temperature

To a mixture of 4-penten-1-oic acid (0.1 g, 1 mmol), NaI (0.149 g, 1 mmol) and $CeCl_3.7H_2O$ (0.186 g, 0.5 mmol) in water (3 mL), H_2O_2 (1 mL) was added. The progress of the reaction was monitored by GC or TLC. The resulting reaction mixture was treated with $Na_2S_2O_4$ solution (10 mol%, 10 mL) and extracted with diethyl ether (2×10 mL). The ethereal solution was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent resulted in the desired crude product which was further purified by plate chromatography technique to give the pure compound in 93% yield (Scheme 1).

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