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$SbCl_3$-Catalyzed conversion of ketones and aldehydes into gem-dihydroperoxides (DHPs) with 30% H_2O_2

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ABSTRACT

A simple and efficient conversion of ketones and aldehydes into corresponding *gem*-dihydroperoxides (DHPs) has been developed by $SbCl_3$-catalyzed oxidation with 30% H_2O_2 at room temperature. The reactions proceeded smoothly under mild conditions at room temperature. Simple experimental procedure, use of inexpensive and non-toxic catalyst, high yields and low reaction times are the main merits of the present method.

Keywords

Gem-dihydroperoxide; antimony trichloride; $SbCl_3$; catalyst; ketone; aldehyde; hydrogen peroxide

Academic Discipline And Sub-Disciplines

Chemistry; Synthetic Organic chemistry

SUBJECT CLASSIFICATION

Oxidative Organic transformation

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1. INTRODUCTION

In recent years, *gem*-dihydroperoxides (DHPs) as stable derivatives of ketones and aldehydes [1], have emerged as widely used effective and high potent oxidants in various transformations including the oxidation of various compounds [2] such as sulfides [3], enantioselective oxidation of 2-substituted 1,4-naphthoquinones [4], and as initiators in polymerization reactions [5]. Also, owing to their important role as useful intermediates in the synthesis of various peroxides including tetraoxanes [6], and their analogues such as silatetroxanes [7], spirobisperoxyketals [8], and tetroxycycloalkanes [9], and epoxidation of α,β-unsaturated ketones [10], much research has been directed towards *gem*-dihydroperoxides in the last few years [1]. It is interesting to note that, *gem*-dihydroperoxides are closely relevant to peroxidic antimalarial drugs [6a,11]. They possess the *gem*-peroxy linkage as a salient structural feature [11e,12] in common with many well-known antimalarial cyclic organic peroxides [1,6a,13].

In literature, different protocols are reported on the synthesis of *gem*-dihydroperoxides most of which suffer from significant drawbacks such as the use of strong acidic media, use of concentrated H_2O_2, and low yields of the products [1]. Most of the methods documented in literature utilize a Brönsted or Lewis acid e.g., HCO_2H [9,11b,14], $NaHSO_4$-SiO_2 [15], H_2SO_4 [16], F_3CCO_2H [17], H_2WO_4 [13c,16], $F_3B.OEt_2$ [13d,17], bismuth (III) triflate [17b], and phosphomolybdic acid [17c] to promote the conversion of ketones, ketals or enol ethers into corresponding DHPs on treatment with aqueous H_2O_2. In addition, various other catalysts such as ceric ammonium nitrate (CAN) [13f], methyltrioxorhenium (prepared from Re_2O_7) [6a], and iodine [13g] have been reported to promote such conversions. However, these methods are not mild enough to offer general applicability and impose limitations such as low yields, long reaction times, use of harmful catalyst and high concentration of H_2O_2, and incapability with sensitive functional groups. Thus, there is still necessity to develop efficient and benign approaches for the synthesis of DHPs. Dussault *et al*. [13h] has reported a remarkably mild and highly efficient protocol for Re_2O_7-catalyzed conversion of ketones, aldehydes or acetals into 1,1-dihydroperoxides by H_2O_2 with a major improvement. In this paper we report the application of antimony trichloride ($SbCl_3$) as an efficient and non-toxic catalyst to activate the mild conversion of ketones and aldehydes into respective DHPs. $SbCl_3$ is a commercially available ionic salt which is soluble in water and many other organic solvents and has been widely used as catalyst in synthetic organic chemistry [18].

2. EXPERIMENTAL

2.1 Material and instruments

Solvents and chemicals were obtained from Aldrich and Merck chemical companies and used without purification. Melting points were determined in open capillary tubes in a Stuart SMP_3 apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded on 90 MHz (22.5) JEOL FX 90Q, 200 (50) MHz Varian and 400 (100) MHz BRUKER spectrometers in $CDCl_3$ and DMSO-d_6 solution using Me_4Si as an internal standard. IR spectra were recorded on a Perkin Elmer GX FT IR spectrometer (KBr pellets).

Caution: Although we did not encounter any problem with these reactions, peroxidic compounds are potentially explosive and should be handled with precautions; all reactions should be carried out behind a safety shield inside a fume hood and transition metal salts or heating should be avoided.

2.2 General procedure for conversion of ketones and aldehydes into corresponding *gem*-dihydroperoxides

A mixture of carbonyl substrate **1** (1 mmol), 30% aqueous H_2O_2 (2 mL) and $SbCl_3$ (0.02 g, 0.1 mmol) in MeCN (3 mL) was stirred at room temperature for an appropriate time (Table 3). After completion of the reaction as monitored by TLC, the mixture was diluted with water (5 mL) and extracted with EtOAc (3×5 mL). The combined organic layer was washed with saturated aqueous sodium bicarbonate solution (3 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced presure. The residue was purified by silica-packed column chromatography (hexane-EtOAc) to afford pure *gem*-dihydroperoxides **2** (Table 3). The products were characterized on the basis of their physical properties and spectral (^1H, ^{13}C NMR and IR) analysis and compared with those reported in the literature [13,18,19,20]. The characteristic data of the new products **2s** and **2q** along with some representative products are given below.

2,2-Dihydroperoxyundecane **(2k)**: ^1H NMR (200 MHz, $CDCl_3$): δ 9.51 (bs, 2H, OOH), 1.76-1.60 (m, 2H), 1.38 (s, 3H), 1.32-1.19 (bs,14H), 0.82 (t, *J* = 7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 112.3, 33.4, 32.0, 29.4, 29.1, 28.4, 23.6, 22.5, 17.6, 13.8, 13.5.

1-(4-Methylphenyl)-1,1-dihydroperoxyethane **(2m)**: ^1H NMR (200 MHz, $CDCl_3$): δ 9.71 (bs, 2H, OOH), 7.30 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 6.28 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 139.5, 129.4, 129.0, 126.7, 109.8, 21.1.

1-(Naphthalen-1-yl)-1,1-dihydroperoxyethane **(2p):** Colorless oil; IR (KBr pellet): 3324, 3052, 2922, 2853, 1594, 1573, 1508, 1461, 1356, 1279, 1240, 1192, 1128, 941, 863, 802, 775, 591 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz): δ 8.83-8.75 (bs, 2H, OOH), 8.10-7.20 (m, 7H, Ar-H), 2.66 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 136.0, 134.4, 131.1, 129.9, 127.8, 126.6, 125.5, 123.0, 107.0, 20.5.

2,2-dihydroperoxy-1-phenylpropane (**2q**)^{new}: White solid, m.p: 98-100 °C. (KBr pellet): 3424, 3244,1626, 1374, 873, 825, 665 cm^{-1} ; ^1H NMR (400 MHZ, $CDCl_3$) δ: 9.95 (bs, 2H, OOH), 6.8-7.3 (m, 5H, Ar), 2.2 (s, 2H, CH_2), 1.54 (s, 3H, CH_3); ^{13}C NMR (100 MHZ, DMSO) δ: 108.4, 110.0, 126.3, 128.5, 128.7, 128.8, 141.9; Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.52. Found: C, 58.61; H, 6.45.

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1,1,2,2-tetrahydroperoxy-1,2-diphenylethane (**2s**)[new]: White solid, m.p: 50-52 °C. (KBr pellet): 3436, 3072, 3013, 2888, 1687, 1602, 1583,1454, 1424,1326,1292,1179,1128, 934,809 cm^{-1}; ^{1}HNMR (400 MHZ, $CDCl_3$) δ: 9.56 (bs, 4H, OOH), 7.4-7.9 (m, 10H, Ar); ^{13}C NMR (100 MHZ, DMSO) δ: 129.0, 129.7, 131.2, 133.3, 167.7; Anal. Calcd for $C_{14}H_{14}O_8$: C, 54.19; H, 4.51. Found: C, 53.97; H, 4.35.

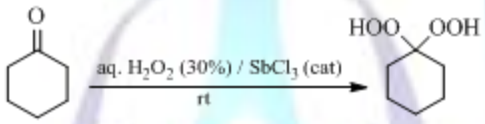
4-Cyanopheny-1,1-dihydroperoxymethane **(2w)**: White solid; mp 107-110 °C; IR (KBr): 3414, 2916, 2235, 1611, 1405, 1333, 1243, 1199, 1122, 1083, 977, 824 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.08 (s, 2H, OOH), 8.04-7.78 (m, 4H, Ar), 7.24 (s, 1H, CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 139.3, 129.4, 128.0, 126.1, 117.0, 112.1.

3. RESULTS AND DISCUSSION

In continuation of our efforts to develop new approaches for synthesis of DHPs [19] and their application in various organic transformations [21], herein, we report $SbCl_3$ as an efficient and hitherto unreported catalyst in promoting the synthesis of *gem*-DHPs from ketones and aldehydes using aqueous H_2O_2 (30%) at room temperature.

To establish the optimum reaction conditions, different solvents such as Et_2O, EtOAc, CH_2Cl_2, $CHCl_3$, CCl_4, CH_3CN, and different catalyst loadings were examined in conversion of cyclohexanone into respective *gem*-dihydroperoxide with aqueous H_2O_2 (30%) at room temperature as model reaction (Table 1). As seen in Table 1, the reaction worked out best in terms of yield (98%) and reaction time (10 min) when CH_3CN was used as the solvent of choice and 10 mol% catalyst loading (entry 7). Further increasing the amount of catalyst showed no improving effect on the yield.

Table 1. Screening the parameters for the model $SbCl_3$-catalyzed conversion of cyclohexanone into 1,1-dihydroperoxycyclohexane with aqueous H_2O_2 (30%) at room temperature[a]



Entry	Solvent	$SbCl_3$ (mmol)	Time (min)	Yield (%)[b]
1	Et_2O	0.1	140	45
2	EtOAc	0.1	60	86
3	CH_2Cl_2	0.1	90	68
4	$CHCl_3$	0.1	100	32
5	CCl_4	0.1	-	-
6	CH_3CN	0.05	30	57
7	CH_3CN	0.1	10	98
8	CH_3CN	0.2	20	78
9	CH_3CN	0,3	30	83

[a]Conditions: cyclohexanone (1 mmol), 30% H_2O_2 (2 mL), solvent (3 mL), room temperature.

[b]Isolated yield.

In addition, the catalytic importance of $SbCl_3$ in this reaction was verified by comparing its efficiency with some other catalysts which have been previously reported to catalyze the same reaction (Table 2). As evident, $SbCl_3$ exhibits superiority over other catalysts listed in Table 2 in terms of the yield and reaction time.

Using these optimized reaction conditions (10 mol% catalyst, room temperature, solvent CH_3CN), the scope and efficiency of the reaction were explored for the synthesis of *gem*-dihydroperoxides **2a-z** through $SbCl_3$-catalyzed reaction of ketones and aldehydes **1a-z** (Scheme 1), and the results are summarized in Table 3.

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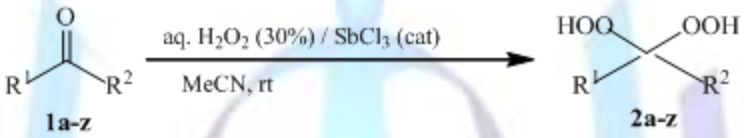
Table 2. Comparison between the catalytic efficiency of $SbCl_3$ with other catalysts reported in the literature for *gem*-dihydroperoxidation of cyclohexanone with aq. H_2O_2 in CH_3CN at room temperature[a]

Entry	Catalyst	Concentration of H_2O_2 (%)	Time (min)	Yield (%)	Ref
1	$SbCl_3$	30	10	98	-
2	Silica sulphuric acid	30	20	98	18
3	$Bi(OTf)_3$	30	18	78	17b
4	phosphomolybdic acid	50	150	95	17c
5	Re_2O_7	50	30	79	13h
6	CAN reagent	50	120	87	13f
7	$NaHSO_4{\cdot}SiO_2$	50	20	98	15

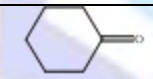
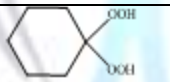
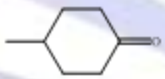
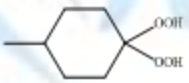
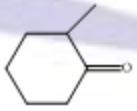
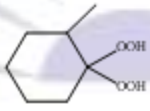
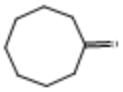
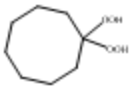
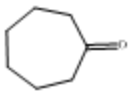
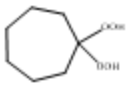
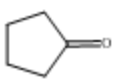
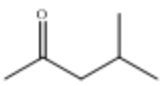
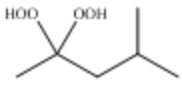
[a]Conditiones: cyclohexanone (1 mmol), catalyst (0.1 mmol), aq. H_2O_2 (2 mmol), CH_3CN (3 mL).



Scheme 1. $SbCl_3$-catalyzed synthesis of *gem*-dihydroperoxides.

As shown in Table 3, generally, the aliphatic ketones **1a-k** react more readily than the aromatic ketones **1l-s** to afford the corresponding *gem*-DHPs in higher yields. It was observed that, under the same reaction condition no conversion to *gem*-DHP was observed for benzophenone as it remained almost intact after 10 hours (entry r). This can be likely due to the strong resonance stabilization and steric effects caused by phenyl groups. Moreover, as previously known by Žmitek [20] and Rieche [22], we noticed that, simple aliphatic aldehydes such as octanal **1y** and dihydrocinnamaldehyde **1z,** react differently to provide 1,1-hydroxyhydroperoxides instead of giving their corresponding *gem*-dihydroperoxides (entries y and z); that is the addition of only one molecule of hydrogen peroxide to the carbonyl group has occurred.

Table 3. Synthesis of *gem*-dihydroperoxides with $SbCl_3$ (cat.) /30% aq. H_2O_2[a]

Entry	Ketone or aldehyde **1**	Product **2**	Time (min)	Yield (%)[b]	Mp (^oC)	Ref.
a			15	97	oil	18
b			20	96	oil	13f
c			22	86	oil	13f
d			25	87	oil	13h
e			19	95	64-66	18
f			60	93	oil	18
g			10	95	oil	18

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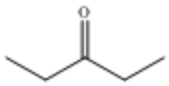
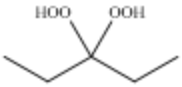
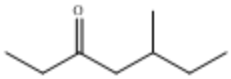
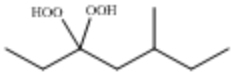
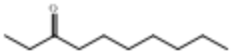
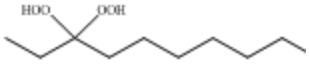
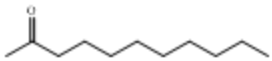
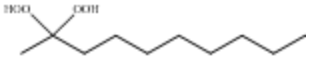
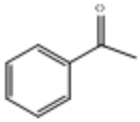
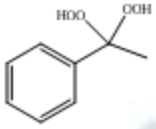
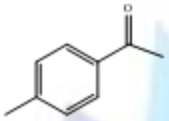
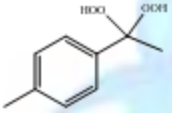
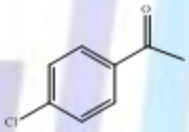
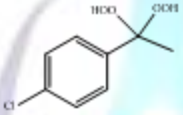
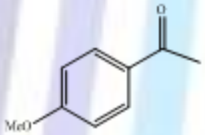
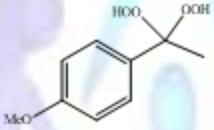
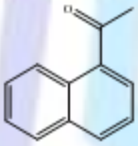
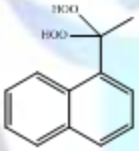
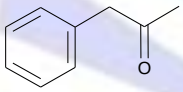
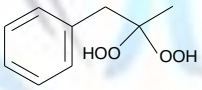
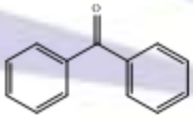
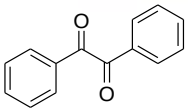
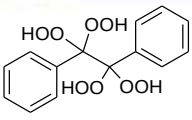
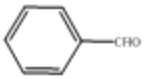
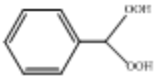
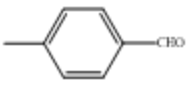
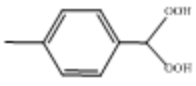
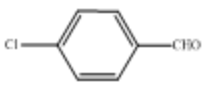
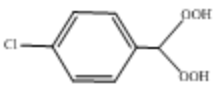
h			15	84	oil	18
i			18	86	oil	22
j			20	93	31-33	22
k			20	90	oil	18
l			120	74	75-77	18
m			140	78	oil	18
n			90	75	oil	18
o			100	76	oil	18
p			160	45	oil	18
q[new]			20	96	50-55	-
r		–	10h		–	18
s[new]			24h	98	98-100	-
t			60	87	oil	18
u			100	86	54-56	18
v			90	75	72-74	18

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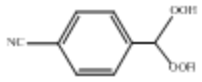
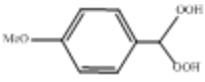
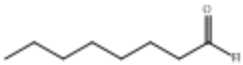
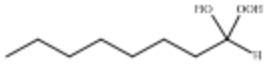
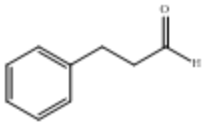
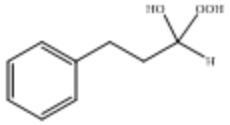
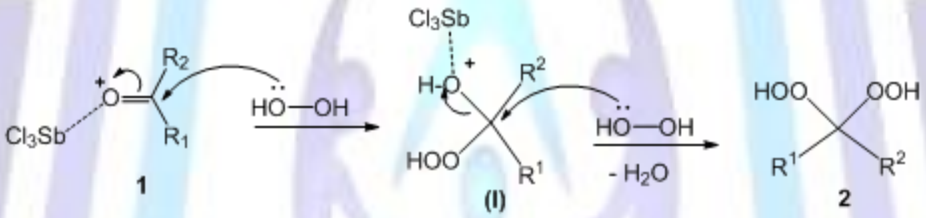
w			60	86	105-107	18
x			55	75	oil	18
y			10	94	oil	18
z			47	93	oil	18

[a]Conditions: carbonyl **1** (1 mmol), 30% aq. H_2O_2 (2 mL), CH_3CN (3 mL), $SbCl_3$ (0.1 mmol), room temperature.

[b]Isolated Yield.

A simple and reasonable mechanism to explain the conversion of ketones and aldehydes **1** into respective *gem*-DHPs **2** is given in Scheme **2**. As shown in this Scheme, the initial step likely involves the nucleophilic addition of hydrogen peroxide on $SbCl_3$-activated carbonyl compound **1** to produce the hydroxy-hydroperoxy intermediate (**I**). Subsequently, dehydrative substitution of hydroxyl group in the intermediat (**I**) occurs through nucleophilic attack by hydrogen peroxide under the activation by $SbCl_3$ to furnish the product **2**.



Scheme 2. Possible mechanism of $SbCl_3$-catalyzed synthesis of *gem*-dihydroperoxides from ketones and aldehydes.

CONCLUSIONS

In summary, a new efficient homogeneous catalyst $SbCl_3$ has been explored for promotion of the synthesis of *gem*-dihydroperoxides from aliphatic and aromatic ketones and aldehydes using aqueous H_2O_2 (30%) in acetonitrile at room temperature. The attractive features of this new approach are: the readily available and non-toxic catalyst, high yields of the products, mild reaction conditions and the operational simplicity.

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