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AN EFFICIENT SYNTHESIS OF GEM-DIHYDROPEROXIDES AND 1,2,4,5-TETRAOXANES CATALYZED BYCHLOROSULFONIC ACIDAS A NEW CATALYST

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ABSTRACT

Chlorosulfonic acid was used as an active, low-cost and reusable solid catalyst for conversion of ketones and aldehydes to corresponding gem-dihydroperoxides using 30% aqueous hydrogen peroxide at room temperature. The reactions proceed with high rates and excellent yields.

Keywords

Gem-dihydroperoxide; Aldehyde; Ketones; Chlorosulfonic acid; Hydrogen peroxide.

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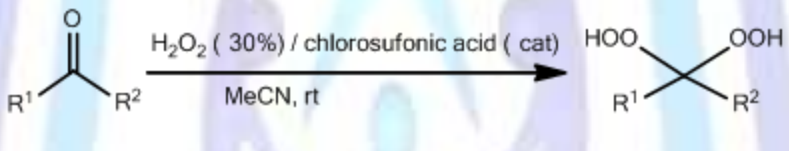
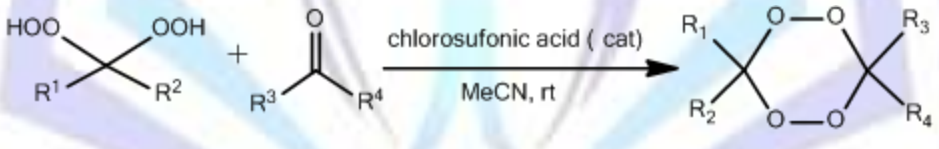
1. INTRODUCTION

Gem-dihydroperoxides (DHPs) which are interested closely durable peroxidic derivatives of ketones and aldehydes, have important roles in synthesis of peroxidic antimalarial drugs [1, 2, 3]. Furthermore, gem-dihydroperoxides are critical fundamental intermediates in synthesis of some categories of peroxides as well as tetraoxanes [4-6], silateraoxans [7], spirobisperoxyketals [8,9], bisperoxyketals [10], and 1,2,4,5- tetraoxacycloalkanes [11,12]. Also, similar to other peroxides such as 3-chloropebenzoic acid, gem-dihydroperoxides have been utilized as the initiators in radical polymerization procedures [13]. Additionally, newly, these compounds have been employed as the powerful oxidants in several organic reactions such as epoxidation of α,β-unsaturated ketones [14,15,] oxidation of sulfides [16-17], oxidation of alcohols [18], enantioselective oxidation of 2-substituted-1,4-naphtoquinones [19] oxidative aromatization of 2-pyrazolines and isoxazolines [20] and some similar reactions [21]. Normally, there are two reported methods for synthesis of gem-dihydroperoxides: (I) reaction of ketals with H_2O_2 in the presence of tungstic acid [22], or $BF_3.Et_2O$ [23], (II) ozonolysis of ketone enol ethers or α-olefines in the presence of aqueous H2O2 [11, 24]. Unfortunately, these methods clearly suffer from notable drawbacks inluding needing for concentrated H_2O_2 and surplus acid, minimal substrate range and formation a mix of peroxidic products, low yield, long reaction time and strong reaction condition [25]. Moreover, little selectivity and drawbacks from existence of ozone sensitive functional groups in the substrates are additional deficiencies in ozonolysis reaction. As a result, to eliminate these disadvantages, lately, in modified method, gem-dihydroperoxides have been synthesized via peroxidation of aldehydes and ketones by aqueous H_2O_2 in the presence of molecular iodine as the catalyst. [26,27] currently, some Lewis or Bronsted acids, including ceric ammonium nitrate (CAN) [28], camphor sulfuric acid (CSA) [29], $NaHSO_4.SiO_2$ [30], Re_2O_7 [31], Bismuth (III) triflate [32] and PMA [33] have been utilized as the catalysts for synthesis of these compounds. As the importance of gem-dihydroperoxides and also 1,2,4,5-tetraoxanes that are key precursors in synthesis of anti-malaria drugs, in duration of our efforts to adapt this methodology and apply novel and more appropriate catalysts, [34], herein, we wish to report using Chlorosulfonic acid as an effective catalyst (Scheme 1) for synthesis of gem-dihydroperoxides from ketones and aldehydes with 30% aqueous H_2O_2 at room temperature. Besides, we successfully used Chlorosulfonic acid for catalyzing facile synthesis of 1,2,4,5-tetraoxanes from direct condensation of obtained gem-dihydroperoxides with different ketones (scheme 2)



Scheme 1. Chlorosulfinic acid-catalyzed peroxidation of aldehydes and ketones to *gem*-dihydroperoxides with H_2O_2 (30 %).



Scheme 2. Chlorosulfinic acid-catalyzed syntheisi of 1,2,4,5-tetraoxanes 4a-4q

Chlorosulfuric acid is commercially available acid that has been used as a proper catalyst in several chemical reactions [35].

2. EXPERIMENTAL

2.1 Material and instruments

Solvents, reagents, and chemical materials were obtained from Aldrich and Merck chemical companies and purified prior to use. Nuclear magnetic resonance spectra were recorded on JEOL FX 90Q using tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded on a PerkinElmer GX FT IR spectrometer (KBr pellets).

Caution: Although we did not encounter any problem with gem-dihydroperoxides, peroxides are potentially explosive and should be handled with precautions; all reactions should be carried out behind a safety shield inside a fume hood and heating should be avoided.

2.2 General procedure for synthesis of gem-dihyroperoxides: To a mixture of carbonyl compound (1 mmol) and ClSA (0.0066 ml, 0.1mmol) in MeCN (3 ml) 30% aqueous H_2O_2 (1 ml) was added, and the mixture was stirred at room temperature for an appropriate time (Tables 2,3 and 4). After completion of reaction as monitored by thin-layer chromatography (TLC), the mixture was diluted with water (5 ml) and extracted by ethyl acetate (3×5 ml). Aqueous layer which contains SA and organic layer that contains products, was separated, dried over anhydrous Mg_2SO_4, and

evaporated under reduced pressure. The residue was purified by silica-packed column chromatography (hexane–EtOAc) to afford pure gem-dihydroperoxides (Tables 2,3 and 4). Products were characterized on the basis of their melting points, elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectral analysis and amount of peroxide in products has been determined by iodometric titration.

2.3 General procedure for synthesis of teraoxanes: To a mixture of ketone (1 mmol) and ClSA (0.0066 ml, 0.1mmol) in MeCN (3 ml) gem-dihydroperoxide (1 mmol) was added and the mixture was stirred at room temperature for an appropriate time (Tables 5). After the completion of the reaction as monitored by thin-layer chromatography (TLC), the mixture was diluted with water (5 ml) and extracted with CH_2Cl_2 (3×5 ml). Then, aqueous layer and organic layer was separated, dried over anhydrous Mg_2SO_4 and evaporated under reduced pressure. The residue was purified by silica-packed column chromatography (hexane–EtOAc) to afford pure 1,2,4,5-tetraoxanes (Tables 5). Products were characterized on the basis of their melting points, elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectral analysis.

The characteristic data for new products are given below.

4-(dihydroperoxymethyl)-N,N-dimethylaniline (table 4, entry 3k): Sticky brown oil. IR vmax /cm^{-1} (nujol mull): 3400, 3092, 1592, 1425, 1363, 1221, 1111, 979; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 10.47 (br, s, 2H, OOH), 7.32-8.17 (m, 4 H), 6.28 (s, 1H), 3.00, (s, 6H); ^{13}C NMR (DMSO-d_6, 22.5 MHz), δ: 143.4, 138.0, 130.5, 127.7, 101.0, 38.5; Anal. Calcd for $C_9H_{13}NO_4$: C, 54.26; H, 6.58%. Found: C, 54.44; H, 6.83%.

2-(1,1-dihydroperoxyethyl)thiophene (table 4, entry 3m): White solid, m.p: 98-101 °C. IR vmax /cm^{-1} (KBr pellet): 3420, 2922, 2829, 1635, 1558, 1458, 1363, 1271, 987, 721, 599, 435, 353; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 8.21 (br, s, 2 H,OOH), 7.20-7.90 (m, 3 H), 2.55 (s, 3H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 142.7, 130.0, 129.3, 126.7, 100.4, 31.5; Anal. Calcd for $C_6H_8O_4S$: C, 40.90; H, 4.58; S, 18.20%. Found: C, 41.18; H, 4.60, S, 19.12%.

1,4-bis(dihydroperoxymethyl)benzene (table 4, entry 3j): White solid, m.p: 210-212 °C. IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 1687, 1611, 1580, 1416, 1387, 1248, 1088, 989, 833, 826, 641; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 9.8-9.9 (br, s, 4 H, OOH), 7.32-7.91 (m, 4 H),(2H), 5.78 (s, 1H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 137.4, 131.9, 131.4, 113.9; Anal. Calcd for $C_8H_{10}O_8$: C, 41.03; H, 4.30%; Found: C, 42.06; H, 4.25%.

7,8,15,16-Tetraoxa-dispiro[5.2.5.2]hexadecane (4a): White solid; m.p: 70-72 °C.; IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.26-2.29 (m, 20H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 108.5, 30.1, 25.8, 22.3; Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83%; Found: C, 62.76; H,8.95%.

3-Methyl-7,8,15,16-tetraoxa-dispiro[5.2.5.2]hexadecane (4b): White solid; m.p: 86-88 °C; IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 3.3 (s, 1H), 1.24-2.34 (m, 18H), 0.94 (d, 3H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 108.38, 108.33, 35.1, 32.2, 32.0, 31.6, 26.0, 25.0, 24.1, 21.8; Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%; Found: C, 65.00; H,8.69%.

3,3'-di-Methyl-7,8,15,16-tetraoxa-dispiro[5.2.5.2]hexadecane (4d): White solid; m.p: 153-155 °C; IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 3.32 (s, 2H), 1.22-1.60 (m, 16H), 0.90 (d, 6H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 108.3, 32.0, 31.7, 30.5, 21.5; Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44%; Found: C, 66.05; H, 9.13%.

3-(4-chlorophenyl)-1,2,4,5-tetraoxaspiro[5.5]undecane (4j): White solid; m.p: 98-100 °C; IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 7.30-7.52 (m, 4H), 6.81 (s, 1H), 1.70-2.60 (m, 8H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 137.8, 130.5, 129.6, 129.5, 109.52, 107.6, 32.4, 32.2, 30.7, 22.8, 22.5; Anal. Calcd for $C_{13}H_{15}ClO_4$: C, 57.68; H, 5.59%; Found: C, 58.12; H, 5.31%.

9-methyl-3-phenyl-1,2,4,5-tetraoxaspiro[5.5]undecane (4n): White solid; m.p: 101-103 °C; ; IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 7.40-7.55 (m, 5H), 6.80 (s, 1H), 3.21-3.34 (m, 1H), 0.99-1.98 (m, 13H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 132.0, 131.3, 129.1, 128.0, 109.2, 108.2, 32.5, 31.8, 30.9, 30.5, 29.9, 21.8; Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%; Found: C, 69.21; H, 7.03%.

3-phenyl-1,2,4,5-tetraoxaspiro[5.5]undecane (4o): White solid; m.p: 78-80 °C; IR vmax /cm-1 (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 7.40 -7.56 (m, 5H), 6.69 (s, 1H), 2.65-2.85 (m, 2H), 1.70-1.92 (m , 8H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 131.9, 131.5, 129.1, 127.8, 109.1, 108.2, 32.0, 30.1, 25.9, 22.5, 22.0; Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83%; Found: C, 65.78; H, 6.90%.

8-phenyl-6,7,9,10-tetraoxaspiro[4.5]decane (4p): White solid; m.p: 73-75 °C; IR vmax /cm^{-1} (KBr pellet): 3338, 3085, 2920, 1697, 1612, 1579, 1419, 1319, 1275, 1203, 1014, 972, 835, 808, 621; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 7.38-7.44 (m, 5H), 6.80 (s, 1H),1.80-2.10 (m, 8H); ^{13}C NMR (DMSO-d_6, 22.5 MHz): δ 132.0, 131.3, 129.0, 127.9, 114.5, 108.0, 35.5, 35.0, 25.5, 24.0; Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%; Found: C, 64.15; H, 6.77%.

3. RESULTS AND DISCUSSION

In an effort to establish the reaction conditions, various reaction parameters were studied to produce 1,1-dihydroperoxycyclohexane by the model reaction of cyclohexanone with 30 % aqueous H_2O_2 under catalytic effect of ClSA, so the results are summarized in Table 1. As we have seen in this Table, the best result in terms of yield and

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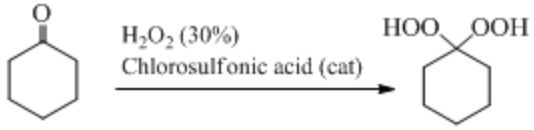
reaction time was provided using MeCN as a solvent at room temperature with 0.1 mmol of catalyst loading (entry 6, table 1).

Table 1. Screening the reaction parameters for the formation of 1,1-dihydroperoxycyclohexane[a]



Entry	Solvent	CSA (mol%)	Time (min)	Yield[b] (%)	
1	Et_2O	0.1	25	70	
2	EtOAc	0.1	20	83	
3	CH_2Cl_2	0.1	50	35	
4	$CHCl_3$	0.1	50	45	
5	CCl_4	0.1	65	40	
6	CH_3CN	0.1	9	98	
7	CH_3CN	0.08	15	92	
8	CH_3CN	0.05	28	68	
9	CH_3CN	0.15	8	90	
10	CH_3CN	0.2	8	70	

[a] Conditiones: cyclohexanone (1 mmol), 30 % aqueous H_2O_2 (1 ml), solvent (3 ml), room temperature.

[b] Isolated yield.

With optimized conditions in hand (aldehyde or ketones (1 mmol), aqueous 30% H_2O_2 (3 ml), 0.1 mmol catalyst, MeCN (3 ml, r.t)) we began to study the scope of the reaction using a range of cyclic aliphatic ketones (Table 2), side chain aliphatic aldehydes and ketones (Table 3) and aromatic aldehydes and ketones (Table 4). According to results summarized in these tables, generally, both cyclic and side chain aliphatic ketones react faster than the aromatic ketones because of the conjugating of carbonyl group with aromatic ring to afford the corresponding gem-dihydroperoxides comparatively in higher yields. This conjugating cause that benzophenone recovered intact after 200 minutes. For cyclic ketones, cyclohexanone reacts faster than cyclopentanone in higher yield (table 2, entries 1a and 1d). Also, interestingly, the aromatic aldehydes and ketones substituted by electron-withdrawing substituent didn't react at all or they reacted in very long time with nearly low yields. It has been explained by Katja Zmitek and Co-workers [28]. They reported that the transition state for this reaction has positive charge on carbonyl group. So, this reaction has high negative reaction constant (ρ= -2.76) that suggests a transition state with a more developed charge in the rate-determining step [28]. For example, we observed that 4-N,N-dimethylamino bebzaldehyde reacts faster than 4-chlorobenzaldehyde (table 4, entry 3k). On the other hands, 4-nitro benzaldehyde converted very slowly to gem-dihydroperoxide in very low conversion (13%) and decomposed after 0.5 hour because of the powerful electron-withdrawing effect of NO_2 group, (table 4, entry 3i). summing up, we suggest that Chlorosulfonic acid activates both carbonyl group and hydrogen peroxide. In fact, chlorosulfonic acid is a powerful acid, so generates H+ which activates the carbonyl group. On the other hands, the chlorine atom in chlorosulfonic acid is a powerful; electronegative atom, consequently it causes hydrogen peroxide (or gem-dihydroperoxide) more nucleophile via hydrogen bonding (scheme 3).

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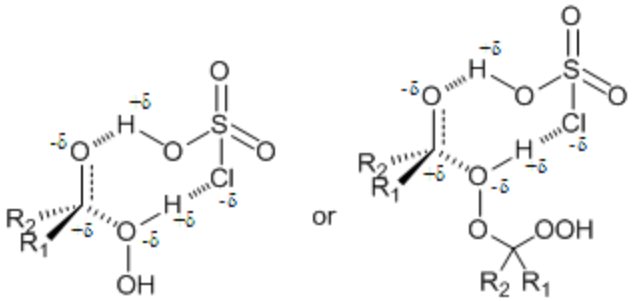
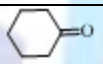
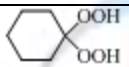
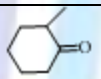
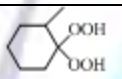
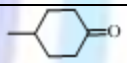
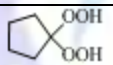
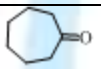
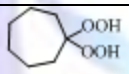
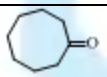
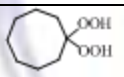
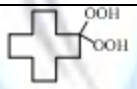
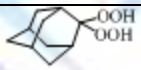


Scheme 3. suggested mechanism for catalitic efffect of chlorosulfonic acid

Table 2. Peroxidation of different cyclic ketones

Entry	Ketone	Product[b]	Time (min)	Yield (%)[c]	Mp (^{o}C)	Ref
1a			9	98	oil	34b
1b			13	91	oil	28
1c			11	95	oil	28
1d			10	92	oil	34b
1e			20	90	64-66	26
1f			14	94	oil	8
1e			25	85	138-140 (decomposed)	26
1h			14	95	148-150	26

[a] Conditions: ketone and aldehyde (1 mmol), CH_3CN (3 ml), ClSA (0.1 mmol), 30% aq. H_2O_2 (1 ml), reactions are carried out at rt.

[b] The structures of the products were established from their physical properties and spectral (^{1}H NMR, ^{13}C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by Iodometric titration.

[c] Isolated Yield.

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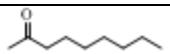
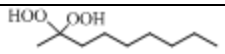
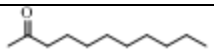
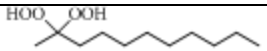
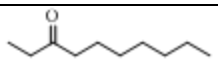
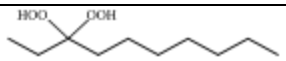
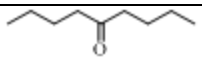
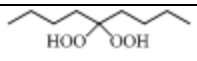
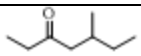
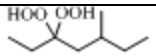
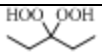
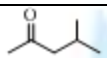
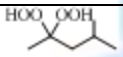
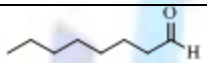
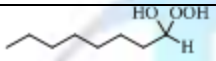
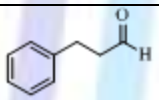
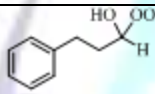
Table 3 Peroxidation of side chain aliphatic ketones and aldehydes

Entry	Ketone	Product[b]	Time (min)	Yield (%)[c]	Mp (^{0}C)	Ref
2a			10	94	oil	34b
2b			12	93	oil	28
2c			12	91	31-33	26
2d			16	90	oil	26
2e			21	76	oil	26
2f			10	95	oil	36
2g			9	96	oil	34b
2h			50	92	oil	34b
2i			45	97	oil	34b

[a] Conditions: ketone and aldehyde (1 mmol), CH_3CN (3 ml), ClSA (0.1 mmol), 30% aq. H_2O_2 (1 ml), reactions are carried out at rt.

[b] The structures of the products were established from their physical properties and spectral (^{1}H NMR, ^{13}C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by Iodometric titration.

[c] Isolated Yield.

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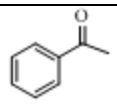
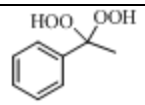
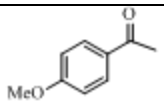
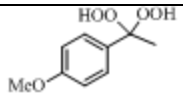
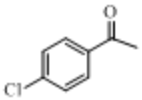
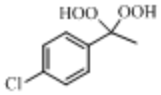
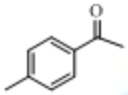
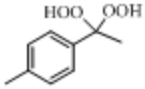
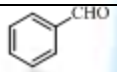
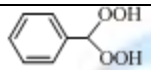
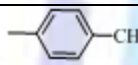
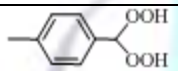
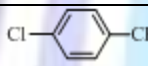
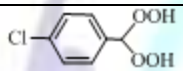
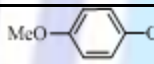
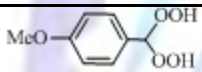
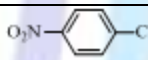
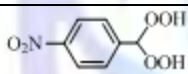
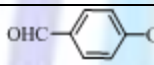
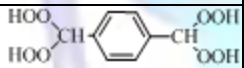
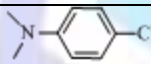
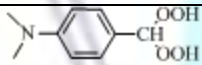
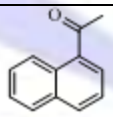
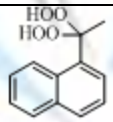
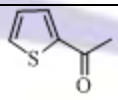
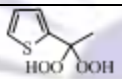
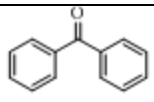
Table 4 Peroxidation of aromatic ketones and aldehydes

Entry	Ketone	Product[b]	Time (min)	Yield (%)[c]	Mp (°C)	Ref
3a			93	75	75-77	34b
3b			80	60	oil	34b
3c			78	55	oil	34b
3d			76	60	oil	34b
3e			40	82	oil	34b
3f			38	86	54-56	34b
3g			45	82	72-74	34b
3h			39	91	oil	34b
3i			170	13	decomposed	28
3j			340	91	210-212	new
3k			31	70	Sticky oil	new
3l			48	93	oil	34b
3m			52	88	98-102	new
3n		–	200	–	–	–

[a] Conditions: ketone and aldehyde (1 mmol), CH_3CN (3ml), ClSA (0.1mmol), 30% aq. H_2O_2 (1 mL), reactions are carried out at rt.

[b] The structures of the products were established from their physical properties and spectral (^1H NMR, ^{13}C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by Iodometric titration.

[c] Isolated Yield.

Moreover, It is interesting that aliphatic aldehydes react with only one molecule of hydrogen peroxide in carbonyl group, so 1,1- hydroxyhydroperoxide derivatives were formed instead of their expected DHPs (table 3, entries 2h and 2i, scheme 4).

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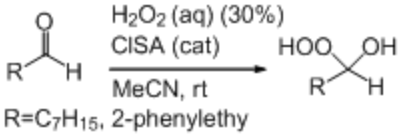
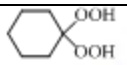
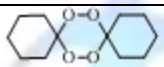
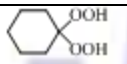
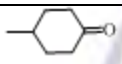
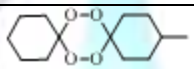
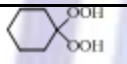
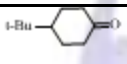
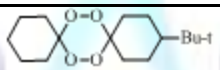
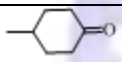
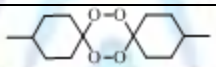
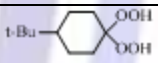
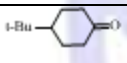
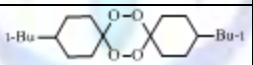
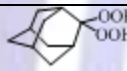
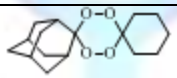
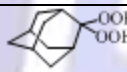
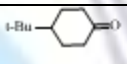
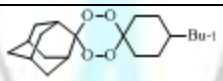
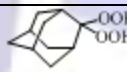
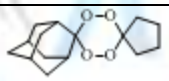
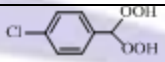
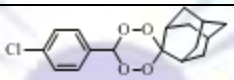
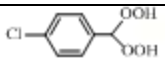
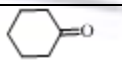
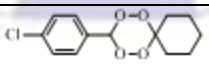
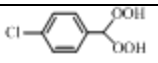
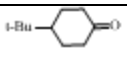
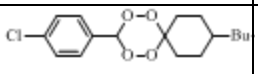
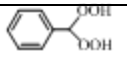
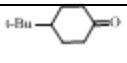
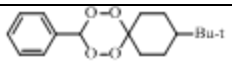
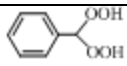
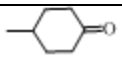
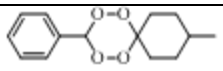


Scheme 4. peroxidation of aliphatic aldehydes

For the first time, terephthalaldehyde was reacted as a dialdehyde and we observed that both of the aldehyde groups has been converted to gem-dihydroeperoxide after 360 minutes (table 3, entry 3j). In addition, we have successfully converted 2-methyltheilnyl ketone as a heterocyclic ketone to corresponding gem-dihydroperoxide without any by-product (table 3, entry 3m). Like other our reported works, benzophenone was recovered intact after 200 minutes (table 3, entry 3n).

In the next step, we used some of the synthesized gem-dihydroperoxides as nucleophiles. These gem-dihydroperoxides reacted with ketones and variety of 1,2,3,4-tetraoxanes were produced. (Scheme 2, table 5). Reaction's condition is similar to synthesis of gem-dihydroperoxides condition.

Table 5. Synthesis of tetraoxanes using of gem-dihydroperoxides

Entry[a]	gem-dihydroperoxide	ketone	Product[b]	Time (min)	Yield (%)[b]	Mp (oC)	Ref
4a				9	88	70-72	new
4b				7	89	86-88	new
4c				6	90	102-104	36
4d				5	90	153-155	new
4e				5	92	191-193	36
4f				8	84	58-62	36
4g				7	82	131-133	36
4h				6	85	0il	36
4i				16	70	73-75	36
4j				11	82	98-100	new
4k				9	80	114-116	36
4l				10	84	122-124	36
4n				11	86	101-103	new
4o				12	86	78-80	new
4p				14	85	73-75	new

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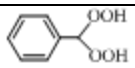
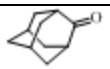
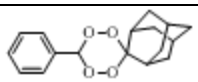
4q				15	72	61-63	36

[a] condition: gem-dihydroperoxide (1 mmol), ketone (1 mmol), MeCN (3 ml), ClSA (0.1mmol), reactions are carried out at rt.

[b] The structures of the products were established from their physical properties and spectral (^{1}H NMR, ^{13}C NMR and IR) analysis and compared with the data reported in the literature and amount the peroxide is determined by Iodometric titration.

[c] Isolated Yield.

Finally, this method for peroxidation of cyclohexanone (entry 1a, table 2) is compared with other reported methodologies in the table 6. As has been noted, this methodology is clearly better which really improves the time reaction, yields and reaction condition.

Table 6. Comparing reported results for peroxidation of cyclohexanone

Entry	Catalyst	Condition	Concetration of H_2O_2	Time (min)	Yield (%)	Ref
1	This method (ClSA)	r. t		11	98	-
2	Silica sulfuric acid	r. t		20	98	34b
3	$Bi(OTf)_3$	r. t		18	78	32
4	phosphomolybdic acid	r. t		150	95	33
5	Re_2O_7	r. t		30	79	31
6	CAN reagent	r. t		120	87	28
7	$NaHSO_4{\cdot}SiO_2$	r. t		20	98	30

CONCLUSIONS

In conclusion, chlorosulfonic acid was explored as a high active, commercially available and simple catalyst towards the conversion of ketones and aldehydes to corresponding gem-dihydroperoxides. These reactions proceeded smoothly with low reactions time at room temperature to furnish the titled products in high to excellent yields. Chlorosulfonic acid catalyst exhibited a high reusability potential and has shown no significant loss of activity after three consecutive runs (entry 1, Table 2). This catalyst makes the process affordable and economical.

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