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Note

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### Synthesis, structure and oxidation of alkynes using a $\mu$ -oxo diiron complex with the ligand bis (1-(pyridin-2-ylmethyl)-benzimidazol-2-yl methyl) ether

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#### ABSTRACT

New ligand bis (1-(pyridin-2-ylmethyl)-benzimidazol-2-ylmethyl ether and its  $\mu$ -oxo diferric complex has been synthesized and characterized. The dimeric [LCIFe–O–FeCl<sub>3</sub>] has been characterized crystallographically, and shows that iron atoms occupy inequivalent coordination sites. One of the Fe (III) atom is coordinated by two benzimidazole nitrogens, one ether oxygen and bridging oxide oxygen, forming the equatorial plane while one Cl<sup>-</sup> ion and the oxygen atom of a DMF molecule occupy the axial fifth and the sixth coordination positions. The second Fe (III) is tetrahedrally coordinated by three Cl<sup>-</sup> ions and the bridging oxide oxygen 0. The bridging oxide anion is unsymmerically coordinated to the two Iron (III) atoms. Oxidation of aromatic alkynes was investigated using this complex as catalyst with small amount of tert-butyl hydroperoxide (TBHP) and Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an alternate source of oxygen. Isolated products were characterized by GC-Mass. Solvent, temperature, Stoichiometry and oxidant variation are studied and reaction conditions have been optimized. Dicarbonyl and  $\alpha$ , $\beta$ -acetylenic ketone are the major product and depend on the nature of the alkyne employed.

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#### 1. Introduction

The oxidation of alkynes carrying methylene and hydroxyl moieties to the corresponding carbonyl derivatives is of importance in organic synthesis. This has been reported with transition metal catalysts using different oxidants [1–4]. It is known that alkynes can be converted into  $\alpha,\beta$  acetylenic ketones [5], dicarbonyl compounds [2,6] and can undergo oxidative cleavage [7]. Earlier reports on the oxidative cleavage of alkynes employed oxidants such as ozone, potassium permanganate, ruthenium tetraoxide, Mo and W polyoxometalates, methylrhenium trioxide, alkaline hydrogen peroxide, [bis(trifluoroacetoxy)iodo]-benzene, and use of these oxidants were found to have low reaction efficiencies [8–18]. The present work was undertaken to study the oxidation or cleavage of alkynes by iron catalyst in the presence of hydroperoxide. It aims to investigate if the product profile is dependent on the catalyst or oxidant, and whether the oxidation occurs at the C=C bond or at the adjacent methylene group. Thus the oxidation and cleavage of alkynes has been investigated using a new µ-oxo bridged dinuclear Fe (III) complex. It is observed that the profile of the products depend markedly upon the solvent system, nature of the oxidant, and reactivity of the alkynes used.

#### 2. Experimental

#### 2.1. Analysis and physical measurements

Elemental analyses of ligand and dimeric  $\mu$ -oxo diiron (III) complex was obtained on VARIO EL III instrument from USIC, University of Delhi, Delhi, India. Electronic spectra were recorded on a Shimadzu 1601 spectrometer at the Department of Chemistry, University of Delhi, Delhi. IR spectra were recorded in the solid state as KBr pellets on a Perkin–Elmer FTIR-2000 Spectrometer in the region of 400–4000 cm<sup>-1</sup>. GCMS spectra were recorded at Advanced Instrumentation and Research Facility, Jawaharlal Nehru University, New Delhi on a GCMS-QP2010 (plus) Schimadzu instrument.

#### 2.2. Materials required

Bis (2-benzimidazolylmethyl) ether (DGB) was prepared as described earlier [19]. Freshly distilled solvents were employed for all the synthesis. All other chemicals were of AR grade.

#### 2.3. X-ray crystallographic data collection and refinement of [LClFe– O–FeCl<sub>3</sub>].2.C<sub>3</sub>H<sub>7</sub>ON

The complex was dissolved in HPLC grade DMF, and slow evaporation at room temperature over a period of 48 h resulted in the formation of golden brown hexagonal shaped crystals. X-ray data for structure determination and refinement for the complex were

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collected on a Nonius CCD using Mo K $\alpha$  ( $\lambda$  = 0.71069). The data were corrected for Lorentz and polarization effects and absorption corrections were applied. A total of 20857 reflections were measured out of 9153 were independent and 4379 were observed  $[I > 2 \sigma(I)]$  for theta 29.19°. The structure was solved by direct methods using siR-97 [20] and refined by full-matrix least squares refinement methods based on  $F^2$ , using SHELX-97 [21]. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their Uiso values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbons. All calculations were performed using WINGX [22] package. Important crystal and refinement parameters are given in (Table 1). There are two DMF molecules in the molecular structure one of which is coordinating to the metal ion. The latter showed disorder in terms of large thermal parameters especially for N7 and C34 and short C-N distance. The disorder could be resolved only for one of the methyl carbons C34 which was split into two positions with a total occupancy of 1.0. The rest were refined with a fixed C-N distance of 1.421(3) Å. Because of the unresolved thermal disorder in the two solvent molecules containing four terminal methyl groups, the cif shows three B level errors relating to the large  $U_{eq}$  (max)/ $U_{eq}$ (min) ratios which are fully justified. A final refinement Overall the structure refined nicely with a final refinement of 474 parameters, with one restraint, gave  $R_1 = 0.0512$ ,  $wR_2 = 0.0951$  for the observed data and  $R_1$  = 0.12187,  $wR_2$  = 0.1086 for the whole data (Table 1).

#### 2.4. Preparation of ligand

2.4.1. Bis (1-(pyridin-2-ylmethyl)-benzimidazol-2-yl methyl) ether [P-DGB] [L]

A solution of Bis (2-benzimidazolylmethyl) ether (DGB) (1 g, 3.6 mmol) in DMF was stirred for 3 h with  $K_2CO_3$  (1.24 g, 9 mmol)

#### Table 1

Crystal	data	and	structure	refinement	for	[LClFe=0	D-FeCl <sub>3</sub> ]
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Identification code	SHELXL
Empirical formula	C34 H38 Cl4 Fe2 N8 O4
Formula weight	876.22
T (K)	153(2)
$\lambda$ (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	-1
a (Å)	11.418(5)
b (Å)	17.255(4)
c (Å)	20.463(5)
α (°)	90
β (°)	102.586(5)
γ (°)	90
$V(Å^3)$	3935(2)
Z	4
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.479
Absorption coefficient	$1.057 \text{ mm}^{-1}$
F(000)	1800
Crystal size (mm)	$0.19 \times 0.16 \times 0.16$
$\theta$ (°)	2.99-29.19
Index ranges	$-15 \leqslant h \leqslant 14$ , $-21 \leqslant k \leqslant 21$ ,
	$-25 \leqslant l \leqslant 24$
Reflections collected	20857
Independent reflections $(R_{int})$	9153 (0.0422)
Completeness to $\theta$ = 25.00°	99.8%
Absorption correction	Multiscan
Maximum and minimum transmission	0.853 and 0.829
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	9153/1/474
Goodness-of-fit on (GOF) $F^2$	0.859
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0540, wR_2 = 0.1084$
R indices (all data)	$R_1 = 0.1314$ , $wR_2 = 0.1234$
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.485 and -0.449

at 70 °C. When turbidity appeared, 2-Picolyl chloride hydrochloride (1.5 g, 9 mmol) was added and the solution was stirred for another 72 h continuously at 70 °C. The solvent was stripped off on a rotatory evaporator and the residue was treated with small amount of distilled water to obtain a brown colored crude product. The product was recrystallised from hot methanol and water (2:1) .A light brownish crystalline powder was obtained that analyzed for the composition C<sub>28</sub>N<sub>6</sub>OH<sub>24</sub>·2.5H<sub>2</sub>O, Yield (%) = 60. *Anal.* Calc.: C, 66.5; N, 16.6; H, 5.7. Found: C, 66.7; N, 16.6; H, 5.8%.  $\lambda_{max}$ (nm), [log  $\varepsilon$ ]: 269 [4.12], 278 [4.14], 287 [4.13].

<sup>1</sup>H NMR ( $\delta$  ppm in DMSO-d<sub>6</sub>): 4.95(s, 4H), 5.60(s, 4H), 7.10–7.17(m, 4H), 7.20–7.25 (m, 2H), 7.40–7.45 (m,4H), 7.53–7.59(m, 2H), 7.64–7.7(m, 2H), 8.40–8.45 (d,2H).

<sup>13</sup>C NMR ( $\delta$  ppm in DMSO-d<sub>6</sub>): 156, 151, 149,142,137,136, 123, 122,119,111,65,49.

IR(KBr pellets):3342  $\nu_{(OH)}$ , 1591  $\nu_{(C=N-benzim, pyr)}$ , 1080  $\nu_{(C-O)}$ , 1458 $\nu_{(C=N-C=C-benzim)}$ , 749  $\nu_{(c=c benz)}$ 

#### 2.5. Preparation of complex

#### 2.5.1. Preparation of [LClFe-O-FeCl<sub>3</sub>]

The ligand [L] (100 mg, 0.22 mmol) was dissolved in methanol (10 ml). A methanolic solution (5 ml) of anhydrous FeCl<sub>3</sub> (35.35 mg, 0.22 mmol) was added to the ligand solution. The solution turned deep red. After 10 min's of stirring a dark reddish-orange colored product was formed which was centrifuged and washed with small amount of cold methanol. The product obtained was then recrystallized from a DMF: methanol (1: 2) mixture, brown colored compound crystallized on cooling and was dried over  $P_2O_5$ . The complex analyzed for the composition  $C_{28}N_6H_{24}$ - $O_2Cl_4$  Fe<sub>2</sub>.2.C<sub>3</sub>H<sub>7</sub>ON, Yield (%) = 55.

Anal. Calc.: C, 46.5; H, 4.3; N,12.7. Found: C, 47.0; H, 4.1; N, 12.4%.

 $\lambda_{\rm max}$  (nm),  $[\log\varepsilon]$  = 269[3.91], 278[3.87], 287[3.79], 312[3.65], 359[3.50].

 $IR(cm^{-1}, KBr) = 1595 v_{(C=Npyr)}, 1108 v_{(C-O)}, 1478 v_{(C=N-C=C-benzim)}, 752 v_{(c=c benz)}$ 

2.6. Oxidation of aromatic alkynes by [LClFe–O–FeCl<sub>3</sub>] using TBHP and  $H_2O_2$ 

#### 2.6.1. Experimental procedure

The complex 5 mg (0.005 mmol), was dissolved in acetonitrile (10 ml), a solution of aromatic alkyne (0.114 mmol) in acetonitrile and 0.02 ml of oxidant (TBHP/or  $H_2O_2$ ) were added to this. The catalyst: substrate: oxidant ratio was kept as, 1:20:20. The reaction mixture was stirred at 60 °C on a water bath for 1 h and monitored via TLC. The reaction mixture was evaporated on a rotatory evaporator to near dryness. The residue was treated with small portions of distilled water and extracted with ethylacetate. The products formed were analyzed using GCMS.

#### 3. Result and discussions

#### 3.1. Description of the crystal structure of [LClFe–O–FeCl<sub>3</sub>].2.C<sub>3</sub>H<sub>7</sub>ON

The molecular structure of the complex is comprised of two iron atoms having inequivalent coordination sites. (Fig. 1) shows the final structure of the dinuclear compound. Fe(1) is six coordinated in a distorted octahedral environment by two benzimidazole nitrogens N(1) and N(4), ether oxygen O(1) and the bridging oxide oxygen O(2), forming the equatorial plane. While one Cl<sup>-</sup> ion and the oxygen of one of the solvent molecules, (DMF) occupies the fifth and the sixth coordination positions. Fe (2) is tetrahedrally



Fig. 1. Showing the final structure of  $\mu$ -oxo bridged diferic complex. The uncoordinated solvent molecule and hydrogen's have been removed. Disorder in the coordinated solvent molecule is shown.

coordinated by three  $Cl^{-}$  ions and the bridging oxide oxygen O(2). The Fe (1)–O(2)–Fe (2) angle is almost linear (175.24°). The O(2)– Fe(1) and O(2)–Fe(2) distances [1.793 and 1.746 Å] are significantly different in accordance with the unsymmetry of the molecule (Table 2). Average Fe-Cl distances of Fe (2)-Cl (2.212 Å) are also significantly shorter than Fe (1)-Cl distance (2.308 Å). The solvent oxygen O(3) is strongly bonded to the metal ion Fe(1) than the ethereal oxygen O(1) with respective bond lengths being 2.180 and 2.353 Å. The bond length O(1)-Fe(1) is found to be relatively longer than the remaining bond lengths in the diiron complex. In similarly ligated Cu(II) complexes [Cu(DGB)(Phen)][ClO<sub>4</sub>]<sub>2</sub> and [Cu(DGB)<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>N<sub>3</sub>O<sub>7</sub>)].4C<sub>3</sub>H<sub>7</sub>NO where DGB is Bis (2-benzimidazolylmethyl) ether, the O(1)-Cu bond length are reported to be [2.571 and 2.583 Å], respectively [23,24]. These are even longer than the O(1)-Fe(1) [2.353 Å] bond length found in the present case.

A plane may be passed through Fe(1) and the major portion of the ligand except the two pyridine rings. Only oxygen O1 is

Table 2						
Selected	bond	lengths	(Å) and	bond	angles (°).	

0.16 Å out of this plane. The two pyridine rings lie on the same side of this plane along with the coordinated solvent molecule and the  $[FeCl_3O]^{2-}$  moiety. The two pyridine rings are almost perpendicular to each other (dihedral angle 85.9(2)°).

#### 3.2. IR spectral properties and electronic spectroscopy

The free ligand L has characteristic IR bands at 1591 and 1458 cm<sup>-1</sup>. These are assigned to pyridyl (mainly  $v_{C=N}$  stretch) and benzimidazole  $v_{C=N-C=C-}$  stretching frequencies, respectively. Small shift upon complexation is attributed to the binding of imine nitrogen's to iron (III) [25,26]. The electronic spectra of ligand L and the [LCIFe–O–FeCl<sub>3</sub>] complex were recorded in HPLC grade DMF. Three peaks in the range 265–285 nm are observed in the free ligand and its complex and are assigned to intraligand  $\pi$ – $\pi$ \* transition of benzimidazole and pyridyl moiety present in the ligating system. In the diiron complex band at 359 nm is assigned as Ox- o  $\rightarrow$  Fe (III) charge transfer bands [27].

Bond lengths (Å)		Bond angles (°)			
N(1)-Fe(1)	2.074(3)	C(1)-N(1)-Fe(1)	120.9(2)	N(1)-Fe(1)-Cl(4)	93.42(8)
N(4)-Fe(1)	2.080(3)	C(7)–N(1)–Fe(1)	133.7(2)	N(4)-Fe(1)-Cl(4)	91.74(8)
O(1)-Fe(1)	2.353(2)	C(10)-N(4)-Fe(1)	120.8(2)	O(3)-Fe(1)-Cl(4)	167.14(7)
O(2)-Fe(1)	1.793(2)	C(11)-N(4)-Fe(1)	133.4(2)	O(2)-Fe(1)-O(1)	164.02(10)
O(3)-Fe(1)	2.180(3)	C(8)-O(1)-Fe(1)	115.33(18)	N(1)-Fe(1)-O(1)	71.58(8)
Cl(4)-Fe(1)	2.3076(14)	C(9)-O(1)-Fe(1)	114.42(18)	N(4)-Fe(1)-O(1)	71.48(9)
Cl(1)-Fe(2)	2.2196(16)	Fe(2)-O(2)-Fe(1)	175.24(15)	O(3)-Fe(1)-O(1)	72.54(9)
Cl(2)-Fe(2)	2.2153(12)	C(32)–O(3)–Fe(1)	129.0(3)	Cl(4)-Fe(1)-O(1)	94.59(6)
Cl(3)-Fe(2)	2.2008(12)	O(2)-Fe(1)-N(1)	106.52(10)	O(2)-Fe(2)-Cl(3)	110.52(8)
O(2)-Fe(2)	1.746(2)	O(2)-Fe(1)-N(4)	108.30(10)	O(2)-Fe(2)-Cl(2)	113.16(9)
		N(1)-Fe(1)-N(4)	142.99(10)	Cl(3)-Fe(2)-Cl(2)	108.79(5)
		O(2)-Fe(1)-O(3)	91.49(10)	O(2)-Fe(2)-Cl(1)	112.36(9)
		N(1)-Fe(1)-O(3)	82.67(10)	Cl(3)-Fe(2)-Cl(1)	105.77(6)
		N(4)-Fe(1)-O(3)	84.26(10)	Cl(2)-Fe(2)-Cl(1)	105.85(6)
		O(2)-Fe(1)-Cl(4)	101.37(8)		



#### 3.3. NMR spectroscopy

<sup>1</sup>H NMR spectrum of the free ligand [L] (Fig. 2) shows signal at 8.4 ppm and is assigned to the H's adjacent to the N atom of the pyridyl group. A singlet is also observed at 5.6 and 4.95 ppm which is assigned to the CH<sub>2</sub> protons linked to pyridine ring and CH<sub>2</sub> protons attached with ether O atom. Multiplets are observed in the range 7.1–7.8 ppm and are assigned to the protons of the benz-imidazole ring and pyridine ring [19]. <sup>13</sup>C NMR spectrum of the ligand (Fig. 3) shows signals at 64 and 49 ppm assigned to methylene carbons linked to ether O atom and to the pyridine ring. Benzene ring and pyridine ring carbons appear in the range (111–124 ppm) and (122–137 ppm) [28], respectively.

#### 4. Reactivity of [LClFe-O-FeCl<sub>3</sub>] using TBHP and H<sub>2</sub>O<sub>2</sub>

#### 4.1. Oxidation of aromatic alkynes

The oxidation of aromatic alkynes using tert-butylhydroperoxide (TBHP) and  $H_2O_2$  as an oxidant in acetonitrile was studied in the presence of the iron (III) complex. In a control experiment in the absence of the Iron complex no product formation occurred. While when the reaction is performed in the presence of the salt  $FeCl_3$  the reaction is very slow with very poor yields. This indicates that the present metal complex is required and is indeed acting as a catalyst. The oxidation of Diphenyl acetylene was studied in more detail to optimize the reaction variables such as solvent, catalyst: substrate: oxidant ratio, type of the oxidant, temperature and length of reaction time.

#### 4.1.1. Solvent dependence

The activity of iron (III) complex was checked in different solvents (acetonitrile, acetone and methanol) with tert-butylhydroperoxide (TBHP) as the oxidant while keeping the catalyst: substrate: oxidant ratio as 1:20:20 (Table 3). Best conversions have been observed in acetonirile. In this solvent% yield of the dicarbonyl product 1 is nearly thrice (47.6%) to that found in acetone (14.2%). Further the products 2, ester and 3, ketone due to over oxidation through oxidative cleavage or rearrangement are substantially low (9 and 10%) as compared to that found in acetone (21.6, 27.4%) as reaction medium. When the reaction is carried out in a hydroxylic solvent like methanol the product profile is quiet different. Besides the dicarbonyl product, formation of new monoketonic products  $\alpha$  hydroxy ketone **4** (10.5%) and  $\alpha$  methoxy ketone 5 (13.5%) are also formed while cleavage products are nil. The formation of the product  $\alpha$  methoxy ketone indicates participation of solvent methanol in the oxidation reaction whereas in



Fig. 3. <sup>13</sup>C NMR of ligand L in DMSO-d<sub>6</sub>.

#### Table 3

Product yields from the oxidation of diphenylacetylene by diiron (III) catalyst in different solvents using tert-butyl hydroperoxide as oxidant, temperature, 60 °C.



<sup>a</sup> Reaction was carried out at temperature 100 °C.

<sup>b</sup> Conversions were determined using 1-Chloronapthalene as internal standard.

non hydroxylic solvents, like acetonitrile and acetone, formation of dicarbonyl and cleavage products shows that these solvent's don't participate in the oxidation reaction. The formation of products **2** and **5** indicate the presence of t-BuO<sup>•</sup> and CH<sub>3</sub>O<sup>•</sup> radicals. This suggests that the reaction proceeds via a radical pathway; the presence of product **4** also supports this mechanism (Scheme I).

#### 4.1.2. Stoichiometry

If the reaction is carried out with the catalyst: substrate: oxidant ratio of 1:20:100 in acetonitrile with TBHP as the oxidant, dicarbonyl product 1 (23.7%) is formed to a lower degree. The

oxidative cleavage products are found to be slightly higher **2** (13.6%) and **3** (15.7%) when compared to the reaction where ratio of catalyst: substrate: oxidant is 1:20:20. Thus increasing the concentration of the oxidant has a disadvantage and does not promote the oxidation reaction, in the desired direction.

#### 4.1.3. Temperature dependence

When the reaction temperature is increased to  $100 \,^{\circ}$ C the expected dicarbonyl product **1** (17.5%) yield is less than half, and there are no cleavage products .While when the temperature is below 60  $^{\circ}$ C, the% yield of all the products was proportionately low. Increasing the length of reaction time does not have any effect on the product yield of all the products. Thus the reaction is not facilitated by increasing the temperature or reaction time, possibly increased thermal energy causes decay or self binding of radicals, that are the main pathway to oxidized products.

#### 4.1.4. Substrate variation

By using the optimal condition obtained for the oxidation of Diphenyl acetylene, various alkynes were investigated in order to determine the versatility of this catalytic system. The results are summarized in (Table 4).

The nature of substrate has a profound effect on the products formed. With the substrates phenyl propyne, phenyl butyne, phenyl pentyne and TBHP as the oxidant, it is found that phenyl propyne gives a lower yield of the dicarbonyl product **6** (14.4%) in comparison to diphenyl acetylene. Besides the cleavage product **2** (27.3%) a new product that leaves the acetylenic bond intact is also observed **7** (29.0%). A similar kind of observation is inferred for oxidation with phenyl butyne. This is the most selective oxidation reaction found in the present series of aromatic alkynes, with a major product **8** (42.6%). This keeps the acetylenic bond intact and oxidation takes place preferably at the methylene group of the side chain, very poor yield of cleavage product **2** is observed.

It is quiet intriguing that phenyl pentyne has a very low reactivity in comparison to its homologs; poor yields of product **2** and **9** are listed. It seems that the carbon chain length had a large effect on the conversion. Remarkably oxidation of phenyl acetylene results in a cleavage product **2** (81.3%) and trace amount of monoketonic product **10**.

#### Table 4

Oxidation of various alkynes by diiron (III) catalyst using TBHP and H2O2 as oxidant, catalyst: substrate: oxidant ratio of 1:20:20, temperature, 60 °C.

Solvent for reaction	Products	Yield (%)	
		TBHP	$H_2O_2$
Ph - C = C - Ph	(1)	47.6	41.8
	(2)	9.04	-
	(3)	10.0	-
$Ph - C = C - CH_3$	$\begin{array}{c} 0 & 0 \\ \  & \  \\ Ph - C - C - CH_{2} \end{array} $ (6)	14.4	33.8
	(2)	27.3	-
	Ph-C=C+O( <b>7</b> )	29.0	-
$Ph \longrightarrow C \longrightarrow C \longrightarrow CH_2 \longrightarrow CH_3$	$P_{h} - C \equiv C - C - C H_{2}^{(8)}$	42.6	-
	(2)	3.3	-
$Ph - C = C - CH_2 - CH_2 - CH_3$	0    H. H. H. <b>(9</b> )	5.7	-
	Ph— $C - C - C - C - C - CH_3$	2.0	
	(2)	3.8	-
Ph→C≡CH	(2)	81.3	_
	0	5.5	-
	$\begin{array}{c} \parallel (10) \\ Ph \longrightarrow C \longrightarrow CH_3 \end{array}$		

#### 4.1.5. Nature of the oxidant

When similar reactions are performed with H<sub>2</sub>O<sub>2</sub> as the oxidant, % yield of products are comparatively low. Hence we find that TBHP is a better oxidant in the present case.

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#### **Appendix A. Supplementary material**

CCDC 840315; contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.ica.2012.04.015.

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