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Catalytic oxidation of benzene by mononuclear copper(II) complexes with a bis(imidazolyl)methane ligand

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Catalytic oxidation of benzene under mild conditions is one of the most challenging reactions in synthetic chemistry. In order to develop a hydroxylation catalyst for benzene, we have designed and synthesized new copper(II) complexes with the bidentate ligand bis(1,4,5-trimethyl-2-imidazolyl)methane (Me_6bim), [Cu(Me_6bim)X_2] (X = Cl, Br). This ligand provides a reaction space which can be easily accessed by exogenous substrates and has an imidazole group, which is a typical ligand of metalloenzymes. These complexes exhibit catalytic oxidation of benzene in the presence of excess H_2O_2 at room temperature in aqueous MeCN solution to yield phenol and 1,4-benzoquinone.

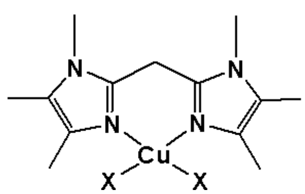
Keywords: Bioinorganic chemistry, Metalloenzymes, Catalysts, Oxidation, Benzene oxidation, Mononuclear copper, Copper, Bis(benzimidazolyl)methane

Phenol is one of the most important feedstocks in the production of resins, fibers and related materials. More than 90 % of the phenol consumed in the world is produced via the so-called cumene method, a three step process which coproduces acetone in a 1:1 molar ratio with respect to phenol.[1] However, due to the inherent environmental and energetic issues related to this process, many efforts are in progress for the development of a new route for phenol production via a one step process through direct oxidation of benzene.

The direct and catalytic transformation of arenes to various useful chemicals via C-H activation is of considerable interest to chemical industries and remains a challenge to chemists.[2] The aromatic ring is resistant to oxidation because of its stability and the high dissociation energy of the C(sp^2)-H bond. Thus, oxygenation almost invariably requires a highly reactive oxidant under severe conditions. Over the last few years, several reports regarding the use of transition metal complexes as catalysts for aromatic C-H oxidation have been published.[3] Re/HZSM-5 and $H_7PMo_8V_4O_{40}$, which were prepared from the reaction of zeolite-supported Re catalysts and molybdovanadophosphoric acids, have been demonstrated to catalyze the aerobic oxidation of benzene to phenol in the presence of NH_3 and CO, respectively, while titanium silicate (TS-1) zeolites were reported to activate H_2O_2 for synthesis of phenol from benzene in one step.[4-6] Sorokin *et al.*[7,8] reported that the iron complex of μ-nitrido-bridged tetra-*tert*-butylphthalocyanine catalyzes a mild oxidation of benzene accompanied by the NIH shift which resembles a biological aromatic oxidation. Interestingly, the iron complex also oxidized methane to methanol and formic acid. Esmelindro *et al.*[9] demonstrated oxidation of benzene to phenol and 1,4-benzoquinone using a mononuclear Cu(II) complex, [Cu$(BMTEA)_2$Cl]Cl (BMTEA = bis (2-thienylmethyl)-1, 2-ethylenediamine), as the catalyst and hydrogen peroxide as the oxidant. This reaction system oxidized benzene to phenol and 1,4-benzoquinone at 25 °C in MeCN to give a turnover number (TON)[9] = 3.85 after 8 h. Carvalho *et al.*[10] also reported that the mononuclear Cu(II) complexes of 2,2-bipyridine or 1,10-phenantroline promote catalytic oxidation of benzene in the presence of H_2O_2 or *tert*-butyl hydroperoxide as the oxidant in CH_3CN/H_2O solution for 24 h, which exhibited a larger TON of 88.

A copper ion is present in the active site of several metalloenzymes and plays a fundamental role in living systems. Particularly important Cu-containing metalloenzymes include tyrosinase and particulate methane monooxygenase (pMMO), which catalyze the hydroxylation of tyrosine to catechol and methane to methanol, respectively.[11,12] Interestingly, both copper ions in tyrosinase and pMMO are coordinated to the N atoms of the imidazole group of histidine residues. To achieve high oxidation capability and selectivity under mild conditions, many copper complexes have been synthesized. These complexes have provided fundamental insights into the spectroscopic and structural properties.[13-16] However, there are few examples of synthetic copper complexes and metalloenzymes with imidazole ligands.[17-21] In addition, the oxidation reactions of various substrates such as $(R)_2S$, $(R)_2SO$, PPh_3, cyclohexene and cyclohexane have also been reported for some complexes.[22-25] However, the high stability of benzene has discouraged attempts to oxidize benzene to phenol.

In order to develop a hydroxylation catalyst for benzene, we designed and synthesized new copper(II) complexes with bis(1,4,5-trimethyl-2-imidazolyl) methane (Me_6bim), [Cu(Me_6bim)X_2] (X = Cl, Br) (**I**), a bidentate ligand which provides a reaction space that can be easily accessed by exogenous substrates. This ligand also includes an imidazole group. Herein, we report that these complexes react catalytically with benzene in the presence of excess H_2O_2 under mild conditions at 25 °C under atmospheric pressure in MeCN solution to give phenol and 1,4-benzoquinone, as identified by gas chromatography.



Structure of [Cu(Me_6bim)X_2] (X = Cl, Br)

(I)

Materials and Methods

Commercially available reagents and solvents were employed. Hydrogen peroxide (30 *w*/*w*%) was purchased from Wako Ltd.

Electronic absorption spectra were recorded on a Jasco V-570 spectrophotometer. IR spectra of solid compounds were measured as KBr pellets using a Jasco FT/IR-410 spectrophotometer. Electrospray ionization time-of-flight mass spectra, ESI-TOF/MS, were obtained with a Micromass LCT spectrometer. X-band ESR spectra were obtained using a Jeol RE-1X spectrometer at 77 K. Elemental analyses were obtained with a Perkin Elmer CHN-900 elemental analyzer. Gas chromatography/mass spectrometry (GC/MS) measurements were carried out on a Shimadzu GCMS-QP2010.

X-ray crystallography

A single crystal of [Cu(Me_6bim)Cl_2] suitable for X-ray diffraction analyses was obtained from acetone/Et_2O solutions after standing for a few days at room temperature. The crystal was mounted on a glass fiber, and diffraction data were collected on a Rigaku/MSC Mercury CCD using graphite monochromated Mo-K_α radiation at 173 K. Crystal data and experimental details are listed in Tables 1 and 2. The structure was solved by a combination of the direct method (SIR2004) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model and only the hydrogen atoms linked to the μ-benzene molecule were positioned from the D-Fourier map and refined. A Sheldrick weighting scheme was

Table 1—Crystal data and structure refinement for [Cu(Me_6bim)Cl_2]

Empirical formula	$C_{13}H_{20}Cl_2CuN_4$
Formula wt	133.78
Crystal color	Orange, block
Crystal dimensions (nm)	0.10 ×0.05×0.05
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
a (Å)	7.69(2)
b (Å)	12.420(3)
c (Å)	16.524(4)
β (deg.)	97.052(3)
Volume (Å^3)	1566.7(7)
Z	4
D_{calc} (g cm^{-3})	1.555
F (000)	765.00
Radiation	Mo-K_α (λ= 0.71070 Å)
Detectometer	Rigaku/MSC mercury CCD
T (C°)	-100.0
2θ max (deg.)	55.0
Reflections measured (Total)	12237
Observations	3517
Variables	203
Reflection / Parameter ratio	17.33
R_1 / R_w (I>2.00σ(I))	0.0449/0.1080
Goodness of Fit	1.007
Max shift/error	0.000

Table 2— Selective bond lengths (Å) and angles (°) of [Cu(Me_6bim)Cl_2]

Bond lengths (Å)			
Cu(1)-N(1)	1.960(3)	Cu(1)-N(2)	1.970(3)
Cu(1)-Cl(1)	2.238(11)	Cu(1)-Cl(2)	2.237(12)
Bond angles (°)			
N(1)-Cu(1)-N(2)	92.69(13)	Cl(1)-Cu(1)-Cl(2)	103.24(4)
Cl(1)-Cu(1)-N(1)	102.45(10)	Cl(1)-Cu(1)-N(2)	127.20(10)
Cl(2)-Cu(1)-N(1)	130.42(10)	Cl(2)-Cu(1)-N(2)	104.15(11)

employed. Plots of $\Sigma w(|F_0| - |F_c|)^2$ versus $|F_0|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. Neutral atomic scattering factors were obtained from the International Tables for X-ray Crystallography by Cromer and Waber.[26] Anomalous dispersion terms[27] were included in F_{calc}, and the values for $\Delta f'$ and $\Delta f''$ used were the values described by Creagh and McAuley.[28] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[29] All calculations were performed using the crystallographic software package, CrystalStructure.[30,31]

The oxidation reaction products were analyzed by GC/MS spectroscopy. GC/MS conditions: Column DB-5 ms; column length 30.0 m; column temperature 60 °C; injection temperature 210 °C; 100 kPa; t_R (min) 7.3 (*o*-benzoquinone), 10.7 (phenol), 13.0 (*o*-dichlorobenzene).

Synthesis of [Cu(Me$_6$bim)Cl$_2$]

To a MeOH (2 mL) solution of Me$_6$bim (46.4 mg, 0.20 mmol), was added $CuCl_2$ (26.9 mg, 0.20 mmol) in MeOH (1 mL) and then the mixture was stirred at ambient temperature. After 12 hrs, the resulting red-brown precipitate was filtered. [Cu(Me$_6$bim)Cl$_2$] was recrystallized from acetone as dark red block crystals; yield 48.3 mg (65.9 %). FT-IR (KBr, cm^{-1}): ν_{as} 2960 (C–CH$_3$), ν_s 2827 (C–CH$_3$), δ_s 1387 (N–CH$_3$). ESI-TOF-Mass (MeCN, ion mode positive): *m/z* 330.0 [M–Cl]$^+$. Anal. (%): Calcd. for $C_{13}H_{20}N_4CuCl_2$: C, 42.6; H, 5.50; N, 15.3. Found: C, 42.3; H, 5.38; N, 15.1.

Synthesis of [Cu(Me$_6$bim)Br$_2$]

To a MeOH (2 mL) solution of Me$_6$bim (46.4 mg, 0.20 mmol), was added $CuBr_2$ (44.7 mg, 0.20 mmol) in MeOH (1 mL). The mixture was then stirred at ambient temperature. After 8 hrs, the resulting red-brown precipitate was filtered. [Cu(Me$_6$bim)Br$_2$] was recrystallized from acetone as dark red block crystals; yield 39.2 mg (43.0 %). FT-IR (KBr, cm^{-1}): ν_{as} 2947 (C–CH$_3$), ν_s 2866 (C–CH$_3$), δ_s 1403 (N–CH$_3$). ESI-TOF-Mass (MeCN, ion mode positive): *m/z* 357.8 [M–Br]$^+$, 607.8 [M – Br + Me$_2$bim]$^+$.

General procedure for benzene oxidation

The oxidation reactions were performed in a 20 mL vial container sealed with a silicon septum under an argon atmosphere, using MeCN solution as the solvent, H_2O_2 as the oxidant, the Cu(II) complexes as catalysts and *o*-dichlorobenzene as an internal standard material for quantitative analysis by gas chromatography. Solvent, catalyst (1 m*M*), substrate (1 *M*), a small amount of *o*-dichlorobenzene and oxidant (2 *M*) were successively added. The total volume was 2 mL. The reaction mixture was stirred at 25 °C for 24 h. The reaction was quenched by the addition of excess of triphenylphosphine (PPh$_3$) and hexane and then the mixture was filtered with a silica bed. The products were analyzed by gas chromatography.

Product analysis by reaction with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO)

An acetone solution (2 mL) of [Cu(Me$_6$bim)Cl$_2$] (0.15 m*M*) was cooled to −80 °C, and then 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) (20 equiv.) was added to the solution. The resulting mixture was stirred for 1 min and immediately changed from purple to orange (**1**). Additionally, H_2O_2 (20 equiv.) was added to the solution and also stirred for 1 min (**2**).

ESI-TOF-Mass of (**1**) (in acetone at -80 °C, positive ion mode): *m/z* 555.1 [M + 2DMPO + H–Cl]$^+$. ESI-TOF-Mass of (**2**) (in acetone at -80 °C, positive ion mode): *m/z* 423.1 [M + DMPO + O–Cl]$^+$.

Results and Discussion

Syntheses and spectroscopic and structural properties of [Cu(Me$_6$bim)X$_2$] (X = Cl, Br)

Two Cu(II) complexes [Cu(Me$_6$bim)X$_2$] (X = Cl, Br) were prepared by the reaction of $CuCl_2$ or $CuBr_2$ with Me$_6$bim in MeOH solution. The electronic absorption and ESR spectral data of samples in MeCN solution are listed in Table 3. The spectra have *d-d* bands in the wavelength range of 950-960 nm. This lower energy range suggests that the complexes have square planar geometry. The spectra also exhibit an intense absorption band at 360-530 nm, which is assignable to LMCT transitions from X (X = Cl, Br) to Cu(II) and from N(imidazole) to Cu(II).[32] The ESR spectra of the complexes showed that their metal geometries are slightly different in solution. Using the parameter $|A_{//}|$ obtained from ESR spectra, we can discuss the distortion around the Cu(II) ions; a value larger than 180 G indicates square planar geometry and a smaller value indicates distortion from planar towards tetrahedral geometry. The $|A_{//}|$ values of

Table 3—Spectroscopic properties of [Cu(Me$_6$bim)X$_2$][a] in MeCN

	UV-vis λ (nm)/ ε (M^{-1} cm^{-1})		ESR	
Complexes	LMCT	*d-d*	$g_\perp$, $g_{//}$	$\lvert A_{//}\rvert$ (G)
[Cu(Me$_6$bim)Cl$_2$]	360/1730, 530/110	950/120	2.08, 2.30	160
[Cu(Me$_6$bim)Br$_2$]	420/800, 530/290	950/220	2.08, 2.29	150

[a](X = Cl, Br)

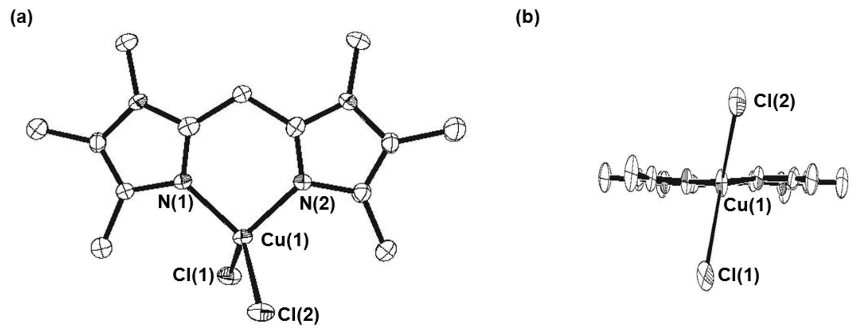
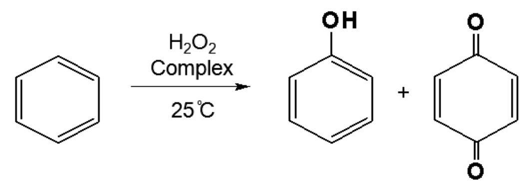


Fig. 1—ORTEP view of [Cu(Me_6bim)Cl_2]. [(a) Top view; (b) Side view].

[Cu(Me_6bim)Cl_2] and [Cu(Me_6bim)Br_2] are $|A_{//}|$ = 160 and 150 G, respectively, indicating that the latter is more distorted from planar geometry.[33] This difference may arise from the steric hindrance of halogen ions because Br^- (1.85 Å) has a larger ionic radius than Cl^- (1.75 Å) and Br^- ion may provide larger steric hindrance between Br^- ions than Cl^- ions. The geometry of the metal center of [Cu(Me_6bim)Br_2] has more distortion from square-planar to a tetrahedral geometry relative to the geometry of [Cu(Me_6bim)Cl_2] in solution.

Crystal structure of [Cu(Me_6bim)Cl_2]

Fortunately, we obtained a single crystal of [Cu(Me_6bim)Cl_2] from an acetone solution. The X-ray crystallographic analysis revealed that [Cu(Me_6bim)Cl_2] is a four-coordinated mononuclear Cu(II) complex with ligands provided by Me_6bim and two Cl^- anions. A perspective view is displayed in Fig. 1 and the selected bond lengths and angles are listed in Table 2. The Cu-N(imidazole of Me_6bim) are Cu(1)–N(1) 1.960(3) Å and Cu(1)–N(2) 1.970(3) Å and the Cu-chloride atoms are Cu(1)–Cl(1) 2.238(11) Å and Cu(1)–Cl(2) 2.237(12) Å. The former and the latter are both within the normal ranges of Cu-N (1.954 – 2.029 Å) and Cu-Cl bonds (2.233 – 2.263 Å) reported previously.[34] The bond angles around the Cu(II) ion are N(1)–Cu(1)–N(2) 92.69(13)°, Cl(1)–Cu(1)–N(1) 102.45(10)°, Cl(2)–Cu(1)–N(1) 130.42(10), Cl(1)–Cu(1)–N(2) 127.20(10)°, Cl(2)–Cu(1)–N(2) 127.20(10), and Cl(1)–Cu(1)– Cl(2) 103.24(4)°. As expected from the EPR parameter $|A_{//}|$ described above, the $CuCl_2$ plane in [Cu(Me_6bim)Cl_2] is distorted from the CuN_2 plane. The dihedral angle between the CuN_2 and $CuCl_2$ planes is 69.6°, showing that it is twisted towards tetrahedral geometry rather than square-planar geometry. The imidazole rings are also twisted away from the CuN_2 plane. The dihedral



Oxidation reaction scheme of benzene

Scheme 1

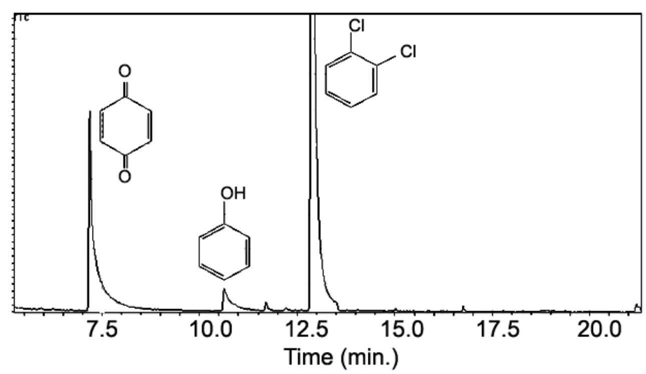


Fig. 2—Chromatogram of the reaction products after 24 hr in MeCN.

angle between the CuN_2 plane and the imidazole ring planes (N1,C6,N2,C3,C2 and N2,C8,N4,C9,C13) are 5.9 and 6.3°, respectively, although the angle between the planes of the imidazole rings is 1.8°.

Oxidation of benzene by [Cu(Me_6bim)X_2] (X = Cl, Br)

The catalytic oxidation of benzene by the Cu(II) complexes was investigated according to Scheme 1. The reaction was carried out using H_2O_2 as an oxidant in MeCN solution at 25 ºC. After 24 hrs, we identified the conversion of benzene to phenol and 1,4-benzoquinone, based on the injection of authentic and internal standards by gas chromatography (Fig. 2). The chemical conversions by the complexes [Cu(Me_6bim)X_2] (X = Cl, Br) employed as catalysts are presented in Table 4. The results clearly indicate that [Cu(Me_6bim)Cl_2] and [Cu(Me_6bim)Br_2] can oxidize benzene to phenol and 1,4-benzoquinone. As is clear from Table 4, 1,4-benzoquinone is always obtained in a higher yield relative to phenol. This indicates the likelihood that the oxidized phenol has been further oxidized to 1,4-benzoquinone. This means that the oxidation reaction proceeds through a hydrogen abstraction by the R-O$^\bullet$ radical formed by homolytic cleavage of H_2O_2 bound to the metal center, as shown in Scheme 2. First, a Cu(II)−hydroperoxo intermediate species is generated by reaction of Cu(II) complex with H_2O_2. Then the Cu(II)−hydroperoxo species undergoes homolytic cleavage of the O−O bond to generate a phenoxyl radical which reacts with benzene to form phenol, and furthermore the para-proton of the obtained phenol is abstracted by another radical to form 1,4-benzoquinone. In order to elucidate this reaction mechanism, we attempted to obtain evidence of the generation of radical species using a UV−vis spectrophotometer at low temperature. This attempt did not succeed because of its high reactivity and low stability. Recently, in the oxidation reaction of 10-methyl-9,10-dihydroacridine and 1,4-cyclohexadiene as exogenous substrates by copper complex[35-37], Itoh *et al.*[38,39] succeeded in trapping the LCu(II)−O$^\bullet$ radical species generated by homolytic cleavage of the O−O bond in LCu(II)−OOH by using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a radical trap reagent. We also carried out this radical trap experiment for confirmation of the intermediates in our system. To an acetone solution of [Cu(Me_6bim)Cl_2] cooled to −80 °C, was added DMPO and H_2O_2. The resultant solution was injected into ESI-MS apparatus. Fortunately, we succeeded in observing the mass spectral features assignable to $[M + DMPO + O-Cl]^+$ and $[M + 2DMPO + H - Cl]^+$ at *m*/*z* 423.1 and 555.1, thus confirming the generation of Cu(II)−O$^\bullet$ species. Based on the above, we propose that the formation of benzene and 1,4-benzoquinone proceeds via the radical reaction.

Table 4—Oxidation products and TON[a] for [Cu(Me_6bim)X_2][b]

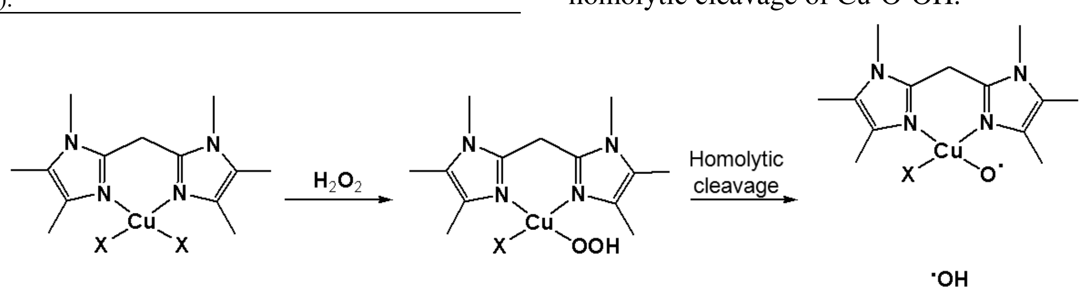
Complexes	Phenol	Quinone
[Cu(Me_6bim)Cl_2]	3.4	16
[Cu(Me_6bim)Br_2]	3.1	12

[a]TON: moles of product per moles of catalyst.
[b](X = Cl, Br).

As shown in Table 4, [Cu(Me_6bim)Cl_2] has higher oxidation activity than [Cu(Me_6bim)Br_2], especially for generation of 1,4-benzoquinone. This may be due to the slight difference in geometries between the two complexes, as expected from their different ESR $|A_{//}|$ values. It thus appears that the Br^- ions of [Cu(Me_6bim)Br_2] provide more steric hindrance relative to the Cl^- ions of [Cu(Me_6bim)Cl_2]. This steric hindrance may lead to less attraction of hydrogen atoms and less reactivity of substrates.

Conclusions

The oxidation of benzene to phenol is well known as a very difficult reaction because benzene is non-polar and has a high C-H dissociation energy. It is therefore challenging to develop a one-step hydroxylation catalyst of for reactions of benzene under mild conditions. We have designed and synthesized new Cu(II) complexes with an imidazole derivative, Me_6bim, [Cu(Me_6bim)X_2] (X = Cl, Br). These complexes have bidentate ligands which provide an easily-accessible reaction space for exogenous substrates and have the imidazole group which is commonly employed in the active sites of metalloenzymes. The [Cu(Me_6bim)Cl_2] complex was found to promote the oxidation of benzene at room temperature in the presence of H_2O_2 to generate phenol and 1,4-benzoquinone. The hydroxylation mechanism elucidated by a combination of DMPO radical trap and ESI-MS methods, proceeds through a radical reaction with the radicals generated by homolytic cleavage of Cu-O-OH.



Proposed reaction mechanism with H_2O_2

Scheme 2

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