Journal of Education for Pure Science- University of Thi-Qar
Vol.12, No2 (December, 2022)
Website: jceps.utq.edu.iq Email: jceps@eps.utq.edu.iq

DOI: http://doi.org/10.32792/utq.jceps.12.02.25

A Low-cost Manganese Complex Catalyst for Phenolic Coupling and Further Oxidation of Phenols

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Received 4/10/2022 Accepted 24/10/2022 Published 01/12/2022

Abstract:

Binuclear manganese (Mn) complexes have been prepared as selective oxidants. Here, the oxidative coupling of phenols under manganese (Mn)-catalyzed conditions were described to form biphenols, ortho-quinones and benzoxepines. Manganese(III) picolinate (Mn (III) (PIC)$_3$ H$_2$O, complex (**1**) is used as a low- cost and easy to prepare catalyst which activates by periodic acid and some organic substrates can be oxidized after the activation process proposing that the manganese is converted to a higher oxidation state. In this study, catalytic oxidation reactions from a mononuclear Mn complex can be used to perform manganese catalysis that usually requires a binuclear complex. The formation of biphenols was successfully determined by using ^{1}HNMR.

Keywords: Catalyst, Phenolic oxidation, Manganase complexes.

Introduction:

Unfunctionalized hydrocarbon and phenolic oxidation is important in organic chemistry and wide studies have been done [1]. So far, the challenge remains for developing an appropriate oxidation processes such as the enhancement of stereo-, chemo- and regioselectivity and the usage of environmentally friendly,

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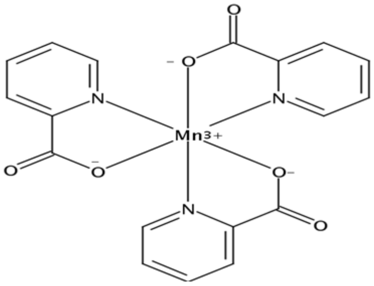
relatively inexpensive oxidants and catalytic metals [2]. The oxidation of phenols has been widely studied, particularly their one-electron (1e) oxidation, due to their relationship to many biological approaches [3-10]. Phenol oxidation by 1e oxidants mostly participates by the generation of phenoxy radicals with losing the phenolic protons. It is a process that requires a proton-coupled electron-transfer which could participate in concerted or stepwise pathways [11-13]. Otherwise, phenol oxidation by metal–oxo species might be involve a mechanism of H-atom abstraction [14-15] as shown in equation 2.

$$\mathrm{PhOH} + \mathrm{M}^{+} \rightarrow \mathrm{PhO}^{\bullet} + \mathrm{H}^{+} + \mathrm{M} \qquad (1)$$

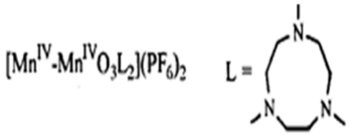
$$\mathrm{PhOH} + \mathrm{M{=}O} \rightarrow \mathrm{PhO}^{\bullet} + \mathrm{M{-}OH} \qquad (2)$$

Binuclear manganese complexes have become of interest in the few past years because of their important role in biological redox systems [16-17]. Consequently, numerous efforts to synthesize and characterize these complexes have been undertaken. Binuclear manganese complexes have been presented in many studies to catalyze many oxidation reactions, such as the oxidation of hydrocarbons [18], alcohols [19], epoxidation of alkenes [20] and bleaching [20]. A study by Hage *et al.* that highlighted the water-soluble alkenes epoxidation with hydrogen peroxide and binuclear complex (**2**) at pH= 10 and they try to realize the bleaching process mechanism [20]. In their study, a considerable hydrogen peroxide excess was required as oxygen was also formed as complex (**2**) demonstrates strong catalase activity. Later, Barton *et al.* suggested that complex (**2**) can activates by oxidants instead hydrogen peroxide that cannot generate oxygen [21]. This can more efficiently oxidize organic substrates. They used periodic acid as a co-oxidant to oxidize 2,4-di-t-butylphenol (**3**) in pyridine as no oxygen was formed and observed to give the biphenyl compound (**4**) 3,3′,5,5′-tetra-tert-butyl 2,2′- biphenol, (TBBP). However, complex (**2**) is an expensive catalyst and requires multiple steps to synthesize and contains an expensive ligand (1,4,7-trimethyl-1,4,7-triazacyclononane). Here, we have used a simple Mn (III) $(\mathrm{PIC})_3\ \mathrm{H_2O}$ complex (**1**) instead of complex (**2**) to carry out the same reaction. First, several attempts were spent to crystalize out and isolate the reactive complex of (**1**) but were failed then we have performed the oxidation of (**3**) to obtain (**4**) to give support for formation of a binuclear complex. The phenolic coupling aspect of (**4**) comes as an experimental evidence for formation of a reactive complex as we could not isolate this complex. The further oxidation of biphenol (**4**) by complex (**1**) and equivalents of periodic acid led to form 3,3′,5,5′-tetra-tert-butyl 2,2′-diphenoquinone, (**5**) (TBDQ), which then rearranges to be 2,4,7,9-tetra-tert-butyloxepino[2,3-b] benzofuran, (**6**) (TBOBF) (Scheme1). Complex (**1**) can be easily synthesized in one step which does not required expensive starting materials. Complex (**1**) has been used in many studies, such as redox chemistry [22-26] and in oxidation reactions [27-29].

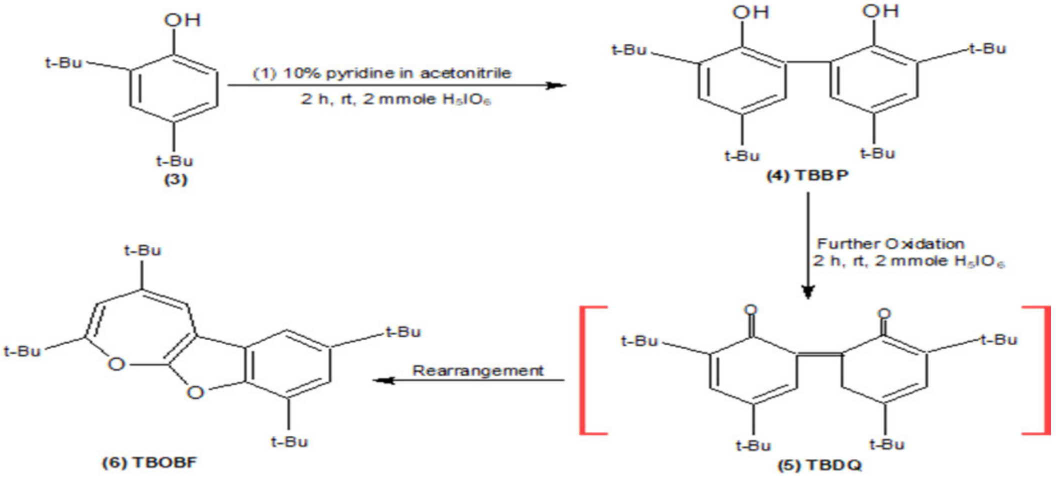
Recent studies have addressed the ability to further oxidize phenol (**3**) under copper (Cu)-catalyzed aerobic oxidation to form TBDQ and TBOBF [30-32] which supports our approach to use this system as evidence for the formation of a reactive Mn complexes.



Complex (**1**)


$[Mn^{IV}\text{-}Mn^{IV}O_3L_2](PF_6)_2$

Complex (**2**)



Scheme 1

2- Experimental Section

2.1- Materials and Chemicals

Periodic acid and picolinic acid were purchased from Aldrich chemical company, manganese (III) acetate from Asia Pacific Specialty Chemicals Company, 2,4-di-t butylphenol from Combi-Blocks company and pyridine from Fluka.

2.2- Synthesis of Manganese (III) picolinate. H_2O (1)

A solution of picolinic acid (2.76 g, 0.224 mmol) in hot acetonitrile (MeCN) (40 ml) was carefully added to a solution of manganese(III) acetate $Mn(OAC)_3$ (2 g, 0.0746 mmol) in hot acetonitrile (25 ml) and stirred until red crystals were formed. The solution was then filtered, and the red crystals were collected in 56 % yield. Crystals were suitable for analysis by X-ray Crystallography.

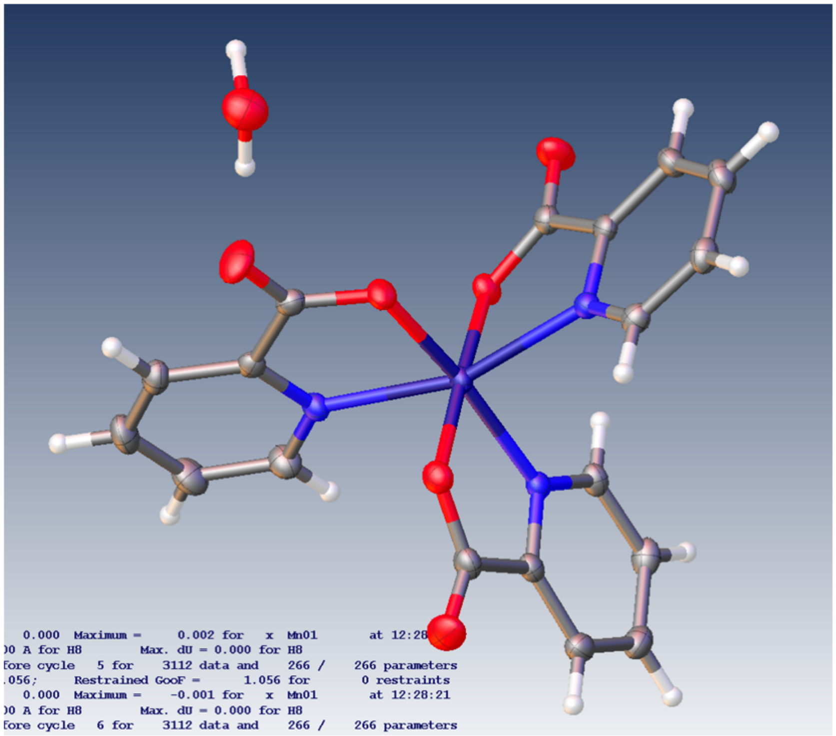
2.3- Synthesis of biphenol (4), ortho-quinone (5) and benzoxepine (6).

A solution of Mn (III) $(PIC)_3$ H_2O (0.02 g, 0.05 mmol), 2,4-di-t-butylphenol (0.206 g, 1mmol) and periodic acid (0.455 g, 2 mmol) in 10% pyridine in acetonitrile (15 ml) was stirred at the room temperature (rt) for 2h and the reaction progress was watched by TLC. The mixture was then extracted with ethyl acetate (3 x 15 ml), the extracts were washed with water and sat. $KHSO_4$ (~2ml) to remove pyridine and washed again with water and sat. Na_2CO_3 (~2ml) to remove the remaining periodic acid. The extracts then evaporated to give a brown product of 3,3′,5,5′-tetra-tert-butyl 2,2′- biphenol, TBBP in 60% yield. To form TBDQ and TBOBF, the same procedure was repeated using an increased amount of periodic acid (4mmol) for 4 h to ensure the further oxidation of TBBP. The product was purified by column chromatography and ^{1}HNMR was performed on all products.

3- Results and Discussions:

The presence of complex (**1**) as an oxidant and catalyst was characterized and confirmed by X-ray Crystallography as shown in Figure 1. Added oxidants (periodic acid and hydrogen peroxide) to complex

(**1**) in pyridine gave a green solution indicate formation of a new complex. Literature reports a Mn^{III}-Mn^{IV} binuclear complex to be green [33]. However, diffusion with ether did not isolate any crystals, so oxidation chemistry investigated to give evidence for a new complex formed.



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  0.000  Maximum =     0.002 for   x  Mn01       at 12:28
00 A for H8        Max. dU = 0.000 for H8
fore cycle   5 for    3112 data and    266 /    266 parameters
.056;     Restrained GooF =      1.056 for      0 restraints
  0.000  Maximum =    -0.001 for   x  Mn01       at 12:28:21
00 A for H8        Max. dU = 0.000 for H8
fore cycle   6 for    3112 data and    266 /    266 parameters
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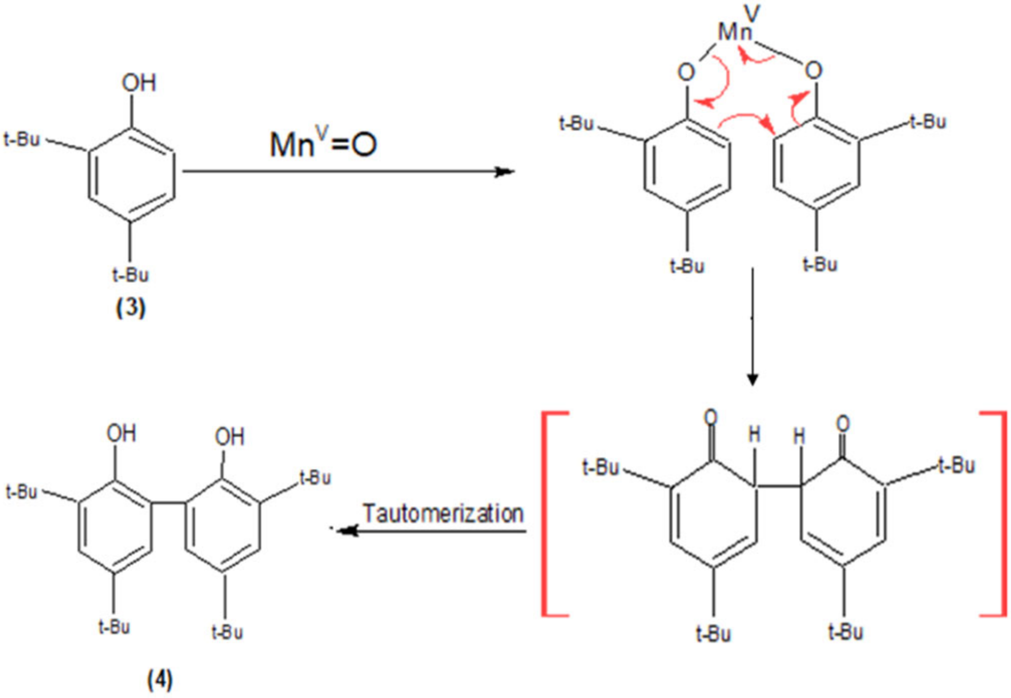
Figure 1: The Molecular structure of complex (**1**)

[Mn violent; O red; H white; N blue]

Periodic acid was selected as an appropriate co-oxidant, where the formation of oxygen was not observed after adding a solution of complex (**1**) in pyridine. 2,4-Di-t-butylphenol (**3**) oxidation in pyridine with complex (**1**) (0.05 mmol) and periodic acid (2 mmol) formed the biphenyl compound (**4**). Further oxidation of (**4**) using an excess of periodic acid (4 mmol) was also observed to TBDQ (**5**) which then rearranged to TBOBF (**6**) as indicated in the literature. However, the absence of complex (**1**) in the reaction of (**3**) with periodic acid displayed a slow and incomplete formulation of (**4**) which was formed after 24h. It clearly seems that a new species have been formed which is responsible for the oxidation process which is clear from the reality that with (**3**), three different products were obtained depending upon the absence of complex (**1**) or not. Previously, the addition of complex (**2**) to (**3**) showed some reaction, suggesting that complex (**2**) is not the oxidizing species which then offered support to their theory of a $Mn^{V}{=}O$ compound [21]. Herein, we have potentially demonstrated a similar $Mn^{V}{=}O$ compound has been formed from complex (**1**) that is an oxidant of (**3**) via $Mn^{V}{=}O$, by oxidative coupling (**4**), (Scheme 2) and substituted ortho-quinone (**5**) is obtained. For further oxidation, a full change in selectivity is noticed for benzoxepine (**6**). The generation of (**6**) is reqular with an oxidative dimerization of (**3**) to biphenol (**4**) via a subsequent oxidation to diquinone (**5**).



Scheme 2

For an evidence of our approach to form TBOBF, Meier's group identified TBOBF as the unknown oxidation product through integrating theoretical and experimental studies [34], a formation mechanism starting with (**3**) as a starting material then coupling oxidation reaction intermediated by appropriate oxidants first forms to TBBP (**4**). In the presence of further oxidant, (**4**) gets oxidized again generating the corresponding diquinone form TBDQ (**5**). Then, spontaneous isomerization of (**5**) occurs generating of pale yellow TBOBF (Scheme 1). The formation of TBOBF (**6**) starting from (**3**) is reported in the literature rarely [35-38]. A ^{1}H NMR spectrum indicated a clear 60% conversion of the starting material (**3**) to biphenolic (**4**) after 2h reaction with complex (**1**) and periodic acid and further oxidation gave TBOBF (**6**) via TBDQ (**5**) (as shown in attached appendices).

4- Conclusion:

We have briefly showed the utilization of manganese picolinate complex to catalyze organic substrates oxidation during an $Mn^{V}=O$ species. The oxidative coupling of phenols under manganese (Mn)-catalyzed conditions were described that allow to form biphenols, ortho-diquinones and benzoxepines. This is a potential alternative catalyst to expensive binuclear manganese complexes.

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