



Methyltrioxorhenium-catalyzed aerobic oxidative coupling of 2-naphthols to binaphthols

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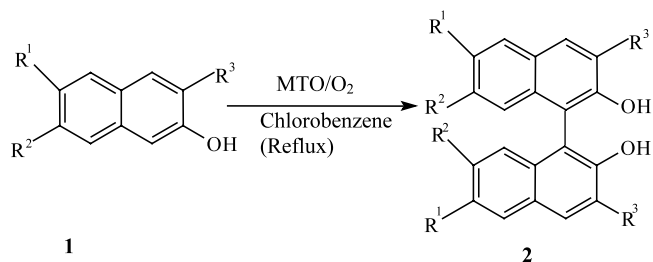
Abstract—A variety of 2-naphthols have been selectively oxidized to their corresponding 1,1'-bi-2-naphthols in excellent yields with molecular oxygen using methyltrioxorhenium as catalyst. © 2003 Elsevier Science Ltd. All rights reserved.

The methyltrioxorhenium (MTO)/hydrogen peroxide oxidation system first reported by Herrmann and co-workers¹ in 1991 for epoxidation of olefins has proved to be an efficient and versatile system for various oxidation reactions.² The important features of MTO as a catalyst are its ease of synthesis, commercial availability, stability in air and efficiency in acting as a homogeneous oxidation catalyst for hydrogen peroxide in both aqueous and organic solvents. Molecular oxygen is an attractive oxidant and the development of synthetic methodologies using molecular oxygen is a rewarding goal both from economic and environmental points of view.³ However, to the best of our knowledge there is only one literature report which describes the oxidation of triphenylphosphines to triphenylphosphine oxides by molecular oxygen using methyltrioxorhenium as the catalyst.⁴

Oxidative coupling of 2-naphthols is an important synthetic transformation as 1,1'-bi-2-naphthols are widely used chiral inducers in synthetic organic chemistry.⁵ A wide variety of stoichiometric methods using FeCl₃,⁶ K₃Fe(CN)₆,⁷ Mn(acac)₃,⁸ and Cu(II)-amine complexes⁹ as oxidative coupling reagents have been reported in literature for this transformation. However, these methods suffer from drawbacks such as the use of an expensive oxidant (AgCl), the production of copious amounts of heavy metal wastes and the need for high temperatures. Recently several catalytic methods using chiral diamine-copper complexes,¹⁰ CuSO₄/Al₂O₃,¹¹ VO(acac)₂,¹² CuCl¹³ and mesoporous molecular sieves¹⁴ as the catalysts and molecular oxygen as the primary

oxidant have also been reported in the literature. Most of these methods require longer reaction times and complex preparations of the catalyst, leaving scope for further improvement in the catalytic oxidative coupling of 2-naphthols.

As part of our studies on oxidation with molecular oxygen as the primary oxidant¹⁵ we report a simple and convenient method for the oxidation of 2-naphthols **1** to their corresponding 1,1'-bi-2-naphthols **2** in excellent yields by using molecular oxygen as the sole oxidant and methyltrioxorhenium as the catalyst (Scheme 1). The oxidation of various substituted 2-naphthols was carried out with molecular oxygen in refluxing chlorobenzene using methyltrioxorhenium as catalyst.¹⁶ All the substrates studied were converted smoothly and selectively to their corresponding *ortho-ortho* coupled products in excellent yields. These results are presented in Table 1 and clearly indicate that 6-bromo-2-naphthol was the most reactive and gave the highest yield of coupled product while 3-(carboxy)-2-naphthol was found to be the least reactive and gave only 20% yield of the coupled product. The oxidative coupling of phenol did not take place, but 2,4-dimethylphenol **3** was selectively oxidized to its *ortho-ortho* coupled product **4** under similar reaction conditions (Scheme 2).



Scheme 1.

Keywords: methyltrioxorhenium; 2-naphthols; 1,1'-bi-2-naphthols; oxidation; molecular oxygen.

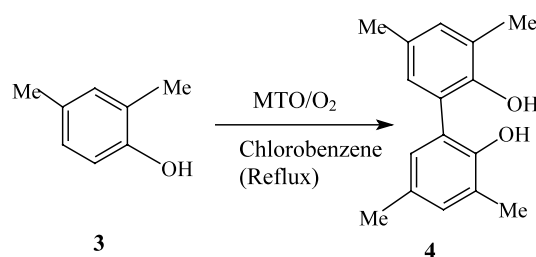
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Table 1. Methyltrioxorhenium catalyzed aerobic oxidation of 2-naphthols^a

Entry	Naphthol 1	Reaction time (h)	Yield (%) ^b
1a	R ¹ =R ² =R ³ =H	12	92
1b	R ¹ =Br; R ² =R ³ =H	10	95
1c	R ¹ =R ³ =H; R ² =OCH ₃	12	90
1d	R ¹ =R ² =H; R ³ =COOCH ₃	20	40
1e	R ¹ =R ² =H; R ³ =COOH	24	20

^a Reaction conditions: 2-naphthol (1 mmol), methyltrioxorhenium (5 mol%) in chlorobenzene (5 ml) at reflux temperature under an oxygen atmosphere.

^b Isolated yields.

**Scheme 2.**

To evaluate the effect of solvents, the aerobic oxidation of 2-naphthol was carried out under similar reaction conditions by using different solvents: chlorobenzene, acetonitrile, 1,2-dichloroethane and toluene. Chlorobenzene was found to be most suitable solvent. The oxidative coupling of 2-naphthols was found to be very slow at room temperature and could be carried out more efficiently in refluxing chlorobenzene.

The mechanism of this reaction is not clear at this stage and further studies in this direction are being carried out.

In summary, we have developed a catalytic aerobic oxidation for the selective oxidative coupling of 2-naphthols to their corresponding 1,1'-bi-2-naphthols. The present method describes the second example of a methyltrioxorhenium catalyzed oxidation reaction using molecular oxygen as the oxidant.

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- Typical experimental procedure:** To a stirred solution of 2-naphthol (144 mg, 1 mmol) in chlorobenzene (5 ml) was added methyltrioxorhenium (12 mg, 5 mol%) and the reaction mixture was refluxed for 12 h under an oxygen atmosphere. The reaction progress was monitored by TLC (SiO₂). After completion of the reaction the solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane. The dichloromethane layer was washed twice with water and dried over anhydrous sodium sulphate followed by evaporation of the solvent. The residue thus obtained was purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded 1,1'-bi-2-naphthol (265 mg, 92%). Similarly other substituted 2-naphthols were oxidized using this procedure and their reaction times and yields are given in the Table. The products were identified by comparing their physical and spectral data with those of authentic compounds reported in literature.