

ORIGINAL PAPER

Methyltrioxorhenium-catalysed oxidation of secondary amines to nitrones in ionic liquids

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

Nitrones serve as starting materials for the synthesis of many heterocycles. Oxidation of secondary amines using hydrogen peroxide and the catalytic amount of methyltrioxorhenium in ionic liquids is a useful method for the preparation of nitrones. Ultrasonic irradiation and ionic liquids have a positive influence on the reaction. The nitrones required were isolated in good yields. Corresponding hydroxylamines, which can be easily oxidised to nitrones, often accompanied the main products. Methyltrioxorhenium in ionic liquids was re-used in several reaction cycles without any deteriorating effect on the course of the reaction.

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Introduction

Nitrones are useful and versatile intermediates in the synthesis of heterocyclic compounds (Gothelf & Jørgensen, 1998). Enantioselective 1,3-dipolar cycloadditions of nitrones to α,β -unsaturated carbonyl compounds provide versatile synthons for the construction of biologically active products, especially pharmaceuticals and agrochemicals (Chow et al., 2007; Jen et al., 2000; Kano et al., 2005; Puglisi et al., 2004; Weseliński et al., 2009).

Nitrones can be prepared by condensation of *N*-alkyl- or *N*-arylhydroxylamines with aldehydes (Andrade et al., 2008; Dicken & DeShong, 1982; Gautheron-Chapoulaud et al., 2001; Hassan et al., 1997; Robl & Hwu, 1985) or by oxidation of secondary amines and the corresponding hydroxylamines, respectively. Oxidation procedures using stoichiometric amounts of dioxirane (Murray & Singh, 1990; Murray et al., 1992), oxaziridines (Cicchi et al., 2000), or Oxone® (2KHSO₅ · KHSO₄ · K₂SO₄) (Gella et al., 2009) usually suffer from poor atom economy and a high E-

factor. Consequently, those catalytic oxidations are preferable that use cheap and environmentally benign oxidants such as oxygen or hydrogen peroxide in the presence of suitable catalysts. Hydrogen peroxide is usually employed as an oxidant in combination with various catalysts, such as Na₂WO₄ (Coşkun & Parlar, 2005; Evans et al., 2006; Mitsui et al., 1984; Murahashi et al., 1985, 1990; Radivoy et al., 2001), salts of Mo(VI), W(VI), or SeO₂ (Ballini et al., 1992; Marcantoni et al., 1995; Nguyen et al., 2009; Yamada et al., 2002), Pt(II) (Colladon et al., 2008), Ti(IV) (Zonta et al., 2008), Ru(IV) (Goti et al., 1994). The effective oxidation of secondary amines to nitrones was also performed with alkyl hydroperoxides as oxidants in Ti(IV) catalysis (Buonomenna et al., 2006; Forcato et al., 2010, 2003). Molecular oxygen acted as the primary oxidant of secondary amines with cyclohexanone mono-oxygenase (Colonna et al., 2004) or methyltrioxorhenium (Yamazaki, 1997) as catalysts.

Methyltrioxorhenium (CH₃ReO₃, MTO) is regarded as a particularly useful catalyst in this respect. The first reaction catalysed by MTO was an epoxida-

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