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Methyltrioxorhenium/urea hydrogen peroxide catalyzed oxidation of *N*-sulfinyl imines: A mild and highly efficient access to *N*-sulfonyl aldimines, ketimines and α-ketiminoesters

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ABSTRACT

A mild and highly efficient access to *N*-sulfonyl imines through the oxidation of corresponding *N*-*tert*-butylsulfinyl imines and *N*-*p*-tosyl-sulfinyl imines with UHP in the presence of catalytic amount MTO was developed. Under mild reaction conditions, this highly selective reaction, provides a general and efficient access to *N*-sulfonyl aldimines, ketimines and α-ketiminoesters in excellent yield. The unstable sulfonylimine intermediates can be afforded with high purity and ready for subsequent reaction without further purification. The application of this method was demonstrated by facile synthesis of quaternary α-amino acids derivatives via allylation of obtained α-ketiminoesters.

N-Sulfonyl imines are versatile intermediates in a variety of organic transformations [1], such as nucleophilic addition reactions [2], hetero-Diels–Alder reactions [3], ene reactions [4], radical reactions [5], as well as reductions [6], and other organic reactions [7]. In light of the synthetic importance of sulfonylimines, a variety of methods have been developed for their preparation [8]. The direct condensation of aldehydes or ketones with sulfonyl amides are most straightforward way to synthesize sulfonylimines. However, due to the weak nucleophilicity of sulfonamide, harsh conditions are normally required and the scope are usually limited to nonenolizable aldehydes. Ruano, J. L. G. and co-workers developed a two-step process for obtaining *N*-sulfonylimines by reaction of the corresponding aldehydes or ketones with sulfinamides and followed by oxidation by dry m-CPBA [8]. The method features a broad substrate scope, including aromatic and aliphatic carbonyl compounds, even those containing enolizable protons. The tiny flaw of this method is obviously, as a pure substance, m-CPBA can be detonated by shock or sparks. α-Sulfonyl ketimines esters, as special *N*-sulfonyl imine derivatives, are useful synthetic intermediates to provide α,α-disubstituted α-amino acids with a quaternary carbon center, which are important building blocks in pharmaceutical research [9]. Despite their importance, the general and efficient synthesis method of α-sulfonyl ketimines esters and derivatives remains elusive [10]. There are one report for the synthesis of α-sulfonyl ketimines esters by condensation methyl benzoylformate and *p*-toluenesulfonamide catalyzed by $TiCl_4$ in CH_2Cl_2 under N_2 to afford (*Z*)-Methyl 2-phenyl-2-(tosylimino)acetate in 30% yield [10a,11].

During recent years, our research have been focusing on the chemistry of *N*-*tert*-butanesulfinyl imines and enantioselective arylation of *N*-sulfonyl imines for asymmetric synthesis of various useful chiral amines [12]. *N*-Sulfonyl α-iminoesters as powerful substrates for the facile synthesis of plenty of α-amino acids via nucleophilic addition reactions have attracted our attention for a long time. However, we found that the *N*-sulfonyl α-iminoesters are quite kinetically unstable and can be easily hydrolyzed to the corresponding amines and α-ketoesters during purification on silica gel. Therefore, a simple and efficient work-up or purification process for the synthesis of α-sulfonyl ketimines esters is a highly desirable.

Methyltrioxorhenium (MTO or CH_3ReO_3) has been widely used as a catalyst in the formation of catalytically active peroxorhenium species, with hydrogen peroxide or urea hydrogen peroxide complex (UHP) as a stoichiometric oxidant [13]. During our studies in synthesis of *N*-sulfonyl α-iminoesters, we noticed that organic disulfides with either alkyl or aryl substituent can be oxidized to thiosulfinates, thiosulfinate or sulfonic acids by hydrogen peroxide in nearly quantitative yield under MTO catalysis [14]. Therefore,

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