# PREPARATION OF NITRONES FROM SECONDARY AMINES. TUNGSTATE CATALYZED OXIDATION OF SECONDARY AMINES WITH HYDROGEN PEROXIDE.

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The metal catalyzed oxidation of amines is of interest in view of biological oxidative deamination processes. The activation of amines with metal catalysts provide various new reactions which include alkyl group exchange reactions and hydrolysis reactions of amines (J. Am. Chem. Soc. 101, 7429 (1979)). These reactions involve dehydrogenation processes which are deeply concerned with the metabolism of amines. In relation to the alternative deamination process which involves the oxidation of amines with molecular oxygen, the catalytic transformation of secondary amines to nitrones is of interest.

We wish to report a novel method for the tangstate catalyzed oxidation of secondary amines with hydrogen peroxide to give the corresponding nitrones as depicted in eq 1. We have already demonstrated the palladium catalyzed transformation of N,N-disubstituted hydroxylamines to the correspond-

$$RNHCH(R^1)-R^2 + H_2O_2 \xrightarrow{Na_2WO_4} RN^+(O^-)=C(R^1)-R^2 \qquad (1)$$

ing nitrones (Tetrahedron Lett., 1049 (1983)). However, the preparation of hydroxylamines sometimes requires tedious procedures. Treatment of secondary amines with three equivalents of 30 % aqueous hydrogen peroxide in the presence of 4 mol % of sodium tungstate at room temperature for 2-4 hr gave the corresponding nitrones highly efficiently. For example, 3,4-dihydroisoquinoline-2-oxide can be prepared from isoquinoline in 89 % isolated yield Since nitrones are valuable intermediates to construct various biologically active nitrogen compounds, the present single step preparation of nitrones from secondary amine is particularly efficient. The nucleophilic reaction of Grignard reagents to the nitrones thus formed provides valuable α-substituted hydroxylamines. The 1,3-dipolar cycloadaition of the nitrones to alkenes is also of interest to construct five-membered heterocyclic compounds. Especially, the cycloaddition of cyclic nitrones provides valuable key intermediates for natural product syntheses. The application of these reactions will be presented.