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Practical Aerobic Oxidation of Alcohols: Ligand Enhanced TEMPO/Mn(NO3)2 Catalyst System

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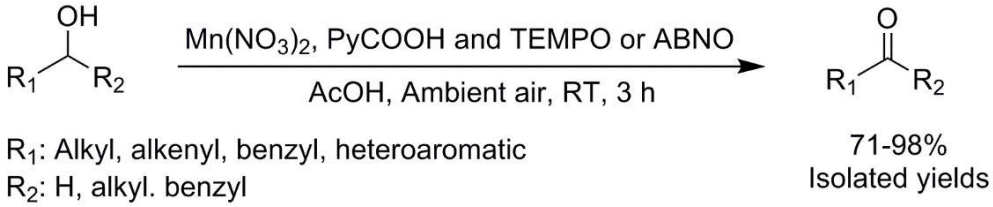
A highly efficient, ligand enhanced TEMPO/Mn(NO3)2 catalyst system for the aerobic oxidation of alcohols is described. From the series of coordinating ligands studied, 2-picolinic acid (PyCOOH) remarkably improves the catalytic activity of TEMPO/Mn(NO3)2. Under ambient air, at room temperature and in acetic acid, the ligand-enhanced catalyst converts various functional group-bearing aliphatic and benzylic primary alcohols to their respective aldehydes with near quantitative conversions (Scheme 1). A change of TEMPO to sterically less demanding 9-azabicyclo[3.3.1]nonane *N*-oxyl (ABNO) turns the Mn-catalyst also capable for oxidation of secondary alcohols to ketones. Mechanistic studies show that alcohols are oxidized by the oxoammonium cation derived from the nitroxyl radical. The active oxidant is re-generated by Mn(NO3)2 and this process is greatly promoted by the coordination of PyCOOH to Mn.



Scheme 1. Aerobic oxidation of alcohols with Mn(NO3)2/pyCOOH/nitroxide catalyst system.