Stable organic nitroxyl radicals, as exemplified by 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO: 1), find their indispensable utility in chemistry and biology. We have particularly been interested in their use as oxidation catalyst that allows facile and efficient conversion of alcohols to the corresponding carbonyl compounds with a safe bulk oxidant such as bleach.

The widely accepted mechanism of TEMPO-catalyzed oxidation of alcohols is shown in Scheme 1 where an oxoammonium ion plays a crucial role. Note that TEMPO exhibits remarkable chemoselectivity of preferring primary alcohols rather than secondary alcohols due to the inherent steric hindrance around the catalytic center. In this connection, TEMPO meanwhile hesitate oxidation of sterically crowded secondary alcohols, exposing a limitation of its synthetic applicability. We designed AZADO (azaadamantan N-oxyl) type nitroxyl radical by merging N-oxyl moiety into adamantane skeleton, with expectation of enhancing robustness and accessibility toward substrates. Thus, it was envisaged that the α-hydrogen of nitroxy group within AZADO skeleton should resist to participating in the well-known isomerization to give a nitrone because of the Bredt’s rule and, therefore, should allow facile access of varieties of substrates to the active center, enabling them to proceed the subsequent oxidation events. We established a reliable synthetic route to 1-Me-AZADO (2) starting from 1-adamantanol. 1-Me-AZADO exhibit superb catalytic activity even for oxidation of sterically crowded secondary alcohols that TEMPO gave insufficient result.

In this seminar, I wish to describe about the versatility of AZABO-catalyzed alcohol oxidation.

Professor Yoshiharu Iwabuchi
Tohoku University

Discovery and Exploitation of AZADOs:
The Highly Active Organocatalysts for Alcohol Oxidation

Date: 8th December 2010 (Wednesday)
Time: 2.15pm – 3.45pm
Venue: NTU SPMS CBC Building Level 2, Conference Room
Host: Asst. Professor Shunsuke Chiba

CBC SEMINAR ANNOUNCEMENT

Professor Yoshiharu Iwabuchi

TOHOKU UNIVERSITY

Discovery and Exploitation of AZADOs:
The Highly Active Organocatalysts for Alcohol Oxidation

Stable organic nitroxyl radicals, as exemplified by 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO: 1), find their indispensable utility in chemistry and biology. We have particularly been interested in their use as oxidation catalyst that allows facile and efficient conversion of alcohols to the corresponding carbonyl compounds with a safe bulk oxidant such as bleach.

The widely accepted mechanism of TEMPO-catalyzed oxidation of alcohols is shown in Scheme 1 where an oxoammonium ion plays a crucial role. Note that TEMPO exhibits remarkable chemoselectivity of preferring primary alcohols rather than secondary alcohols due to the inherent steric hindrance around the catalytic center. In this connection, TEMPO meanwhile hesitate oxidation of sterically crowded secondary alcohols, exposing a limitation of its synthetic applicability. We designed AZADO (azaadamantan N-oxyl) type nitroxyl radical by merging N-oxyl moiety into adamantane skeleton, with expectation of enhancing robustness and accessibility toward substrates. Thus, it was envisaged that the α-hydrogen of nitroxy group within AZADO skeleton should resist to participating in the well-known isomerization to give a nitrone because of the Bredt’s rule and, therefore, should allow facile access of varieties of substrates to the active center, enabling them to proceed the subsequent oxidation events. We established a reliable synthetic route to 1-Me-AZADO (2) starting from 1-adamantanol. 1-Me-AZADO exhibit superb catalytic activity even for oxidation of sterically crowded secondary alcohols that TEMPO gave insufficient result.

In this seminar, I wish to describe about the versatility of AZABO-catalyzed alcohol oxidation.