Nitroxyl radicals (1) contain the N, N-disubstituted NO group with one unpaired electron delocalised over the nitrogen-oxygen bond. One of the most popular nitroxyl radicals is 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 2), a remarkably stable radical, that has found many applications in organic synthesis since it was first synthesised by Lebelev and Kazarnovskii in 1960. 

TEMPO is normally prepared by oxidation of the corresponding tetramethylpiperidine or tetramethylpiperidine hydroxide, but it is also commercially available from several sources. Many analogues have also been prepared, mainly from their common precursor 2,2,6,6-tetramethyl-4-piperidone. 

Due to its inert nature, TEMPO is widely used in electron spin resonance spectroscopy as a probe for biological systems, and also as a radical trap. Optically active nitroxyl radicals have been stereoselectively coupled with transient prochiral carbon radicals. One of the most important synthetic applications of TEMPO is its use in the oxidation of several organic substrates, such as amines, phosphines, phenols, anilines, and particularly primary and secondary alcohols.

References and Notes