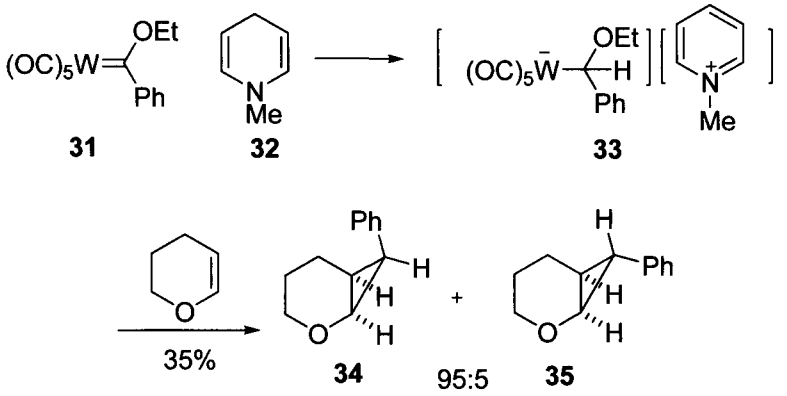
Pyridine *N*-oxides are also versatile intermediates in organic synthesis.[15] They are obtained by oxidation of pyridine using oxidizing agents such as peracids, H_2O_2/AcOH, H_2O_2/manganese tetrakis(2,6-dichlorophenyl)-porphyrin, H_2O_2/methyltrioxorhenium, dimethyldioxirane, bis(trimethylsilyl) peroxide, Caro's acid, oxaziridines,[16] trifluoroacetic anhydride (TFAA)/H_2O_2–urea complex,[17] O_2/ruthenium,[18] H_2O_2/molecular sieves,[19] O_2/cobalt,[20] trichloroisocyanuric acid/AcOH,[21] bromamine-T/$RuCl_3$,[22] and TBHP/$MoCl_5$.[23] Besides activating the ring for substitution reactions, the *N*-oxide moiety can also serve as an effective nitrogen-protecting group.[24]

Short-lived carbenes can react with pyridine to form the corresponding pyridinium ylide, which are far more stable than the starting carbenes. For example, pyridinium tungstate **33**, prepared from phenyl ethoxy carbene **31** and dihydropyridine **32**, serves as an effective cyclopropanation reagent to give products **34** and **35** in a 95:5 ratio and in 35% yield.[25]



The Zincke reaction

The Zincke reaction[26–28] is an overall amine exchange process that converts Zincke salt, i.e., *N*-(2,4-dinitrophenyl)pyridinium salts (e.g., **36**), generated by reaction of pyridine or its derivatives with 2,4-dinitrochlorobenzene, to *N*-aryl or *N*-alkyl pyridiniums **37** upon treatment with the appropriate aniline or alkyl amine. This reaction proceeds via nucleophilic addition, ring opening, amine exchange, and electrocyclic reclosure, a sequence that also requires a series of proton transfers. The Zincke process has been applied to the preparation of a wide range of pyridinium salts, in particular, those unattainable by direct *N*-arylation or *N*-alkylation, such as electron-deficient, weakly nucleophilic pyridines and α-substituted electrophiles. In addition, α-chiral alkyl amines provide the corresponding *N*-alkyl pyridinium salts with retention of configuration in the Zincke process.