

SYNLETT Spotlight 18

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Oxidodiperoxymolybdenum(pyridine) (hexamethylphosphoric Triamide)

Compiled by Douglas B. Weibel

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

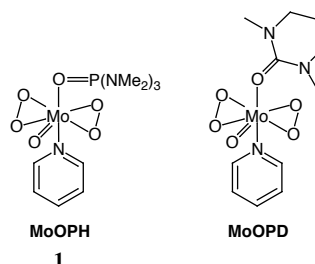
Douglas Weibel received his B.Sc. in 1996 from the University of Utah, where he conducted research with Professor C. Dale Poulter. He then spent a year working with Professor Yoshinori Yamamoto at Tohoku University, Sendai, Japan. He is currently working on his Ph.D. with Professor Jerrold Meinwald at Cornell University.



Oxidodiperoxymolybdenum(pyridine)(hexamethylphosphoric triamide) **1** (MoOPH, Vedejs reagent, Mimoun complex) is a versatile enolate anion hydroxylating reagent first realized by Vedejs.¹ MoOPH swiftly hydroxylates anions from lactones,¹ ketones,² esters,³ aldehydes,⁴ nitriles,⁵ sulfones,⁶ amides,⁷ phenols,⁸ and isoxazolines.⁹ Beyond functionalizing a wide array of substrates, MoOPH carries out oxidations with excellent regio- and stereoselectivity.

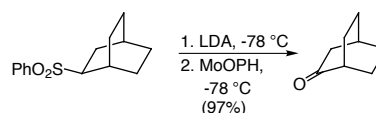
Preparation: MoOPH can be prepared from MoO₃,¹⁰ but has recently been realized by a more convenient and higher yielding procedure arising from MoO₃•H₂O.¹¹ Due to the

toxicity of HMPA, a less hazardous and chemically equivalent reagent (MoOPD) has been developed using DMPU in place of HMPA.¹²

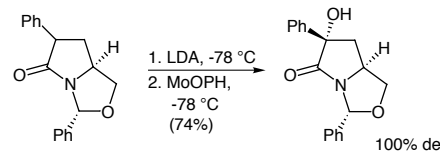


Abstracts

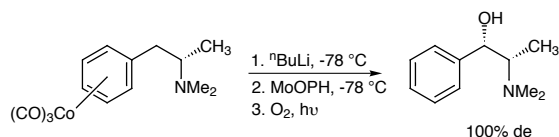
(A) α -Sulfonyl carbanions conveniently undergo oxidative desulfonylation to form ketones in the presence of MoOPH.⁷



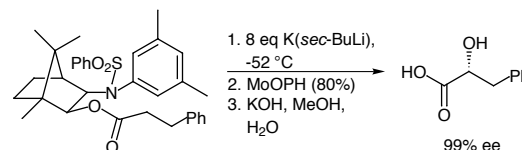
(B) Remarkable *endo* selectivity is observed in the hydroxylation of enolate anions generated from bicyclic lactams with MoOPH and MoOPD.¹³



(C) Coordination of chromium tricarbonyl to (*S*)-(-)-*N,N*-dimethylamphetamine followed by α -deprotonation and MoOPH oxidation yields optically pure (1*R*,2*S*)-*N*-methylpseudoephedrine.¹⁴



(D) The α -hydroxylation of chiral 3-phenylpropionic acid esters with MoOPH proceeds with high diastereoselectivity, providing access to optically pure α -hydroxycarboxylic acids.¹⁵



References

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