

# SYNLETT Spotlight 18

## Oxidodiperoxymolybdenum(pyridine) (hexamethylphosphoric Triamide)

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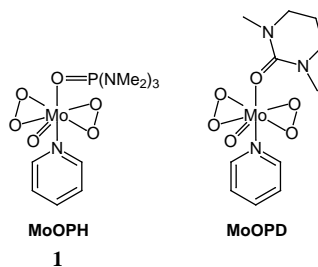


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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

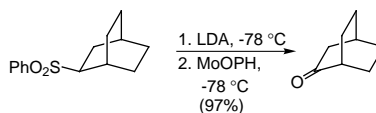
**Preparation:** MoOPH can be prepared from MoO<sub>3</sub>,<sup>10</sup> but has recently been realized by a more convenient and higher yielding procedure arising from MoO<sub>3</sub>·H<sub>2</sub>O.<sup>11</sup> Due to the

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

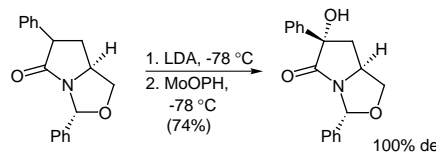


### Abstracts

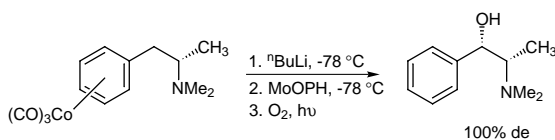
(A)  $\alpha$ -Sulfonyl carbanions conveniently undergo oxidative desulfonylation to form ketones in the presence of MoOPH.<sup>7</sup>



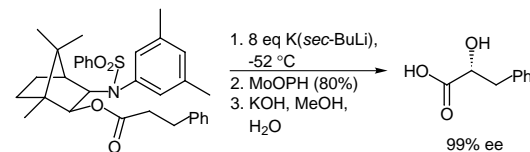
(B) Remarkable *endo* selectivity is observed in the hydroxylation of enolate anions generated from bicyclic lactams with MoOPH and MoOPD.<sup>13</sup>



(C) Coordination of chromium tricarbonyl to (*S*)-(-)-*N,N*-dimethylamphetamine followed by  $\alpha$ -deprotonation and MoOPH oxidation yields optically pure (1*R*,2*S*)-*N*-methylpseudoephedrine.<sup>14</sup>



(D) The  $\alpha$ -hydroxylation of chiral 3-phenylpropionic acid esters with MoOPH proceeds with high diastereoselectivity, providing access to optically pure  $\alpha$ -hydroxycarboxylic acids.<sup>15</sup>



### References

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