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Chiral Tetraaminophosphonium Salt-Mediated Asymmetric Direct Henry Reaction
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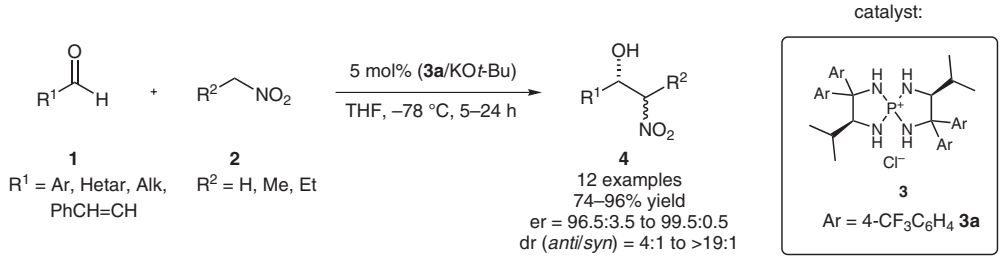
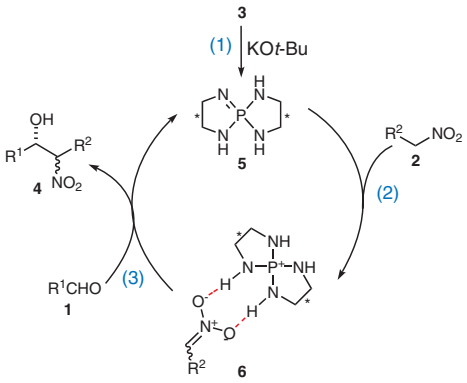
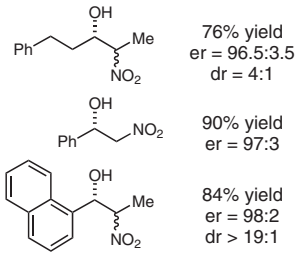
Chiral Tetraaminophosphonium Salts: A New Catalyst Motif



Proposed mechanism:



Selected examples:



Significance: Ooi and co-workers have introduced chiral tetraaminophosphonium chlorides of type **3** as catalysts of the asymmetric Henry reaction of a broad range of aldehydes **1** and nitroalkanes **2**. The authors' working hypothesis includes (1) the in situ generation of triaminoiminophosphorane **5** upon deprotonation of **3** with KO*t*-Bu. (2) Phosphorane **5** will subsequently deprotonate nitroalkanes **2**. The resulting chiral phosphonium nitronate ion pair **6** benefits from hydrogen bonding and enables (3) a highly stereoselective addition of aldehydes **1** in the final step. The ability of phosphonium salts **3** acting as hydrogen bonding donors via the N-H protons could be demonstrated by an X-ray crystal structure of one representative (Ar = Ph).

Comment: The authors could show that tetraaminophosphonium salts besides serving as precursors of P-1 phosphazenes exhibit truly catalytic potential. Access to phosphonium chlorides **3** is given by means of a concise ex-chiral-pool synthesis starting from L-valine. In the future, chiral P-spirocyclic salts of type **3** and related structures might also compete with the well-established N-spirocyclic or cinchona alkaloid derived ammonium salts in phase-transfer catalysis. Ensuing reports on the use of chiral phosphonium salts in further reactions proceeding via anionic intermediates are expected.

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Category
Organo- and Biocatalysis

Key words
tetraamino-phosphonium salts
Henry reaction
ion pairing
hydrogen bonding