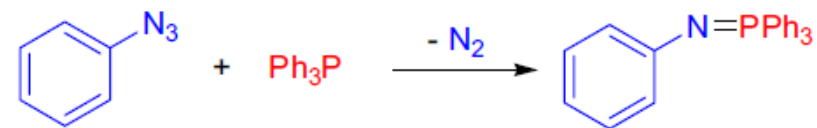
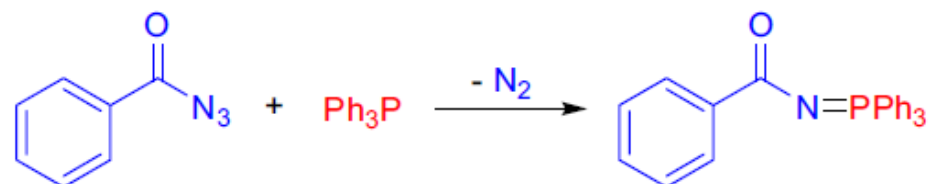


Staudinger Reaction

Staudinger (1919):

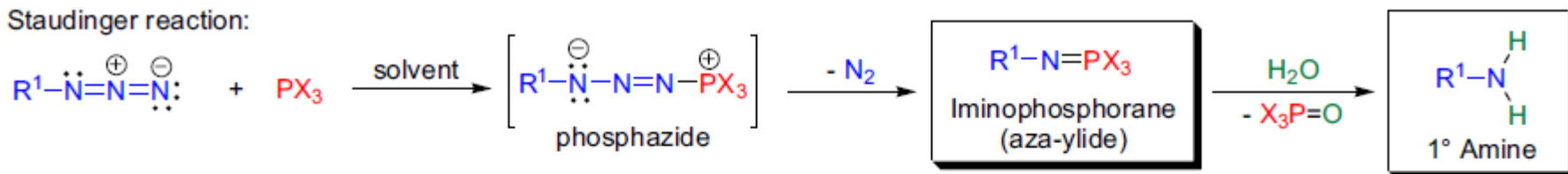


phenyl azide

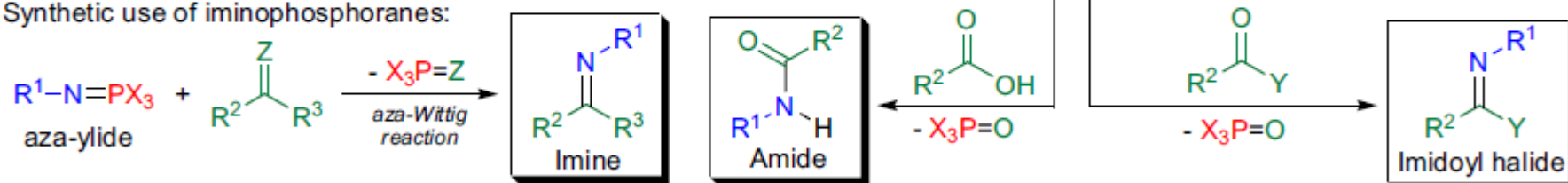


benzoyl azide

Staudinger reaction:



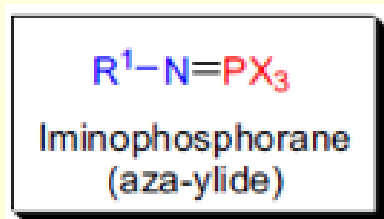
Synthetic use of iminophosphoranes:



R^1 = alkyl, aryl, heteroaryl, RC(O) , RSO_2 , RP(O) , R_2P , R_3Si , R_3Sn , R_3Ge ; R^{2-3} = H, alkyl, aryl, heteroaryl; X = alkyl, aryl, O-alkyl, O-aryl, NH_2 , NR_2 , Cl, F, NCO, (also the combination of these ligands); Y = Cl, Br; Z = O, S; solvent: THF, Et_2O

Features

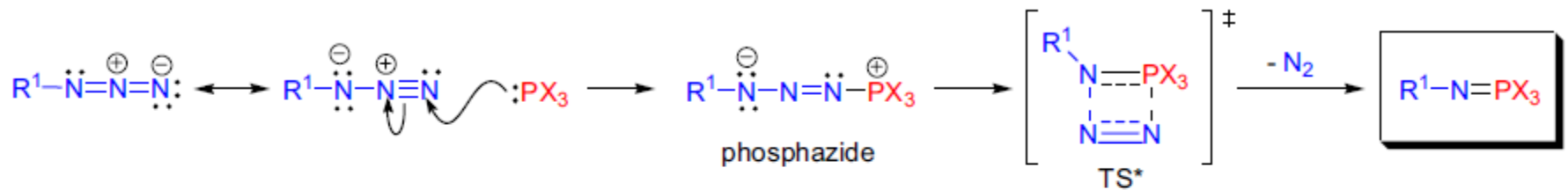
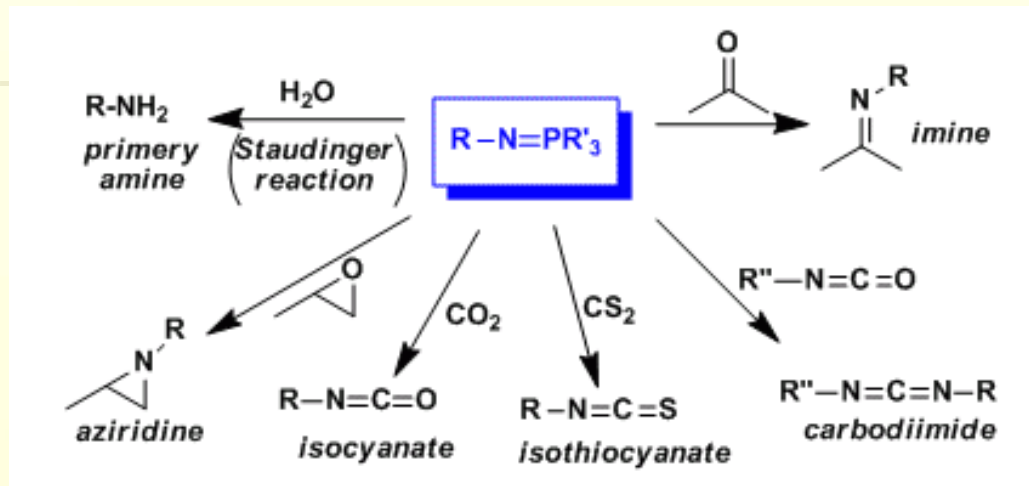
- 1) the reaction is usually very fast and takes place in almost quantitative yield without the formation of side products;
- 2) virtually any trivalent phosphorus compound undergoes the reaction;
- 3) the structure of the azide component can also be widely varied;
- 4) the iminophosphorane products derived from alkyl- or arylazides and trialkyl- and triarylphosphines are stable compounds that can be isolated, but alkoxy groups on the P atom tend to undergo alkyl migration.



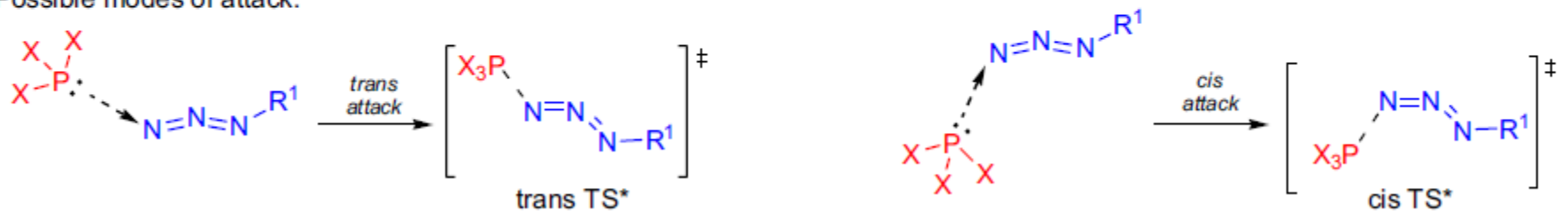
The iminophosphoranes are versatile synthetic intermediates:

- 1) hydrolysis with water gives rise to primary amines (this reduction of azides is highly chemo- and stereoselective);
- 2) inter- or intramolecular reaction with carbonyl or thiocarbonyl compounds affords imines (*aza-Wittig reaction*);
- 3) carboxylic acids convert iminophosphoranes to *N*-substituted amides;
- 4) acyl halides condense to generate imidoyl halides;
- 5) ozonolysis produces nitro compounds.

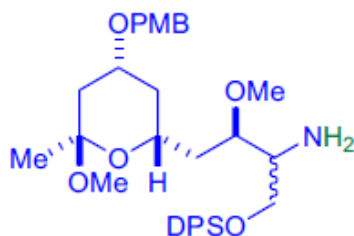
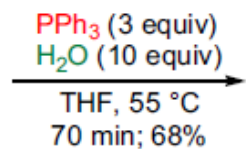
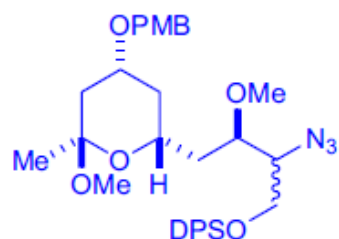
Mechanism



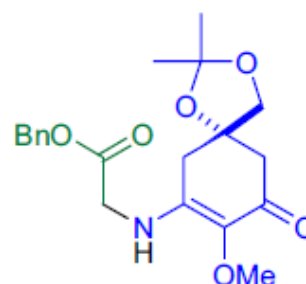
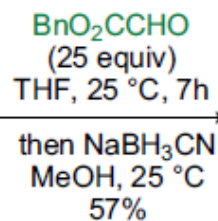
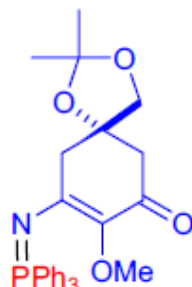
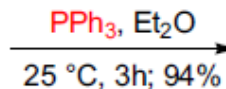
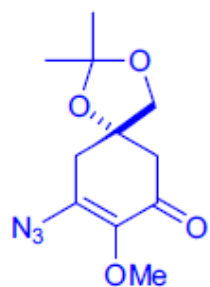
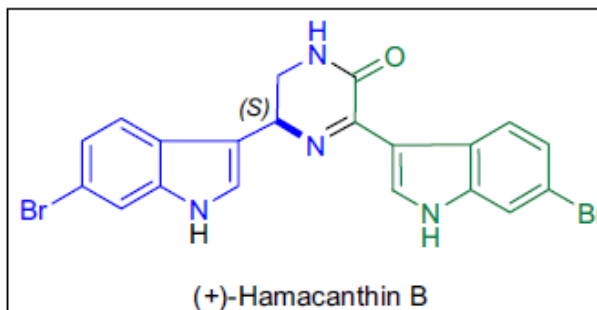
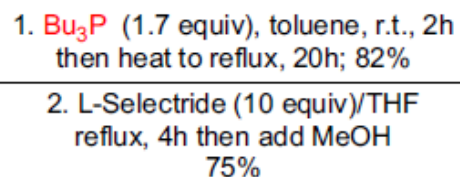
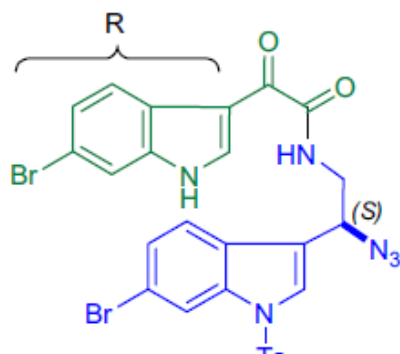
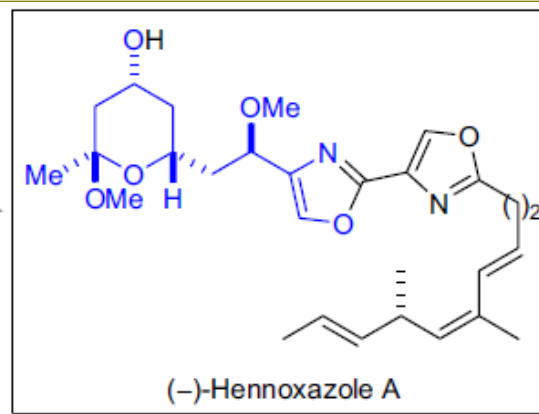
Possible modes of attack:



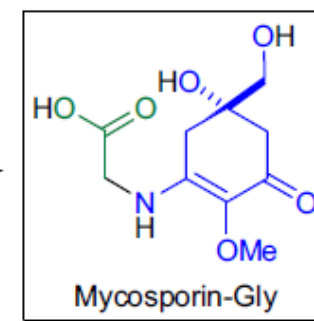
Applications



steps



steps



Applications

