SYNLETT
Spotlight 309

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

Well-Documented Applications of *p*-Phenylenediamine in the Synthesis of Heterocycles and Heterocrown Ethers

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Dedicated to my mentor Professor Manabendra Ray.

Introduction

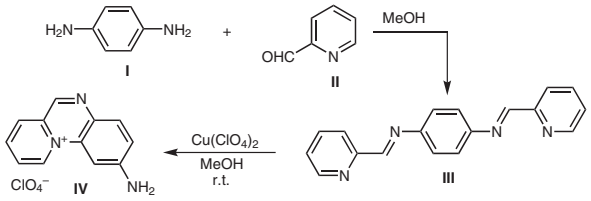
The broad importance of *p*-phenylenediamine functionality is reflected from its wide applications in various fields of chemistry, such as in the production of pigments, dye intermediates, hair dyes, rubber antioxidants, photographic developer and lithography plates, *p*-aromatic polyamide fiber, etc. Apart from these wide applications in industrial chemistry, it is a reagent of choice for the synthesis of heterocycles, heterocrown ethers, and amine-terminated aromatic polyamide dendrimers.[1–5]

Preparation and Properties:

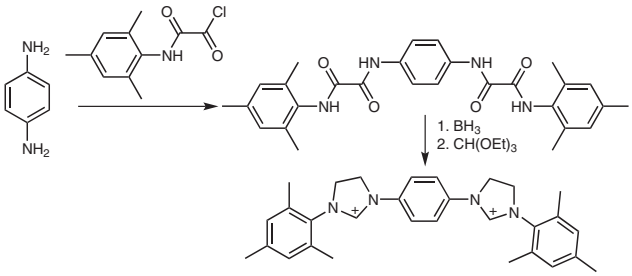
p-Phenylenediamine is a commercially available and cheap compound. In industry, a number of methods are used to prepare this functionality including the *p*-nitroaniline or *p*-dinitrobenzene reduction processes and *p*-dichlorobenzene or *p*-nitrochlorobenzene ammonolysis. Pure *p*-phenylenediamine is a white to slightly red crystalline solid. On exposure to air it gets oxidized and the colour becomes black.

Abstracts

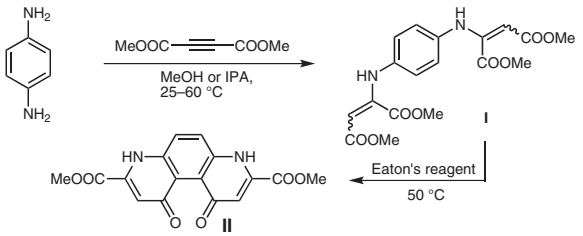
(A) *Synthesis of Quinoxalines:*
Quinoxalines are an important class of heterocyclic compounds, some of which are found to be useful as fluorophores, dyes, and antibiotics. *p*-Phenylenediamine **I** reacted with pyridine-2-carboxaldehyde **II** in methanol at room temperature to produce an imine **III** which upon treatment with copper(II) salts produced the highly fluorescent novel quinoxaline derivative **IV**.[6]



(B) *Synthesis of Bis-N-Heterocyclic Carbene (NHC) Precursors:*
p-Penylenediamine was used as a spacer for the synthesis of a bis-N-heterocyclic carbene (NHC) precursor of a homo-bimetallic ruthenium-type catalyst.[7] This catalyst was used for the dimer ring-closing metathesis.



(C) *Synthesis of Bis-Quinolone Derivatives:*
Zewge et al. developed a general and high-yielding synthetic strategy for the synthesis of bis-quinolones using *p*-phenylenediamine as a key material.[8] The first step was the formation of enamine **I** by the reaction between *p*-phenylenediamine and dimethyl acetylenedicarboxylate (DMAD) in alcoholic solvents. Finally, the enamine was cyclized to the corresponding bis-quinolones **II** using Eaton's reagent as an efficient cyclizing agent.



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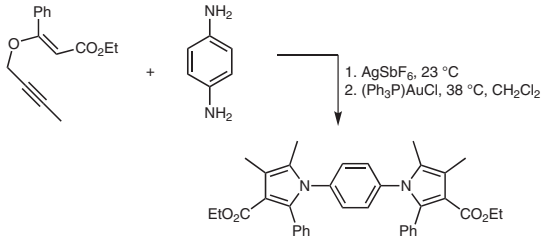
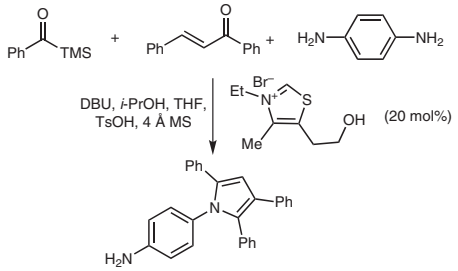
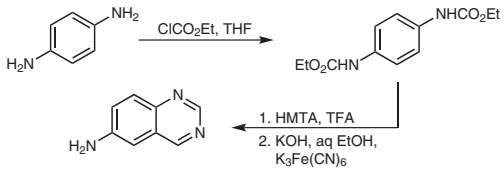
(D) *Synthesis of Pentasubstituted Pyrroles:*
Binder and Kirsch reported that both amine groups of *p*-phenylenediamine could be converted simultaneously into the corresponding pentasubstituted pyrrole by using a combination of propargyl vinyl ether, silver(I) and silver(II) salt in dichloromethane through a convenient one-pot process.[9] Basically this is an example of a one-pot, three-step cascade reaction: first the silver(I)-catalyzed propargyl Claisen rearrangement, followed by amine condensation and finally gold(I)-catalyzed 5-*exo*-dig heterocyclization.



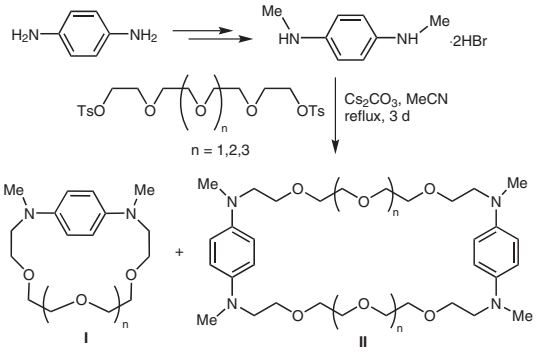
(E) *Synthesis of Polysubstituted Aromatic Pyrroles:*
Scheidt and co-workers reported that one amine group of the *p*-phenylenediamine could selectively be converted into the 2,3,5-trisubstituted pyrrole by following a newly developed one-pot synthetic strategy.[10] The reaction between benzoyltrimethylsilane, chalcone, and *p*-phenylenediamine under the newly developed conditions produced the desired trisubstituted pyrrole.



(F) *Synthesis of 6-Aminoquinazolines:*
Chilin et al. introduced a new synthetic pathway to quinazolines. They were successful enough to convert selectively one amino group of *p*-phenylenediamine into the corresponding pyrimidine ring furnishing 6-aminoquinazoline as the only product.[11]



(G) *Synthesis of Crownophanes:*
Sibert et al. incorporated the electrochemically active *p*-phenylenediamine unit into the body of crown ether and produced a macrocyclic hybrid crown/cyclophane structure called as 'Wurster's crownophanes'. During the synthesis of this type of crownophanes, Sibert et al. isolated two types of crownophanes, one smaller (**I**) and one larger (**II**).[4]



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