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

Compiled by Rik Rani Koner

Rik Rani Koner was born in Bankura, West Bengal, India in 1980. She received her M.Sc. degree (2004) in organic chemistry from Visva-Bharati University. In the meantime, she received her Ph.D. degree under the supervision of Professor Manabendra Ray. Her research interests focus on the synthesis and characterization of metallo-organic frameworks and aniline-based polymers with functional groups.

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India
E-mail: rikuchem@gmail.com
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.\(^1\)\(^2\)\(^3\)\(^4\)

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.\(^6\)

\[
\text{H}_2\text{N} - \text{NH}_2 + \text{OH} - \text{N} - \text{N} - \text{MeOH} \rightarrow \text{MeOH}
\]

(B) Synthesis of Bis-N-Heterocyclic Carbene (NHC) Precursors:
\( p \)-Phenylenediamine 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.

\[
\text{NH}_2 \rightarrow \text{MeOH} \rightarrow \text{CuClO}_2 \rightarrow \text{MeOH} \rightarrow \text{III}
\]

(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.

\[
\text{MeOOC} \rightarrow \text{COOMe} \rightarrow \text{Eaton's reagent} \rightarrow 50^\circ \text{C}
\]

\(^{1-5}\) Synthesis of Quinoxalines:
\(^{1-5}\) Synthesis of Bis-N-Heterocyclic Carbene (NHC) Precursors:
\(^{1-5}\) Synthesis of Bis-Quinolone Derivatives:

SYNLETT 2010, No. 6, pp 0987–0988
Advanced online publication: 02.03.2010
DOI: 10.1055/s-0029-1219397; Art ID: V31509ST
© Georg Thieme Verlag Stuttgart · New York
(D) Synthesis of Pentasubstituted Pyrroles:
Binder and Kirsch reported that both amine groups of p-phenylene-
diamine 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 con-
venient 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-trisub-
stituted pyrrole by following a newly developed one-pot synthetic
strategy.10 The reaction between benzoyltrimethylsilane, chalcone,
and p-phenylenediamine under the newly developed conditions pro-
duced 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 fur-
nishing 6-aminoquinazoline as the only product.11

(G) Synthesis of Crownophanes:
Sibert et al. incorporated the electrochemically active p-phenylene-
diamine unit into the body of crown ether and produced a macro-
cyclic 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

References