

Benzidine Rearrangement Reactions of Polyether Tethered Cyclic *N,N'*-Diaryl Hydrazides

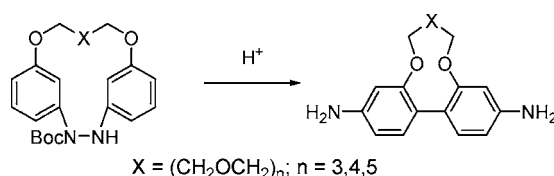
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ABSTRACT



N,N'-Diaryl hydrazides tethered with a polyether group at the meta positions undergo [5,5]-sigmatropic (benzidine) rearrangement reactions to furnish 4,4'-diamino-biphenyls (benzidines) strapped with a polyether unit at the 2,2'-positions.

The acid-catalyzed [5,5]-sigmatropic rearrangement of hydrazobenzenes, conventionally known as the benzidine rearrangement,¹ affords 4,4'-diamino biaryls (benzidines), useful synthetic building blocks for azo dyes, polyaromatics, polyimides, and polyfluorenes.² In addition, their *N*-arylation products are important hole transporting materials for light-emitting display devices.³ However, the conventional benzidine rearrangement reaction itself has little synthetic value because of the formation of inseparable isomeric byproducts⁴ as well as the lack of general synthetic methods for the starting hydrazobenzenes.⁵

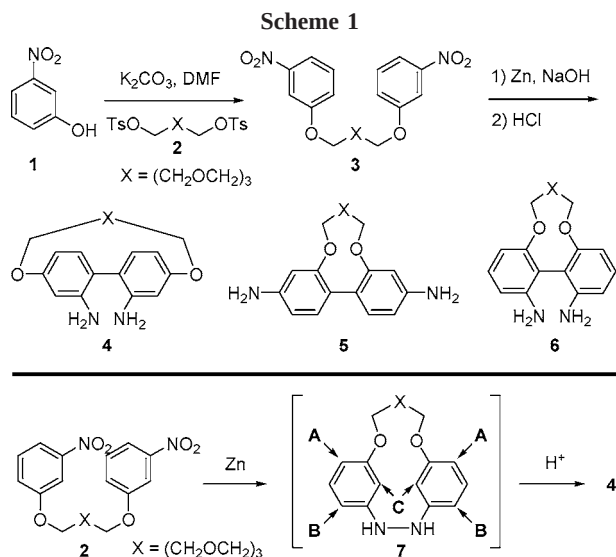
We have recently demonstrated that *N,N'*-diaryl hydrazides undergo acid-catalyzed [3,3]- and [5,5]-sigmatropic rearrangement reactions to afford 2,2'-diamino-1,1'-biaryls and 4,4'-diamino-1,1'-biaryls (benzidines), respectively.⁶ More importantly, *N,N'*-diaryl hydrazides are much more readily accessed than *N,N'*-diaryl hydrazines (hydrazobenzenes), by means of the Pd- or Cu(I)-catalyzed coupling reactions of *N*-aryl hydrazides with aryl halides.^{6,7}

Benzidines incorporating alkyl, polyether, or polyaza chains are versatile chemical motifs, easily convertible into biphenyl-based cyclophanes⁸ by various synthetic methods

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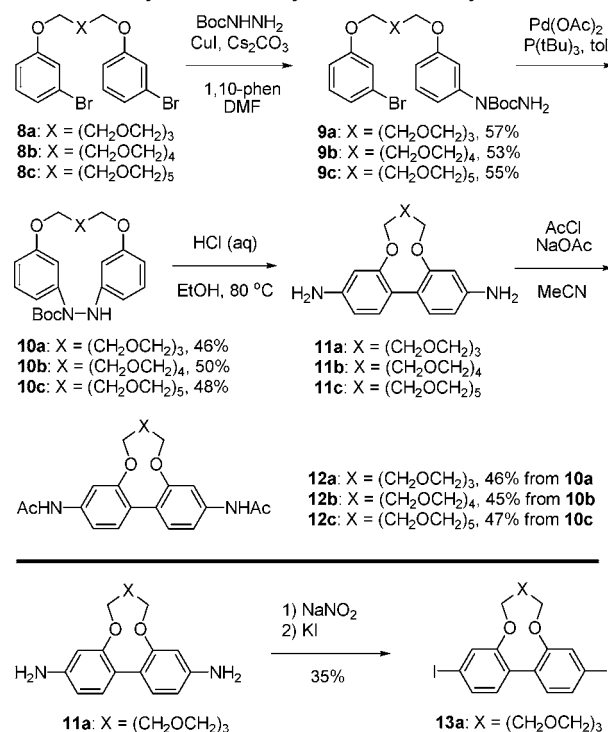
including the Sandmeyer reaction. Benniston and co-workers investigated the synthesis of 4,4'-diamino-biphenyl **5** tethered with alkyl or alkoxy linkers from bis(*m*-nitrophenyl) ether **3** via a reaction sequence consisting of a Zn-mediated partial reduction and in situ acid-catalyzed benzidine rearrangement.⁹ Unfortunately, the reaction did not proceed to give the desired benzidine rearrangement product **5**, but instead **4**, resulting from the [3,3]-sigmatropic rearrangement in an overall yield of 16% (Scheme 1). Evidently, the rearrange-



ment reaction took place at the sites B, rather than A, of the putative hydrazobenzene intermediate **7**.

The potential importance as synthetic intermediates to a diverse array of polyether cyclophanes together with this reported failure led us to investigate the benzidine rearrangement reactions of cyclic *N,N'*-diaryl hydrazides strapped with a polyether chain. Scheme 2 shows our synthesis which commenced with the preparation of **8** from *m*-bromophenol and polyether bistosylates. The Cu(I)-catalyzed coupling reactions of bis(*m*-bromophenyl) ethers **8a–c** provided monohydrazides **9a–c** in 53–57% yields (82–85% based on recovered starting bromide **8a–c**). Their cyclization reactions under Pd catalysis furnished diaryl hydrazides **10a–c** in 46–50% yields, setting the stage for the ensuing benzidine rearrangement reactions. When heated in EtOH with a catalytic amount of aq. HCl, hydrazides **10a–c** were found to undergo rearrangement reactions to the corresponding benzidines **11a–c** as indicated by their crude ¹H NMR spectra. However, their purification by silica-gel column

Scheme 2. Synthesis of Polyether Tethered Cyclic Benzidines



chromatography was unsuccessful, because of the interference of unidentified decomposed byproducts. Full characterizations were made upon acetylation to the acetamides **12a–c**, which were separated in analytically pure form in all cases. The structural integrity of **11a–c** was further corroborated by the conversion of **11a** to the known diiodide **13a**¹⁰ via the standard Sandmeyer protocol.

In summary, we have demonstrated that *N,N'*-diaryl hydrazides strapped with a polyether chain can undergo the benzidine rearrangement reaction to give the corresponding 4,4'-diamino-2,2'-biphenyls with a polyether unit at the 3,3'-positions.

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Supporting Information Available: Experimental procedures and compound characterizations for benzidine acetamides **12a–c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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