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

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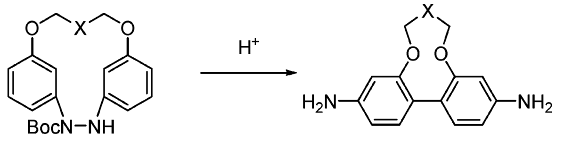
ABSTRACT



X = (CH$_2$OCH$_2$)$_n$; n = 3,4,5

***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 byproducts[4] 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 cyclophanes[8] by various synthetic methods

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(1) (a) Hoffman, A. W. *Proc. R. Soc. London* **1863**, *12*, 576. (b) Dewar, M. J. S. In *Molecular Rearrangement*; de Mayo, P., Ed.; Interscience: New York, 1969; Vol 1, p 323. (c) Banthorpe, D. V. *Chem. Rev.* **1970**, *70*, 295. (d) Olah, G. A.; Dunne, K.; Kelly, D. P.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 7438. (e) Cox, R. A.; Buncel, E. In *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; p 775. (f) Bunton, C. A.; Rubin, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4236. (g) Shine, H. J.; Kupczyk-Subotkowska, L.; Subotkowski, W. *J. Am. Chem. Soc.* **1985**, *107*, 6674. (h) Park, K. H.; Kang, J. S. *J. Org. Chem.* **1997**, *62*, 3794. (i) Park, K. H.; Park, M.-K.; Cho, Y. H. *Bull. Korean Chem. Soc.* **1998**, *19*, 1090.

(2) (a) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203. (b) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127* (21), 7662.

(3) (a) Popovic, Z. D.; Aziz, H. *J. Appl. Phys.* **2005**, *98*, 13510. (b) Tung, C.-H.; Zhang, L.-P.; Li, Y.; Cao, H.; Tanimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 5348.

(4) (a) Cheng, J. D.; Shine, H. J. *J. Org. Chem.* **1975**, *40*, 703. (b) Zhu-Ohlbach, A.; Gleiter, R.; Bleiter, R.; Schmidt, H. L.; Reda, T. *Eur. J. Org. Chem.* **1998**, *11*, 2409. (c) Buncel, E. *Can. J. Chem.* **2000**, *78*, 1251. (d) Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. *Macromolecules* **1993**, *26*, 2779. (b) Shine, H. J.; Trisler, J. C. *J. Am. Chem. Soc.* **1960**, *82*, 4054.

(5) They are generally prepared from nitroarenes via the reductive coupling reaction with NaBH$_4$ or from azobenzenes through a Zn-mediated reduction process that are moderately effective only for symmetric hydrazobenzenes.

(6) (a) Kang, H.-M.; Lim, Y.-K.; Shin, I.-J.; Kim, H.-Y.; Cho, C.-G. *Org. Lett.* **2006**, *8*, 2047. (b) Lim, Y. K.; Jung, J. W.; Lee, H.; Cho, C.-G. *J. Org. Chem.* **2004**, *69*, 5778.

(7) (a) Peters, M. V.; Goddard, R.; Hecht, S. *J. Org. Chem.* **2006**, *71*, 7846. (b) Peters, M. V.; Stoll, R. S.; Goddard, R.; Buth, G.; Hecht, S. *J. Org. Chem.* **2006**, *71*, 7840. (c) Lim, Y.-K.; Choi, S.; Park, K. B.; Cho, C.-G. *J. Org. Chem.* **2004**, *69*, 2603. (d) Kim, K.-Y.; Shin, J.-T.; Lee, K.-S.; Cho, C.-G. *Tetrahedron Lett.* **2004**, *45*, 117. (e) Lim, Y.-K.; Pang, S.-J.; Paik, S. U.; Cho, C.-G. *Bull. Korean Chem. Soc.* **2003**, *24*, 543. (f) Lim, Y.-K.; Lee, K.-S.; Cho, C.-G. *Org. Lett.* **2003**, *5*, 979. (g) Lee, K.-S.; Lim, Y.-K.; Cho, C.-G. *Tetrahedron Lett.* **2002**, *43*, 7463.

(8) (a) Shishkina, S. V.; Shishkin, O. V.; Grygorash, R. Y.; Mazepa, A. V.; Rakipov, I. M.; Yakshin, V. V.; Kotlyar, S. A.; Kamalov, G. L. *J. Mol. Struct.* **2007**, *832*, 199. (b) Burguete, M. I.; Diaz, P.; García-España, E.; Luis, S. V.; Miravet, J. F.; Querol, M.; Ramirez, J. A. *Chem. Commun.* **1999**, 649. (c) Artz, S. P.; Cram, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 2160. (d) Rebek, J. *Acc. Chem. Res.* **1984**, *17*, 258.

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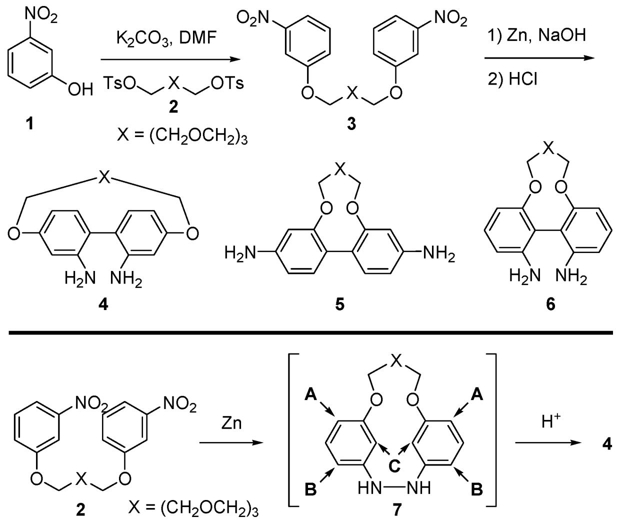
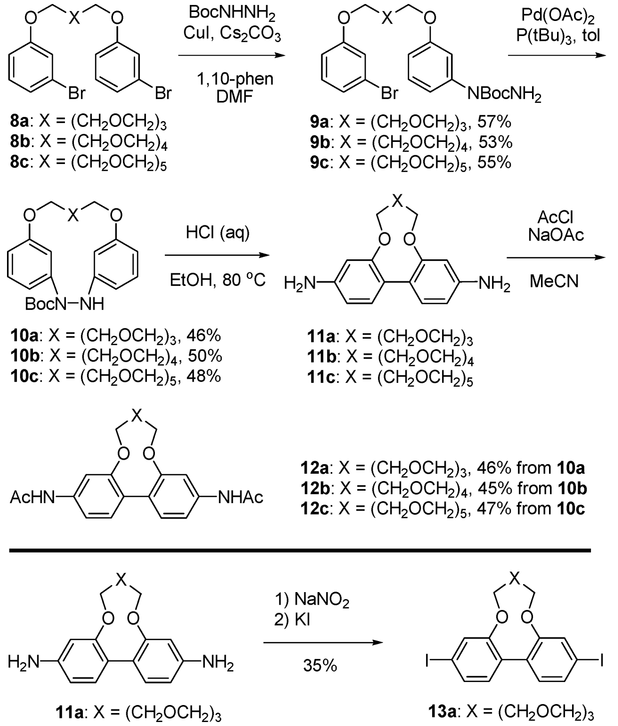
including the Sandmeyer reaction. Benniston and co-workers investigated the synthesis of 4,4′-diamino-biphenyl **5** tethered with alkyl or alkoxy linkers from bis(*m*-nitrophenyl) ether **3** via a reaction sequence consisting of a Zn-mediated partial reduction and in situ acid-catalyzed benzidine rearrangement.[9] 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 rearrangement reaction took place at the sites B, rather than A, of the putative hydrazobenzene intermediate **7**.

Scheme 1



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 ^{1}H NMR spectra. However, their purification by silica-gel column 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.

Scheme 2. Synthesis of Polyether Tethered Cyclic Benzidines



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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(9) Benniston, A. C.; Clegg, W.; Harriman, A.; Harrington, R. W.; Li, P.; Sams, C. *Tetrahedron Lett.* **2003**, *44*, 2665.

(10) (a) Benniston, A. C.; Harriman, A.; Li, P.; Patel, P. V.; Sams, C. A. *J. Org. Chem.* **2006**, *71*, 3481. (b) Benniston, A. C.; Li, P.; Sams, C. *Tetrahedron Lett.* **2003**, *44*, 3947.