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[9,9]-Sigmatropic Shift in a Benzidine-Type Rearrangement

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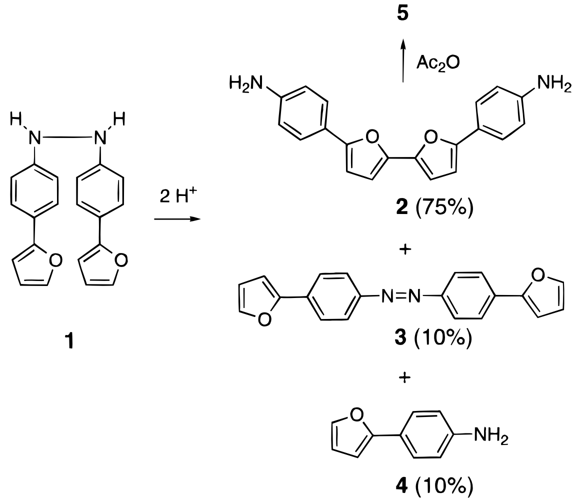
We have discovered a [9,9]-sigmatropic shift in the acid-catalyzed benzidine rearrangement of bis[4-(2-furyl)-phenyl]diazane (**1**). This [9,9] shift provides the first example of such a shift not only in the benzidine rearrangements[1] but also in organic reactions. Our findings also support the new formulation by Shine and co-workers that the benzidine rearrangements follow the patterns for sigmatropic processes.[2] Thus, hydrazo **1** underwent exceptionally clean rearrangement to give the HCl salt of 5,5′-bis(4-aminophenyl)-2,2′-bifuryl (**2**), which was precipitated from the reaction solution almost free from impurities, contrary to the ordinary benzidine rearrangements that require tedious workup procedures in order to get the pure product. Overall, 75% of the rearrangement product **2** and 20% of disproportionation products such as the corresponding azo **3** [bis[4-(2-furyl)-phenyl]diazene] and fission amine **4** [4-(2-furyl)aniline] and small amounts of unidentified products accounted for the rearrangement of **1** in 95% ethanol at 0 °C (Scheme 1).

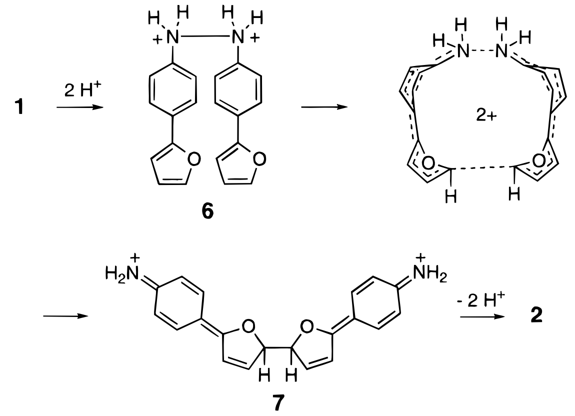
Characterization of product **2** was achieved with spectroscopic data[3] such as MS and ^{1}H and ^{13}C NMR and further confirmed by making its diacetyl derivative **5**. All the spectroscopic data such as ^{1}H, ^{13}C, and 2-D NOESY NMR spectra fit the structure of **5** well.[4]

The specific rate constant in the rearrangement of **1** was 7.65 M^{-2} min^{-1} (at 0 °C in *ca.* 95% ethanol and 0.10 N in HCl), and the disappearance of **1** was found to be second order in acid concentration.[5] The rate constant shows that the disappearance of **1** is 5.3−11 times faster than that of hydrazobenzene **8** and 2.4 times faster than that of 4,4′-divinylhydrazobenzene, but is slower than that of *p*-hydrazobiphenyl by a factor of 1.7. Comparisons could be made with the data reported previously; *i.e.*, the specific rate constants for rearrangement of hydrazobenzene **8** were 1.44 M^{-2} min^{-1} (0.15 °C in 95% ethanol and 0.102 N in acid)[6] and 0.70 M^{-2} min^{-1} (0 °C in 75% ethanol and 0.10 N in acid)[7] and of 4,4′-divinylhydrazobenzene and *p*-hydrazobiphenyl (**14**) 3.16 M^{-1} min^{-1} (0 °C in 95% ethanol and 0.053 N in acid)[6] and 13.05 M^{-2} min^{-1} (0 °C in 95% ethanol containing about 8% water and 0.128 N in acid),[8] respectively.

Scheme 1



Scheme 2



The fast and clean conversion of **1** to **2** selectively by a [9,9]-sigmatropic shift was surprising in view of the fact that other bondings such as [3,3]- and [7,7]-sigmatropic shifts would be also thermally allowed processes. A reasonable explanation for the unique rearrangement of **1** may lie in the structure of the transition state leading to **2**. That is, diprotonated hydrazo **6** (Scheme 2) is expected to adopt a transition state in which aromatic rings are parallel to each other and are bent to a certain degree while maintaining an aromatic character.

In this bent transition state, one may imagine skeletons of phenyl and furyl as those of cyclohexadienyl and 2-butenyl, respectively. Then this transition structure

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[1] (a) Park, K. H. *Heavy-Atom Kinetic Isotope Effects in Solving Mechanisms of Benzidine Rearrangements: Hydrazobenzene and 2,2′-Dimethoxyhydrazobenzene.* Ph.D. Dissertation, Texas Tech University, 1983. (b) Dewar, M. J. S. In *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: New York, 1969; Vol. 1, pp 323−343. (c) Shine, H. J. In *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Interscience: New York, 1969; Vol. 2, pp 191−247. (d) Shine, H. J. In *Aromatic Rearrangements*; Elsevier: New York, 1967; pp 126−179. (e) Cox, R. A.; Buncel, E. In *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; pp 775−859. (f) Banthorpe, D. V. *Chem. Rev.* **1970**, *70*, 295−322. (g) Olah, G. A.; Dunne, K.; Kelly, D. P.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 7438−7447. (h) Bunton, C. A.; Rubin, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4236−4246.

[2] (a) Rhee, E. S.; Shine, H. J. *J. Am. Chem. Soc.* **1986**, *108*, 1000−1006. (b) Shine, H. J. In *Isotopes in Organic Chemistry*; Buncel, E., Saunders, W. H., Jr., Eds.; Elsevier: Amsterdam, 1992; Vol. 8, Chapter 1.

[3] ^{1}H NMR (300 MHz, acetone-d_6) δ: 7.50 (d, J = 8.6 Hz, 4H, Ph-H), 6.72 (d, J = 8.6 Hz, 4H, Ph-H), 6.68 (d, J = 3.4 Hz, 2H, furyl-H), 6.62 (d, J = 3.4 Hz, 2H, furyl-H), 4.88 (s, 4H, NH_2). MS *m/e* 316 (M$^+$). IR: 3400, 3300, 3200, 1630, 1605, 1505, 1460, 1270, 1180, 1020 cm^{-1}.

[4] ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.08 (s, 2H, NH), 7.71 (d, J = 8.7 Hz, 4H, Ph-H), 7.66 (d, J = 8.7 Hz, 4H, Ph-H), 6.98 (d, J = 3.4 Hz, 2H, furyl-H), 6.87 (d, J = 3.4 Hz, 2H, furyl-H), 2.05 (s, 6H, C(O)-CH_3). ^{13}C: 24.07, 106.89, 107.92, 119.21, 124.07, 124.67, 138.92, 144.69, 152.63, 168.43. MS: *m/e* 400 (M$^+$). IR (KBr): 3295 (br s, NH), 1658 (C=O), 1583, 1515, 1401, 1300, 1018, 823, 779 cm^{-1}.

[5] By measuring [**1**] at time *t* with Bindschedler's Green, specific rate constants depending on the acid concentration were obtained as follows. k = 7.67 M^{-2} min^{-1} at [HCl] = 0.1 M and [**1**]$_o$ = 0.01 M. k = 7.62 M^{-2} min^{-1} at [HCl] = 0.2 M and [**1**]$_o$ = 0.01 M. See the following references for the titration method using Bindschedler's Green. (a) Dewar, M. J. S. *J. Chem. Soc.* **1946**, 777−780. (b) Croce, L. J.; Gettler, J. D. *J. Am. Chem. Soc.* **1953**, *75*, 874−879. (c) Cohen, M. D.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 880−883. (d) Shine, H. J.; Trisler, J. C. *J. Am. Chem. Soc.* **1960**, *82*, 4054−4058. (e) Clovis, J. S.; Hammond, G. S. *J. Org. Chem.* **1963**, *28*, 3290−3297.

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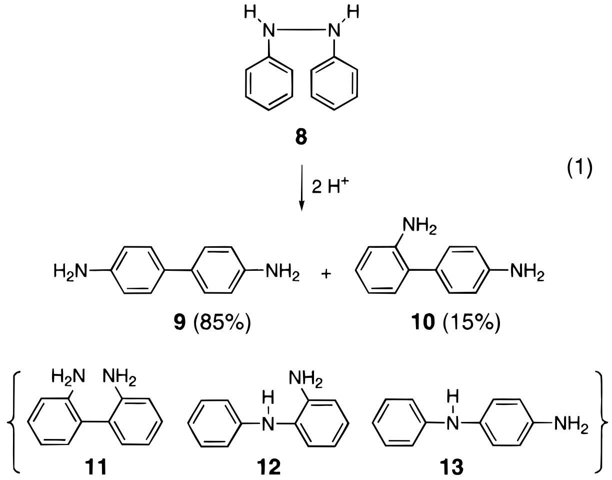
would allow the distance between the 9,9′-carbons to be shorter for efffective bonding, while making those between the 3,3′- and 7,7′-carbons larger. Regarding the mechanism of the benzidine rearrangement, a new understanding has emerged in the last 16 years based on heavy-atom kinetic isotope effects (KIE).

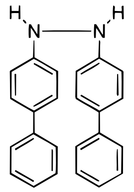
The essence of the new understanding lies in the successful demonstration of sigmatropic shifts in benzidine rearrangements. Thus, hydrazobenzene **8** has been shown with nitrogen and carbon KIE (eq 1)[9] to give *p*-benzidine **9** in a concerted way and diphenyline **10** in a nonconcerted way by [5,5]- and [3,5]-sigmatropic shifts, respectively.



Analogously, rearrangement products that are structurally similar to *o*-benzidine (**11**) and *p*-semidine (**13**) have been shown to be formed in a concerted way, conforming with [3,3]- and [1,5]-sigmatropic shifts, respectively. On the other hand, formation of rearrangement products such as *o*-semidine (**12**) have been shown to be nonconcerted, corresponding with a [1,3]-sigmatropic shift. Accepting that the benzidine rearrangements are sigmatropic shifts,[10] the possibility of a larger sigmatropic shift than [5,5] would be anticipated. In this regard, our example of a [9,9]-sigmatropic shift clearly supports the new understanding of the benzidine rearrangement.

Among the previous reports dealing with the hydrazoaromatics, none has described rearrangement by any sigmatropic shift larger than [5,5]. *p*-Hydrazobiphenyl (**14**) is reported to disproportionate (75% at 0 °C, 88% at 25 °C) and concurrently to rearrange (25% at 0 °C, 12% at 25 °C), forming an *o*-semidine-type product,[8] though a larger shift such as [7,7] or [9,9] would theoretically be possible. 4,4′-Divinylhydrazobenzene is documented to give only a polymeric compound without any rearrangement product.[6] The rearrangement of 3,3′-divinylhydrazobenzene is described to give 2,2′-divinylbenzidine.[11]

With this in mind, we further studied the rearrangement of *p*-hydrazobiphenyl (**14**), bis[4-(2-thienyl)phenyl]diazane (**15**), bis[3-(2-furyl)phenyl]diazane (**16**), and bis[3-(2-thienyl)phenyl]diazane (**17**) in order to compare the results with those of **1**.



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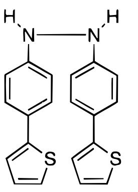

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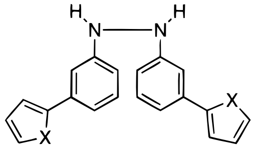

16: X=O **17**: X=S

The revisit of *p*-hydrazobiphenyl (**14**) in this work was to seek, hopefully, any rearrangement product formed by larger sigmatropic shift than [5,5]. However, we could only confirm *o*-semidine and disproportionation products as reported previously.[8] The rearrangement of **15** gave two rearrangement (∼46%) and disproportionation products (∼50%). Though characterization of the two rearrangement products is not complete, the ^{1}H NMR spectrum of an isolated product indicates the involvement of a [9,9] shift. On the other hand, each rearangement of **16** and **17** gave a *p*-benzidine-type compound by a [5,5] shift.[12]

Several remarks are noteworthy in these benzidine-type rearrangements. One question is why 2-furyl derivative **1** would undergo a [9,9] shift much more favorably than **15** while others (**14**, **16**, and **17**) would not? A possible reason for this would be some sort of $O\cdots H-O-H\cdots O$ hydrogen bonding between the two furyl oxygens holding the molecule in an appropriate conformation, uniquely in the 2-furyl derivative **1** but not in the other cases. The other is the possibility of two successive [5,5]s instead of a [9,9] shift. The only certain way of ruling the possibility in or out would be by measuring a carbon KIE at the appropriate phenyl and furyl positions, successively. Nevertheless, our experimental results seem to provide at least two arguments that weigh againt two [5,5]s. One argument is the faster rate constant of **1** than that of **8**. When **8** rearranges by a [5,5] shift, all that remains is deprotonation. One would expect that to be faster than the second [5,5] shift needed in the case of **1**, so that **8** might be expected to rearrange faster than **1**. A second argument is the good product yield (75%). Supposing the two successive [5,5]s, perhaps cleavage products would be expected from the intermediate, which would be formed in between the two [5,5]s.

In conclusion, a [9,9]-sigmatropic shift has been discovered for the first time in the acid-catalyzed rearrangement of bis[4-(2-furyl)phenyl]diazane (**1**). Further, this example supports Shine's new formulation that the benzidine reaarrangements follow the patterns of sigmatropic processes.

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Supporting Information Available: Experimental procedures and characterization data of **5** (9 pages).

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[9] In earlier reports, the ratio 70:30 for **9**:**10** was quoted; see any reference in ref 1. Recently remeasured ratio of **9** to **10** in 75% aqueous ethanol is 85:15; see ref 10.

[10] Subotkowski, W.; Kupczyk-Subotkowska, L.; Shine, H. J. *J. Am. Chem. Soc.* **1993**, *115*, 5073−5076.

[11] Wiley, R. H.; Smith, N. R. *J. Am. Chem. Soc.* **1948**, *70*, 2295−2296.

[12] Each rearrangement of **16** and **17** gave *p*-benzidine-type compound in 21% and 17% isolated yield, respectively, in addition to disproportionation products such as corresponding diazene and fission amine.