## Attempted Generation of the Potentially Aromatic 6,7-Diphenyldibenzo[*e,g*][1,4]diazocine Dianion Leads with Profound Rearrangement to the Isomeric *N*-(2-Amino-1,2-diphenylethenyl)carbazole Dianions

John J. Eisch,\*,<sup>†</sup> Renuka N. Manchanayakage,<sup>†</sup> and Arnold L. Rheingold<sup>‡</sup>

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902-6000, and Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0332

jjeisch@binghamton.edu

Received July 1, 2009

## ABSTRACT



The attempted generation of the potentially aromatic 6,7-diphenyldibenzo[*e*,*g*][1,4]diazocine dianion from sodium in THF leads with profound rearrangement to the isomeric *N*-(2-amino-1,2-diphenylethenyl)carbazole dianions and, after hydrolysis, to a 55:45 mixture of *Z*- and *E*-isomers of *N*-(2-amino-1,2-diphenylethenyl)carbazoles. These isomers were separated and their individual structures determined by X-ray diffraction. Since treatment of the starting diazocine first with *tert*-butyllithium and then with water also yielded the same *Z*- and *E*-isomeric mixture, electron transfer reduction is clearly involved.

Our ongoing interest in the chemical properties of proposed<sup>1</sup> and actual<sup>2</sup> cyclic conjugated imines has led us to examine the electron-transfer reduction of dibenzo[e,g][1,4]diazocines such as **1**, having a nonplanar eight-membered ring<sup>3</sup> and having received previous attention as a heterocyclic model for cyclooctatetraene.<sup>4,5</sup> The central question of our study has been whether the eight-membered ring of **1** might

become planar upon the addition of two electrons (2) because of the potential aromaticity of such a dianion (Scheme 1). Such a structural change would parallel the known behavior of nonplanar cyclooctatraene, which forms a planar dianion upon two-electron reduction.<sup>6</sup> Previous studies of 1 seemed to be in accord with such a reduction, since the reduction of

ORGANIC LETTERS

2009 Vol. 11, No. 18

4060-4063

<sup>&</sup>lt;sup>†</sup> State University of New York at Binghamton.

<sup>&</sup>lt;sup>\*</sup> University of Čalifornia, San Diego.

<sup>(1)</sup> Eisch, J. J.; Chan, T. Y.; Gitua, J. N. Eur. J. Org. Chem. 2008, 39, 392–397.

<sup>(2)</sup> Eisch, J. J.; Abraham, T. Tetrahedron Lett. 1976, 1647–1650.

<sup>(3)</sup> Finder, C. J.; Newton, M. G.; Allinger, N. L. J. Chem. Soc., Perkin Trans. 2 1973, 1928–1932.

<sup>(4)</sup> Allinger, N. L.; Youngdale, G. A. J. Org. Chem. 1959, 24, 306–308.

<sup>(5)</sup> Allinger, N. L.; Szkrybalo, W.; DaRooge, M. A. J. Org. Chem. 1963, 28, 3007–3009.

<sup>(6) (</sup>a) Katz, T. J. J. Am. Chem. Soc. **1960**, 82, 3784. (b) Goldberg, S. Z.; Raymond, K. N.; Harmon, C. A.; Templeton, D. H. J. Am. Chem. Soc. **1974**, 96, 1348.

1 by sodium amalgam in ethanol was interpreted to have produced the 5,6,7,8-tetrahydro derivative 3 of 1 (assumed *trans*-6,7-diphenyl), based upon elemental analyses and infrared spectra data<sup>4,7,8</sup> If 3 were indeed formed in such a reduction, 2 would seem to be a necessary precursor (but cf. infra<sup>4</sup>).



We therefore undertook the reduction of 1 with sodium metal in anhydrous THF at 25 °C. Hydrolysis of the reaction solution, after 5 h and after separation of the residual sodium, showed complete consumption of 1 and gave an 82% yield of a colorless powder, whose mass spectrum (70 eV) had the appropriate parent peak of 360 for structure 4 but whose infrared spectrum displayed two sharp N-H stretching bands at 3378 and 3480 cm<sup>-1</sup>. Such bands are inconsistent with the secondary amine of structure 4 having a symmetry plane but instead would require a primary amine 5. Amine 5 was recrystallized from 95% ethanol to yield as separate crystals pale yellow cubes of 5a, mp 166-167 °C, and colorless needles of 5b, mp 166-167 °C, in a 55:45 ratio (Figure 1, Scheme 2). Picking apart such crystals<sup>9</sup> under low-power  $(30 \times)$ microscopic magnification and determining their individual structures by X-ray diffraction showed that 5a and 5b are the Z- and E-isomers, respectively, of N-(2-amino-1,2diphenylethenyl)carbazole (Figure 1).

Although there remains no doubt of the structures of **5a** and **5b** in the solid state and of the isolated solid **5** as therefore a mixture of **5a** and **5b**, dissolution of the individual solids, **5**, **5a**, and **5b**, in CDCl<sub>3</sub> and NMR spectral measurements give an unexpected result. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the three samples were superimposably identical and the decoupled <sup>13</sup>C spectrum of each displayed exactly 16 singlets. One interpretation of these spectral data is that in solution CDCl<sub>3</sub> sets up an equilibration between **5a** and **5b** and that D-bonding of CDCl<sub>3</sub> with the amino group of



Figure 1. Thermal ellipsoid (30%) diagrams for the Z-isomer of N-(2-amino-1,2-diphenylethenyl)carbazole (**5a**) (orthorhombic, pale yellow block-type crystals, mp 166–167 °C) and the *E*-isomer of N-(2-amino-1,2-diphenylethenyl)carbazole (**5b**) (triclinic, colorless needles, mp 124–125 °C). Selected bond lengths (Å) and angles of **5a**: N(1)–C(12) 1.388(2), N(1)–C(1) 1.390(2), N(1)–C(13) 1.436(2),N(2)–C(20)1.387(2),C(13)–C(20)1.356(2),C(12)–N(1)–C(13) 124.08(14),N(1)–C(1)–C(13) 126.04(14), C(1)–N(1)–C(13) 124.08(14),N(1)–C(1)–C(2)128.55(15),N(1)–C(1)–C(6)109.56(14), N(1)–C(13)–C(14) 115.13(14), C(13)–C(20)–N(2) 122.47 (16). **5b**: N(1)–C(12) 1.396(4), N(1)–C(1) 1.396(4), N(1)–C(13) 1.440(4), N(2)–C(20) 1.378(4), C(13)–C(20) 1.354(5), C(12)–N(1)–C(1) 108.4(3), C(12)–N(1)–C(13) 127.0(3), C(1)–N(1)–C(13) 124.6(3), N(1)–C(1)–C(2)128.4(3),N(1)–C(1)–C(6)109.5(3),N(1)–C(13)–C(14) 115.3(3), C(13)–C(20)–N(2) 122.3(3).



either isomer favors the solvated *E*-isomer **6b** over *Z*-isomer **6a** for steric reasons (Scheme 3).<sup>10</sup>

Chemical confirmation of structures **5a** and **5b** was obtained through the quantitative hydrolysis of their mixture

<sup>(7)</sup> Täuber, E. Ber. Dtsch. Chem. Ges. 1892, 25, 3287.

<sup>(8)</sup> Täuber, E. Ber. Dtsch. Chem. Ges. 1893, 26, 1703.

<sup>(9)</sup> A.L.R. scrutinized under magnification the crystalline sample of **5** intended for XRD analysis and was able to discern the two distinct crystal habits and to separate crystals of **5a** and **5b** for individual XRD analysis.

<sup>(10)</sup> The complete <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5**, **5a**, and **5b** in  $CDCl_3$  are available for inspection in the Supporting Information.

in refluxing acetic acid with 5 N HCl to yield the known ketone 7 (Scheme 4).<sup>4</sup> The minor products isolated from the original reduction of 1 (Scheme 1) were carbazole (8, 9%) and benzyl phenyl ketone (9, 9%), both of which can be viewed as further C–N cleavage products of the dianions of **5a** and **5b**, followed by hydrolysis.



From these surprising findings it follows that the previously reported tetrahydro derivative does not have proposed structure **3**, but rather that of an *N*-(2-amino-1,2-diphenyl-ethyl)carbazole derivative (**10**) of **5**. In better accord with such a primary amine structure for **10** is the reported presence of two infrared stretching bands at 3425 and 3333 cm<sup>-1.4</sup>



The formation of disodium salts **13a** and **13b** in the course of the sodium reduction of **1** appears to be best explained by the intramolecular coupling of the asterisked N- and C-centered radicals in the nonplanar bis-radical anion **11** to yield **12**, which undergoes anionic elimination and aromatization to produce the anions **13a** and **13b** (Scheme 5). There



is ample precedent for such intramolecular formation and coupling of bis-radical anions by alkali metals. For example, treatment of *o*-diphenylbenzene (**14**) with lithium metal in THF at 25 °C and hydrolysis leads via **15a** to tetrahydro derivative **15b**, whose subsequent dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) yields 65% of triphenylene (**16**) (Scheme 6).<sup>11</sup> In an analogous manner, 1,1'-binaphthyl is transformed into perylene in 55% yield.<sup>11</sup>



Furthermore, that such a rearrangement can be effected by electron-transfer agents other than metals received corroboration by treating **1** in THF at -78 °C with *tert*butyllithium. After bringing such a mixture to 25 °C and hydrolyzing, again the principal products were **5a** and **5b**. This reagent in pentane has been shown to effect by electron transfer the reductive dimerization of diphenylacetylene into (E,E)-1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene.<sup>12a,b,13</sup>

This last experiment provides insight into the original work of Allinger and co-workers,<sup>4</sup> who observed the extraordinary transformation of 1 into 7 by two consecutive reactions: first,

<sup>(11)</sup> Eisch, J. J.; Kovacs, C. A. In *Polynuclear Aromatic Compounds*; Ebert, L. B., Ed.; Advances in Chemistry Series 217; American Chemical Society: Washington, D.C., 1988; Chapter 6, pp 96, 103–4, where experimental procedure and discussion are available.

<sup>(12)</sup> Such a reductive dimerization of this alkyne by *tert*-butyllithium is readily understood as an electron-transfer formation of Li<sup>+</sup>[PhC=CPh]<sup>-</sup> and coupling of such radical-anions. (a) Mulvaney, J. E.; Garlund, Z. G.; Garlund, S. L. J. Am. Chem. Soc. 1963, 85, 3897-3898. (b) The reaction between 1 in THF at -78 °C and a pentane solution of *tert*-butyllithium (1.7 M, Aldrich) was conducted on a 1.50 mM scale of 1 and a 3-fold molar excess of *tert*-butyllithium for 1 h, and then the reaction mixture was brought to and maintained at 25  $^{\circ}$ C for 3 h before quenching with wet diethyl ether. Usual workup and <sup>1</sup>H NMR analysis showed the typical absorptions of 5a and 5b in CDCl<sub>3</sub> solution (cf. Scheme 3). All of these operations occurred without incident since the tert-butyllithium in pentane and the reaction mixture were maintained under an atmosphere of anhydrous, deoxygenated argon. Later in 2008, a fatal accident occurred at UCLA when a chemistry research assistant died from injuries sustained while conducting an organic synthesis procedure employing tert-butyllithium in pentane: Chem. Eng. News, Online, Latest News, Jan 22, 2009. The details of the experiment and some analysis of the circumstances of the tragic accident have now been reported: Chem. Eng. News, Aug 3, 2009. We advise anyone considering experimentation with tert-butyllithium to study the foregoing reports and to employ instead tert-butyllithium in less volatile solvents, such as cyclohexane or heptane, and to work under an argon atmosphere. Appropriate safety measures for working with air- and moisture-sensitive

the treatment of 1 with LiAH<sub>4</sub> in refluxing THF, followed by hydrolysis, and second, heating the resulting crude product with aqueous HCl and acetic acid. To explain such a surprising formation of 7, these workers<sup>4</sup> proposed successive hydride attack on 1 followed by intramolecular nucleophilic amide attack and hydrolysis. Since our results show that attack of *tert*-butyllithium on 1 can produce **5a** and **5b** by an electron-transfer process, we suggest that LiAlH<sub>4</sub> in THF can similarly achieve electron-transfer reduction of 1 into **5a** and **5b**. Previous workers have proposed electron-transfer processes for reductions with LiAlH<sub>4</sub>.<sup>14</sup>

Finally, this work suggests that diazocine **1** may prove to be the most effective electron trap for the detection of electron transfer in organometallic reactions with organic substrates.<sup>15</sup>

(14) In such a precedent for the electron-transfer reduction by LiAlH<sub>4</sub> in THF we offer the pertinent study of the reduction of alkyl iodides: Ashby, E. C.; Pham, T. N.; Amrollah-Madjdabadi, A *J. Org. Chem.* **1991**, *56*, 1596–1603.

Acknowledgment. This work is dedicated to the memory of Glen Allan Russell (1925–1998), late Distinguished Professor of Chemistry, Iowa State University, outstanding mentor and pioneer of organic electron-transfer reaction mechanisms. Support for this research stems from a Senior Scientist Award (J.J.E.) made by the Alexander von Humboldt Foundation, Bonn, Germany.

**Supporting Information Available:** Crystallographic (CIF) data for structures **5a** and **5b** in the solid state; criteria of purity of starting materials and separated final products for key transformations; experimental procedures; and copies of the fully displayed <sup>1</sup>H and <sup>13</sup>C NMR spectra of the following solutions in CDCl<sub>3</sub>: (1) starting diazocine, compound **1**; (2) isolated mixture of **5a** and **5b**, compound **5**; (3) *Z*-isomer, mp 166–167 °C, compound **5a**; (4) *E*-isomer, mp 124–125 °C, compound **5b**; and (5) compound **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

## OL901503S

compounds are discussed extensively in the following reference: Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1981; Vol. 2, Part I, pp 1–81, in detail and Part II, pp 87–191, *passim*.

<sup>(13)</sup> Another apparent electron-transfer cyclization by *n*-butyllithium in THF is the transformation of 2-(2,2-diphenyl-1-ethenyl)biphenyl into 9-(diphenylmethyl)fluorene in 25% yield. Eisch, J. J.; Chobe, P. *Polynuclear Aromatic Compounds*; Ebert, L. B., Ed.; Advances in Chemistry Series, No. 217; American Chemical Society: Washington, D.C., 1988; pp 97–105.

 $<sup>\</sup>left(15\right)$  Eisch, J. J. Doetschman, D. C. UV spectral and EPR studies in progress.