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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

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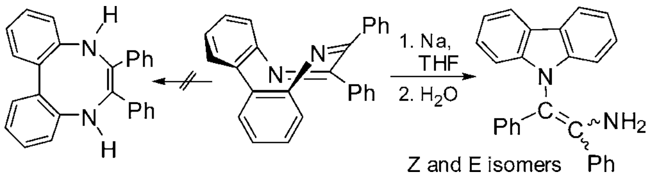
ABSTRACT



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[1] and actual[2] 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[3] and having received previous attention as a heterocyclic model for cyclooctatetraene.[4,5] 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.[6] Previous studies of **1** seemed to be in accord with such a reduction, since the reduction of

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

(2) Eisch, J. J.; Abraham, T. *Tetrahedron Lett.* **1976**, 1647–1650.

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

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

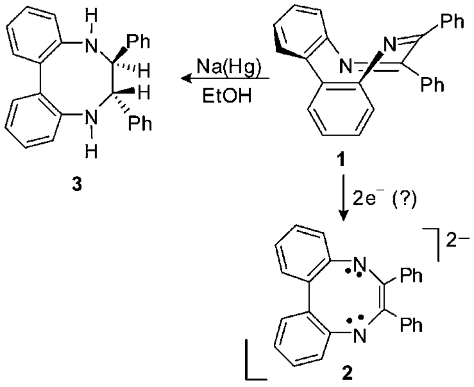
(5) Allinger, N. L.; Szkrybalo, W.; DaRooge, M. A. *J. Org. Chem.* **1963**, *28*, 3007–3009.

(6) (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.

10.1021/ol901503s CCC: $40.75

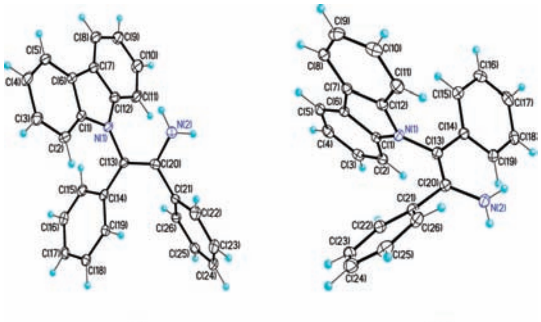
1 by sodium amalgam in ethanol was interpreted to have produced the 5,6,7,8-tetrahydro derivative **3** of **1** (assumed *trans*-6,7-diphenyl), based upon elemental analyses and infrared spectra data[4,7,8] If **3** were indeed formed in such a reduction, **2** would seem to be a necessary precursor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

Scheme 1



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^{-1}. 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[9] under low-power (30×) 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-1,2-diphenylethenyl)carbazole (Figure 1).

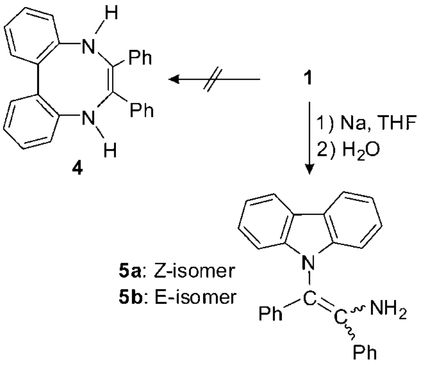
Although there remains no doubt of the structures of **5a** and **5b** in the solid state and of the isolated solid **5** as therefore a mixture of **5a** and **5b**, dissolution of the individual solids, **5**, **5a**, and **5b**, in $CDCl_3$ and NMR spectral measurements give an unexpected result. The ^{1}H and ^{13}C NMR spectra of the three samples were superimposably identical and the decoupled ^{13}C spectrum of each displayed exactly 16 singlets. One interpretation of these spectral data is that in solution $CDCl_3$ sets up an equilibration between **5a** and **5b** and that D-bonding of $CDCl_3$ with the amino group of either isomer favors the solvated *E*-isomer **6b** over *Z*-isomer **6a** for steric reasons (Scheme 3).[10]



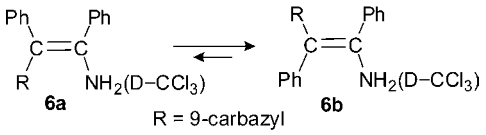
5a **5b**

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(1) 108.22(13), C(12)−N(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).

Scheme 2



Scheme 3



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

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(7) Täuber, E. *Ber. Dtsch. Chem. Ges.* **1892**, *25*, 3287.

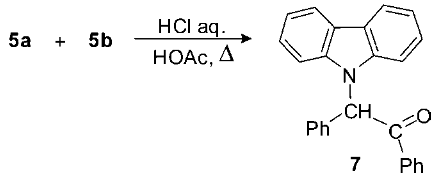
(8) Täuber, E. *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 1703.

(9) 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.

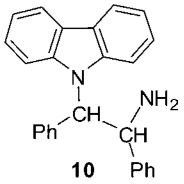
(10) The complete ^{1}H and ^{13}C NMR spectra of **5**, **5a**, and **5b** in $CDCl_3$ are available for inspection in the Supporting Information.

in refluxing acetic acid with 5 N HCl to yield the known ketone **7** (Scheme 4).[4] 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.

Scheme 4



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-diphenylethyl)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^{-1}.[4]



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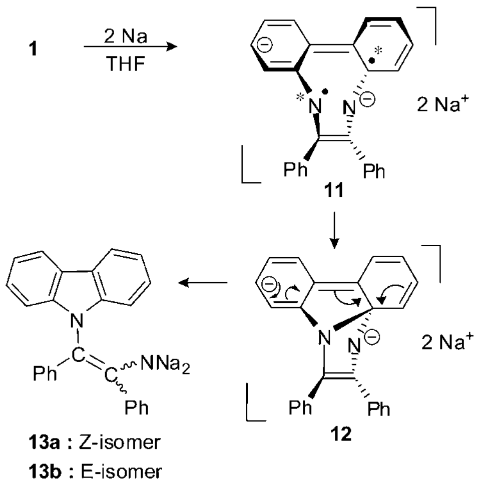
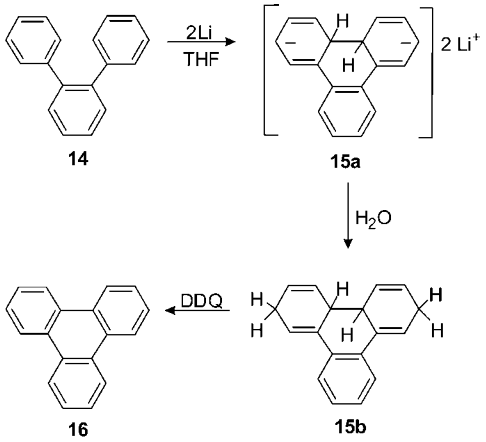
The formation of disodium salts **13a** and **13b** in the course of the sodium reduction of **1** appears to be best explained by the intramolecular coupling of the asterisked N- and C-centered radicals in the nonplanar bis-radical anion **11** to yield **12**, which undergoes anionic elimination and 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).[11] In an analogous manner, 1,1′-binaphthyl is transformed into perylene in 55% yield.[11]

Scheme 5



Scheme 6



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.[12a,b,13]

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

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[11] 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.

[12] Such a reductive dimerization of this alkyne by *tert*-butyllithium is readily understood as an electron-transfer formation of $Li^+[PhC{=}CPh]^-$ 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 °C for 3 h before quenching with wet diethyl ether. Usual workup and ^1H NMR analysis showed the typical absorptions of **5a** and **5b** in $CDCl_3$ 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 $LiAH_4$ 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[4] 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 $LiAlH_4$ in THF can similarly achieve electron-transfer reduction of **1** into **5a** and **5b**. Previous workers have proposed electron-transfer processes for reductions with $LiAlH_4$.[14]

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.[15]

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 ^1H and ^{13}C NMR spectra of the following solutions in $CDCl_3$: (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.

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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*.

(13) 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.

(14) In such a precedent for the electron-transfer reduction by $LiAlH_4$ 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.

(15) Eisch, J. J. Doetschman, D. C. UV spectral and EPR studies in progress.