One-Pot Synthesis of *N*-Substituted Diaza[12]annulenes

Isao Yamaguchi,* Yoshiaki Gobara, and Moriyuki Sato

Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan iyamaguchi@riko.shimane-u.ac.jp

Received June 28, 2006

The authors have retracted this paper on November 15, 2007 (*Org. Lett.* 2007, 24, 5139) due to uncertainties regarding what products are formed in the reaction described.



N-Substituted diaza[12]annulenes are obtained by one -pot reaction of *N*-(2,4-dinitrophenyl)pyridinium chloride with amines in moderate to high yields. The ¹H NMR spectrum reveals that diamagnetic ring current is generated in the diaza[12]annulene ring. The *N*-substituted diaza-[12]annulenes are electrochemically active in solution.

Annulenes have attracted much attention since the first report on [8]annulene in 1911.¹ Many efforts have been devoted to probing the (anti)aromaticity of [4*n*]annulenes by using NMR spectroscopy and computational methods.^{2–4} The addition of π -electrons to the [4*n*]annulenes that are antiaromatic in the Hückel sense has been carried out to alter their aromaticity and magnetic properties.^{5–8} Among the [4*n*]annulenes, studies on [12]annulenes and hetero[12]annulenes are very limited due to their decreased thermal stability.^{6,9–11} Stevenson reported that [12]annulenes show diamagnetic properties.^{10a}

To our knowledge, the subtraction of two π -electrons from a [4*n*]annulene to provide a dicationic [4*n*]annulene contain-

- (3) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301.
- (4) Sondheimer, F. Acc. Chem. Res. **1972**, 5, 81.
- (5) (a) Strauss, H. K.; Katz, T. J.; Fraenkel, G. K. J. Am. Chem. Soc. **1963**, 85, 2360. (b) Cox, R. H.; Harrison, L. W.; Austin, W. K., Jr. J. Phys. Chem. **1973**, 77, 200.
 - (6) Oth, J. F. M.; Schröder, G. J. Chem. Soc. B 1971, 904.
- (7) (a) Oth, J. F. M.; Baumann, H.; Gilles, J. M.; Schröder, G. J. Am. Chem. Soc. **1972**, 94, 3498. (b) Baumann, H.; Oth, J. F. M. Helv. Chim. Acta **1980**, 63, 618.
- (8) Oth, J. F. M.; Woo, E. P.; Sondheimer, F. J. Am. Chem. Soc. 1973, 95, 7337.
- (9) (a) Oth, J. F. M.; Gilles, J.-M.; Schröder, G. Tetrahedron Lett. **1970**, 61. (b) Oth, J. F. M.; Röttele, H.; Schröder, G. Tetrahedron Lett. **1970**, 67.
- (10) (a) Stevenson, G. R.; Concepcion, R.; Reiter, R. C. J. Org. Chem. **1983**, 48, 2777. (b) Gard, M. N.; Reiter, R. C.; Stevenson, C. D. Org. Lett. **2004**, 6, 393.

10.1021/ol061585q CCC: \$37.00 © 2006 American Chemical Society Published on Web 08/16/2006

ing $(4n - 2)\pi$ electrons has no precedent. The aromaticity and chemical properties of dicationic [4n]annulenes and hetero[4n]annulenes remain elusive.

The introduction of a substituent on the nitrogen atoms of a diaza[12]annulene will give a dicationic species. It is known that the thermal and electronic properties of *N*-substituted aza[4n + 1]annulenes (n = 2, 3, and 4) vary depending on the *N*-substituent.^{12–14} Investigation of the aromaticity and chemical properties of the *N*-substituted diaza[12]annulenes will provide new information about hetero[4n]annulenes. However, there is only one report on such a diaza[12]annulene,¹¹ and its *N*-substitution reaction to generate a dicationic species has not yet been performed.

Herein, we report the one-pot synthesis of *N*-substituted diaza[12]annulenes and an investigation of their aromaticity and their structural, optical, and electrochemical properties. A plausible reaction pathway is also reported.

N-Substituted diaza[12]annulenes (**3**) were obtained by a 2:2 reaction of *N*-(2,4-dinitrophenyl)pyridinium chloride (**1**) with substituted amines¹⁵ (**2**) in 40-83% yields (Scheme 1).

ORGANIC LETTERS 2006 Vol. 8, No. 19 4279-4281

Willstater, R.; Waser, E. Ber. Dtsch. Chem. Ges 1911, 44, 3423.
 Kennedy, R. D.; Lioyd, D.; McNab, H. J. Chem. Soc., Perkin Trans.

¹ **2002**, 1601.

⁽¹¹⁾ Bindra, A. P.; Elix, J. A. *Tetrahedron* **1970**, *26*, 3749.

⁽¹²⁾ Anastassiou, A. G.; Eachus, S. W.; Gellura, R. P.; Gelbrian, J. H. Chem. Commun. **1970**, 1133.

^{(13) (}a) Anastassiou, A. G.; Reichmanis, E.; Elliott, R. L. *Tetrahedron Lett.* **1973**, 3805. (b) Anastassiou, A. G.; Elliott, R. L.; Reichmanis, E. *J. Am. Chem. Soc.* **1974**, *96*, 7823.

^{(14) (}a) Schröder, G.; Heil, G.; Röttle, H.; Oth, J. F. M. Angew. Chem. **1972**, 84, 474. (b) Schröder, G.; Frank, G.; Röttle, H.; Oth, J. F. M. Angew. Chem. **1974**, 86, 237. (c) Röttle, H.; Heil, G.; Schröder, G. Chem. Ber. **1978**, 111, 84.



The results of these reactions are summarized in Table 1. Reaction of $\mathbf{1}$ with 4-haloaniline (entries 4–7) gave a mixture

Table 1.	Results of Reaction of N-(2,4-
Dinitrophe	enyl)pyridinium Chloride (1) with Amines (2)

			yield, %	
$entry^a$	2	Ar	3^b	4 ^c
1	2a	2,5-Me-C ₆ H ₃	3a , 40	0
2	2b	p-MeO-C ₆ H ₄	3b , 83	0
3	2c	p-F-C ₆ H ₄	3c , 62	0
4	2d	p-Cl-C ₆ H ₄	3d , 73	4d , 6
5	2e	$p ext{-}Br ext{-}C_6H_4$	3e , 76	4e , 3
6	2f	p-I-C ₆ H ₄	3f , 46	4f , 3
7	$2\mathbf{g}$	n-hexyl	3g , 40	0

^{*a*} Ethanol solution of **1** and **2** in a 1:2 molar ratio was refluxed for 12 h under nitrogen. ^{*b*} Isolated yield. ^{*c*} Estimated from ¹H NMR spectrum of a mixture of **3** and **4**.

of *N*-halophenyl diaza[12]annulene dichloride and *N*-halophenylpenta-2,4-dienylidene-1-*N*-halophenylinium chloride (**4**).¹⁶ The diaza[12]annulenes obtained were soluble in water and polar aprotic solvents such as *N*,*N*-dimethylformamide, dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidinone. The structures of **3** and **4** were confirmed by FAB-MS, ¹H and ¹³C NMR spectroscopy, and elemental analysis.

Figure 1 depicts the ¹H NMR spectrum of **3a** in DMSO*d*₆. Peaks at δ 9.29, 8.83, and 8.33 are assigned to H^a, H^c, and H^b of the diaza[12]annulene ring, respectively. Observation of these three signals of the diaza[12]annulene ring in a 2:1:2 integral ratio suggests that the diaza[12]annulene ring has a *C*₂-symmetric conformation. As judged from the coupling constants, $J_{H_a-H_b} = 5.9$ Hz and $J_{H_b-H_c} = 6.6$ Hz, the diaza[12]annulene ring may form an all-cis geometrical structure at 20 °C, as shown in Figure 1. ¹³C NMR data also support this structure.¹⁷ A previous report predicted the allcis structure to be the most stable of the six geometries of [12]annulene isomers.¹⁸



Figure 1. ¹H NMR spectrum of 3a in DMSO- d_6 at 20 °C.

The ¹H NMR peak positions and *J* values corresponding to the hydrogen atoms of the diaza[12]annulene ring of 3a-gwere essentially the same, independent of the structure of the *N*-substituent. The appearance of the ¹H NMR peaks of the diaza[12]annulene ring at lower magnetic field positions by about 2–3 ppm compared with those of the outer hydrogens of the [12]annulenes^{9b} and hetero[12]annulenes^{11,19} has been ascribed to the generation of diamagnetic ring currents in the diaza[12]annulene ring. Such a downfield shift of the ¹H NMR peak induced by diamagnetic ring current was also observed in the [12]annulene anion.⁶

The diaza[12]annulenes give rise to two absorption bands in the ranges of 255-284 and 351-396 nm, and their relative intensities vary depending on the structures of the *N*substituents, as summarized in Table 2. It is reported that

Table 2. Absorption and Electrochemical Oxidation Potential

 Data of Diaza[12]annulene Dichloride (3)

		1	
entry	3	$ ext{absorption},^a ext{nm} \ (\log \epsilon, ext{M}^{-1} ext{cm}^{-1})$	$E_{\rm a}, {}^c{\rm V}$ (vs Ag ⁺ /Ag)
1	3a	255 (3.95), 351 (2.85)	0.79
2	3b	$264 (5.56), 333 (5.18), {}^{b} 396 (4.51)$	0.77
3	3c	268 (4.53), 297 (3.88)	1.15
4	3d	266 (4.79), 365 (3.92)	1.07
5	3e	284 (4.01)	1.00
6	3f	$269\ (4.51),\ 292\ (4.56),\ 369\ (4.05)$	0.99
7	$3\mathbf{g}$	$258\ (4.17),\ 336\ (3.58),\ 395\ (3.31)$	0.73

 a In EtOH. b Shoulder peak. c In DMSO solution including Et₄NBF₄ (0.1 M). Sweep rate was 50 mV s^{-1}.

N-substituted aza[9]annulenes exhibit two absorption bands and their intensities are affected by the structures of the *N*-substituents.¹² Diaza[12]annulene **3b** exhibited absorptions at longer wavelengths than those exhibited by **3a**, probably

⁽¹⁵⁾ Reactions of 1 with 4-nitroaniline and with 4-aminoacetophenone did not give both 3 and 4. A possible reason for the results is that low basicity of the amines prevents nucleophilic addition to the pyridinium ring of 1.

⁽¹⁶⁾ It was reported that reaction of **1** with amine in a 1:1 molar ratio gave *N*-arylpenta-2,4-dienylidene-1-*N*-arylinium chloride. See: Becher, J. *Synthesis* **1980**, 589.

⁽¹⁷⁾ Three ^{13}C NMR signals due to the diaza[12]annulene ring were observed at δ 142.2, 146.1, and 142.0.

⁽¹⁸⁾ Castro, C.; Karney, W. L.; Vu, C. M. H.; Burkhardt, S. E.; Valencia, M. A. J. Org. Chem. 2005, 70, 3602.

⁽¹⁹⁾ Holms, A. B.; Sondheimer, F. J. Am. Chem. Soc. 1970, 92, 5284.





due to the expansion of the π -conjugation system from the diaza[12]annulene ring to the 4-methoxyphenyl groups.

The steric effect of the methyl group at the 2-position of the 2,4-dimethylphenyl ring of **3a** may hinder the expansion of the π -conjugation system. The absorption data often give valuable information in predicting the planarity of the annulene ring. The reported tetrabenzodiaza[12]annulene has a nonplanar ring structure, and exhibits absorptions at 235 and 300 nm.¹¹ The diaza[12]annulene ring of **3** seems to have a more planar structure than that of tetrabenzodiaza[12]annulene, as judged from the absorption data.

Cyclic voltammetry measurements suggested that the diaza[12]annulenes underwent electrochemical oxidation in a DMSO solution including Et₄NBF₄. Figure 2 depicts CV



Figure 2. CV curves of **3a** and **3g** in a DMSO solution including Et_4NBF_4 (0.1 M). Sweep rate was 50 mV s⁻¹.

curves of **3a** and **3g**. As summarized in Table 2, the oxidation potential is dependent on the *N*-substituent; **3g** with electrondonating *n*-hexyl substituents (entry 7) shows a peak at a lower oxidation potential than the compounds with electronwithdrawing substituents, **3c**-**f** (entries 3-6). Scheme 2 shows a plausible preparation mechanism for the diaza[12]annulene dichloride (**3**) and *N*-arylpenta-2,4dienylidene-1-*N*-arylnium chloride (**4**), where nucleophilic addition of amine to the pyridinium ring of **1** occurs first, followed by ring-opening of the dihydropyridyl ring and elimination of 2,4-dinitroaniline by reaction of the ringopening compound with **2** to provide **4** (path a). The reaction of *N*-(2,4-dinitrophenyl)penta-2,4-dienylidene-1-*N*-arylinium chloride with amine to give **4** has been reported.²⁰ The **3**:**4** preparative ratios obtained by reaction of **1** with aromatic amines depend on the basicity of the amine. These results indicate that the nucleophilic addition of the NH group of **4** to the pyridinium ring of **1** is a crucial step for generation of the diaza[12]annulene ring.

In summary, *N*-substituted diaza[12]annulenes were obtained in moderate to high yields by the one-pot reaction of N-(2,4-dinitrophenyl)pyridinium chloride with amines. The ¹H NMR spectra of the products revealed that a diamagnetic ring current was generated in the diaza[12]annulene ring. Cyclic voltammetry analysis indicated that the diaza[12]annulenes were electrochemically active in solution. Diaza-[12]annulenes with 4-halophenyl substituents would be a useful starting material for functional compounds and polymers. These approaches are under investigation in our laboratory.

Acknowledgment. The authors wish to thank Dr. H. Fukumoto (Tokyo Institute of Technology) for help with MS measurements.

Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL061585Q

⁽²⁰⁾ Kavalek, J.; Lycka, A.; Machacek, V.; Sterba, V. Collect. Czech. Chem. Commun. 1974, 39, 2056.