of Ms. Ruth Records. We furthermore acknowledge Dr. Craig vanAntwerp's contribution[9] to the synthesis of (*S*)-(3-$^{2}H_{1}$)cyclohexanone (**6**) and Dr. A. Kergomard (Department of Chemistry and Biology, University of Clermont, France) for providing us with the results of his work prior to publication.[27]

Registry No. 1, 68737-98-4; **2**, 68687-98-9; **3**, 68778-92-7; **4**, 68687-91-2; **5**, 75348-02-6; **6**, 66529-33-7; **7**, 1195-31-9; **10**, 68687-94-5; **11**, 68687-95-6; **12**, 68678-49-9; **13**, 68737-96-2; **14**, 1195-31-9; **16**, 68687-97-8; **18**, 56782-80-0; **19**, 61062-51-9; **20**, 61116-80-1; **21**, 68687-92-3; **22**, 5856-74-6; **24**, 68687-86-5; **25**, 75419-01-1; **27**, 68737-95-1; **28**, 75419-02-2; **30**, 68687-87-6; **32**, 68687-88-7; **34**, 68687-89-8; **36** (isomer 1), 68687-88-7; **36** (isomer 2), 75348-03-7; **38**, 68687-90-1; **42**, 75348-04-8; **43**, 75348-05-9; **44**, 75348-06-0; **45** (isomer 1), 75348-07-1; **45** (isomer 2), 75348-08-2; **46**, 75365-51-4; **48**, 24965-94-4; **49**, 66529-34-8; **51**, 66529-35-9.

Evidence against the Intramolecular Cyclization of *o*-Azidobenzenediazonium Ions

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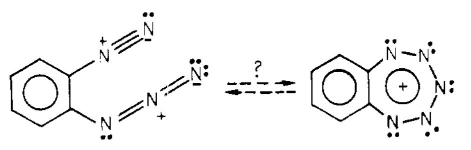
Received June 6, 1980

The question regarding the possibility that *o*-azidobenzenediazonium ions might cyclize to give pentaaza analogues of benzotropylium ions was investigated experimentally. Samples of 4-chloro-2-azidobenzenediazonium ion (**5**) and 5-chloro-2-azidobenzenediazonium ion (**6**) were prepared separately by diazotization of the corresponding chloroazidoanilines and were treated subsequently with cuprous chloride. From each of these Sandmeyer reactions only the unrearranged product was obtained: 2,5-dichloroazidobenzene from **5** and 2,4-dichloroazidobenzene from **6**. The absence of detectable amounts of crossover products in both reactions (within the limits of detection of about 5–10%) demonstrates that the conversions of ions **5** and **6** to the hypothetical benzotropylium-like cyclized ion **7** are not kinetically significant processes. The failure of this type of cyclization is attributed to a high energy barrier for the reorganization of the 12π-electron system in ions **5** and **6** to the 10π-electron system in ion **7**.

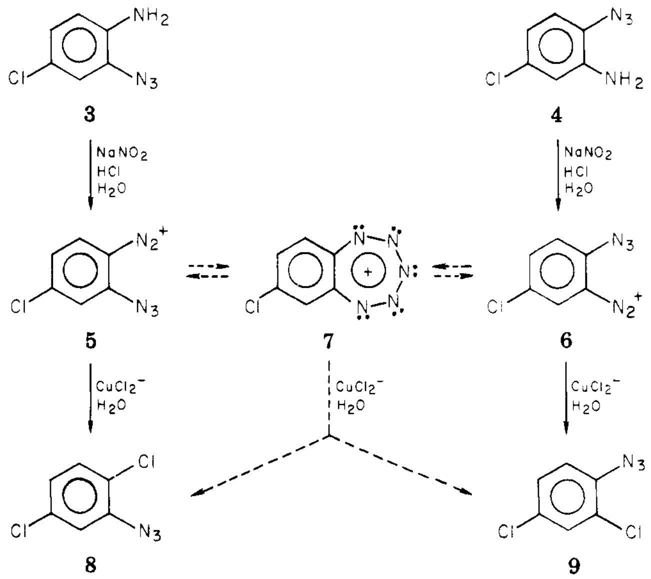
We considered the possibility that the *o*-azidobenzenediazonium ion (**1**) might cyclize to give the resonance-stabilized benzotropylium-like ion **2**. To test this idea,



1 2

we prepared samples of 4-chloro-2-azidoaniline (**3**) and 5-chloro-2-azidoaniline (**4**) and treated them separately with nitrous acid followed by cuprous chloride. As illustrated in Scheme I, if the azidodiazonium ions **5** and **6** fail to give the cyclized ion **7** under these conditions, then the two Sandmeyer reactions would yield different products with no crossover. Specifically, diazotization of amine **3** would generate diazonium ion **5**, which on treatment with cuprous chloride would produce exclusively 2,5-dichloroazidobenzene (**8**); diazotization of amine **4** would generate diazonium ion **6**, which on treatment with cuprous chloride would produce exclusively 2,4-dichloroazidobenzene (**9**). If, however, the azidodiazonium ions **5** and **6** equilibrate with the cyclized ion **7** under these conditions, then the same mixture of Sandmeyer products **8** and **9** would be obtained by starting either from amine **3** or from amine **4**.[2]

Scheme I



Results and Discussion

A sample of amine **3** was prepared from 4-chloro-2-nitroaniline (**10**) by the method of Hall and Patterson.[3] A sample of amine **4** was prepared analogously from 5-chloro-2-nitroaniline (**11**).[3]

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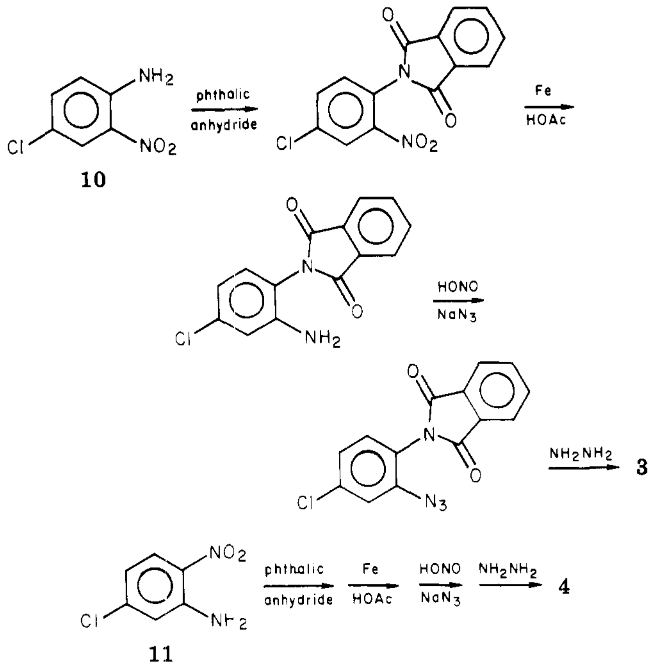
(1) (a) Taken from the M.A. thesis of Donna S. Amenta, Bryn Mawr College, 1971. (b) Presented at the 168th ACS National Meeting, Atlantic City, NJ, Sept 1974; American Chemical Society: Washington, D. C., 1974; ORGN 74.

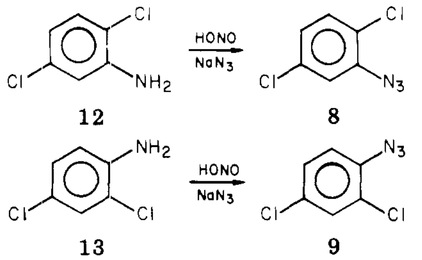
(2) In the only other studies of substituted *o*-azidobenzenediazonium ions of which we are aware, the ions (including **5**) were treated with sodium azide to synthesize the corresponding *o*-diazidobenzenes,[3] thereby precluding any information about possible crossover products.

(3) Hall, J. H.; Patterson, E. *J. Am. Chem. Soc.* **1967**, *89*, 5856–5861.

0022-3263/80/1945-5236$01.00/0 © 1980 American Chemical Society



Authentic samples of the dichloroazidobenzenes **8** and **9** were prepared independently from the corresponding dichloroanilines **12** and **13**, respectively. These two isomeric dichloro azides are readily detected in each other's presence by infrared spectroscopy: 2,5-dichloroazidobenzene (**8**) has a peak of medium intensity at 740 cm^{-1} and no significant absorption at 762 cm^{-1}, whereas 2,4-dichloroazidobenzene (**9**) has a peak of medium intensity at 762 cm^{-1} and no significant absorption at 740 cm^{-1}. Using this analytical method, one could detect as lower limits approximately 5% **8** as a contaminant in a sample of **9** and approximately 10% **9** as a contaminant in a sample of **8**.

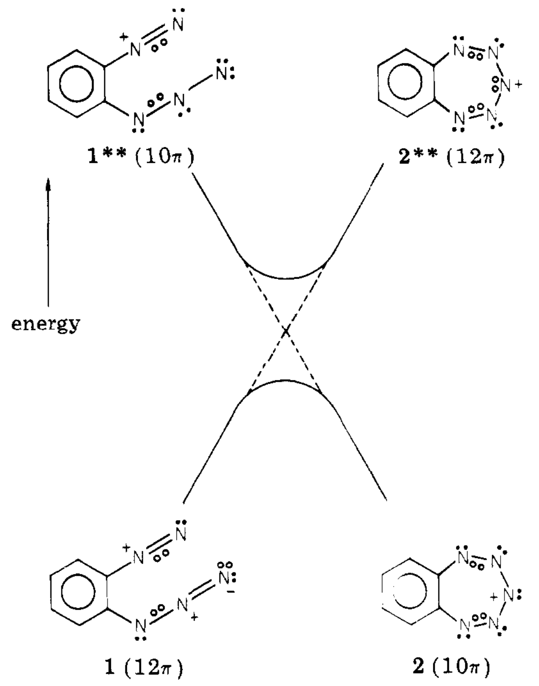


The Sandmeyer reactions of amines **3** and **4** were carried out by treating the amines with nitrous acid at 0 °C and allowing the resulting diazonium ion solutions to stand for 1 h at 0 °C before treatment with cuprous chloride. The crude product (83% yield) derived from amine **3** was identified as 2,5-dichloroazidobenzene (**8**) by infrared analysis. Detectable amounts of the 2,4-dichloro isomer **9** were not present. Similarly, the crude product (59% yield) derived from amine **4** was identified as 2,4-dichloroazidobenzene (**9**), and detectable amounts of the 2,5-dichloro isomer **8** were not present. In a subsequent experiment with amine **3**, the reaction conditions were modified to allow the solution of diazonium ion **5** to stand for 7 days at room temperature before treatment with cuprous chloride. Once again, the crude product (64% yield) consisted of the unrearranged isomer **8** and none of the rearranged isomer **9**.

Thus we conclude that *o*-azidobenzenediazonium ions do not readily undergo cyclization of the **1** → **2** type.

This behavior can be understood by considering the correlation diagram illustrated for the unsubstituted system in Scheme II. In this diagram, the out-of-plane electrons (those in orbitals having a node in the molecular plane) associated with the nitrogen atoms are designated by open circles. The azidodiazonium ion **1** in its ground state has a total of 12 out-of-plane electrons (formally an aromatic sextet, two NN π bonds, and one N lone pair), whereas the cyclized ion **2** in its ground state has only 10 out-of-plane electrons. The cyclization of **1**, represented by moving from left to right in Scheme II, would start out leading not toward **2** but rather toward **2****, a species in a doubly excited state. Therefore this cyclization would be energetically unfavorable in its early stages. A cyclization pathway leading initially toward **2** rather than **2**** would be possible only by starting from **1****, a doubly excited form of the azidodiazonium ion. Because of an avoided crossing of the **1** → **2**** and **1**** → **2** pathways, a direct pathway from **1** to **2** would exist in principle, but the **1** → **2** cyclization would be expected to have a high activation energy as illustrated in Scheme II.[4]

Scheme II



Experimental Section

Elemental analyses were performed by M-H-W Laboratories, Garden City, MI. Melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 257 grating infrared spectrophotometer. Reported gas–liquid chromatographic analyses were accomplished with an F. and M. Model 402 chromatograph equipped with a 6 ft × 0.25 in. glass column packed with 5% SE-52 on 100–140-mesh Gas-Chrom Z (Applied Science).

4-Chloro-2-azidoaniline (3). The procedures of Hall and Patterson were followed.[3]

Fusion of 34.5 g (0.20 mol) of 4-chloro-2-nitroaniline (**10**) and 29.6 g (0.20 mol) of phthalic anhydride gave 48.7 g (79%) of crude 5-chloro-2-phthalimidonitrobenzene, mp 200–202 °C (lit.[3] mp 202 °C).

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(4) In view of the results of other studies of the ease of bending of azido and other related groups,[5] it seems unlikely that the failure of *o*-azidobenzenediazonium ions to undergo cyclization results from difficulties in achieving the bond-angle deformations around nitrogen atoms that would be required.

(5) (a) Roberts, J. D. *Chem. Ber.* **1961**, *94*, 273–278. (b) Roberts, J. D. "Notes on Molecular Orbital Calculations"; Benjamin: New York, 1962; pp 131–139. (c) Ugi, I.; Perlinger, H.; Behringer, L. *Chem. Ber.* **1959**, *92*, 1864–1866. (d) Burke, L. A.; Leroy, G.; Nguyen, M. T.; Sana, M. *J. Am. Chem. Soc.* **1978**, *100*, 3668–3674.

Treatment of 31.7 g (0.10 mol) of crude 5-chloro-2-phthalimidonitrobenzene with Fe and HOAc gave 18.6 g (66%) of crude 5-chloro-2-phthalimidoaniline, mp 177–188 °C (lit.[3] mp 183 °C).

Diazotization of 35.2 g (0.13 mol) of crude 5-chloro-2-phthalimidoaniline followed by treatment with NaN_3 gave 18.5 g (48%) of crude 5-chloro-2-phthalimidoazidobenzene, mp 180–185 °C (lit.[3] mp 195 °C dec). After the diazotization, 13.8 g of starting material was recovered.

Treatment of 36.7 g (0.12 mol) of crude 5-chloro-2-phthalimidoazidobenzene with 85% $NH_2NH_2{\cdot}H_2O$ gave 4.8 g (23%) of crude 4-chloro-2-azidoaniline (**3**), mp 65.5–67.4 °C (lit.[3] mp 70 °C), along with 23.8 g of recovered starting material.

5-Chloro-2-azidoaniline (4). The procedures were based on those of Hall and Patterson.[3] Fusion of 29.0 g (0.17 mol) of 5-chloro-2-nitroaniline (**11**), prepared as described previously,[6] and 24.8 g (0.17 mol) of phthalic anhydride gave 27.4 g (42%) of crude 4-chloro-2-phthalimidonitrobenzene, mp 191–195 °C; recrystallization from 95% EtOH gave material with mp 197.4–197.8 °C.

Anal. Calcd for $C_{14}H_7ClN_2O_4$: C, 55.55; H, 2.33; N, 9.25. Found: C, 55.32; H, 2.25; N, 9.18.

Treatment of 31.1 g (0.10 mol) of crude 4-chloro-2-phthalimidonitrobenzene with Fe and HOAc gave 22.6 g (80%) of crude 4-chloro-2-phthalimidoaniline, mp 177–183 °C; recrystallization from 95% EtOH gave material with mp 171.8–172.8 °C.

Anal. Calcd for $C_{14}H_9ClN_2O_2$: C, 61.66; H, 3.33; N, 10.27. Found: C, 61.49; H, 3.40; N, 10.25.

Diazotization of 23.0 g (0.084 mol) of crude 4-chloro-2-phthalimidoaniline followed by treatment with NaN_3 gave 18.0 g (71%) of crude 4-chloro-2-phthalimidoazidobenzene, mp 150 °C. After the diazotization, 4.5 g of starting material was recovered. Recrystallization of the crude product from 95% EtOH gave material with mp 147.8-149.0 °C.

Anal. Calcd for $C_{14}H_7ClN_4O_2$: C, 56.29; H, 2.36; N, 18.76. Found: C, 56.08; H, 2.38; N, 18.99.

Treatment of 6.2 g (0.021 mol) of crude 4-chloro-2-phthalimidoazidobenzene with 85% $NH_2NH_2{\cdot}H_2O$ gave 1.9 g (54%) of crude 5-chloro-2-azidoaniline, mp 55–57 °C, along with 1.2 g of recovered starting material. Recrystallization of the crude product from petroleum ether (bp 30–60 °C) gave material with mp 57.0–57.8 °C.

Anal. Calcd for $C_6H_5ClN_4$: C, 42.75; H, 2.99; N, 33.24. Found: C, 42.96; H, 2.91; N, 32.94.

2,5-Dichloroazidobenzene (8) and 2,4-Dichloroazidobenzene (9). The method of Hall and Patterson[3] was employed to transform 20.9 g (0.13 mol) of 2,5-dichloroaniline (**12**), mp 49–50 °C, into 12.1 g (50%) of 2,5-dichloroazidobenzene (**8**): mp 28–30 °C (lit.[7] mp 30 °C); IR (KBr or CS_2) 740 cm^{-1}. Similar treatment of 20.9 g (0.13 mol) of 2,4-dichloroaniline (**13**), mp 61.4–62.2 °C, gave, after recrystallization from 95% EtOH, 13.7 g (56%) of 2,4-dichloroazidobenzene (**9**): mp 52.8–53.4 °C (lit.[7] mp 54 °C); IR (KBr or CS_2) 762 cm^{-1}.

Sandmeyer Reaction of 5-Chloro-2-azidoaniline (4). A solution of 36.3 mL (0.44 mol) of concentrated HCl and 1.7 g (0.010 mol) of **4** in 20 mL of H_2O was cooled to 0 °C, and the amine was diazotized with 0.69 g (0.010 mol) of $NaNO_2$ dissolved in a minimum of H_2O. The resulting solution was stirred at 0 °C for 1 h and then filtered to remove 0.4 g of insoluble material. The filtrate was added slowly with swirling to a solution of $CuCl_2^-$ that had been freshly prepared from 2.75 g (0.011 mol) of $CuSO_4{\cdot}5H_2O$, 0.64 g (0.011 mol) of NaCl, 0.57 g (0.0055 mol) of $NaHSO_3$, 0.44 g (0.011 mol) of NaOH, and 5.0 mL (0.06 mol) of concentrated HCl. The resulting mixture was allowed to stand at room temperature for 30 min until the evolution of N_2 had ceased and then was extracted with three 50-mL portions of Et_2O. The combined Et_2O extract was dried over anhydrous $MgSO_4$. The dried Et_2O solution was filtered and the filtrate evaporated under reduced pressure to yield 1.1 g (59%) of crude 2,4-dichloroazidobenzene (**9**). The infrared absorption spectrum of this material, both in KBr and CS_2, showed an absorption peak at 762 cm^{-1} and no significant absorption at 740 cm^{-1}. Gas–liquid chromatographic analysis of the crude product showed a major component with retention time identical with that of an independently synthesized sample of **9** and three minor components with longer retention times.

Sandmeyer Reaction of 4-Chloro-2-azidoaniline (3). The same procedure that was described above for the Sandmeyer reaction of amine **4** was employed to convert 2.0 g (0.012 mol) of **3** into 1.9 g (83%) of crude 2,5-dichloroazidobenzene (**8**). The infrared absorption spectrum of this material, both in KBr and CS_2, showed an absorption peak at 740 cm^{-1} and no significant absorption at 762 cm^{-1}. Gas–liquid chromatographic analysis of the crude product showed a major component with retention time identical with that of an independently synthesized sample of **8** and three minor components with longer retention times. One of the minor components had a retention time identical with that of an authentic sample of 2-azido-4-chlorophenol prepared from 2-amino-4-chlorophenol by treatment with HONO and NaN_3.

Registry No. 3, 17537-17-6; **4**, 75458-14-9; **8**, 75458-15-0; **9**, 1965-25-9; **10**, 89-63-4; **11**, 1635-61-6; **12**, 95-82-9; **13**, 554-00-7; phthalic anhydride, 85-44-9; 5-chloro-2-phthalimidonitrobenzene, 75458-16-1; 5-chloro-2-phthalimidoaniline, 75458-17-2; 5-chloro-2-phthalimidoazidobenzene, 75458-18-3; 4-chloro-2-phthalimidonitrobenzene, 17537-07-4; 4-chloro-2-phthalimidoaniline, 17537-08-5; 4-chloro-2-phthalimidoazidobenzene, 17537-13-2.

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(6) Mallory, F. B.; Schueller, K. E.; Wood, C. S. *J. Org. Chem.* **1961**, *26*, 3312–3316.

(7) Chattaway, F. D.; Garton, F. L.; Parkes, G. D. *J. Chem. Soc.* **1924**, *125*, 1980–1991.