tane–ethyl acetate), was a mixture of **5a**, **6a**, and a small quantity of **9**. No evidence was observed for the presence of **7a**.

1,1-Bis{4-[3-[(*N*,*N*-dibenzylamino)oxy]-2,5-dioxopyrrolidin-1-yl]phenyl}methane (12). By the procedure used to prepare **7a**, compound **12** was prepared from 5.3 g (25 mmol) of **6a** and 4.5 g (12 mmol) of **11** in 50 mL of THF (16 h at reflux temperature). The residue was purified by preparative HPLC (silica gel, 7:3, heptane–ethyl acetate eluent) followed by recrystallization from nitromethane to give 6.0 g (61%) of a white solid: mp 141–149 °C; IR (CH_2Cl_2) ν 1790, 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) (200 MHz) δ 2.15 (dd, 2 H, J_{AB} = 20 Hz, J_{AX} = 5 Hz), 2.49 (dd, 2 H, J_{BA} = 20 Hz, J_{BX} = 8 Hz), 3.93 (s, 2 H), 4.09 (AB q, 8 H, $^2J_{HCH}$ = 16 Hz), 4.57 (dd, 2 H, J_{XA} = 5 Hz, J_{XB} = 8 Hz), 7.19 (d, 4 H), 7.29 (d, 4 H), 7.43 (complex m, 20 H). Anal. Calcd for $C_{49}H_{44}N_4O_6$: C, 75.0; H, 5.6; N, 7.1. Found: C, 75.1; H, 5.8; N, 7.0.

Reaction of *N*,*N*-Dibenzylhydroxylamine with *N*,*N*-1,2-Phenylenedimaleimide. By the procedure used to prepare **7a**, compound **14a** was prepared from 5.3 g (25 mmol) of **6a** and 3.4 g (12 mmol) of **13a** in 50 mL of THF (72 h at reflux temperature). The residue was purified by preparative HPLC (silica gel, 7:3, heptane–ethyl acetate eluent) to give two products. The higher R_f component was isolated to give 5.9 g (71%) of a white solid, **14a**: IR (CH_2Cl_2) ν 1800, 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) (200 MHz) δ 2.21 (dd, 2 H, J_{AB} = 19 Hz, J_{AX} = 4 Hz), 2.43 (dd, 2 H, J_{BA} = 19 Hz, J_{BX} = 8 Hz), 3.95 (AB q, 8 H, $^2J_{HCH}$ = 13 Hz), 4.43 (dd, 2 H J_{XA} = 4 Hz, J_{XB} = 8 Hz), 7.39 (complex m, 24 H). Anal. Calcd for $C_{42}H_{38}N_4O_6$: C, 72.6; H, 5.5; N, 8.1. Found: C, 72.6; H, 5.4; N, 7.9. The lower R_f component was isolated to give 0.6 g (10%)[32] of a white solid, **14b**: ^1H NMR ($CDCl_3$) (200 MHz) δ 2.05 (dd, 1 H, J_{AB} = 20 Hz, J_{AX} = 6 Hz), 2.45 (dd, 1 H, J_{BA} = 20 Hz, J_{BX} = 8 Hz), 3.63 (AB q, 4 H, $^2J_{HCH}$ = 12 Hz), 4.43 (dd, 1 H, J_{XA} = 6 Hz, J_{XB} = 8 Hz), 6.77 (s, 2 H), 7.33 (complex m, 14 H). Anal. Calcd for $C_{28}H_{23}N_3O_5$: C, 69.8; H, 4.8; N, 8.7. Found: C, 70.0; H, 5.1; N, 8.5.

Reaction of *N*,*N*-Dibenzylhydroxylamine with *N*,*N*-1,3-Phenylenedimaleimide. By the procedure used to prepare **7a**, compound **14c** was prepared from 5.3 g (25 mmol) of **6a** and 3.4 g (12 mmol) of **13b** in 50 mL of THF (72 h at reflux temperature). The residue was purified by preparative HPLC (silica gel, 7:3, heptane–ethyl acetate eluent) to give two products. The higher R_f component was isolated to give 3.8 g (46%) of a white solid, **14c**: ^1H NMR ($CDCl_3$) (200 MHz) δ 2.09 (dd, 2 H, J_{AB} = 18 Hz, J_{AX} = 4 Hz), 2.43 (dd, 2 H, J_{BA} = 18 Hz, J_{BX} = 8 Hz), 3.67 (AB q, 8 H, $^2J_{HCH}$ = 13 Hz), 4.51 (dd, 2 H, J_{XA} = 4 Hz, J_{XB} = 8 Hz), 7.33 (complex m, 24 H). Anal. Calcd for $C_{42}H_{38}N_4O_6$: C, 72.6; H, 5.5; N, 8.1. Found: C, 72.3; H, 5.4; N, 7.7. The lower R_f component was isolated to give 1.2 g (21%)[32] of a white solid, **14d**: ^1H NMR ($CDCl_3$) (200 MHz) δ 2.05 (dd, 1 H, J_{AB} = 20 Hz, J_{AX} = 6 Hz), 2.39 (dd, 1 H, J_{BA} = 20 Hz, J_{BX} = 8 Hz), 3.97 (AB q, 4 H, $^2J_{HCH}$ = 12 Hz), 4.53 (dd, 1 H, J_{XA} = 6 Hz, J_{XB} = 8 Hz), 6.85 (s, 2 H), 7.27 (complex m, 14 H). Anal. Calcd for $C_{28}H_{23}N_3O_5$: C, 69.8; H, 4.8; N, 8.7. Found: C, 69.5; H, 4.9; N, 8.8.

Kinetic Rate Studies. The progress of the reaction of **5a** (100 mmol) with **6a** (100 mmol) in 16 mL of benzene-d_6 at 65.5 °C (thermally regulated oil bath) was monitored by ^1H NMR spectroscopy (90 MHz) both in the presence and absence of *m*-dinitrobenzene (110 mmol). Toluene (100 mmol) was used as an internal standard.

Acknowledgment. S.D.P. wishes to thank CIBA-GEIGY Corp. for permission to publish this paper and support of the work and Jo Behrens for preparation of the manuscript.

Registry No. **5a**, 941-69-5; **5b**, 541-59-3; **5c**, 930-88-1; **5d**, 1631-25-0; **5e**, 17450-30-5; **6a**, 621-07-8; **6b**, 3710-84-7; **7a**, 117022-01-2; **7b**, 117022-02-3; **7c**, 117022-03-4; **7d**, 117022-04-5; **7e**, 117022-05-6; **7f**, 117039-48-2; **8**, 117022-06-7; **9**, 117022-07-8; **10**, 117022-08-9; **11**, 13676-54-5; **12**, 117022-09-0; **13a**, 13118-04-2; **13b**, 3006-93-7; **14a**, 111363-49-6; **14b**, 117022-10-3; **14c**, 117022-11-4; **14d**, 117022-12-5; $(PhCH_2)_2NH$, 103-49-1.

(32) Yield of monoadduct based upon starting maleimide.

Synthesis of 4-Aryl-3,5-bis(alkoxycarbonyl)-1,4-dihydropyrazines

Robert J. Chorvat*,[1] and Kurt J. Rorig

Department of Medicinal Chemistry, G. D. Searle and Co., Skokie, Illinois 60077

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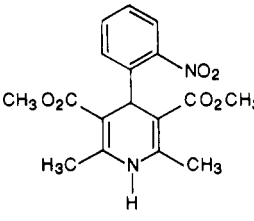
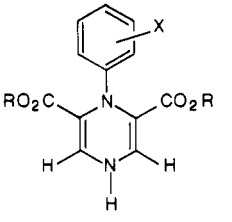
Members of the 4-aryl-3,5-bis(alkoxycarbonyl)-1,4-dihydropyridines are clinically useful agents for the treatment of cardiovascular diseases such as angina pectoris[2] and hypertension.[3] These compounds exert their spasmolytic and vasodilating activity through their ability to inhibit movement of calcium through certain membrane channels, thus interfering with the calcium dependent processes associated with contraction of vascular smooth muscle.[4,5] Representative of the compounds in this series is nifedipine **1**, which is currently marketed as an antianginal and antihypertensive agent.



1



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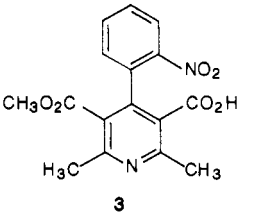

3

Our interest in this series centered around the identification of analogues that would possess significant calcium antagonist activity and a longer duration of action than nifedipine and related compounds. One such series was expected to be the 4-aryl-3,5-bis(alkoxycarbonyl)-1,4-dihydropyrazines **2**. Due to the presence of the aryl-substituted nitrogen atom at the 4-position of the heterocyclic ring, oxidative aromatization of this ring should be metabolically less favorable. Metabolism studies of nifedipine indicated that a main metabolite is the biologically inert pyridine acid **3**.[6] Thus, agents resistant to this transformation would be expected to possess more favorable pharmacokinetics and less frequent dosing regimens.

(1) Current address: Du Pont Critical Care, 1600 Waukegan Road, Waukegan, IL 60085.

(2) Antman, E.; Muller, J.; Goldberg, S.; MacAlpin, R.; Rubenfire, M.; Tabatznik, B.; Liang, C.; Heupler, F.; Achuff, S.; Reichek, N.; Geltman, E.; Kerin, N. Z.; Neff, R. K.; Braunwald, E. *N. Engl. J. Med.* **1980**, *302*, 1269.

(3) Guazzi, M.; Olivari, M. T.; Polese, A.; Fiorentini, C.; Margrini, F.; Moruzzi, P. *Clin. Pharmacol. Ther.* **1977**, *22*, 528. Hornung, R. S.; Gould, B. A.; Jones, R. I.; Sonecha, T. N.; Raferty, E. B. *Am. J. Cardiol.* **1983**, *51*, 1323.

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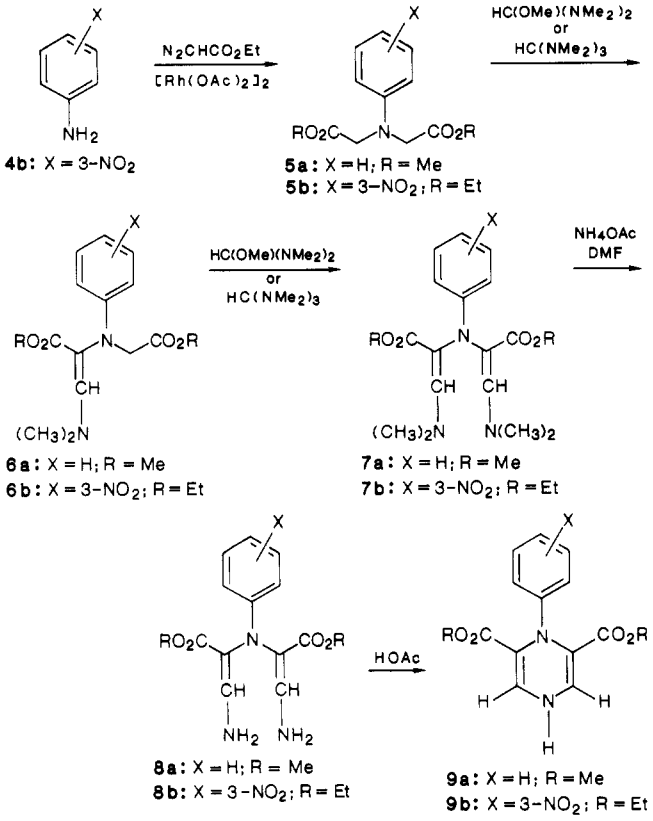
(5) Rosenberger, L. B.; Triggle, D. J. In *Calcium and Drug Action*; Weiss, G. B., Ed.; Plenum: New York, 1978.

(6) Kondo, S.; Kuchiki, A.; Yamamoto, K.; Akimoto, K.; Takahashi, K.; Awata, N.; Sugimoto, I. *Chem. Pharm. Bull.* **1980**, *28*, 1.

0022-3263/88/1953-5779$01.50/0

Scheme I



Our approach to this series[7] (Scheme I) proceeded from the aniline *N,N*-bis(alkyl acetates) **5a**[8] and **5b**. The latter nitroaniline derivative was prepared from **4b** by treatment with ethyl diazoacetate in refluxing benzene in the presence of a catalytic amount of rhodium acetate dimer.[9] Functionalization of both methylene groups of these ester appendages was accomplished using either bis(dimethylamino)methoxymethane in the case of **5a** or tris(dimethylamino)methane in the case of **5b**. Both reagents required elevated temperature and protracted heating times to produce the bis[(dimethylamino)methylene] compounds **7a** and **7b**. Shorter reaction times and lower temperatures produced reaction mixtures containing a preponderance of the mono[(dimethylamino)methylene] adducts **6**, detected by the presence of methylene resonances at ca. 4.2 ppm.

The bisadduct **7a** was readily transaminated with ammonium acetate in DMF to afford the stable crystalline vinylogous carbamate **8a**. Brief heating of the material in glacial acetic acid readily produced the dihydropyrazine **9a** in high yield.

The nitrophenyl bisadduct **7b** was more resistant to transamination and required longer reaction times. As a consequence, the desired product **8b** was accompanied by various other components (as observed by TLC). Rather than isolating this compound, it was converted in its crude state to the dihydropyrazine **9b** by brief treatment with hot glacial acetic acid. Both dihydropyrazines are characterized by olefinic proton resonances at 7.48 (**9a**) and 7.76 ppm (**9b**).

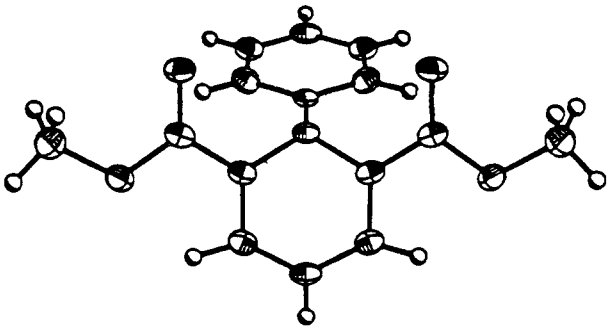


Figure 1. ORTEP drawing of compound **9a** (X = H; $R = CH_3$).

X-ray crystallography[10] confirmed the structure of **9a** (Figure 1) and revealed a unique characteristic of these compounds in the crystal state. The plane of the 4-phenyl ring fails to assume an orthogonal relationship to the plane of the heterocyclic ring system. This orthogonal conformation between these rings generally exists in the dihydropyridine systems.[11] Lack of significant calcium antagonism and vasodilating activity of these compounds[12] suggest that this orthogonal conformation may be a necessary feature for biological activity of this compound type.[13,14]

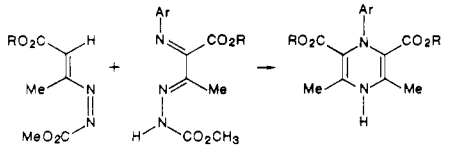
In summary, we have prepared 4-aza analogues of the clinically useful dihydropyridine calcium antagonists via a novel enamine ester pathway. The preferred crystal state conformation of these compounds correlates with the lack of biological activity of this series.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were recorded on Varian T-60, Varian FT-80, or GE QE-300 spectrometers with Me_4Si as an internal standard. UV spectra were obtained on a Beckman DK-2A instrument by the group of A. J. Damascus. Compounds were subjected to elemental analysis by the group of E. Zielinski. Mass spectra were determined on an AEI MS 30 by Dr. J. Hribar and associates.

***N,N*-Bis[1-methoxy-3-(dimethylamino)-1-oxo-2-propen-2-yl]phenylamine (7a).** A 1.0-g (4.2-mmol) portion of diester **5a** in 2.0 g of 85% bis(dimethylamino)methoxymethane (12.9 mmol) was heated at ca. 115 °C for 18 h in a nitrogen atmosphere. The volatiles were then swept away with a stream of nitrogen, and the remaining oil was again treated as above with another 2-g portion of reagent for 32–40 h. Upon removal of the volatiles, an oil remained that was composed of about a 4:1 mixture of bis- to monoadducts, **6a** and **7a**, respectively. This mixture was used

(7) During the course of this investigation, a report on the synthesis of 4-aryl-1,4-dihydropyrazine-3,5-dicarboxylic acid derivatives appeared in the patent literature: DE3400765 to Bayer AG, 7-24-85. The preparation of these compounds was reported via the following reaction:



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(9) Salzmann, T. N.; Ratcliff, R. W.; Christensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161.

(10) The single crystal X-ray determination was performed at Colorado State University by J. Reibenspies under the direction of O. Anderson, with a Nicolet R3m-E diffractometer purchased with funds from the NSF (Grant CHE-8103011). The ORTEP drawing of **9** (X = H, R = Me) is shown.

(11) Fosshein, R.; Svarteng, K.; Mostad, A.; Romming, C.; Shefter, E.; Triggle, D. J. *J. Med. Chem.* **1982**, *25*, 126.

(12) Compounds **9a** and **9b** showed little antagonism of calcium-dependent contractions in a potassium depolarized aortic ring assay and minimal blood pressure lowering effect in the SHR test at high doses.

(13) Seidel, W.; Meyer, H.; Born, L.; Kazda, S.; Dompert, W. In *Abstracts, Division of Medicinal Chemistry*; 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8–13, 1984.

(14) Baldwin, J. J.; Claremon, D. A.; Lumma, P. K.; McClure, D. E.; Rosenthal, S. A.; Winquist, R. J.; Faison, E. P.; Kaczorowski, G. J.; Trumble, M. J.; Smith, G. M. *J. Med. Chem.* **1987**, *30*, 690.

for the subsequent reaction without purification: characteristic ^{1}H NMR resonances ($CDCl_3$) **7a** δ 2.80 (12 H, s, NCH_3's), 3.57 (6 H, s, OCH_3's), 7.27 (2 H, s, olefinic H's); **6a** δ 3.0 (6 H, s, NCH_3's), 3.53 (3 H, s, OCH_3), 3.70 (3 H, s, OCH_3), 4.2 (2 H, m, CH_2), 7.40 (1 H, s, olefinic H).

***N*,*N*-Bis(3-amino-1-methoxy-1-oxo-2-propen-2-yl)-phenylamine (8a).** To 3 g of crude adduct **7a** in 10 mL of DMF was added 6 g of ammonium acetate, and the reaction mixture was heated on a steam bath for 4 h. Water and ether were then added to the cooled solution, and the layers were separated. The aqueous phase was extracted with two additional portions of ether, and the combined extracts were washed with a saturated salt solution and dried (Na_2SO_4). Solvent removal gave about 2 g of sticky solid. Trituration with ether afforded 1.2 g (~60% yield, based on the bisadduct present in crude product) of **8a**. Recrystallization from MeOH produced light salmon colored crystals: mp 183–195 °C; UV (MeOH) 248–9 (ε 45 500); NMR ($CDCl_3$) 3.70 (6 H, s, OCH_3's), 7.70 (2 H, t, J = 6 Hz, olefinic H's); MS, m/e 291 (M^+, 100). Anal. Calcd for $C_{14}H_{17}N_3O_4$: C, 57.67; H, 5.84; N, 14.42. Found: C, 57.69; H, 5.78; N, 14.07.

1-Phenyl-2,6-bis(methoxycarbonyl)-1,4-dihydropyrazine (9a). A solution of 230 mg (0.79 mmol) of **8a** in 1 mL of glacial HOAc was heated on a steam bath for 20 min. The solvent was then swept away with a stream of nitrogen, and the residue was triturated with MeOH. The solid was collected, washed with ether, and air-dried to give 160 mg (74%) of **9a** as yellow crystals: mp 198–200 °C dec; UV (MeOH) 245 (ε 9100), 277 (ε 7300); NMR ($CDCl_3$ + 1 drop CD_3OD) δ 3.75 (6 H, s, OCH_3's), 6.70–7.30 (5 H, m, phenyl H's), 7.48 (2 H, s, dihydropyrazine H's); MS, m/e 274 (M^+, 67), 215 (60), 197 (100). Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.38; H, 5.14; N, 10.21. Found: C, 61.27; H, 4.99; N, 10.16.

***N*,*N*-Bis(2-ethoxy-2-oxo-1-ethyl)-3-nitrophenylamine (5b).** To 6.9 g (50 mmol) of 3-nitroaniline (**4b**) in 100 mL of benzene containing 15 mg of rhodium(II) acetate dimer was added about half of a solution of 12.5 g (110 mmol) of ethyl diazoacetate (EDA) in 25 mL of benzene. Upon warming the solution nitrogen evolution commenced with an accompanying exotherm. After the mixture was maintained at 45–50 °C for 30 min, the remaining EDA solution was added dropwise over a 15-min period and the reaction mixture was then refluxed for 1 h. Another 5-g (44-mmol) portion of EDA and 15 mg of rhodium catalyst were again added, and refluxing was continued for a 1-h period. The solvent was then removed in vacuo, and the residue, which showed ca. 2:1 ratio of bis/monoalkylated anilines (10% ethyl acetate/toluene–silica gel) was chromatographed on silica gel with ethyl acetate/toluene as the solvent to provide 9.15 g (61%) of **5b**. Recrystallization from ether/Skelly B gave chunky crystals: mp 62–63 °C; NMR ($CDCl_3$) δ 4.18 (4 H, s, NCH_2's). Anal. Calcd for $C_{14}H_{18}N_2O_6$: C, 54.19; H, 5.85; N, 9:03. Found: C, 53.98; H, 5.68; N, 9:03.

***N*-[1-Ethoxy-3-(dimethylamino)-1-oxo-2-propen-2-yl]-*N*-(2-ethoxy-2-oxo-1-ethyl)-3-nitrophenylamine (6b) and *N*,*N*-Bis[1-ethoxy-3-(dimethylamino)-1-oxo-2-propen-2-yl]-3-nitrophenylamine (7b).** To 2.5 g (8 mmol) of diester **5b** in 6 mL of DMF was added 3.0 g (20 mmol) of tris(dimethylamino)methane, and the reaction mixture was heated in a nitrogen atmosphere at ca. 95 °C for 18 h. After that time another 1-g (7-mmol) portion of reagent was added, and the heating continued for an additional 24 h. The solvent was then removed, and the residue was chromatographed over silica gel with ethyl acetate/toluene as the eluent, affording 1.7 g (58%) of the monoadduct **6b** as the main product (CH_2 resonance at 4.2 ppm) and 0.64 g (19%) of bisadduct **7b** as an oil: NMR ($CDCl_3$) δ 2.83 (12 H, s, NCH_3's), 7.35 (2 H, s, olefinic H's).

1-(3-Nitrophenyl)-2,6-bis(ethoxycarbonyl)-1,4-dihydropyrazine (9b). To 0.5 g (1.19 mmol) of bisadduct **7b** in 2 mL of DMF was added 1.5 g of ammonium acetate, and the reaction mixture was heated on a steam bath for 16 h. After cooling, water was added and the aqueous solution was extracted three times with $CHCl_3$. The combined extracts were washed with a saturated salt solution and dried (Na_2SO_4). Solvent removal gave an oil, which was taken up into 2 mL of HOAc and heated on a steam bath for 30 min. About 1 mL of MeOH was then added, and upon cooling, needles formed in the solution and were collected, affording 197 mg (48%) of **9b**. Recrystallization from aqueous MeOH gave long yellow needles: mp 201–202 °C dec; NMR (DMSO-d_6) δ 1.27 (6 H, t, J = 6 Hz, CH_3's), 4.27 (4 H, q, J = 6 Hz, CH_2's), 6.90–7.15 (1 H, m, phenyl H), 7.27–7.67 (3 H, m, phenyl H's), 7.76 (2 H, s, dihydropyrazine H's); MS, m/e 347 (M^+, 100). Anal. Calcd for $C_{16}H_{17}N_3O_6$: C, 55.33; H, 4.93; N, 12.10. Found: C, 55.10; H, 4.88; N, 12.35.

Supplementary Material Available: Tables of final atomic coordinates for the non-hydrogen atoms, bond distances and angles, thermal parameters and final hydrogen coordinates for **9a**, X = H, R = CH_3 (3 pages). Ordering information is given on any current masthead page.

New Aspects of the Electroreduction of Azo Compounds: Disproportionation Reaction of the Protonated Radical Anion ARNHNAR• of Benzo[*c*]cinnoline

Yves Mugnier* and Etienne Laviron

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences, 6 bd Gabriel, 21000 Dijon, France

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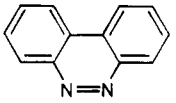
The electrochemistry of azo and hydrazo compounds in aqueous solvents has been extensively studied.[1] Fewer studies are concerned with the electrochemical behavior of these compounds in aprotic media.[2,3] Recently, Cheng and Hawley[3] have examined the influence of proton donors of different acidities in the case of azobenzene.

We report in this note some new aspects of the electrochemical mechanism of the reduction of azo compounds, taking benzo[*c*]cinnoline (**1**) and its hydrazo derivative **6** as an example.[4] This work was carried out in tetrahydrofuran with n-$Bu_4N^+PF_6^-$ as supporting electrolyte.



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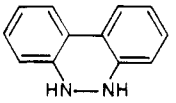

6

Compound **1** exhibits two one-electron waves A and B (Figure 1a) (A, $E_{1/2}$ = −1.55 V; B, $E_{1/2}$ = −2.16 V vs the SCE electrode). Electrolysis at the potential of wave A leads quantitatively to the anion radical ARNNAR•⁻ **2**, characterized by ESR spectroscopy;[5] it gives one oxidation wave A′ and one reduction wave B (Figure 1b). A controlled potential electrolysis at the potential of wave A′ gives back quantitatively **1**.

Addition of 1 equiv of a proton donor (benzoic acid) to the solution of the anion radical **2** causes an important modification of the voltammogram. Wave A′ and B disappears; two oxidation waves A'_3 and A'_4 and two reduction waves A and B appear (Figure 1c).

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