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$^\bullet$ of Benzo[*c*]cinnoline

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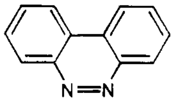
Received May 12, 1988

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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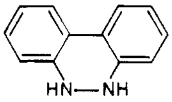

6

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$^{\bullet-}$ **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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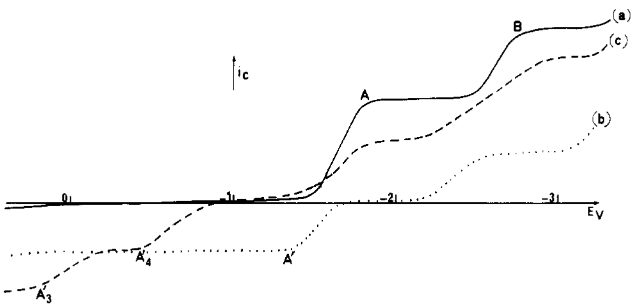


Figure 1. Voltammograms on a platinum rotating disk electrode: (a) Benzo[c]cinnoline; (b) after one-electron reduction at −1.8 V; (c) after addition of 1 equiv of benzoic acid.

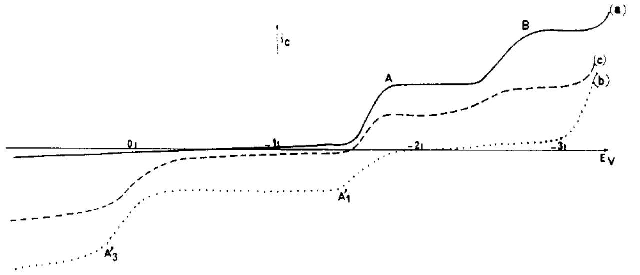


Figure 2. Voltammograms on a platinum rotating disk electrode: (a) benzo[c]cinnoline; (b) after two-electron reduction at 2.7 V; (c) after one-electron oxidation at −1 V.

The electrolysis of **1** at the potential of wave B consumes two electrons, and the voltammogram shows two oxidation waves A'_1 and A'_3 (A'_1, $E_{1/2} = -1.53$ V) (Figure 2b).

After reoxidation on the plateau of wave A'_1 with consumption of 1 F, the solution obtained shows two reduction waves A and B and the oxidation wave A'_3 (Figure 2c).

Wave A'_3 ($E_{1/2} = +0.05$ V) is due to the oxidation of dihydrobenzo[c]cinnoline (**6**) as shown by examining the behavior of this compound (**6** also exhibits a reduction wave at −2.48 V). The results can be rationalized on the basis of Scheme I.

The dianion $ARNNAR^{2-}$ generated by the two-electron reduction of **1** at the potential of wave B is a strong base and a protonation reaction by residual water or by the supporting electrolyte occurs,[6] affording the monoprotonated dianion $ARNHNAR^-$ **4**, which exhibits wave A'_1. The dianion **3** is relatively stable on the time scale of cyclic voltammetry. The species **4** is stable in tetrahydrofuran under argon. The oxidation of **4** at the potential of wave A'_1 gives, with consumption of 1 F, the radical $ARNHNAR^{\bullet}$ **5**, which rapidly disproportionates to the azo (waves A and B) and hydrazo (wave A'_3) derivatives.

The radical **5** is also obtained when 1 equiv of proton donor (benzoic acid) is added to the solution of the anion radical **2**; it immediately disproportionates to **1** and **6**.

The disproportionation reaction can a priori follow two routes:

$$5 + 5 \rightarrow 2 + 7 \qquad (1)$$

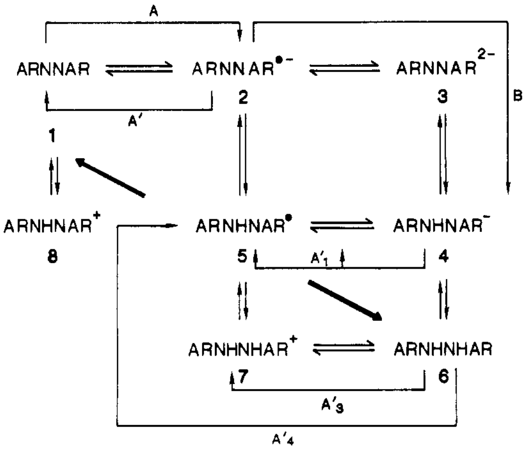
$$2 + 7 \rightarrow 1 + 6 \qquad (2) \quad (I)$$

or

$$5 + 5 \rightarrow 4 + 8 \qquad (3)$$

$$8 + 4 \rightarrow 1 + 6 \qquad (4) \quad (II)$$

Scheme I



Along route I, reaction 1 is thermodynamically unfavorable since **5** is more acidic than **2** and less than **7**. However, reaction 2 must be very fast, since the difference of the redox potentials of system **1**/**2** and **6**/**7** is very large ($\Delta E \simeq 1.6$ V).

The reverse is true along route II. It seems thus difficult to chose a priori which of the two routes if followed. However, if the reaction took place via II, only **1** would be obtained during the oxidation of **4**, since the latter would be oxidized as soon as it is formed by reaction 3.

Wave A'_4 is due to the oxidation of **6** according to an EC mechanism. The chemical step corresponds to a deprotonation of **7** by the nucleophilic species $C_6H_5COO^-$ obtained during the protonation of **2**:

$$\underset{2}{ARNNAR^{\bullet -}} + C_6H_5CO_2H \rightleftharpoons \underset{5}{ARNHNAR^{\bullet}} + C_6H_5CO_2^- \qquad (1')$$

$$2\underset{5}{ARNHNAR^{\bullet}} \rightleftharpoons \underset{6}{ARNHNHAR} + \underset{1}{ARNNAR} \qquad (2')$$

$$\text{wave } A'_4 \begin{cases} \underset{6}{ARNHNHAR} \rightleftharpoons \underset{7}{ARNHNHAR^+} & (3') \\ \underset{7}{ARNHNHAR^+} + C_6H_5CO_2^- \rightleftharpoons \underset{5}{ARNHNAR^{\bullet}} + C_6H_5CO_2H & (4') \end{cases}$$

followed by reaction 2′.

This was verified by adding 1 equiv of C_6H_5ONa to the solution of **6**; wave A'_4 is observed by voltammetry.

The disproportionation of **5**, the existence of which we have proved by direct experiments, has never been mentioned as a possible intermediate reaction during the reduction of azo compounds,[1-3] although it also takes place in the case of azobenzene itself, phenazine, etc.[7]

Experimental Section

The electrochemical procedures were carried out under argon. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 M) in all cases; the salt (Fluka) was twice recrystallized from ethanol, dried, and deoxygenated before use.

The voltammetric experiments were carried out on a platinum disc electrode (ϕ 1.2 mm). For the controlled potential electrolysis, a platinum grid was used. The reference electrode was a saturated calomel electrode separated from the solution by a sintered-glass disk. The auxiliary electrode was a platinum wire electrode. A Tacussel UAP 4 Unit connected to a Tektronix oscilloscope (linear potential sweep experiments), a three electrode Tacussel Tipol polarograph, an Amel 552 potentiostat, and a Tacussel IG 5 integrator were used.

Benzo[c]cinnoline is commercially available.

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Dihydro-5,6-benzo[*c*]cinnoline. This derivative is prepared by electrolysis of benzo[c]cinnoline at −1.1 V in aqueous medium (ethanol–water, 1/2, NaCl 0.2 M). After a two-electron reduction, the solution is cooled, and the dihydro derivative is separated by filtration under argon and characterized by its melting point (122 °C) and its ^1H NMR data. This derivative has been previously prepared by catalytic hydrogenation of benzo[c]cinnoline.[4]

Acknowledgment. We thank M. T. Compain for her technical assistance.

Homogeneous Nucleophile Exchange. 2. Silver-Free, Direct Synthesis of Primary Alkyl Sulfonates from Alkyl Halides

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Received August 16, 1988

Recently, on finding that homogeneous quaternary ammonium halide catalyzed alkyl halide exchange[1] never had been systematically explored, we used this process to develop a rapid, simple, solvent-free method for bromide–chloride, chloride–iodide, and bromide–iodide exchange and applied it to high-yield syntheses of certain α,ω-hetero dihalides.[2] The ability to achieve, in particular, reversible chloride–iodide exchange encouraged us to attempt the unprecedented homogeneous conversion of alkyl halides to alkyl sulfonates; some initial successes are reported herein.

Although, historically, the major role of sulfonate ions has been as leaving groups in S_N1 or S_N2 type processes, Zefirov noted recently[3] that nucleophilicity scales such as the Swain–Scott scale "completely ignore the nucleophilic properties of ... such a typical nucleofuge as the *p*-toluenesulfonate ion". Indeed, Kevill[4] has demonstrated the ability of arenesulfonate ions (as tetrabutylammonium salts) to react in S_N2 fashion with trimethyl- and triethyloxonium ion, methyl triflate, and methyl perchlorate, and MacDonald has reported oxidatively assisted displacement of iodide by tosylate.[5] However, unassisted S_N2 type displacement of halide ions by sulfonate ions has not been previously demonstrated. Synthetically, alkyl sulfonates usually are made from the corresponding alcohols or from halides through the agency of silver sulfonates.[6]

In our approach to halide–sulfonate exchange, two observations from Cl–I exchange were used: High temperatures were needed to achieve practical rates (>160 °C for Cl–I), and R′X in eq 1 had to be selectively distilled out to drive the reaction forward. Cheaply available methyl tosylate allowed both of these conditions to be met. In the first experiment (eq 2), we were pleased to find that the reaction could be pushed essentially to completion (disappearance of CH_3OTs) in 2 h. Also, high chemoselectivity was indicated by the near absence of bromoethyl tosylate and dimethylene ditosylate; 97% pure 2-chloroethyl tosylate was isolated in 68% yield (not optimized). Rough thermal comparison with Cl–I exchange conditions suggests that displacement of bromide by tosylate is relatively facile.

$$\mathrm{RX + R'OTs \xrightarrow[\text{heat}]{\text{catalyst}} ROTs + R'X} \qquad (1)$$

$$\mathrm{X = Cl, Br, I}$$

$$\underset{\text{bp } 106\ ^\circ\text{C}}{\mathrm{ClCH_2CH_2Br}} + \underset{144\ ^\circ\text{C } (5\text{ mm})}{\mathrm{CH_3OTs}} \xrightarrow[135\ ^\circ\text{C}]{\mathrm{Bu_4N^+Br^-}} \underset{\text{bp } 153\ ^\circ\text{C } (0.3\text{ mm})}{\mathrm{ClCH_2CH_2OTs}} + \underset{\text{bp } 4\ ^\circ\text{C}}{\mathrm{CH_3Br}} \qquad (2)$$

The above success led us to attempt benzenesulfonate–chloride exchange (eq 3); ^1H NMR analysis indicated ca. 30% conversion under the conditions shown, but reaction mixture darkening and deceleration of gas evolution made it appear likely that catalyst decomposition was occurring.

$$\mathrm{Cl(CH_2)_6Cl + CH_3O_3SPh \xrightarrow[170\ ^\circ\text{C}]{\mathrm{Bu_4N^+Br^-}} Cl(CH_2)_6O_3SPh + CH_3Cl} \qquad (3)$$

Workup gave a 23% isolated yield of 6-(chlorohexyl)-1-benzenesulfonate. A simple primary alkyl chloride thus can be replaced, but more severe conditions (and possibly more catalyst) are required, as expected.

On the other hand, sulfonate–iodide exchange was anticipated to occur readily, and we were particularly interested in selective conversion of the now economically available chloroiodomethane[2] to chloromethyl tosylate; this simple compound has not been reported previously. The reaction indicated in eq 4 therefore was attempted.

$$\mathrm{ClCH_2I} + \underset{10\%\text{ excess}}{\mathrm{CH_3OTs}} \xrightarrow[\text{heat}]{\mathrm{Bu_4N^+Br^-}} \mathrm{ClCH_2OTs + CH_3I} \qquad (4)$$

However, it was found that, under the conditions used, $ClCH_2OTs$ was transformed into $CH_2(OTs)_2$ faster than it was being formed (eq 5). Because $ClCH_2OTs$ is the first known example of an α-tosyloxy halide, this behavior was not entirely predictable, but it is consistent with reports that α-alkoxy and α-acyloxy substituents greatly increase halide nucleofugality.[7] It is known also that α-halides greatly *decrease* leaving-group nucleofugality;[8] the iodide in $ClCH_2I$ therefore is less reactive than is an ordinary primary alkyl iodide.

$$\mathrm{ClCH_2OTs + CH_3OTs \xrightarrow[\text{heat}]{\mathrm{Bu_4N^+OTs^-}} TsOCH_2OTs + CH_3Cl} \qquad (5)$$

The known, stable $CH_2(OTs)_2$[6a] readily crystallizes out of the reaction mixture; originally made by reaction of CH_2I_2 and AgOTs, and rarely studied since,[9] it now can

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