C, 54.2; H, 3.88; Cl, 11.6.

Registry No.—**1a,** 54014-67-4; **1b,** 52156-15-7; **2,** 61723-13-5; **3a,** 62723-15-7; **3b,** 61723-17-9; **4,** 61723-19-1; **5,** 61723-21-5; **6a,** 61723-23-7; **6b,** 61723-25-9; **7a,** 61723-27-1; **7b,** 61723-29-3; **8a,** 61723-31-7; **8b,** 61723-33-9; **10,** 61723-34-0; **11,** 61723-35-1; **12,** 61723-36-2; **13a,** 61723-37-3; **13b,** 61723-38-4; acetone, 67-64-1; butanone, 78-93-3; methyl isopropyl ketone, 563-80-4; acetophenone, 98-86-2; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; indanone-1, 83-33-0; tetralone-1, 529-34-0; sodium thiocyanate, 540-72-7; sodium *p*-toluenesulfinate, 824-79-3; potassium ethylxanthate, 140-89-6; pyridine, 110-86-1.

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(4) Postdoctoral Fellow.

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(11) Unpublished work of Dr. Cyril Parkanyi, University of Texas, El Paso, Texas. We are grateful to Dr. Parkanyi for making the data available to us.

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Reaction of Electrogenerated Nitrobenzene Radical Anion with Alkyl Halides

John H. Wagenknecht

Corporate Research Department, Monsanto Company, St. Louis, Missouri 63166

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Nitrobenzene radical anion formed by the electrochemical reduction of nitrobenzene reacts rapidly with alkyl halides. Electrochemical reduction of nitrobenzene in the presence of alkyl halides leads to a high yield of *N,O*-dialkylphenylhydroxylamines.

The electrochemical reduction of nitrobenzene in aprotic solvents has been studied in detail during the past two decades.[1,2] Nitrobenzene is reduced in two steps, first to a radical anion (eq 1) and then at more negative electrode potentials directly to a dianion (eq 2). Both steps are reversible, but generally the dianion reacts rapidly with solvent, electrolyte, or trace impurities so that the dianion may be observed only under rigorously controlled conditions.[3] The radical anion of nitrobenzene, however, is much less reactive. It has been detected even in strongly basic aqueous solution by ESR spectroscopy.[4,5] The reaction of nitrobenzene radical anion with various proton donors has been studied in detail[1–3] and, generally, if a proton donor is present during nitrobenzene reduction, then phenylhydroxylamine is formed (eq 3). The electrogenerated nitrobenzene radical anion is generally considered to be quite stable and, therefore, reactions other than with proton donors have been studied very little.

$$C_6H_5NO_2 \overset{1e}{\rightleftarrows} C_6H_5NO_2^{-}\cdot \tag{1}$$

$$C_6H_5NO_2 \overset{2e}{\rightleftarrows} C_6H_5NO_2^{2-} \tag{2}$$

$$C_6H_5\text{-}NO_2 \xrightarrow[4e^-]{4H^+} C_6H_5\text{-}NHOH + H_2O \tag{3}$$

This paper deals with the reduction of nitrobenzene in dimethylformamide in the presence of simple alkyl halides, which have been found to react rapidly with nitrobenzene radical anion leading in several steps to substituted phenylhydroxylamines. A similar product was obtained when nitrobenzene was reduced in the presence of acetic anhydride, producing *N,O*-diacetylphenylhydroxylamine.[6] Alkyl halides recently have been found to react with many types of electrogenerated anions and radical anions, such as those formed by reduction of ketones and imines,[7] activated olefins,[8–10] Schiff bases,[11] and disulfides.[12]

Results and Discussion

The stability of nitrobenzene radical anion is demonstrated by cyclic voltammetry (Figure 1) carried out at a hanging mercury drop electrode in dimethylformamide (DMF) containing 0.1 M tetraethylammonium perchlorate (TEAP). The presence of an anodic peak, on reversing the direction of voltage sweep just after the initial reduction peak of nitrobenzene, indicates that the nitrobenzene radical anion is not being rapidly consumed in a follow-up chemical reaction. As shown in Figure 1, addition of 1-bromobutane to the solution causes the anodic peak to decrease in size, indicating that the radical anion is reacting with butyl bromide.

Although it is possible to determine the rate of the reaction of nitrobenzene radical anion with 1-bromobutane by cyclic voltammetry or cyclic chronopotentiometry, the theoretical treatment of this set of reactions (eq 12–16) is complex. A sense of the relative rates of reaction of nitrobenzene radical anion with 1-bromobutane and 1-iodobutane may be gained from cyclic chronopotentiometry (Figure 2). In the absence of a follow-up reaction the reverse transition time is one-third of the forward electrolysis time.[13] Reactions consuming the radical anion cause the reverse transition time to be shorter. For a solution of 1.3 mM nitrobenzene, the decrease in the reverse transition time is about the same when 0.5 M 1-bromobutane is present as it is when 0.05 M 1-iodobutane is present. In other words, it requires ten times as much 1-bromobutane as 1-iodobutane to obtain the same apparent rate of disappearance of nitrobenzene radical anion.

The preparative electrochemical reduction of nitrobenzene at −1.3 V vs. SCE (the potential at which nitrobenzene radical anion is formed) in the presence of 1-chlorobutane, 1-bro-

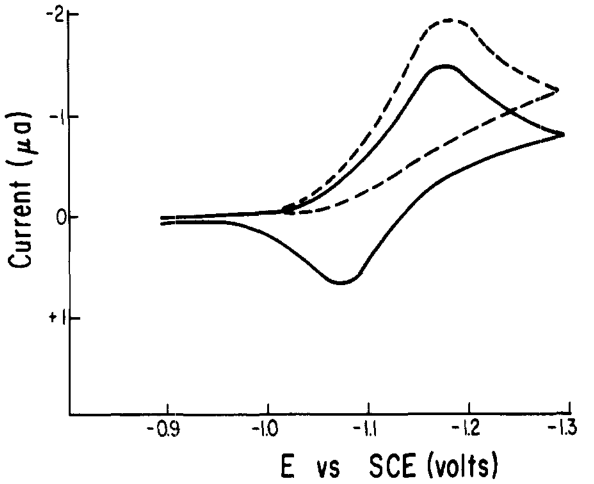
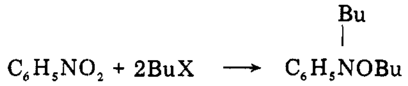


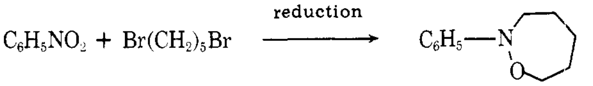
Figure 1. Cyclic voltammograms of nitrobenzene (1.275 mM) in DMF containing 0.1 M TEAP at a hanging Hg drop electrode in the absence (solid line) and presence (dashed line) of butyl bromide (0.3 M). Scan rate 50 mV/s.

mobutane, or 1-iodobutane produces in each case a good yield of *N,O*-dibutylphenylhydroxylamine (eq 4). Chloromethane



$$C_6H_5NO_2 + 2BuX \longrightarrow C_6H_5\overset{\displaystyle Bu}{\overset{|}{N}}OBu \qquad (4)$$

or methyl-*p*-toluenesulfonate each react to form *N,O*-dimethylphenylhydroxylamine. The dihaloalkane (1,5-dibromopentane) reacts to form a cyclic compound, *N*-phenylperhydro-1,2-oxazepine (eq 5). All of these reactions required 4 Faradays of electricity per mol of nitrobenzene present.

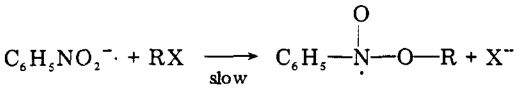


(5)

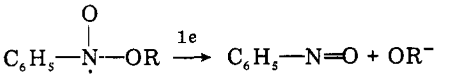
These reactions are examples of a simple method for synthesis of a large variety of trisubstituted hydroxylamines. A few trisubstituted phenylhydroxylamines have been prepared[14] before, but the synthetic utility of previous methods is limited.

The reaction scheme proposed for the formation of the substituted phenylhydroxylamines follows:

$$C_6H_5NO_2 \xrightarrow{1e^-} C_6H_5NO_2^{-}\cdot \qquad (6)$$

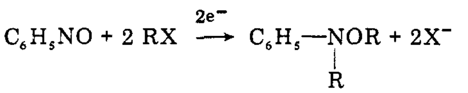


$$C_6H_5NO_2^{-}\cdot + RX \xrightarrow[\text{slow}]{} C_6H_5\text{—}\overset{\displaystyle O}{\overset{|}{\underset{\cdot}{N}}}\text{—O—R} + X^- \qquad (7)$$



$$C_6H_5\text{—}\overset{\displaystyle O}{\overset{|}{\underset{\cdot}{N}}}\text{—OR} \xrightarrow{1e} C_6H_5\text{—N=O} + OR^- \qquad (8)$$

$$OR^- + RX \longrightarrow ROR + X^- \qquad (9)$$



$$C_6H_5NO + 2\ RX \xrightarrow{2e^-} C_6H_5\text{—}\underset{\displaystyle R}{\underset{|}{N}}OR + 2X^- \qquad (10)$$

Equation 7 is thought to be the slow step, because cyclic voltammetry and cyclic chronopotentiometry of nitrosobenzene showed that the rate of reaction of nitrosobenzene radical anion with 1-bromobutane was much faster than that of nitrobenzene radical anion with 1-bromobutane. Values for the rate constant were not determined for the reaction of nitrosobenzene radical anion with 1-bromobutane because other reactions, such as dimerization or reaction with unreduced nitrosobenzene,[15,16] were consuming nitrosobenzene radical anion.

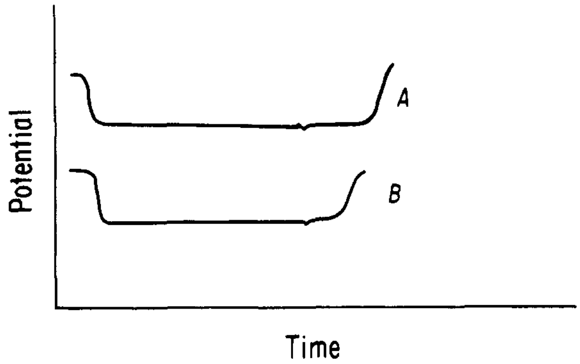
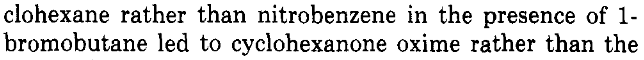


Figure 2. Cyclic chronopotentiogram of 1.36 mM nitrobenzene in DMF containing 0.1 M TEAP at a hanging Hg drop electrode in the absence (A) and presence (B) of butyl bromide (0.54 M).

Dibutyl ether was present in the electrolysis product of the reduction of nitrobenzene in the presence of 1-bromobutane (eq 9).

Equation 10 is shown as a single step because an electrolysis of nitrosobenzene in the presence of 1-bromobutane at −0.9 V vs. SCE did not produce *N,O*-dibutylphenylhydroxylamine, while reduction at −1.5 V vs. SCE did produce *N,O*-dibutylphenylhydroxylamine. At −1.5 V vs. SCE nitrosobenzene is converted directly to the dianion[16] which would be expected to react rapidly with 1-bromobutane. Even at −1.5 V vs. SCE, the yield of *N,O*-dibutylphenylhydroxylamine was not as high as was obtained from nitrobenzene, presumably because of the disproportionation reaction (eq 11). Dimerization of the

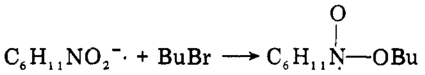


(11)

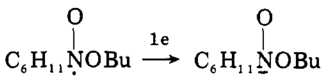
nitrosobenzene radical anion or coupling of nitrosobenzene and its radical anion are presumably the competing reactions which lower the yield of the substituted hydroxylamine at −1.5 V vs. SCE and effectively inhibit the reaction when the reduction is carried out at −0.9 V vs. SCE.

An attempt to carry out a similar reaction using nitrocyclohexane rather than nitrobenzene in the presence of 1-bromobutane led to cyclohexanone oxime rather than the expected *N,O*-dibutyl-N-cyclohexylhydroxylamine. A similar electrolysis of nitrocyclohexane in the absence of 1-bromobutane gave only traces of cyclohexanone oxime. Those results may be rationalized by the following reaction scheme:

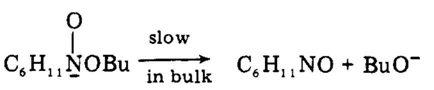
$$C_6H_{11}NO_2 \xrightarrow{1e} C_6H_{11}NO_2^{-}\cdot \qquad (12)$$



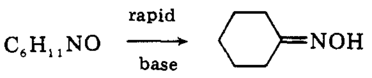
$$C_6H_{11}NO_2^{-}\cdot + BuBr \longrightarrow C_6H_{11}\overset{\displaystyle O}{\overset{|}{\underset{\cdot}{N}}}\text{—OBu} \qquad (13)$$



$$C_6H_{11}\overset{\displaystyle O}{\overset{|}{\underset{\cdot}{N}}}OBu \xrightarrow{1e} C_6H_{11}\overset{\displaystyle O}{\overset{|}{\underset{-}{N}}}OBu \qquad (14)$$



$$C_6H_{11}\overset{\displaystyle O}{\overset{|}{\underset{-}{N}}}OBu \xrightarrow[\text{in bulk}]{\text{slow}} C_6H_{11}NO + BuO^- \qquad (15)$$



(16)

The scheme is similar to that proposed for nitrobenzene, except that nitrosocyclohexane is rapidly converted by base (eq 16) to the oxime which is not reducible at the potential of the reaction. In the absence of an electrophile to react rapidly with the nitrocyclohexane radical anion, the most likely reaction is cleavage of the C–N bond[17] to form nitrite ion and cyclohexyl radical.

Experimental Section

Cyclic voltammetry and cyclic chronopotentiometry were carried out at a hanging Hg drop using a Princeton Applied Research Model 173 potentiostat driven by a Princeton Applied Research Model 175 universal programmer. The cell used for electroanalytical experiments had a working volume of 50 mL. It contained the hanging mercury drop working electrode, Pt wire secondary electrode, and SCE reference which was isolated from the electrolyte by a fine glass frit. The solution was deaerated with N_2 before analysis.

NMR spectra were obtained with a Varian T-60 NMR spectrometer. Mass spectra were obtained on a Varian MAT CH7A mass spectrometer. Gas chromatographic analyses were performed using a 6 ft × 0.125 in. column packed with 5% OV-17 on 80–100 mesh Chromosorb W.

General Electrolysis Procedure. The electrolyses were carried out in a coarse glass frit divided H cell with a 7-cm diameter Hg pool cathode and 1 in.^{2} Pt foil anode. The cathode compartment contained 300 mL of DMF with 0.2 M electrolyte, 0.05 mol of nitro compound, and 0.2 mol of alkyl halide or tosylate. The cathode potential was monitored by a saturated calomel electrode separated from the bulk catholyte by a porous ceramic plug. All electrolyses were carried out under N_2 at a constant cathode potential using a Wenking Model PCA 72H Potential Control Amplifier. The total electricity passed during the electrolysis was measured by passing the current through a dc motor coupled to an odometer.

The dimethylformamide used as a solvent was dried over Linde 3A molecular sieves. The electrolyte was 0.2 M tetrabutylammonium bromide or iodide or tetraethylammonium *p*-toluenesulfonate or chloride predried in a vacuum desiccator. The choice of anion was dictated by the alkyl halide or tosylate used.

The electrolyses were generally carried to completion as indicated by the current being less than 10% of the initial current. The catholyte was then diluted with twice its volume of benzene and extracted three times with water. The benzene solution was dried over anhydrous $MgSO_4$ and then the benzene was removed on a rotary evaporator to give the crude product. When tetrabutylammonium iodide was used, the crude product was extracted with ether to separate the products from the electrolyte.

Reduction of Nitrobenzene in the Presence of 1-Bromobutane. The electrolysis was run at −1.3 V vs. SCE with the initial current being 150 mA. After 47 h, 0.185 Faraday of electricity had been passed (3.7 Faraday/mol nitrobenzene). Ten grams (90%) of crude product was obtained. The crude *N,O*-dibutylphenylhydroxylamine was distilled at reduced pressure (0.05 mm), the major portion distilling at 80 °C accompanied by some decomposition. Redistillation of a portion gave a colorless liquid, bp 65 °C (0.025 mm), n^{22}_{D} 1.4920. Another portion of the first distillate was purified by chromatography on silica gel eluting with 50/50 benzene/hexane. Evaporation of the solvent gave an oil which by GC analysis was identical with the redistilled material. Both samples gave satisfactory elemental analyses. ^{1}H NMR ($CDCl_3$) δ 0.97 (6 H, t, CH_3), 1.53 (8 H, m, CH_2), 3.26 (2 H, t, J = 7 Hz, CH_2N), 3.78 (2 H, t, J = 6.5 Hz, CH_2O), 7.18 (5 H, m, aromatic).

Reduction of Nitrobenzene in the Presence of 1-Iodobutane. The electrolysis was carried out at −1.3 V vs. SCE for 64 h, and a total of 0.24 Faraday passed (4.8 Faradays/mol nitrobenzene). The crude product (10.2 g) was 90% *N,O*-dibutylphenylhydroxylamine (83%) by GC analysis.

Reduction of Nitrobenzene in the Presence of 1-Chlorobutane. The electrolysis was carried out at −1.35 V vs. SCE for 40 h, and a total of 0.19 Faraday had passed (3.8 Faradays/mol nitrobenzene). The crude product contained 7.6 g (69%) of *N,O*-dibutylphenylhydroxylamine by GC analysis.

Reduction of Nitrosobenzene in the Presence of 1-Bromobutane. The catholyte contained 5.35 g of nitrosobenzene and 15 g of 1-bromobutane. The electrolysis was carried out at −1.1 V vs. SCE for 20 h, and 0.03 Faraday of electricity was passed (0.6 Faraday/mol nitrosobenzene). The crude product (5.4 g) contained no *N,O*-dibutylphenylhydroxylamine by GC analysis.

A second electrolysis, as above except carried out at −1.5 V vs. SCE, was operated for 20 h, and 0.084 Faraday of electricity passed (1.68 Faradays/mol of nitrosobenzene). The crude product contained 3 g (27% yield) of *N,O*-dibutylphenylhydroxylamine by GC analysis.

Reduction of Nitrobenzene in the Presence of Chloromethane. The catholyte consisted of 300 mL of DMF containing 0.2 M $Et_4N^+Cl^-$, 6.15 g of nitrobenzene, and saturated with chloromethane. Chloromethane was bubbled through the catholyte continuously during the electrolysis. The electrolysis was run at −1.3 V vs. SCE for 40 h, and a total of 0.193 Faraday of electricity was passed (3.86 Faradays/mol nitrobenzene). The crude product (6.2 g) was estimated to be 85% *N,O*-dimethylphenylhydroxylamine by GC (80% yield). Distillation of the crude product gave pure *N,O*-dimethylphenylhydroxylamine: bp 67–68 °C (10 mm); n^{22}_{D} 1.5170; ^{1}H NMR ($DCCl_3$) δ 3.00 (3 H, s, CH_3N), 3.63 (3 H, s, CH_3O), 7.03 (5 H, m, aromatic).

Reduction of Nitrobenzene in the Presence of Methyl *p*-Toluenesulfonate. The electrolysis was run at −1.3 V vs. SCE for 42 h, and 0.19 Faraday was passed (3.8 Faradays/mol of nitrobenzene). Analysis of the crude product by GC indicated the presence of 2.5 g (36% yield) of *N,O*-dimethylphenylhydroxylamine along with considerable amounts of unidentified material.

Reduction of Nitrobenzene in the Presence of 1,5-Dibromopentane. The electrolysis was run at −1.3 V vs. SCE for 44 h, and a total of 0.19 Faraday passed (3.8 Faradays/mol nitrobenzene). The crude product (11.5 g) was distilled, the major component boiling at 71–77 °C (0.025 mm) with some decomposition. Further purification by chromatography on silica gel eluting with 80/20 hexane/benzene gave, after solvent evaporation, an oil which contained only one component by GC analysis. The mass spectral data and NMR were consistent with *N*-phenylperhydro-1,2-oxazepine: ^{1}H NMR ($DCCl_3$) δ 1.82 (6 H, m, CH_2), 3.33 (2 H, m, CH_2N), 3.97 (2 H, m, CH_2O), 7.02 (5 H, m, aromatic); mass spectrum $M^{+}\cdot$ *m/e* (rel intensity) 177 (42), 159 (100), 158 (63), 130 (39), 122 (31), 106 (30), 105 (44), 104 (39).

Reduction of Nitrocyclohexane in the Presence of 1-Bromobutane. The electrolysis was run at −1.8 V vs. SCE for 20 h, and a total of 0.053 Faraday was passed (1 Faraday/mol nitrocyclohexane). GC analysis of the crude product indicated that it contained 3 g of cyclohexanone oxime. Distillation gave pure cyclohexanone oxime, bp 208 °C, identical with an authentic sample.

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Registry No.—Nitrobenzene, 98-95-3; 1-bromobutane, 109-65-9; *N,O*-dibutylphenylhydroxylamine, 61915-46-6; 1-iodobutane, 542-69-8; 1-chlorobutane, 109-69-3; nitrosobenzene, 586-96-9; chloromethane, 74-87-3; *N,O*-dimethylphenylhydoxylamine, 61915-47-7; methyl *p*-toluenesulfonate, 80-48-8; *N*-phenylperhydro-1,2-oxazepine, 61915-48-8; 1,5-dibromopentane, 111-24-0; nitrocyclohexane, 1122-60-7; nitrobenzene radical anion, 12169-65-2.

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