imidazolin-1′-yl)thiazole (**9**) (instead of 2-aminothiazole) and 1 equiv of the reagent **1b** (instead of 2 equiv as used in method A) were employed. The yields were comparable within ±5% to that obtained by method A.

Acknowledgment. This work was supported by Research Grant 14499-GB1 from the Petroleum Research Fund, administered by the American Chemical Society. One of the authors (R.S.H.) gratefully acknowledges the University of Maryland Baltimore County, for the award of a Faculty Summer Research Fellowship. We are indebted to Dr. Patrick Callery of the University of Maryland, Baltimore, for the mass spectral data and to Dr. Yui-Fai Lam of the University of Maryland, College Park, for the ^{13}C NMR spectra.

Registry No. **1a**, 88945-40-8; **1b**, 88945-41-9; **4**, 540-61-4; **4**·HCl, 6011-14-9; **6**, 88945-42-0; **8**, 88945-43-1; **9**, 88945-44-2; **10**, 88945-45-3; **11**, 31354-57-1; **12**, 88945-46-4; 2-aminothiazole, 96-50-4; 2-aminopyrimidine, 109-12-6.

Reduction of Aromatic Nitro Compounds by Ethylenediamine. A New Selective Reagent for the Synthesis of Symmetric Azo Compounds

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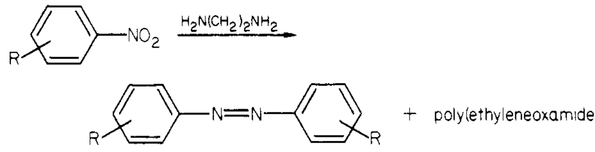
Ethylenediamine selectively reduces aromatic nitro compounds $RC_6H_4NO_2$ (R = H, *m*-CH_3, *p*-CH_3, and *m*-Ph) at 150 °C to symmetric azo compounds $RC_6H_4N{=}NC_6H_4R$ in good yield but does not reduce their ortho-substituted analogues. The diamine does not react with *o*- or *p*-nitroanilines but reduces the meta isomer to 1,3-diaminobenzene and 3,3′-diaminoazobenzene. Its reaction with *o*- and *p*-halonitrobenzenes gives substitution products $H_2NCH_2CH_2NHC_6H_4NO_2$. Nitrosobenzene is reduced to aniline and azobenzene, while α-nitroso-β-naphthol is converted to 1,4-phenanthroline. Among a variety of other amines tested, only 1,3-propylenediamine reduces nitrobenzene to azobenzene. A mechanism for the reaction is proposed.

Introduction

Methods for selective reduction of aromatic nitro compounds to azo compounds are of continuing interest.[1-5] Although many reagents have been developed for this reduction, most of them give low yields of azo compounds. An exception is zinc powder in basic solution, which converts nitrobenzene to azobenzene in 85% yield.[1b] $NaBH_4$,[1h] $LiAlH_4$, $NaAlH_4$,[1e-j] and $NaH_2Al(OCH_3)(OC_2H_5)$[1f] have also been used for this reduction. While both boron and aluminum hydrides reduce nitro compounds to azo compounds in good yields, the former are less reactive and require a much higher temperature for the reduction.

In our studies on the catalytic reduction of aromatic nitro compounds by alcohols and alkyl amines[6] we have discovered that ethylenediamine reduces aromatic nitro compounds to the corresponding azo compounds in good yield (eq 1). We now report the results of this investigation.



(1)

Table I. Reduction of Aromatic Nitro Compounds by Ethylenediamine

nitro compd	product and yield[a]
nitrobenzene	azobenzene 75%, aniline (10%)
p-nitrotoluene	4,4′-azotoluene 97%
m-nitrotoluene	3,3′-azotoluene 86%, *m*-toluidine (12%)
o-nitrotoluene	no reaction
p-nitroaniline	no reaction
m-nitroaniline	3,3′-diaminoazobenzene 24%, phenylenediamine 75%
o-nitroaniline	no reaction
m-nitrobiphenyl	3,3′-diphenylazobenzene 68%
nitrosobenzene	azobenzene (16%), aniline (83%)
α-nitroso-β-naphthol	1,4-phenanthroline (65%)

[a] Isolated yields; yield in parentheses were estimated by NMR.

Results and Discussion

The reduction is performed by heating a mixture of the nitro compound and 4–10 equiv of ethylenediamine at 150 °C for 10–22 h. The reaction is carried out in a vessel that can contain the pressure (~2 atm) developed by the ethylenediamine. Yields of azo compounds prepared by this method are presented in Table I. Nitrobenzene is reduced mainly to azobenzene and ca. 10% aniline as shown by NMR spectroscopy. The attachment of a methyl

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group to different positions on the nitrobenzene ring leads to a change in reactivity. While *p*- and *m*-nitrotoluenes are reduced to azo compounds in high yields, the ortho isomer is not reduced. Since the electronic contribution of the ring methyl group to the nitro group is essentially equal for *o*- and *p*-nitrotoluenes, this difference in reactivity can be attributed to steric hindrance by the ortho substituent. Similarly, 3-nitrobiphenyl is reduced to the corresponding azo compound by ethylenediamine, but the 2-nitro isomer shows very little reaction with the diamine.

A dramatic difference in reactivity in the reaction of ethylenediamine with *o*-, *m*-, and *p*-nitroanilines was also observed. *m*-Nitroaniline is reduced to 1,3-diaminobenzene and a smaller amount of 3,3′-diaminoazobenzene, whereas the other two nitroanilines are unreactive. Thus it appears that the presence of a strong electron-releasing group at the ortho or para position greatly inhibits the reactivity of a nitro compound by increasing the electron density at the nitro group. This notion is supported by the observations that *p*-nitrophenol and *N*-(2-aminoethyl)-*p*-nitroaniline do not undergo reduction by ethylenediamine. In these compounds a strong electron-releasing group is attached in the para position to the nitro group.

Both *p*- and *o*-halonitrobenzenes react with ethylenediamine to give the corresponding *N*-(2-aminoethyl)-nitrobenzenes, which do not undergo reduction because of the strong electron-releasing ability of the *N*-(2-aminoethyl) group. Such a nucleophilic substitution is commonly observed for halo nitro aryls.[1g,7]

Among several other amines tested for this reduction, only 1,3-propylenediamine was effective, although less so than ethylenediamine. Hexamethylenediamine, *N*-methyl derivatives of ethylenediamine, and monoamines were inactive.

Ethylenediamine does not further reduce azo compounds under the condition for the reduction of nitro compounds, but it does react with nitroso compounds. As shown in Table I nitrosobenzene is reduced to aniline and a small amount of azobenzene, while α-nitroso-β-naphthol was converted to 1,4-phenanthroline in 65% yield.

The formation of azo compounds in the reaction of ethylenediamine with nitro compounds indicates that the diamine is oxidized. Formation of ammonia in the reduction was indicated by its odor when the reaction vessel was opened and confirmed by a strong peak, m/e 17, in the mass spectrum of the gas over the reaction mixture. Addition of chloroform to the mixture after completion of reduction yielded a polymer precipitate that dissolved only in CF_3COOH and *o*-cresol among many solvents tested. The NMR and IR spectra, microanalysis data, and solubility properties led us to conclude that the polymer is a polyoxamide with the formula $-[COCONH(CH_2)_2NH(H_2O)]-$ (1). The attachment of a water molecule to each $-COCONHCH_2CH_2NH-$ group is a consequence of the high polarity of the amide group and the facile hydrogen bonding between water and the amide group. An authentic sample of $-(COCONHCH_2CH_2NH)-_n$, prepared by the condensation polymerization of oxalic acid with ethylenediamine, was identical with polymer 1 in solubility properties and IR spectrum.

Evidence for the presence of the monomer **2** of **1** is found

$$\underset{\mathbf{2}}{H_2NCH_2CH_2NHCOCONHCH_2CH_2NH_2}$$

in the ^1H NMR spectrum of a solution of nitrobenzene and ethylenediamine, which reveals two A_2B_2 triplets at δ 3.54 and 2.76, corresponding to the methylene protons attached to the amide group and to the amino group, respectively. The polar character of this compound allowed us to separate it from other components in the reaction solution by extraction with water followed by vacuum removal of water and ethylenediamine. Because of the high affinity of **2** for water, it was not possible to remove all the water, and only a viscous liquid was obtained. The liquid was converted to **1** and ethylenediamine on heating at elevated temperature, confirming its identity as the monomer.

Based on the above results, the formation of **1** can be viewed via the following reaction sequence, in which ethylenediamine is first oxidized to oxamide (**3**). This

$$H_2N(CH_2)_2NH_2 \xrightarrow{C_6H_5NO_2} \underset{\mathbf{3}}{H_2NCOCONH_2} \xrightarrow[-NH_3]{H_2N(CH_2)_2NH_2}$$
$$\underset{\mathbf{2}}{H_2N(CH_2)_2NHCOCONH(CH_2)_2NH_2} \xrightarrow[-H_2N(CH_2)_2NH_2]{\text{heat}}$$
$$\underset{\mathbf{1}}{-(COCONH(CH_2)_2NH)-_n}$$

compound then reacts with exccess ethylenediamine to give **2** and ammonia. Further condensation of **2** yields **1** by releasing one molecule of ethylenediamine per molecule of **2**.

Our results show that ethylenediamine is oxidized to oxamide with a total oxidation state change of 8, even in the presence of excess ethylenediamine. Moreover, the diamine is oxidized at both carbons, leading to symmetric products. Counting the total oxidation state changes in the nitro compound and ethylenediamine, the oxidation of one molecule of diamine results in the formation of one molecule of azo compound.

Mechanism

A mechanism involving nucleophilic attack of ethylenediamine on the nitrogen of the nitro group can be envisaged (Scheme I). With longer chain diamines, intermediates similar to **4**, except for ring size, would be formed. The relative ease of formation of a five- or six-membered ring explains the unique reactivity of ethylenediamine and propylenediamine. Prototropic rearrangements similar to those of steps iii–viii have been reported.[7-11]

The steric interaction of an ortho methyl group with the three groups at the nitrogen center in **4** explains the difference in reactivity of *o*-nitrotoluene and *p*-nitrotoluene. A model of **4** indicates that an ortho methyl group would lead to a strong nonbonded interaction between the bulky substituents of the nitrogen center and the methyl group.

The suggested mechanism accounts for the fact that both ends of ethylenediamine are oxidized even in the presence of excess diamine. As shown by a number of experiments, azo compounds are not further reduced by ethylenediamine. Consequently, the possibility that the aniline produced comes from the reduction of azobenzene is ruled out. Possible reaction pathways leading to the formation of aniline are proposed in steps xi–xii.

A possible alternative for the formation of azo compounds is the reaction of aniline with an intermediate nitroso compound. However, this route is also ruled out by the observation that no cross product was detected by adding a different aryl amine to the solution of nitro compound and ethylenediamine.

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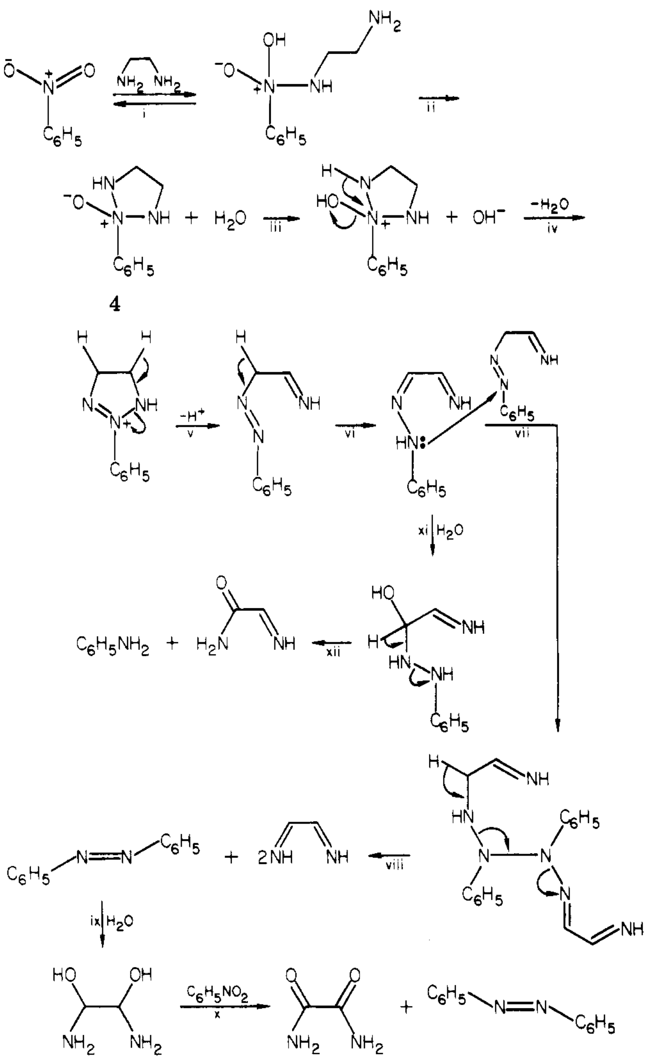
Scheme I



Experimental Section

General Procedures. Infrared spectra were recorded on a Jasco A-100 spectrometer, and NMR spectra were measured on Jeol FX-100 and JEOL C-60 HL NMR spectrometers. Gas chromatographic analyses were performed on a Shimadzu GC-7AG using a Versamide 900 column. Melting points were determined on a Fisher Johns apparatus and are uncorrected.

Reaction of Nitrobenzene with Amines. A mixture of nitrobenzene (5.0 mmol) and amine (20 mmol) in a vacuum-sealed tube or an evacuated round-bottomed flask sealed with a rubber septum was heated at 150 °C for 10 h. The solution was cooled and analyzed by ^{1}H NMR spectroscopy. The relative amounts of aniline, azobenzene, and nitrobenzene were determined by ratios of areas under characteristic NMR peaks for each compound: aniline, δ 7.0 (t, 2 H); azobenzene, δ 7.88 (m, 2 H); nitrobenzene, δ 8.20 (d, 2 H). The identity of each component and the yields were confirmed by GC. The results of the two methods were in good agreement. Under these conditions, ethylenediamine reacted with nitrobenzene to give azobenzene (80%) and aniline (10%); 1,3-propylenediamine gave only azobenzene (54%).

Reaction of Nitro Compounds with Ethylenediamine. Azobenzene. To 5.0 mL (6.0 g, 0.049 mol) of nitrobenzene in a round-bottomed flask was added 30.4 mL (27.4 g, 0.46 mol) of ethylenediamine. The flask was sealed with a rubber septum, evacuated, and heated at 150 °C for 10 h. Addition of 20 mL of chloroform gave a precipitate that was removed by filtration. The filtrate was evaporated to dryness and washed with 3 N HCl to afford an orange crystalline material. Recrystallization from ethanol afforded 3.4 g (75%) of azobenzene: mp 65–66 °C (lit.[12] 68 °C); mass spectrum, *m/e* 182 (M$^+$); IR and NMR spectra of the product agreed with reported spectra.

4,4′-Azotoluene. Similar reduction of *p*-nitrotoluene gave the azo compound in 97% yield; mp 141–142 °C (lit.[12] 143 °C); mass spectrum, *m/e* 210 (M$^+$).

3,3′-Azotoluene. Similar reduction of *m*-nitrotoluene gave the azo compound in 78% yield; mp 53–54 °C (lit.[12] 54–55 °C); mass spectrum, *m/e* 210 (M$^+$).

3,3′-Diphenylazobenzene. *m*-Nitrobiphenyl was reduced by the same procedure with a reaction time of 22 h. The product was isolated by PLC (SiO_2) using $CHCl_3$ as eluent: yield 68%; mp 127–128 °C; mass spectrum, *m/e* 334 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 8.14 (d, J = 1 Hz, 1 H), 7.88 (d of t, J = 8 Hz, 1 H), 7.76–7.24 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 152.9 (s), 142.0 (s), 140.2 (s), 129.4 (d), 129.3 (d), 128.7 (d), 127.5 (d), 127.0 (d), 121.5 (d). Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.19; H, 5.43; N, 8.37. Found: C, 85.89; H, 5.22; N, 8.06.

***N*-(2-Aminoethyl)-*p*-nitroaniline.** A mixture of *p*-chloronitrobenzene (0.788 g, 5 mmol) and ethylenediamine (2.74 g, 46 mmol) in an evacuated flask sealed with a rubber septum was heated at 150 °C for 10 h. Evaporation of the solution to dryness followed by washing with 1 N NaOH afforded the product as a yellow material in essentially quantitative yield: mp 139–141 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.90 (t, J = 6 Hz, 2 H), 3.16 (t, J = 6 Hz, 2 H), 6.66 (d, J = 10 Hz, 2 H), 7.29 (b), 8.00 (d, J = 10 Hz, 2 H); IR (KBr) 1600 (s), 1300 (s,b) cm^{-1}; mass spectrum, *m/e* 181 (M$^+$). Under the same conditions, *p*-bromonitrobenzene gave the same product.

Poly(ethyleneoxamide). The polymer was prepared from nitrobenzene, *p*-nitrotoluene, or *m*-nitrotoluene. A solution containing 0.05 mol of the nitro compound and 0.4 mol of ethylenediamine was heated at 150 °C for 10 h. Addition of 20 mL of $CHCl_3$ to the solution precipitated the polymer, which was filtered, washed with water, methanol, and acetone, and dried in vacuo: IR (Nujol) 3200 (s), 1650 (s), 1520 (m), 1245 (w), 1220 (m), 820 (m) cm^{-1}; ^{1}H NMR (C_6D_6 and CF_3COOH) δ 3.74 (b); ^{13}C NMR (C_6D_6 and CF_3COOH) δ 41.4 (t), 164.3 (s). Anal. Calcd for $H_2NCH_2CH_2NH\text{-}[COCONHCH_2CH_2NH(H_2O)]_n\text{-}H$ with n = 5.92 (estimated from the mole ratio of C/N determined by microanalysis): C, 36.63; H, 6.51, N, 23.04. Found: C, 36.66; H, 6.50; N, 23.04. The polymer did not melt, but decomposed above 300 °C. Among a variety of solvents tested, it dissolved only in CF_3COOH and *o*-cresol. The IR spectrum and solubility of this polymer were identical with those of a polymer synthesized by reaction of oxalic acid with ethylenediamine. Its $\nu_{C=O}$ (1650 cm^{-1}) was the same as that of oxamide.[13]

1,4-Phenanthroline. To 0.865 g (5 mmol) of α-nitroso-β-naphthol in a round-bottomed flask was added 2.6 g (44 mmol) of ethylenediamine. The solution was heated at 150 °C for 10 h. After the same workup procedure used for azobenzene the crude product was vacuum sublimed at 70 °C to afford 1,4-phenanthroline in 65% yield: mp 55–57 °C; mass spectrum, *m/e* 180 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 9.16 (t, J = 4 Hz, 2 H), 8.04–7.65 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.1 (d), 142.9 (d), 142.4 (s), 141.4 (s), 133.0 (s), 131.5 (d), 130.7 (s), 128.7 (d), 127.7 (d), 127.3 (d), 126.6 (d), 124.3 (d). Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.54. Found: C, 80.19; H, 4.69; N, 15.71.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this work.

Registry No. 1 (SRU), 36812-63-2; 2, 4312-20-3; 2 (homopolymer), 88841-78-5; ethylenediamine, 107-15-3; nitrobenzene, 98-95-3; *p*-nitrotoluene, 99-99-0; *m*-nitrotoluene, 99-08-1; *o*-nitrotoluene, 88-72-2; 3-nitrobiphenyl, 2113-58-8; 2-nitrobiphenyl, 86-00-0; *o*-nitroaniline, 88-74-4; *m*-nitroaniline, 99-09-2; *p*-nitroaniline, 100-01-6; *p*-nitrophenol, 100-02-7; *N*-(2-aminoethyl)-*p*-nitroaniline, 6332-77-0; 1,3-propylenediamine, 109-76-2; hexamethylenediamine, 124-09-4; azobenzene, 103-33-3; 4,4′-azotoluene, 501-60-0; 3,3′-azotoluene, 588-04-5; 3,3′-diphenylazobenzene, 88841-77-4; *p*-chloronitrobenzene, 100-00-5; *p*-bromonitrobenzene, 586-78-7; 1,4-phenanthroline, 230-33-1; α-nitroso-β-naphthol, 131-91-9; 3,3′-diaminoazobenzene, 21371-44-8; *m*-phenylenediamine, 108-45-2; nitrosobenzene, 586-96-9.

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