injection temperature, 200°; flow rate, ~30 cc/min. The relative retention for CCl_4, $C_6H_5NO_2$, $p\text{-}O_2NC_6H_4Cl$ was 1:20:24, respectively.

To determine the yield of $C_6H_4NO_2$ and $p\text{-}O_2NC_6H_4Cl$, standard solutions of $C_6H_5NO_2$ and $p\text{-}O_2NC_6H_4Cl$ dissolved in CCl_4 were prepared and stored in sealed 1-ml glass vials. These standards were analyzed in triplicate prior to and following the reaction samples.

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Registry No.—NAT, 16186-97-3; PAT, 981-18-0; *p*-nitrophenyl radical, 2395-99-5.

Formation of Radical Anions from Vicinal Diamines and Strong Bases[1]

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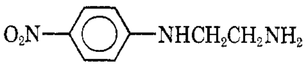
Ethylenediamine (EDA) reacts with butyllithium to form the pyrazine radical anion. On standing, in the presence of EDA and *N*-lithioethylenediamine, this radical is slowly converted to a dihydropyrazine radical. Other vicinal diamines were also found to yield pyrazine-type radicals when treated with strong base. The large amounts of hydrogen gas evolved during these reactions is attributed to loss of metal hydride from the metalated EDA.

In the course of the kinetic study of the reaction mechanism of the prototropic propargylic rearrangement of 3-hexyne with sodium amide in ethylenediamine (EDA) at room temperature,[3] the rate of rearrangement was found to be dependent on the time given to the interaction of sodium amide with EDA before introduction of the hexyne. The suspension of sodium amide in EDA gradually changes color from gray to purple to deep blue. Subsequent investigation by electron paramagnetic resonance (epr) revealed the presence of organic radicals in this and other reactions involving strong bases and vicinal diamines. Although further research has indicated that the rearrangement may not be related to the formation of these radicals,[4] the radicals themselves are of sufficient interest to warrant separate presentation.

Results

A. Detection of Radicals in Base-Treated Vicinal Diamines.—When strong bases [$NaNH_2$, $LiNH_2$, LiH, or butyllithium (BuLi)] are treated with excess EDA (a 10:1 molar ratio of diamine to base was commonly used) in a drybox at room temperature, intense blue solutions are obtained. Regardless of the base used, identical epr spectra resulted (Figure 1). The radical concentration was estimated to be 0.005 *M* by comparison with a standard solution of diphenylpicrylhydrazyl. Additional hyperfine structure was observed when tetrahydrofuran (THF) solvent was added to the EDA–BuLi mixture. Fully deuterated EDA, on treatment with BuLi, gave a five-line spectrum (Figure 2).

The reaction between EDA and BuLi results in a golden yellow color (no λ_{max} in the visible region 400–800 nm) if air is very carefully excluded using vacuum line techniques. Exposure to a trace of oxygen results in a gradual color change from yellow to purple (λ_{max} 585 nm) with little or no change in the epr signal. Extensive degassing does not reverse the color change. Excess oxygen, however, destroys the purple color as well as the radical signal. The radical signal can also be quenched by the addition of nitrobenzene, which results in formation of the nitrobenzene radical anion and *N*-(*p*-nitrophenyl)ethylenediamine (1).



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If either the yellow or the blue solution containing the radical (produced from EDA and BuLi) are allowed to stand for several days (under vacuum at room temperature) a different epr spectrum gradually develops (Figure 3).

Other diamines were also treated with strong base and examined by epr. The results are tabulated in Table I.

B. Formation of a Radical on Treatment of Pyrazine with Butyllithium.—Treatment of a dilute solution of

Table I

Base-Treated Diamines Which Were Analyzed by Epr[a]

Diamine	Color	Epr signal
EDA	Blue[b]	Figure 1[c]
EDA-d_8	Blue	Figure 2
Propylenediamine	Red	Yes
N,*N*′-Dimethylethylenediamine	Green	Figure 4
2-Methyl-1,2-diaminopropane	Brown	Yes
N-Methylethylenediamine	Green	Yes
o-Phenylenediamine	Blue	Yes
cis-1,2-Diaminocyclohexane	Red-brown	Yes
trans-1,2-Diaminocyclohexane	Cloudy white	No
1,3-Diaminopropane	Cloudy white	No
N,*N*-Dimethylethylenediamine	Yellow	No

[a] A 10:1 molar ratio of diamine to BuLi was used. [b] The color is golden yellow if air is very carefully excluded. [c] Upon standing the spectrum gradually changes (Figure 3).

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[1] Presented, in part, at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971.

[2] Postdoctoral Research Associate, 1970–1971.

[3] J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, **31**, 2069 (1966).

[4] P. Barelski, Ph.D. Thesis, Southern Illinois University, 1971.

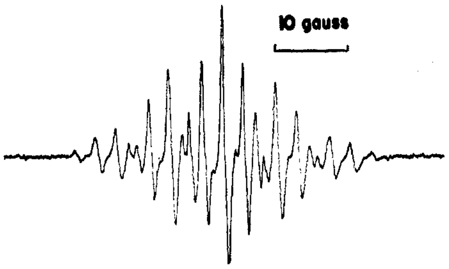


Figure 1.—First-derivative epr spectrum of radical formed from EDA and butyllithium.

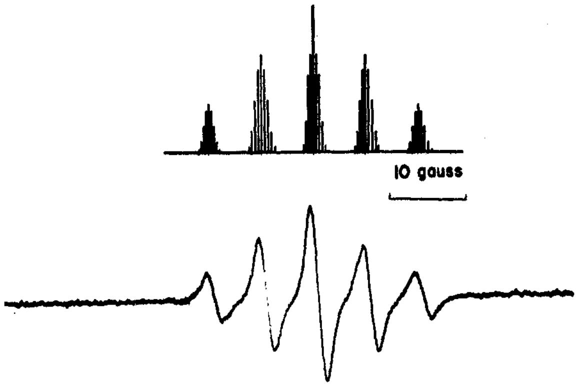


Figure 2.—First-derivative epr spectrum of radical formed from EDA-d_8 and butyllithium. The reconstruction refers to pyrazine-d_4 with a_N = 7.2 and a_D = 0.4.

pyrazine in THF ($\sim 10^{-2}$ *M*) with BuLi resulted in a yellow solution (no λ_{max} in the visible region) which gave the epr spectrum shown in Figure 5. This solution also turned blue on exposure to a trace of air.

C. Evolution of Hydrogen Gas on Treatment of Vicinal Diamines with Base.—Considerable amounts of hydrogen gas were evolved during the reaction between EDA and strong base. These and other results are given in Table II.

Table II

Gaseous Products from the Reaction of Vicinal Diamines with Strong Bases[a]

Reactants		Products		
BuLi	EDA	Butane	H_2	NH_3
1	15	0.9	0.2	0
1	1	0.8	0.4	0.05
1	0.8	0.7 (.05)[b]	0.4 (0.1)[b]	0 (.02)[b]
$NaNH_2$	EDA			
1	10		0.02	0.2
1	1		0.06	0.1
BuLi	DMEDA[c]			
1	1	0.9	0 (0.2)[b]	0

[a] All data are in molar ratios. [b] Data in parentheses refers to the additional gas evolved after heating to 110° for 2 hr. [c] Refers to *N,N'*-dimethylethylenediamine.

D. Reaction of EDA with Alkali Metals.—EDA was refluxed over sodium metal and then distilled. The distillate as analyzed by vpc showed EDA plus eight other peaks. Piperazine and diethylenetriamine were identified by comparison with authentic samples. Pyrazine was identified, as a product, by vpc retention time and nmr.

When EDA was refluxed over lithium metal a purple solution developed which gave an epr spectrum identical with that shown in Figure 1. A white solid, identified as bis(Δ^2-2-imidazolinyl) (2) was isolated from this reaction.

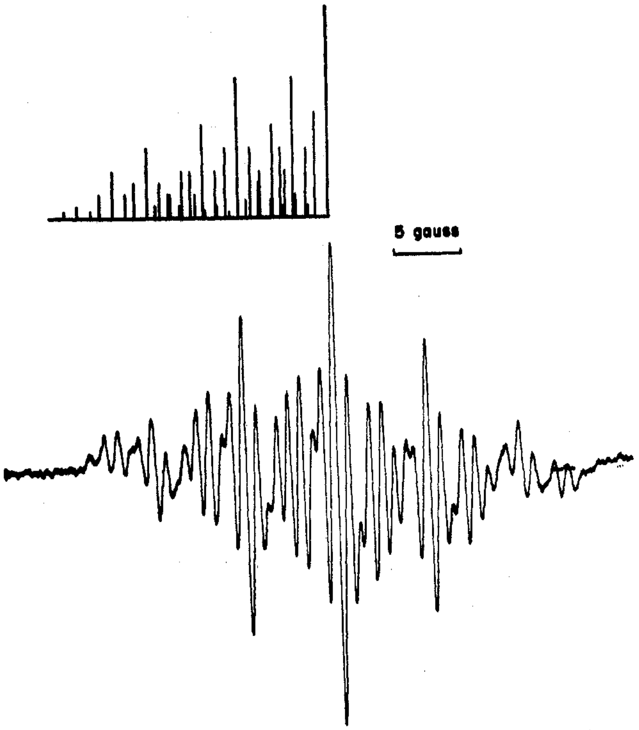


Figure 3.—First-derivative epr spectrum of radical formed in butyllithium–EDA after 1 week. The reconstruction refers to dihydropyrazine with a_N = 6.6, a_H = 2.4 (four equivalent), and a_H = 1.0 (two equivalent).

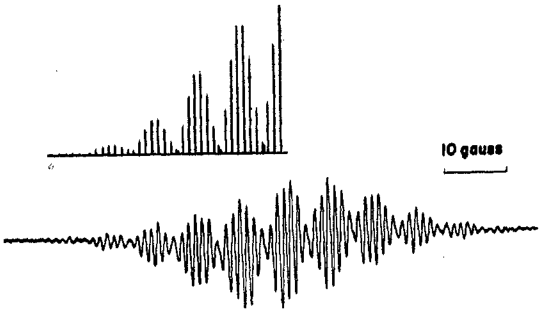
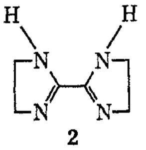


Figure 4.—First-derivative epr spectrum from reaction of *N,N'*-dimethylethylenediamine with butyllithium. The reconstruction refers to *N,N'*-dimethyldihydropyrazine with a_N = 6.7, a_H (methyl) = 6.7, a_H (ring) = 1.0, and a_{Li} = 1.0.



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Discussion

Radicals Formed in EDA.—The initially detected radical formed in the reaction of EDA with strong base (or lithium metal) is the pyrazine radical anion. Relative peak intensities and spacings (Figure 1) may be satisfactorily described as the result of hyperfine interaction of the unpaired electron with two equivalent nitrogen atoms (a_N = 7.3 G) and four equivalent hydrogen atoms (a_H = 2.7 G). We reduced pyrazine in THF with potassium metal and obtained an epr spectrum which was essentially identical with that ob-

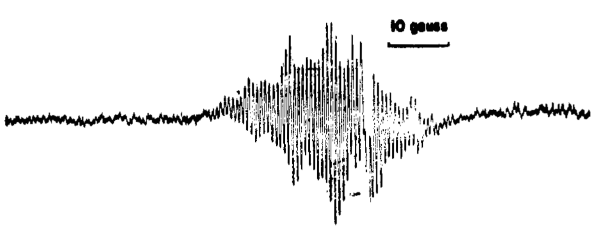


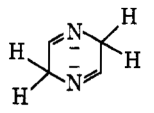
Figure 5.—First-derivative epr spectrum resulting from the reaction of butyllithium with pyrazine in THF.

tained from base treated EDA (literature values:[5] $a_N = 7.22$ G, $a_H = 2.66$ G). Furthermore, treatment of fully deuterated EDA with BuLi resulted in an epr spectrum (Figure 2) consistent with the perdeuterated pyrazine radical anion ($a_N = 7.3$ G, a_H (theoretical) = 0.4 G).

Generally aromatic radical anions are generated either by alkali metal reduction or by electrolytic reduction.[6] However, Russell and coworkers[7] have reported on the generation of radical reduction products in reactions between carbanions or organometallics and neutral unsaturated compounds. For example, phenazine[8] was reduced to its radical anion by treatment with potassium *tert*-butoxide in dimethyl sulfoxide. Similarly, we have found that pyrazine can be conveniently reduced with butyllithium in THF (see Figure 5 for the epr spectrum). This spectrum shows the additional quartet hyperfine structure from the alkali metal ($a_{Li} = 0.7$ G) as reported by Carrington and Santos-Veiga.[5] This additional hyperfine structure was also observed when THF solvent was added to the blue EDA–BuLi mixture containing the pyrazine radical.

The pyrazine radical, when generated from EDA and butyllithium, is not stable. A different epr spectrum (Figure 3) was obtained after the EDA–BuLi mixture had been allowed to stand at room temperature under vacuum for 1 week. This observation was reproducible, starting with either the blue or the yellow EDA–BuLi mixture. The new spectrum is consistent with a pyrazine nucleus to which two additional equivalent hydrogens have been added ($a_N = 6.6$ G, two equivalent; $a_H = 2.4$ G, four equivalent; $a_H = 1.0$ G, two equivalent). Two interpretations were considered. Since hydrogen gas is evolved during the reaction, a weak interaction between hydrogen gas and the pyrazine radical was suggested. However, the bulk of the hydrogen gas is evolved during the first hour of the reaction; yet the new radical is not observed until after several days. Also, five freeze–pump–thaw cycles did not alter the epr spectrum. The favored interpretation, then, is that the new signal is due to the radical anion of a dihydropyrazine (**3**, **4**, or **5**).

3



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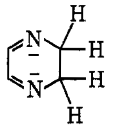

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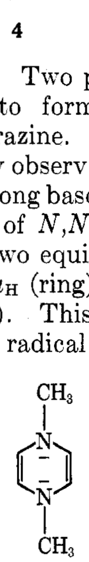
Radicals from Other Vicinal Diamines.—The complex spectrum resulting from the reaction of butyllithium and propylenediamine could be due to a mixture of 2,6-dimethylpyrazine radical anion[9] and 2,5-dimethylpyrazine radical anion.[9] This is consistent with the observation that pyrazine is formed from the EDA (also, see below). Two propylenediamine molecules could combine to form 2,6-dimethylpyrazine and/or 2,5-dimethylpyrazine.

The spectrum initially observed from *N*,*N'*-dimethylethylenediamine and strong base (Figure 4) is consistent with the radical anion of *N*,*N'*-dimethyldihydropyrazine (**6**) ($a_N = 6.7$ G, two equivalent; a_H (methyl) = 6.7 G, six equivalent; a_H (ring) = 1.0 G, four equivalent; $a_{Li} = 1.0$ G, one). This radical would be completely analogous to the radical anion (**6**) of **3**.



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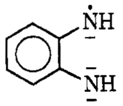
Other vicinal dimaines (see Table I) also gave epr spectra when treated with butyllithium. These were not sufficiently resolved (or were too complex) to permit interpretation. Apparently, diamines which are vicinal (1,3-diaminopropane gave no epr signal) and which involve only primary or secondary amino groups (*N*,*N*-dimethylethylenediamine gave no epr signal) are required for formation of these pyrazine-type radicals. Interestingly, the cis isomer of 1,2-diaminocyclohexane gave an epr signal, whereas the trans isomer did not.

Russell and coworkers[8] assigned the radical obtained from *o*-phenylenediamine and potassium *tert*-butoxide in dimethyl sulfoxide as **7**.



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The Origin of Pyrazine.—Since epr spectroscopy is a very sensitive technique, one must always be concerned with the possibility of impurities in the materials used. In particular, pyrazine was suspected as an impurity in EDA. However, no pyrazine could be detected in the starting EDA using vapor phase chromatography and nmr. The limit of sensitivity for both techniques was approximately 0.001 *M*. The radical (prepared from a 10:1 molar ratio of EDA to BuLi) concentration was estimated to be 0.005 *M* by comparison with a standard solution of diphenylpicrylhydrazyl (the accuracy of this technique is believed to be ±50%).

To confirm that pyrazine was being produced from the EDA, a EDA–BuLi mixture was quenched with nitrobenzene. The recovered EDA was found to contain pyrazine in a concentration of 10^{-2} to 10^{-3} *M* (detected both by vpc and nmr). Hence, small quantities of pyrazine (the yield was around 0.02%) are formed when EDA reacts with butyllithium. Pyra-

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[5] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

[6] R. S. Alger, "Electron Paramagnetic Resonance," Interscience, New York, N. Y., 1968, pp 265–272.

[7] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

[8] G. A. Russell, R. Konaka, E. T. Strom, W. C. Danen, K. Chang, and G. Kaupp, *ibid.*, **90**, 4646 (1968).

[9] C. A. McDowell and K. F. G. Paulus, *Mol. Phys.*, **7**, 543 (1964).

zine was not detected when EDA was mixed only with nitrobenzene.

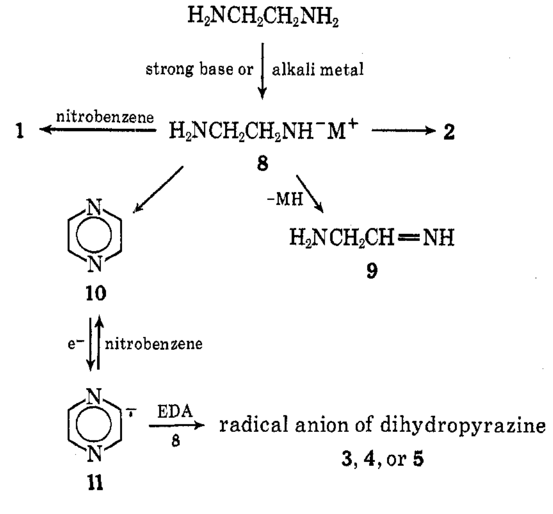
The formation of pyrazine may be a problem if extremely pure EDA is required. The recommended[10] and commonly used preparation of anhydrous EDA involves as a final step, the distillation from sodium metal. We found significant amounts of pyrazine (~10^{-2} *M*) in EDA which had been refluxed for 36 hr over sodium and then distilled. Pyrazine (bp 115.5°) and EDA (bp 116.5°) cannot be effectively separated by ordinary distillation.

Color Changes.—The observation of a deep blue coloration on treatment of EDA with sodium amide has been reported by other workers.[11] We have observed that a trace amount of air is required for the development of this color from the initially formed yellow solutions. A similar color change was noted when the pyrazine radical (prepared by reaction of pyrazine in THF with BuLi) was exposed to air.

Heterocyclic radical anions frequently dimerize.[12,13] Ward[12] was unable to prepare the pyridine radical anion in 1 2-dimethoxyethane owing to its rapid dimerization. Schmulbach, Hinckley, and Wasmund[13] observed that a yellow solution of pyridine radical anion (in pyridine solvent) changes to an intense blue color on standing This they attributed to formation of 4,4′-bipyridyl radical anion. We, however, observed little or no change in the pyrazine radical signal accompanying the color change. The exact structure of the chromophore responsible for the blue color remains a mystery.

Mechanistic Aspects.—We feel that the chemistry involved in the reaction of EDA with strong base or alkali metal can be, at least in part, explained according to Scheme I.

Scheme I

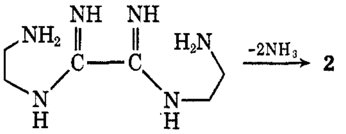


The initial step in the reaction almost certainly involves the formation of **8**. In fact, *N*-lithioethylenediamine has been prepared and isolated from the reaction between EDA and lithium metal powder.[14] This compound has been found useful as a metalating agent,[14,15] as a catalyst in the rearrangement of olefins[16–18] and acetylenes,[4] and as a reagent which dehydrogenates cyclic dienes.[16,17] Product **1** might arise as a result of nucleophilic attack, by **8**, at the para position of nitrobenzene. However, since electron transfer from **8** to nitrobenzene is probably diffusion controlled, a radical coupling is more likely.

The evolution of significant amounts of hydrogen gas most likely results from the loss of metal hydride (which reacts with EDA to produce hydrogen gas and more **8**) from **8**.[19] This would be completely analogous to the loss of lithium hydride on the thermal decomposition of alkyllithium compounds (*e.g.*, butyllithium decomposes into 1-butene and LiH on heating to 100°).[20] Two pieces of evidence require that the hydrogen gas arise from the EDA and not from the butyllithium. First, the evolution of butane is nearly quantitative and no butene is observed. Second, the use of perdeuterated EDA yields only D_2.

The product, **9**, resulting from loss of metal hydride, is an aldimine. Aldimines of the type RCH=NH are not stable.[21]

The imidazole derivative, **2**, has been reported previously from the reaction of lithium metal with EDA.[22] However, these workers reported that the presence of hydrocarbons, such as tetralin or isopropylbenzene, were required for the formation of that product. We obtained **2** in the absence of hydrocarbon. Woodburn and O'Gee[23] obtained **2** from the reaction of EDA with cyanogen at 0°. They proposed **12** as a precursor. In light of the preceding observations, it is not hard to visualize a process leading to **2** (or **12**) involving **8** and **9** as precursors.



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The mode of formation of pyrazine from **8** and/or **9** would be largely spectulation at this time.[24] Its reduction to **11** most likely involves the transfer of an electron from **8** to **10**, analogous to that described by Russell.[7]

$$10 + 8 \longrightarrow 11 + H_2NCH_2CH_2\underset{-}{\dot{N}}H$$

The further reduction of **11** to a dihydropyrazine radical is not surprising. There is some evidence in the literature that hydrocarbon radical anions (*e.g.*, naphthalene radical anion) undergo partial ring satura-

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(10) L. M. Mukherjee and S. Bruckenstein, *Pure Appl. Chem.*, **13**, 419 (1966).

(11) J. C. Warf and V. Gutmann, *Inorg. Nucl. Chem. Lett.*, **6**, 583 (1970).

(12) R. L. Ward, *J. Amer. Chem. Soc.*, **83**, 3623 (1961).

(13) C. D. Schmulbach, C. C. Hinckley, and D. Wasmund, *ibid.*, **90**, 6600 (1968).

(14) O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **28**, 2775 (1963).

(15) O. F. Beumel, Jr., and R. F. Harris, *ibid.*, **30**, 814 (1965).

(16) L. Reggel, S. Friedman, and I. Wender, *ibid.*, **23**, 1136 (1958).

(17) B. S. Tyagi, B. B. Ghatge, and S. C. Bhattacharyya, *ibid.*, **27**, 1430 (1962).

(18) P. Kaspar, unpublished results.

(19) Some hydrogen gas could result during the formation of pyrazine from EDA. However, the amount of gas given off is considerably more than can be accounted for in this way.

(20) W. H. Glaze, J. Lin, and E. G. Felton, *J. Org. Chem.*, **31**, 2643 (1966).

(21) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1965, p 291.

(22) L. Reggel, J. P. Henry, and I. Wender, *J. Org. Chem.*, **26**, 1837 (1961).

(23) H. M. Woodburn and R. C. O'Gee, *ibid.*, **17**, 1235 (1952); H. M. Woodburn and J. R. Fisher, *ibid.*, **22**, 895 (1957).

(24) H. G. Viehe (personal communication) has suggested a mechanism involving reaction of a vicinal enediamine with the corresponding saturated diamine forming a tetrahydropyrazine structure. See A. Halleux and H. G. Viehe, *J. Chem. Soc. C*, 1726 (1968), for a discussion of the chemistry of vicinal enediamines.

tion owing to attack by solvent.[25] A sequence involving protonation of **11** (by EDA) followed by a one-electron reduction, another protonation, and a final one-electron reduction would lead to the required radical anion. This sequence is similar to that proposed for the Birch reduction.[26] Experiments involving reduction of dihydropyrazines, if stable, would be desirable to unambiguously confirm the radical assignments.

Experimental Section

Instrumentation.—First-derivative epr spectra were obtained using a Varian 4502-15 epr spectrometer with 100-kcps field modulation. Magnetic field settings and scan rates were obtained from the Varian Mark II Field Unit. Visible spectra were recorded with a Beckman DK-1A spectrophotometer. Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as internal standard. Ir spectra were obtained on a Beckman Model IR-5A spectrophotometer. Mass spectra were determined using a CEC 21-104 mass spectrometer. The gas–liquid partition chromatographic data were obtained on a Varian-Aerograph Model 1800 chromatograph linked to a Varian Aerograph Model 20 recorder. A 10 ft × 0.25 in. aluminum column packed with 10% DC 710 silicone–10% KOH on Chromosorb W was used.

Epr Solutions.—Most solutions were prepared using a vacuum line (mercury diffusion pump, mechanical oil vacuum pump, liquid nitrogen trap) capable of producing a vacuum of 10^{-3} mm. In general, the solutions were prepared by vacuum transferring the diamine to the epr apparatus containing the strong base (cooled with liquid nitrogen). The epr apparatus consisted of a reaction flask equipped with a stopcock, for attachment to the vacuum system, and a side arm with a $\mathrm{\$}\ {}^{7}/_{25}$ ground-glass joint to which a quartz epr tube was attached. Just above the $\mathrm{\$}\ {}^{7}/_{25}$ joint was a sintered-glass filter. After the base and diamine had reacted (about 1 hr was allowed), a portion of the mixture was filtered into the epr tube and the spectrum was recorded. All spectra were recorded at room temperature.

The concentration of the radical, generated by reaction of a 10:1 molar ratio of EDA to butyllithium, was estimated by comparison with a solution of diphenylpicrylhydrazyl. Comparison of peak heights for the overmodulated spectra at identical instrumental settings indicated a radical concentration of 5×10^{-3} *M*.

Chemicals.—Ethylenediamine (Aldrich or Matheson Coleman and Bell) was distilled from sodium with a minimum of refluxing (bp 116–117°) and stored over "Linde" type 4A Molecular Sieve. The solvent was vacuum transferred from sodium before use. No impurities could be detected in the EDA prepared in this manner. The perdeuterated EDA was custom prepared by Merck Sharp and Dohme and was twice distilled from butyllithium before use. Commercial *N*,*N*′-dimethylethylenediamine (Aldrich) was found to contain ~8% 1,4-dimethylpiperazine as determined by vpc and mass spectral analysis. This diamine was purified by distillation (bp 119–120°) on a spinning-band column. *o*-Phenylenediamine (Matheson Coleman and Bell) was recrystallized from hot water and dried in a vacuum desiccator (mp 102–103°). Propylenediamine, 2-methyl-1,2-diaminopropane, *N*-methylethylenediamine, 1,3-diaminopropane, and *N*,*N*-dimethylethylenediamine (all from Aldrich) were distilled from sodium prior to use. The cis and trans isomers of 1,2-diaminocyclohexane (Aldrich) were separated according to the literature.[4,27]

Nitrobenzene (Fisher) was distilled prior to use. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from a potassium hydroxide activated alumina mixture and stored over sodium. Lithium hydride (all from Matheson Coleman and Bell), sodium amide (Robert's Chemicals Inc.,), and butyllithium (1.5 *M* in hexane, Foote Mineral) were used as received. Pyrazine (Wyandotte) was vacuum sublimed before use.

Reactions of Diamines with Strong Bases.—These reactions were carried out on the vacuum line by vacuum transferring the diamine to the reaction flask containing the strong base. When butyllithium was used, the hexane solvent was removed prior to the addition of diamine. Generally, a 10:1 molar ratio of diamine to strong base was employed. A typical reaction sequence is described below.

Butyllithium (10 ml, 1.5 *M*) was placed in a 50-ml round-bottomed flask in a drybox (nitrogen gas, P_2O_5 desiccant). The flask was attached to the vacuum line and the bulk of the hexane was distilled from the solution. To this concentrated butyllithium (cooled with liquid nitrogen) was vacuum transferred 10 ml of dry EDA which had been degassed by two freeze–pump–thaw cycles. Gases were evolved, as the mixture was gradually allowed to warm to room temperature, and a golden yellow solution resulted. A small amount of material remained undissolved. Exposure to a trace of air gradually resulted in a deep purple color.

Determination of Gaseous Products.—The gases evolved during the reaction between butyllithium and vicinal diamines were hydrogen and butane. The butane was identified by ir (10-cm cell) and mass spectrometry. The hydrogen gas was identified by mass spectrometry. Quantitative data was obtained by using a calibrated vacuum manifold (volume determined with carbon dioxide) and a mercury manometer. The hydrogen and butane were separated with liquid nitrogen.

Reaction of EDA with Alkali Metals.—EDA (150 ml) was added to a dry three-neck flask fitted with reflux condenser, sodium hydroxide drying tube, and nitrogen inlet tube. The system was flushed with nitrogen and 0.3 g of freshly cut sodium was added. The surface of the metal turned blue. Hydrogen was evolved on heating. After 1 day of stirring and refluxing, the sodium was completely consumed. The dark viscous brown mixture was distilled to dryness leaving a black tar which was soluble in hot water. The distillate as analyzed by vpc showed EDA (major component) plus eight other peaks. Piperazine and diethylenetriamine was identified by retention times of the known compounds. Pyrazine was identified by retention time and nmr.

EDA (20 ml) was put into a dry 250-ml flask fitted with a magnetic stirring bar, reflux condenser, and drying tube. The system was flushed with nitrogen, and lithium wire (1.0 g) was added. The mixture turned dark blue, was refluxed for 24 hr, and then was distilled to dryness. Analysis of the distillate by vpc showed no pyrazine, piperazine, or diethylenetriamine; only EDA and an unidentified smaller peak with a longer retention time. The nonvolatile residue was quenched with water, and a water-insoluble white solid was filtered out and recrystallized from methanol: yield 4.2 g; mp 305–310°; mass spectrum *m/e* 138 (decomposes slowly around 300° without melting,[22] *m/e* 138[22]); ir (Nujol) 3.15 (N—H) and 6.48 μ (C=N).

Generation of Pyrazine Radical Anion from Pyrazine.—The pyrazine radical anion was prepared by reduction of a 10^{-3} *M* solution of pyrazine in THF with potassium metal ($a_N = 7.2$ G, $a_H = 2.7$ G; see ref 6, pp 265–272, for a general description of the technique used). The pyrazine radical anion was also prepared by vacuum transferring 15 ml of 10^{-2} *M* pyrazine in THF to 0.015 mol of butyllithium ($a_N = 7.2$ G, $a_H = 2.7$ G, $a_{Li} = 0.7$ G). In both cases initially the color of the solution was golden yellow.

Quenching of the Radical with Nitrobenzene.—To a purple solution made from 10 ml of 1.5 *M* butyllithium and 10 ml of EDA was vacuum transferred 0.5 ml of nitrobenzene. An exothermic reaction resulted and the color changed from purple to brownish-red. The new epr spectrum was due to the nitrobenzene radical anion [$a_N = 12.2$ G, a_H (para) = 3.8 G, a_H (ortho) = 3.7 G, and a_H (meta) = 1.1 G]. The EDA, which had been vacuum transferred to another flask, was found to contain a trace amount of pyrazine as determined by vpc (column 90°, injector 150°, flow 80 ml/min, EDA retention time 10.5 min, pyrazine retention time 19.5 min) and nmr (δ 8.57). No pyrazine could be detected in a sample of the starting EDA.

In another experiment, the quenched EDA–BuLi mixture was taken up in 20 ml of water and extracted with 30 ml of ether. The ether layer was dried and condensed to a volume of about 5 ml. The yellow crystals, which formed after the ether extract had been allowed to stand for 2 days, were recrystallized from absolute ethanol: mp 138–140° (lit.[28] mp 144° for 1);

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nmr (CDCl$_3$, δ) 8.1 (d, 1 H, J = 9 cps), 6.6 (d, 1 H, J = 9 cps), 3.2 (m, 4 H), 1.4 (m, 3 H); mass spectrum m/e (rel intensity) 181 (16), 152 (73), 151 (48), 135 (37), 105 (100), 65 (40), 50 (38), 44 (84), and 40 (81).

Registry No.—**1**, 6332-77-0; **2**, 934-03-2; **6** (radical anion), 11089-69-3; EDA, 107-15-3; EDA-d_8, 34281-22-6; DMEDA, 108-00-9; pyrazine radical anion, 11089-67-1; pyrazine radical anion-d_8, 11089-66-0; dihydropyrazine radical anion, 11089-68-2; nitrobenzene, 98-95-3; butyllithium, 109-72-8; sodium, 7440-23-5; lithium, 7439-93-2; nitrobenzene radical anion, 15753-78-3; pyrazine, 290-37-9; hydrogen, 1333-74-0.

Anodic Oxidations. VII. The Reaction Mechanism in the Electrochemical Oxidation of *N*,*N*-Dimethylformamide in Acetic Acid and in Methanol

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The anodic oxidation of *N*,*N*-dimethylformamide has been studied in methanol and in acetic acid, with fluoroborates, nitrates, and acetates as the supporting electrolytes. The operation of two oxidation mechanisms has been demonstrated. In the one, the primary reaction is an electron transfer from the amide to give a cation radical. In the other, the initiating reaction is an electron transfer from nitrate ion to give a nitrate radical. With a nitrate salt as the supporting electrolyte, both mechanisms operate, and the conditions under which each occurs have been defined.

There is evidence that, in acetic acid containing acetate ion, *N*,*N*-dimethylamides oxidize at a lower potential than acetate ion.[1,2] and the first step in the oxidations to form *N*-acetoxymethyl-*N*-methylamides is an electron transfer from the amide substrate. Nevertheless, when these reactions are run at constant current for preparative purposes, the coulombic efficiencies are low, and a significant portion of the charge passed is used in the Kolbe oxidation of acetate ion to give ethane and carbon dioxide.[1b]

The anodic oxidation of *N*,*N*-dimethylamides in alcohols, with nitrate salts as supporting electrolytes, is a good method for preparing *N*-alkoxymethyl-*N*-methylamides.[1c] However, there is uncertainty as to the mechanism. Current–potential curves, during electrolysis, support discharge of nitrate ion as the initiating reaction,[1c] but cyclic voltammetric curves show very similar peak potentials for *N*,*N*-dimethylformamide and for nitrate ion, suggesting that the amide and the anion oxidize simultaneously.[3]

The present research was undertaken to resolve some of these uncertainties. The anodic oxidation of *N*,*N*-dimethylformamide in both alcohols and acetic acid was studied using quaternary ammonium fluoroborates as the supporting electrolytes. Since the fluoroborate anion is known to oxidize at very high potentials,[4] it is certain that, in these systems, the amide oxidation is initiated either by direct oxidation of the amide or by oxidation of the solvent. For comparison purposes, these oxidations were also studied with quaternary ammonium nitrates as the supporting electrolytes.

Results

The electrochemical preparation of *N*-alkoxymethyl-*N*-methylformamides, using ammonium nitrate as the supporting electrolyte, has been described.[1c] In comparable oxidations, with a quaternary ammonium fluoroborate as the supporting electrolyte, the yields of product, isolated by distillation, varied from 60 to 90%. In a similar experiment in methanol, with sodium methoxide as the supporting electrolyte, the coulombic yield of *N*-methoxymethyl-*N*-methylformamide was 15%. In acetic acid the coulombic yield of isolated *N*-acetoxymethyl-*N*-methylformamide was >50% with a fluoroborate electrolyte but only 5.3% with sodium acetate as the supporting electrolyte.

The experiments compiled in Table I were carried out to obtain more accurate data on coulombic yields and to compare the reactions in the presence of fluoroborates with those using nitrates as supporting electrolytes. The solutions electrolyzed contained 0.05 mol of the supporting electrolyte, 0.13 mol of *N*,*N*-dimethylformamide and 140 ml of either acetic acid or the appropriate alcohol. The amount of charge passed was in every case 0.112 F, and the products formed were determined by vpc.

To elucidate the reaction mechanisms in these systems, the interdependence of the electrode potential and the electric current for the anodic oxidation of *N*,*N*-dimethylformamide was studied by potentiostatic steady-state measurements and by cyclic voltammetry. As was anticipated, electrooxidations in the presence of the fluoroborate anion proved the most straightforward in mechanism. The polarization curves shown in Figure 1 correspond to the steady-state behavior of the electrolyte (tetrabutylammonium fluoroborate in methanol) (curve a) and of added dimethylformamide at two different concentrations (curves b and c). In the absence of added dimethylformamide, the oxidation of methanol is self-inhibiting, and the current density remains low (i < 10 mA cm^{-2}) until the oxidation of

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[1] (a) S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Amer. Chem. Soc.*, **86**, 2745 (1964); (b) *J. Org. Chem.*, **31**, 128 (1966); (c) *J. Amer. Chem. Soc.*, **88**, 4657 (1966).

[2] L. Eberson and K. Nyberg, *ibid.*, **88**, 1686 (1966).

[3] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapter 9. The values given in Table 9-7 of this chapter for the peak potentials for the oxidation of aliphatic amides are in error and should all be higher by 0.6 V (private communication from Professor C. K. Mann).

[4] M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968).