with previous work, and that it both deshields H_a and shields H_e substantially.

The rest of Table VI considers the effect of α_a alkylation on the C_2 chemical shifts by comparing adamantyl to bicyclo[3.3.1]nonyl derivatives. Admittedly, a fairly substantial geometrical change has taken place upon introducing the methylene group, for the C_3–C_6 distance decreased by about 15% from 2.96 to 2.52 Å.[5] Even so, our data suggest a considerably less important chemical shift increment for α than for β substitution, as might be expected if steric hindrance were a very important factor in causing the shift differences.

Returning to the Δ_{ae} values for 1–5, it seems quite clear from Table VI that the effect of the two β_a alkyl groups on $\Delta_{ae}(3)$ will be to give a negative value of nearly the magnitude observed, since $\Delta_{ae}(3)$ would be expected to be in the range of +0.4–+0.6 (as it is for cyclohexane,[14] N-methylpiperidine (C_4),[20] and protonated N-methylpiperidine (C_2)[26]) if the alkyl effects are not taken into account. The smaller negative $\Delta_{ae}(2)$ values observed for 1 and 3 do *not* seem explainable on the basis of double α_a alkylation. In fact, the measured α_a effect indicates a tendency to make $\Delta_{ae}(2)$ more positive.

We suggest that anisotropic effects of the nitrogens are at least partially responsible for the negative $\Delta_{ae}(2)$ values observed. The lone pair on nitrogen ought to create "shielding" and "deshielding" zones, just as
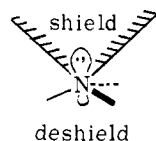
deshield

olefinic and ketonic π electrons do, and, by analogy, one ought to expect shielding on the side of the lone pair and deshielding on the back side. Compounds

(14) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, 41, 2041 (1964).

like those studied here are ideal for observation of such an effect because of the fact that the nitrogens cannot invert, which obviously would exchange shielding and deshielding areas, and average out such effects. We suggest, then, that H_{2a} is relatively deshielded by its proximity to the back side of N_5, whereas H_{2e} feels a much smaller effect because of its greater distance from N_5 (and, indeed, should be shielded relatively to H_{2a} by the N_1 lone pair) and that this is a major factor in causing negative Δ_{ae} values at C_2.

Another case where nitrogen back-side deshielding effects seem to be readily detectable is in causing the large chemical shift differences observed in frozen conformations of hexahydrotetrazane derivatives.[15]

Experimental Sections

(15) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, 94, 3138 (1972).
(16) S. F. Nelsen and P. J. Hintz, *ibid.*, 94, 7114 (1972).

Electrochemical Oxidation of Tetraalkylhydrazines. Effects of Hydrazine and Hydrazine Radical Cation Geometry

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Abstract: A series of 25 tetraalkylhydrazines were studied by cyclic voltammetry at a gold electrode in acetonitrile (0.1 M in sodium perchlorate) and found to give chemically reversible one-electron oxidations with no evidence for radical cation decay, even at scan rates of about 0.01 V/sec. The observed $E_{1/2}$ values were spread over an 850-mV range from −0.28 to +0.56 V (*vs.* sce). The results are discussed in terms of inductive effects and conformational effects in the hydrazine and the hydrazinium radical cations. Nitrogen and ring inversion are apparently rapid compared to electron transfer for these compounds. Irreversible oxidation potentials for four hydrazines which give radical cations that decompose rapidly, even at scan rates up to 100 V/sec, are presented, and reasons for the lesser stability are discussed.

The discovery that the radical cation of tetramethylhydrazine (1) was stable enough at room temperature to give an esr spectrum which persists for several

minutes[1] encouraged us to study the hydrazine–hydrazinium radical couple I ⇌ I·+. This was expected to be

(1) S. F. Nelsen, *J. Amer. Chem. Soc.*, 88, 5666 (1966).
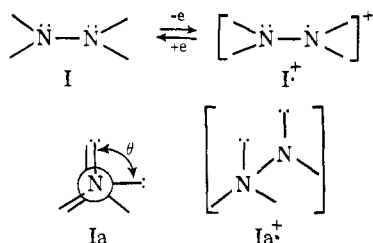
an interesting redox couple not only because there are only two atoms that must bear most of the charge but also because of the differences in geometry expected for the neutral hydrazine and its radical cation. In hydrazines, the lone-pair–lone-pair interaction is destabilizing,[2] leading to an electronic preference for a nearly 90° dihedral angle (θ in Ia) between the lone-pair orbital axes.[3] Steric interactions in cyclic systems lead to tetraalkylhydrazines assuming a variety of θ values depending on substituent.[4] For the radical cation, however, a "three-electron bond" between the two nitrogens is present, and we expect the electronic interaction to be stabilizing and the preferred θ value to be 0° (as in I·+a). Considerable flattening from the essentially tetrahedral geometry at nitrogen of the hydrazine form might also be expected; from esr data, $N_2H_4\cdot^+$ has been claimed to be flat and sp^2 hybridized at nitrogen.[4c] The substantial difference in geometry between I and I·+ is quite different from the situation occurring for most conjugated neutral–radical ion redox couples and might lead to interesting behavior. We therefore initiated cyclic voltammetry (cv) of the electrolytic oxidation of tetraalkylhydrazines and report our results here.

Results and Conclusions

Preliminary investigations at a platinum electrode revealed highly distended waves for several hydrazines. Although we believe the reasons for such behavior are an interesting problem, this aspect has not yet been investigated extensively. Much more ideal behavior was observed at a gold electrode, and all of the data reported here refer to oxidations at a gold sphere electrode in acetonitrile containing 0.1 M sodium perchlorate as a supporting electrolyte and an sce reference electrode.

To calibrate the ability of our instrument to give undistorted cv curves, we examined the oxidation of $N,N,$-N',N'-tetramethyl-p-phenylenediamine (II), which is known to undergo a reversible one-electron oxidation at platinum (polarographic $E_{1/2} = -0.10$ $vs.$ Ag|0.01 M Ag⁺ in acetonitrile[5]).

II
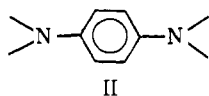
Since iR drop is not compensated for in our cv experiments, "artifical" increases in ΔE_p (the difference

(2) For a general discussion of orbital interactions, see R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(3) For CNDO calculations on hydrazine itself, see M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

(4) (a) J. E. Anderson, *ibid.*, **91**, 6374 (1969); (b) R. A. Y. Jones A. R. Katritzky, and R. Scattergood, *Chem. Commun.*, 644 (1971);, (c) J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, **39**, 1904 (1963).

(5) A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 4130 (1964).

in peak potentials for the oxidation and reduction waves) are expected as the concentration and scan rate are increased and more current is passed (Table 1).

Table I. Cv Data for II (7.08 × 10⁻⁴ M)

Scan rate, V/sec	ΔE_p, mV	$E_{1/2}$, V[a]
0.0186	60	+0.020
0.0465	65	0.022
0.0930	70	0.025
0.140	75	0.023
0.186	80	0.025
0.930	95	0.028
1.86	95	0.028
9.30	130	0.035
18.6	160	0.040

[a] Calculated as $(E_p(\text{ox}) - E_p(\text{red}))/2$.

At slow scan rates, ΔE_p was close to the theoretical value of 57 mV. Using the approximation of $E_{1/2}$ as the mean of the oxidation and reduction peak potentials, the difference between $E_{1/2}$ at slow scan rates ($\Delta E_p = 60$ mV) and that at faster scan rates was only observed to approach 10 mV at a scan rate of over 1 V/sec, where ΔE_p had risen to about 100 mV. Our reproducibility in reading $E_{1/2}$ off the cv curves is not better than ±5 mV. Our basic cv data for 25 hydrazines which show no evidence for radical cation decay on the time scale of the cv experiments (and which we will refer to as "stable" hydrazinium ions) are collected in Table II.

Several hydrazines showed obvious decomposition of the hydrazinium ions during the time scale of the cv experiments. For **27** we were able to observe rereduction at faster scan rates, and so $E_{1/2}$ could be measured, but for **28–31** no rereduction wave could be detected even at our fastest scan rate (100–200 V/sec). See Table III for the data.

Considering first the compounds in Table II, eleven yielded ΔE_p values under 80 mV, nine in the range 85–100 mV, and five greater than 100 mV at the scan rates recorded. We also include tetraphenylhydrazine (**26**) in Table II as an example of an aryl hydrazine; its low ΔE_p value and the data of Table I indicate that our instrumentation will yield close to theoretical ΔE_p values. Although some instrumental distortion is certainly present in the data of Table II, we are confident that the large ΔE_p values observed are not caused entirely by machine error. Experiments are under way with iR-compensated instruments to investigate the cause of the slight distortions observed; we presently hypothesize that the most likely reason is detectably slow electron-transfer rates but shall return to this point in a future publication. It may be noted from Table II that quite generally compounds with a high degree of α branching showed the broader cv curves, and the lower ΔE_p values (approaching the theoretical 57 mV) were seen for the least branched compounds, although those with a bicyclic alkyl substituent were often also relatively "ideal." Small deviations from theoretical behavior for most of the entries in Table I could probably be detected if sufficiently accurate data were obtained. Our major point here is that nearly electrochemically reversible behavior is being observed at the slow scan rates used.

Table II. Cv Data[a] for Tetraalkylhydrazines Which Give "Stable" Hydrazinium Ions
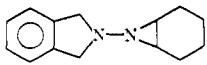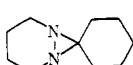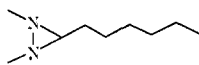
Compound	No.	Scan rate, V/sec	$E_{1/2}$, V	ΔE_p, mV	Compound	No.	Scan rate, V/sec	$E_{1/2}$, V	ΔE_p, mV
	1	0.060	−0.28	90		13	0.052	0.18	110
	2	0.052	−0.04	85		14	0.061	0.18	60
	3	0.062	0.00	70		15	0.053	0.22	90
	4	0.050	0.00	120		16	0.055	0.24	70
	5	0.120	0.02	90		17	0.056	0.24	65
	6	0.050	0.06	75		18	0.050	0.24	110
	7	0.050	0.06	85		19	0.013	0.25	65
	8	0.054	0.10	80		20	0.057	0.28	70
	9	0.061	0.10	80		21	0.062	0.30	100
	10	0.050	0.12	100		22	0.064	0.32	55
	11	0.052	0.13	130[b]		23	0.054	0.42	90[d]
	12	0.055	0.14	95[c]		24	0.008	0.56	130
						25	0.008	0.56	70
					Ph₂NNPh₂	26	0.054	0.76	60

[a] Concentrated 2–9 × 10⁻⁴ M unless noted. [b] 20.6 × 10⁻⁴ M concentrated; significant instrumental broadening certain. [c] 28.1 × 10⁻⁴ M. [d] 30.5 × 10⁻⁴ M.

From current–scan rate plots, wave shapes, and the fact that esr spectra of the hydrazinium ions could be observed by esr for all of the entries **1–24**, we are confident that chemically reversible, one-electron oxidations are occurring for all of the hydrazines studied. The $E_{1/2}$ values measured should reasonably accurately reflect the true E^0 values for the redox reaction of removing an electron from the neutral hydrazine, to the extent that diffusion coefficients for the neutral and cationic forms are the same, which we believe to be a good assumption. The 840-mV range of $E_{1/2}$ values observed for these compounds of rather similar structure is clearly caused by several factors.

Inductive effects play an important part, as is evidenced by the 500–560-mV shift of $E_{1/2}$ between the pyrazolidines **4** and **6** compared to the oxadiazolidines **24** and **25** of equivalent substitution. Similarly, replacement of the β,β'-methylene groups of dimethyl-hexahydropyridazine (**14**) by NCH₃ groups (giving **22**) leads to a 140-mV anodic shift in $E_{1/2}$. A smaller shift is reasonable on an inductive basis since nitrogen is less electronegative than oxygen, but, as discussed below, steric effects in the hydrazinium ion in six-ring systems may well lead to a relatively lower shift in this comparison. An inductive shift in the same direction appears to be observed for replacement of a β,β' C—C

Table III. Cv Data for Tetraalkylhydrazines Which Give "Unstable" Hydrazinium Ions

Compound	No.	Concn. $\times 10^4 M$	Scan rate, V/sec	$E_{1/2}$, V	Other
	27	18.9	1.34	0.96	$\Delta E_p = 100$ mV
	28	3.01	0.058	Irrev[a]	$E_p{}^{ox} = 0.63$
	29	4.18	0.099	Irrev[a]	$E_p{}^{ox} = 1.07$
	30	13.2	0.111	Irrev[a]	$E_p{}^{ox} = 1.15$
	31	5.0	0.080	Irrev[a]	$E_p{}^{ox} > 2$

[a] No rereduction wave was detected; scan rates up to 100 V/sec were investigated.

bond by a C=C bond. In three hexahydropyridazine–tetrahydropyridazine comparisons, $\Delta E_{1/2}$ values of 100 mV were observed (**18** vs. **12**, **20** vs. **14**, and **9** vs. **3**), and for the diazabicyclo[2.2.1]heptyl compounds **16** and **8**, there was a 140-mV $E_{1/2}$ difference.

An inductive effect in the opposite direction might have been predicted for α-alkyl substitution, since a C–C bond should be electron releasing relative to a C–H bond. Oxidation peak potentials generally shift cathodically with increasing α substitution for alkylamines,[6] but these numbers do not necessarily reflect E^0 changes. It is very likely that the effect of C–alkyl for C–H substitution upon $E_{1/2}$ is strongly geometry dependent, since a C–C bond can interact with a nitrogen "lone pair" orbital to lead to significant interactions which raise the lone-pair energy. Such orbital mixing is strongly dependent on the dihedral angle between the C–C bond and lone-pair axis, reaching a maximum where the two have a 180° dihedral angle.[2] This effect is very important for 1,4-diazabicyclo[2.2.2]-octane (III),[7] in which favorable geometry is required

III
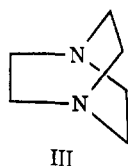
by the caged structure. Another complication is that alkyl substitution has a significant effect upon the molecular geometry of many of the hydrazines studied. Consideration of the data in Table II indicates that the effect upon $E_{1/2}$ of α alkylation (from whatever the source) remains under 40 mV per alkyl group, and the inductive effect may be considerably smaller than this figure.

It is clear that ring strain causes the oxidation of hydrazines to be more difficult. For the three three-membered ring-containing hydrazines (**28**, **30**, and **31**), not only is the hydrazine unusually difficult to oxidize but the hydrazinium ion is so unstable that irreversible

(6) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, p 284.
(7) (a) T. M. McKinney and D. H. Geske, J. Amer. Chem. Soc., 87, 3013 (1965); (b) R. Hoffmann, A. Imamura, and W. J. Hehre, ibid., 91, 3122 (1969).
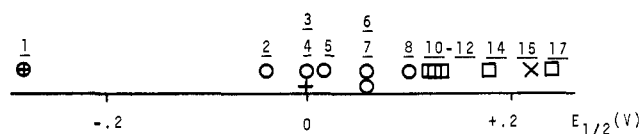
Figure 1. $E_{1/2}$ values for saturated five- and six-membered ring tetraalkylhydrazines: (O) five-membered ring; (□) six-membered ring; (+) bicyclo[2.2.2]octyl; (×) tetramethylhydrazine.

cv curves are observed. Since flattening at nitrogen occurs upon oxidation, an anodic shift upon increasing ring strain is not surprising. We suggest that the major reason that **3** is 100 mV easier to oxidize than **8**, and **9** is 140 mV easier to oxidize than **16**, is also a ring strain effect, for changing the bridging methylene chain from two to one carbon should cause flattening at nitrogen to be more difficult for **8** and **16** than for **3** and **9**.

Another case where geometrical difficulties in the hydrazinium ion form appear to be responsible for a more difficult oxidation is that of di-tert-butyloxa-diazolidine (**27**). This compound is 400 mV more difficult to oxidize than the diethyl and diisopropyl compounds (**24** and **25**) and also has an unstable hydrazinium ion, in contrast to the examples with smaller alkyl groups. Because hydrazinium ions have a strong electronic preference for the geometry shown in I·+a, with $\theta = 0°$ for the "nonbonding" orbitals at nitrogen, **27**·+ is severely sterically hindered; it would require eclipsed tert-butyl groups to attain such geometry. Somewhat similarly, **29** cannot attain the necessary syn geometry at a hydrazine group because of the cage structure. Its radical cation is so unstable that no rereduction could be observed, which means that $E_{1/2}$ is even greater than the 1.07-V peak potential observed. Unusually high oxidation potentials and shortened hydrazinium ion lifetimes are thus observed when the C–N–N angle of a hydrazine is constrained to be small or when syn geometry ($\theta = 0°$) cannot be attained.

Turning to some subtler effects of structure upon oxidation potential, we have 14 examples of completely saturated tetraalkyl monohydrazines which contain only five- and six-membered rings; yet the $E_{1/2}$ values spread over the remarkable range of 540 mV. These data are shown graphically in Figure 1. It is clear that neither alkyl inductive effects nor simple ring strain

arguments based upon flattening at nitrogen can explain the values observed. The most striking correlation revealed by Figure 1 is that both pyrazolidine and 2,2-diazabicyclo[2.2.2]octyl systems are consistently easier to oxidize than hexahydropyridazines.

We suggest that the major reason for this lies in the preferred geometry for the six-ring hydrazinium ion. As we have reported previously,[8] the esr spectra of $10 \cdot^+$ and $11 \cdot^+$ demonstrate that the hydrazine linkage assumes the geometry shown in $I \cdot^+a$ ($\theta = 0°$) but that the ring is not in the half-chain conformation expected if the hydrazinium group were flat. It adopts a conformation of boat-like symmetry, in which C_3 and C_6 approach each other enough to allow interference of substituents upon these carbons (see IV). In contrast

IV
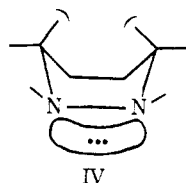
to boat cyclohexane conformations, twisting of the cis C_3, C_6 substituents out of each other's way should be made difficult by the strong electronic preference for $\theta = 0$ at the hydrazinium linkage. Inversion at nitrogen which is rapid on the esr time scale is necessary to explain the symmetry of the observed esr spectra. We suggest, then, that an important reason for five ring and 2,3-diazabicyclo[2.2.2]octylhydrazines oxidizing more easily than hexahydropyridazine systems is that the destabilizing cis interaction shown in IV is reduced or eliminated in the former compounds.

Differences in eclipsing interactions between hydrazine and hydrazinium ion geometries appear to be of importance in giving the large spread in Table I. For example, in going from tetramethylhydrazine (15) to dimethylpyrazolidine (6), one dimethyl eclipsing interaction is eliminated in the cation and the latter oxidized 160-mV cathodic of the former. Making a similar change in the 2,3-diazabicyclo[2.2.2]octyl series causes a 280-mV increment in $E_{1/2}$ (1 vs. 3).

As pointed out in the introduction, the destabilizing electronic interaction between the lone-pair electrons in a hydrazine depends upon the dihedral angle, θ, between the orbitals. Since the size of this interaction should directly affect the energy of the molecular orbital from which an electron is being removed, one might expect that conformations of hydrazines with different θ values would have different oxidation potentials. Yet hydrazines are conformationally mobile due to hydrazine nitrogen inversion and ring flipping and if electron transfer were slower than conformational changes, a single oxidation peak would be expected, since all of the oxidations could proceed through the most easily oxidized conformation. We suggest that this is the case at the scan rates studied, since compounds such as 12, which low-temperature nmr demonstrates to be a rapidly equilibrating mixture of various conformations, give a single oxidation wave.

If slow enough conformational changes were taking place, or high enough scan rates could be employed, we would expect to be able to observe the effect of θ value upon the oxidation potential. We wish to sug-

gest that such effects are discernible in some of the data presented here. For the cis-diaziridine 38 ($\theta \sim 0°$) $E_p^{ox} = 1.15$ V and the trans compound 39 (θ probably somewhat greater than 120°) $E_p^{ox} > 2$ V. Nitrogen inversion is greatly inhibited in these systems by the three-membered ring; double nitrogen inversion cannot be detected for either compound by high-temperature nmr,[9] and electron transfer seems very likely to be faster than nitrogen inversion. Although irreversible oxidation waves are observed because of instability of the hydrazinium ions, causing E_p^{ox} to be shifted from the true E^0 by an amount depending upon the rate of decomposition of the hydrazinium ion, such a large difference in oxidation potential cannot be accounted for just by having $38 \cdot^+$ decompose more rapidly than $39 \cdot^+$, since the shift in E_p^{ox} is only 30 mV per factor of 10 in the rate of the following reaction.[10] The E_p^{ox} values observed are in the order expected upon the basis of lone-pair–lone-pair electronic interaction.

We also suggest that the remarkably cathodic $E_{1/2}$ observed for 2 is caused by electronic interaction in the hydrazine. Although there is only a 60-mV $E_{1/2}$ shift between 3 and 6, the shift between 1 and 5 is 300 mV, although the gross structural changes seem similar. We point out that 1 should have a θ value closer to 0° by virtue of steric hindrance between the bicyclic bridge and the pyrazolidine ring increasing quite rapidly as θ is increased. In 1,5-diazabicyclo[3.3.0]octane (5), θ ought to be larger, since it should increase until steric destabilization balances the electronic destabilization.

Experimental Section

2,2-Diethyl-5,8-ethanohexahydropyrazolo[1,2-a]pyridazine (1) was prepared by the method of Stetter and Woernle,[11] except that we oxidized the potassium salt of 4,4-diethylpyrazoline-3,5-dione with tert-butyl hypochlorite in the presence of cyclohexadiene to obtain the Diels–Alder adduct.[12] Our material had bp (24 mm) 155–159° [lit. bp (10 mm) 135–136°].

1,1'-Bipyrrolidine (2) was isolated from the photolysis of the corresponding 2-tetrazene, following the procedure Watson[13] used for tetramethylhydrazine. The distillate, bp (20 mm) 93–94° [lit.[14] bp (13 mm) 77–78°], was purified by vpc at 65°.

2,3-Dimethyl-2,3-diazabicyclo[2.2.2]octane (3), 2,3-dimethyl-2,3-diazabicyclo[2.2.1]heptane (8), 2,3-dimethyl-2,3-diazabicyclo[2.2.2]-oct-5-ene (9), and 2,3-dimethyl-2,3-diazabicyclo[2.2.1]hept-5-ene (16) were all prepared by the procedures of Anderson and Lehn.[15]

1,2-Diisopropylpyrazolidine (4) was prepared by refluxing 5.0 g (0.043 M) of N,N'-diisopropylhydrazine and 8.7 g (4.3 × 10^{-2} M) of 1,3-dibromopropane in 100 ml of absolute ethanol containing 15 g of potassium carbonate for 17 hr, filtering, distilling off the alcohol, and distilling the product, bp (135 mm) 107–116° (4.3 g, 65%). Final purification was by vpc at 50°: high-resolution mass spectrum, calcd for $C_9H_{20}N_2$, 156.1626; found, 156.1608.

N,N'-Diethylpyrazolidine (7) was prepared in 22% yield by the method used for 4, employing N,N'-diethylhydrazine in methanol, bp 138–143°. The product was purified by vpc at 30°: exact mass calcd for $C_7H_{16}N_2$, 128.1313; found, 128.1307.

N,N'-Dimethylpyrazolidine (6) was prepared by the method used for 4 in 33% yield, employing N,N'-dimethylhydrazine dihydrochloride in methanol, bp 75–95°. The product was purified by vpc at 30°: exact mass calcd for $C_5H_{12}N_2$, 100.1000; found, 100.0996.

(8) S. F. Nelsen and P. J. Hintz, J. Amer. Chem. Soc., 94, 1610 (1972).

(9) A. Mannschreck, R. Radeglia, E. Grundemann, and L. R. Ohne, Chem. Ber., 100, 1778 (1967).

(10) R. S. Nicholson, Anal. Chem., 37, 1351 (1965).

(11) H. Stetter and P. Woernle, Justus Liebigs Ann. Chem., 724, 150 (1969).

(12) General method of T. J. Kealy, J. Amer. Chem. Soc., 84, 966 (1962).

(13) J. S. Watson, J. Chem. Soc., 3677 (1956).

(14) M. Rink and M. Mehtia, Naturwissenschaften, 48, 51 (1961).

(15) J. E. Anderson and J. M. Lehn, J. Amer. Chem. Soc., 89, 81 (1967).

1,5-Diazabicyclo[3.3.0]loctane (5) was prepared by the method of Buhle, Moore, and Wiselogle,[16] employing a 28-cm spiral wire column for the final distillation, bp (26 mm) 73-75° [lit. bp (26 mm) 74-75°].

1,2-cis-3,6-Tetramethylhexahydropyridazine (10) was prepared by the method of Anderson and Lehn,[15] bp (110 mm) 106-109° [lit. bp (19 mm) 64-66°]. Our product was an 85:15 mixture of cis and trans isomers (10 and 11) which were separated by vpc at 55°.

1,2-trans-3,6,-Dimethyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine was prepared in 44% yield by irradiation of a mixture of 8.5 g (49 mM) of diethyl azodicarboxylate, cis-2,trans-4-hexadiene, and 20 ml of the benzene with a sunlamp for 6 hr, at which time the color due to the azo compound had entirely faded; bp (0.55 mm) 109-114°. About 10% isomerization to the cis-3,6-dimethyl compound is inferred from the result of converting this material to 11 (+10).

1,2-trans-3,6-Tetramethylhexahydropyridazine (11). trans-3,6-Dimethyl-1,2-dicarbethoxyhexahydropyridazine (4.0 g, 16 mM) (prepared by catalytic reduction of the Diels–Alder adduct) in 20 ml of ether was dripped into 1.7 g (46 mM) of LiAlH₄ in 500 ml of ether and stirred 18 hr. After decomposition of the excess LiAlH₄ with 1.7 ml of water, 1.7 ml of 15% sodium hydroxide, and 5.1 ml of water, the mixture was filtered, washed with ether, and dried with magnesium sulfate, and the ether was removed by distillation. The residue was distilled to give 1.5 g (69%) of a 90:10 mixture of trans and cis isomers (nmr) which were separated by vpc at 55°; exact mass calcd for C₈H₁₈N₂, 142.1470; found, 142.1486.

1,2,3-Trimethylhexahydropyridazine (12) was prepared in 82% yield by LiAlH₄ reduction of the hydrogenated isoprene-diethyl azodicarboxylate adduct,[17] using the method described for 11: bp (105 mm) 95-98°; exact mass calcd for C₇H₁₆N₂, 128.1313; found, 128.1312.

1,2,4,5-Tetraisopropylhexahydro-s-tetrazine (13) was prepared in very poor yield by addition of 1.0 g (0.12 mM) of formalin to 2.3 g (20 mM) of N,N'-diisopropylhydrazine cooled to −25° and stored at −10° for 12 hr. Benzene was added and the mixture was refluxed with a Dean-Stark trap until no more water separated. The mixture was distilled and after distillation of the oxadiazolidine (27), the fraction boiling at 66-70° (0.3 mm) was collected, crystallized from Skelly B, and sublimed, mp 56-57.5° (lit.[18] 57-58°). Although the yield was only 0.25 g (5%), we were unable to repeat the preparation of Schmitz,[18] who used the hydrochloride.

1,2-Dimethylhexahydropyridazine (14) was prepared by the method of Snyder and Michels,[19] bp 138-141° (lit. bp 140-141°).

Tetramethylhydrazine (15) was prepared by the method of Beltrami and Bissell,[20] bp 71-72° (lit. bp 73°).

1,6-Diazabicyclo[4.4.0]decane (17) was prepared by the method of Stetter and Spangenberger;[21] the distillate, bp (65 mm) 100-105° [lit. bp (18 mm) 79-80°], was purified by vpc.

1,2,3-Trimethyl-1,2,3,6-tetrahydropyridazine (18) was prepared by LiAlH₄ reduction of the isoprene-diethyl azodicarboxylate adduct[17] in 71% yield: bp (160 mm) 107-109°; exact mass calcd for C₇H₁₄N₂, 126.1157; found, 126.1160.

1,2,4,5-Tetraethylhexahydro-s-tetrazine (19). A mixture of 3.0 g (34 mM) of N,N'-diethylhydrazine and 2.0 g of formalin was refluxed 2 hr, and the water was azeotropically removed by addition of 20 ml of benzene and refluxing with a Dean-Stark Trap. After distillation of the solvent, the residue was fractionated, giving 1.2 g (17%) of 21: bp (100 mm) 165-169°; exact mass calcd for C₁₀H₂₄N₄, 200.2001; found, 200.1983.

1,2-Dimethyl-1,2,3,6-tetrahydropyridazine (20) was prepared by the method of Anderson and Lehn,[15] bp (atm) 142-145° [lit. bp (15 mm) 48°]. It was purified by vpc before use.

1,2,4,5-Tetramethylhexahydro-s-tetrazene (22) was prepared by the method of Schmitz,[18] bp (12 mm) 67-68° [lit. bp (11 mm) 58-60°].

2,5-trans-Dimethyl-3,4-cyclotetramethyleneoxadiazolidine (23) was prepared by adding 0.86 g (12 mM) of hexahydropyridazine drop-

wise to 0.60 g (14 mM) of freshly distilled acetaldehyde at 0°, stirring in the cold for 1.5 hr, and removing the water azeotropically by addition of benzene and use of a Dean-Stark Trap. The yield was 0.4 g (25%): bp (0.3 mm) 60°; exact mass calcd for C₈H₁₆N₂O, 156.1263; found, 156.1268.

3,4-Diisopropyl-1,3,4-oxadiazolidine (24) was prepared by refluxing the hydrazine and formaldehyde in benzene (see 13), bp (25 mm) 84-86° [lit.[22] bp (13 mm) 64-65°].

3,4-Diethyl-1,3,4-oxadiazolidine (25) was prepared as 24, using N,N'-diethylhydrazine, in only 17% yield; 21 is the major product. For 25: bp (25 mm) 63-63.5°; exact mass calcd for C₆H₁₄N₂O, 130.1106; found, 130.1114.

3,4-Di-tert-butyl-1,3,4-oxadiazolidine (27) was prepared as 24, using N,N'-di-tert-butylhydrazine: bp (25 mm) 95°; exact mass calcd for C₁₀H₂₂N₂O, 186.1732; found, 186.1732.

7-(1,3-Dihydro-2-isoindolyl)-7-azabicyclo[4.1.0]heptane (28) was prepared by lithium aluminum hydride reduction of the N-phthalimidonitrene–cyclohexene adduct[23] and isolated in 28% yield by sublimation: mp 60-62°; nmr (C₆D₆) τ 2.95 (s, 4 H), 5.97 (s, 4 H), 7.8-9.2 (complex m, 10 H).

1,5-Diazaspiro[5.5]undecane was prepared by condensation of cyclohexanone and 1,3-diaminopropane, following the general procedure of Bergmann, et al.[24] The product was distilled, bp (0.3 mm) 89-92°, and solidified upon standing but was used to prepare 38 without extensive purification: nmr (CCl₄) τ 7.13 (br t, 4 H), 8.57 (br s, 12 H), 9.21 (br s, 2 H).

6,6-Cyclopentamethylene-1,5-diazabicyclo[3.1.0]hexane (30) was prepared from 1,5-diazaspiro[5.5]undecane by the sodium hypochlorite procedure of Schmitz and Schinkowski:[25] bp (15 mm) 66°; exact mass calcd for C₉H₁₆N₂, 152.1314; found 152.1304.

1,2-Dimethyl-3-n-hexyldiaziridine (31) was prepared by the method of Schmitz and Schinkowski:[25] bp (3.2 m m) 52-55° [lit. bp (1 mm) 42-4°]; nmr (s-tetrachlorobenzene) τ 7.52 (s, 3 H), 7.54 (s, 3 H), 7.67 (br t, 1 H), J = 5.5 Hz), 8.25-8.75 (br m, 10 H), 9.02 (br t, 3 H, J = 6.5 Hz) (the N-methyls appeared as a singlet in CDCl₃).

Cyclic Voltametry Measurements. The instrument used was built by John Buschek according to plans designed by Professor D. Evans and used a Wavetek 112-triggered VCG wave generator. A Hewlett Packard 7004B X-Y recorder was used to collect data at scan rates under 200 mV/sec and a Tektronix 564B storage oscilloscope and Model 100 camera at greater scan rates. A Sargent Welch standard calomel electrode was used as the reference electrode and a mercury pool counterelectrode was employed. A gold sphere electrode (0.058-in. diameter) was employed and cleaned by immersing in nitric acid and rinsing with water and acetone, and was dried in a stream of nitrogen between scans. The electrochemical data reported here did not seem sensitive to the method of cleaning the electrode, and neither lifetimes nor currents were observed to vary with how many scans had been performed. This is a marked difference to our experience with tertiary amines.

The solvent was always 0.1 M sodium perchlorate in acetonitrile, and an sce reference electrode was employed. The samples of 1-28, 30, 31, and 25 were all collected by preparative vpc for final purification, immediately sealed in the collection tube, and stored at −15° until use for electrochemical data. A 5 ft × 0.25 in. 15% XF-1150 on Chromosorb W 60-80 column and a Varian Aerograph A90-P.3 vpc were employed.

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