

Single-Electron Oxidation Equilibria of Tetraalkylhydrazines. Comparison of Solution E° Values and Vapor-Phase Ionization Potentials

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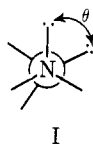
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Abstract: E° values measured by cyclic voltammetry (acetonitrile, vs. SCE) for 56 tetraalkylhydrazines with saturated alkyl groups vary between extremes of +0.52 (for 1,2-di-*tert*-butyldimethylhydrazine, **20**) and -0.25 V (for 4,4-diethyl-2,6-diazatricyclo[5.2.2.0^{2,6}]undecane, **54**). Vapor-phase vertical ionization potentials (IP₁) for 45 of these compounds have been determined by photoelectron spectroscopy (PES), which vary from 8.27 eV (for tetramethylhydrazine, **1**) to 6.92 eV (for **54**). The size of the lone pair-lone pair interaction in the neutral hydrazine (measured by PES) has a larger effect on IP₁ than upon E° . A plot of IP₁ vs. E° for acyclic, *n*-alkyl-substituted hydrazines gives a straight line with a slope of over ten; α -branched alkyl and cyclic compounds often deviate considerably from this line. A major factor causing differences in E° among hydrazines is argued to be strain differences between the cation (nearly flat at nitrogen, lone pairs coplanar) and the neutral hydrazine (nearly tetrahedral at nitrogen, lone pairs nearly at right angles unless structural constraints force other angles).

Introduction

The stability of tetraalkylhydrazine radical cations and the electrochemical reversibility of the hydrazine-hydrazine radical cation redox equilibrium combine to allow easy measurement of the standard electrochemical potential, E° , for the half-reaction $H \rightleftharpoons H^+ + e^-$ by cyclic voltammetry (CV). We previously reported¹ that E° for several tetraalkylhydrazines is rather sensitive to alkyl group structure, and suggested that inductive effects and the conformational changes which accompany electron removal were responsible. Subsequent photoelectron spectroscopy (PES) measurements^{2,3} and low-temperature ¹³C NMR experiments⁴ have revealed a good deal more about hydrazine conformations, as have electron spin resonance⁵ experiments about hydrazine radical-cation geometries, and we now return to the question of how alkyl group structure affects E° . We consider acyclic and cyclic compounds containing five-, six-, and seven-membered rings in this study.

The two highest-occupied MO's of a hydrazine are (usually⁶) predominantly the symmetric and antisymmetric lone-pair orbital combinations n_+ and n_- , although it is realized that orbital mixing with the hydrocarbon substituents also occurs. The difference in energy between n_+ and n_- varies with the lone pair-lone pair dihedral angle θ (see I), and n_+ and n_- are



predicted to cross as θ is varied from 0 (n_- antibonding, and highest in energy) to 180° (n_+ antibonding, and highest in energy).^{2,3} The separation between the first two ionization potentials, $\Delta = IP_2 - IP_1$ has been found to vary with θ at least semiquantitatively, as predicted by approximate molecular-orbital calculations (INDO² and MINDO³). For a series of tetraalkylhydrazines, the INDO Δ vs. θ curves, when scaled to give Δ ($\theta = 0^\circ$) of 2.3 eV (the experimental value for two tetraalkylhydrazines which are believed to have θ of about 0°) gives reasonable θ values for several cyclic and bicyclic tetraalkylhydrazines for which θ can be predicted approximately on structural grounds.^{2c} The large variation in the energy of the HOMO predicted by these calculations as θ is varied for tetramethylhydrazine and observed by PES for more substituted tetraalkylhydrazines is an attractive candidate for





























a major cause of the variation of E° with alkyl group structure. As Miller and co-workers⁷ have pointed out for the widest range of structural types, there exists a remarkably linear experimental correlation of electrochemical potential in solution with ionization potential in the vapor phase. This correlation was best for aromatic compounds (where there was not only more data, but also data for which thermodynamically significant E° values had been measured), but compounds of a wide variety of structural types which undergo rapid irreversible following reactions in solution and thus have kinetically influenced CV peak potentials also fit surprisingly well, presumably because the kinetic shifts of the oxidation peaks are relatively small, as Miller suggests.⁷ We therefore have examined the correlation of vapor phase IP₁ with solution phase E° , hoping to be able to evaluate the importance of lone pair-lone pair interaction in changing the ease of oxidation of hydrazines.

Results

Several of the previously reported¹ E° values of tetraalkylhydrazines have been redetermined and a number of new compounds added. The only change in E° greater than 30 mV from the previously reported values is for tetramethylhydrazine itself, for which our new value of 0.28 V vs. SCE is 60 mV higher, and is certainly the better value. The new values have all been determined at a planar gold electrode. Planar electrodes may be cleaned by polishing a new surface, and it is far easier to obtain reproducible data using them. A clean, planar platinum electrode gives similar E° and ΔE_p values to a clean planar gold electrode (in contrast to our observations with less clean bead electrodes¹), but gold electrodes degrade less rapidly with use and all of the data we report (Table I) were determined in gold. We believe the reproducibility in E° to be ± 10 mV, both from multiple runs and the comparison of different compounds with similar types of structural changes. To see if large solvent effects were present, we have determined E° for several compounds in methylene chloride (see Table II). The same pattern of E° shifts with structure was observed, and a shift of 0.19 ± 0.02 V to higher E° was observed upon changing the solvent to methylene chloride.

Although many of the PES IP₁ values in Table I are taken from the work of Buschek,² several new values have been determined. The IP₁ values for two tetraalkylhydrazines, tetraethyl (**10**) and triisopropylmethyl (**19**), were redetermined for comparison with our previous values,^{2c} and the new values of IP₁ were 5 meV higher and 20 meV lower, respectively,

Table I. Vapor-Phase Vertical Ionization Potential (IP₁) and Solution-Phase E° Values for Some Tetraalkylhydrazines

Compd no.	Compd	IP ₁ , eV	$\Delta(\text{IP}_2 - \text{IP}_1)$, eV	E° , V vs. SCE	Compd no.	Compd	IP ₁ , eV	$\Delta(\text{IP}_2 - \text{IP}_1)$, eV	E° , V vs. SCE
1	Me ₂ NNMe ₂	8.27 ^a	0.55	0.28 ^b					
2	EtMeNNMe ₂	8.18 ^a	0.53	0.27 ^b					
3	<i>n</i> -PrMeNNMe ₂	8.14 ^b	0.51	0.27 ^b	38		7.55 ^a	0.84	0.13 ^c
4	<i>n</i> -BuMeNNMe ₂	8.12 ^a	0.54	0.27 ^b					
5	Et ₂ NNMe ₂	8.10 ^a	0.52	0.26 ^b					
6	<i>n</i> -Pr ₂ NNMe ₂	7.98 ^b	0.51	0.25 ^b	39		7.76 ^a	0.92	0.15 ^d
7	<i>n</i> -Bu ₂ NNMe ₂	8.07 ^{b,f}	0.50	0.25 ^b					
8	EtMeNNMeEt	8.08 ^b	0.51	0.26 ^b	40		7.46 ^b	0.99	-0.01 ^b
9	Et ₂ NNEtME	8.02 ^b	0.50	0.25 ^b					
10	Et ₂ NNEt ₂	7.94 ^b	0.51	0.24 ^b					
11	Et ₂ NN- <i>n</i> -Pr ₂	7.87 ^a	0.52	0.24 ^b	41				0.22 ^b
12	Et ₂ NN- <i>n</i> -Bu ₂	7.77 ^b	0.52	0.24 ^b					
13	<i>n</i> -Pr ₂ NN- <i>n</i> -Pr ₂	7.74 ^b	0.62	0.24 ^b	42				0.17 ^b
14	<i>n</i> -Bu ₂ NN- <i>n</i> -Bu ₂			0.24 ^b					
15	<i>i</i> -PrMeNNMe ₂	8.09 ^a	0.53	0.25 ^b					
16	<i>i</i> -PrMeNN- <i>i</i> -PrMe	7.92 ^b	0.52	0.24 ^b	43		7.81 ^b	0.67	0.18 ^b
17	<i>i</i> -Pr ₂ NNMe ₂	7.65 ^b	0.72	0.24 ^b	44		7.61 ^a	2.31	0.23 ^d
18	<i>i</i> -Pr ₂ NN- <i>i</i> -PrMe	7.60 ^b	0.60	0.21 ^b	45		7.51 ^b	~2.3	0.25 ^b
19	<i>t</i> -BuMeNNMe ₂	7.89 ^b	0.59	0.44 ^b					
20	<i>t</i> -BuMeNN- <i>t</i> -BuMe	7.67 ^a	0.51	0.52 ^b	46		7.66 ^a	1.78	0.10 ^b
21	Me ₂ NN- <i>i</i> -Bu ₂			0.29 ^b	47		7.34 ^a	1.95	0.17 ^e
22		7.97 ^a	0.58	0.12 ^b	48		7.46 ^a	1.82	0.00 ^{c,d}
23		7.91 ^b	0.56	-0.03 ^b	49		7.43 ^a	1.46	0.07 ^b
24		7.95 ^a	0.55	0.15 ^b	50		7.87 ^a	1.57	0.03 ^b
25		7.60 ^b	0.66	0.01 ^b	51		7.63 ^a	2.32	0.10 ^b
26		8.09 ^a	0.54	0.31 ^b	52		7.58 ^a	1.76	-0.04 ^b
27		7.89 ^a	0.52	0.35 ^b	53		7.53 ^a	2.21	-0.06 ^b
28		7.87 ^b	0.59	0.20 ^b	54		6.92 ^a	2.32	-0.25 ^b
29		8.09 ^b	0.72	0.18 ^b	55				0.03 ^b
30				0.05 ^b	56		7.88 ^a	0.54	0.10 ^b
31				0.07 ^b					
32				0.06 ^b					
33		7.78 ^a	2.30	0.06 ^c					
34		8.06 ^a	0.88	0.06 ^c					
35		7.81 ^a	0.99	0.03 ^d					
36		7.81 ^a	2.32	0.18 ^d					
37		7.83 ^a	0.95	0.14 ^c					

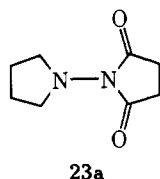
^a Determined by J. M. Buschek. ^b Determined by V. Peacock (this work). ^c Determined by H. J. Hintz. ^d Determined by L. Echegoyen. ^e Determined by R. T. Landis. ^f Note Added in Proof: The IP₁ reported for 7 is seriously in error. We have found this is because the σ bond onset starts to overlap the tail of the second lone pair peak. Using the same data, but a more reasonable baseline for fitting of gaussian lone pair peaks to the data, we obtain IP₁ = 7.96, Δ = 0.54 eV. Use of this better IP₁ for 7 considerably improves the correlation in Figure 3.

Table II. E° for Tetraalkylhydrazines in Methylene Chloride

Compd	E° (CH_2Cl_2) ^a	ΔE° from CH_3CN
1	0.47	0.19
2	0.45	0.19
10	0.43	0.19
13	0.43	0.19
7	0.46	0.21
21	0.48	0.19
22	0.31	0.19
26	0.49	0.18
29	0.35	0.17

^a 0.1 M $(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$ supporting electrolyte, vs. SCE.

which is within our experimental error, which we believe to be about 30 meV. Rademacher and Koopman^{3d} have recently reported, in contrast to our conclusion^{2d} that 1,1'-bispyrrolidine (**23**) exists only in a gauche conformation, that there is an appreciable amount of a second conformation with $\theta \sim 150^\circ$, inferred from the presence of a maximum at 9.93 eV in the PE spectrum which was nearly as intense as the overlapping gauche maxima at lower energy. Upon checking our spectrum, we found a rather smaller peak near 9.9 eV than that reported by Rademacher and Koopman, but there was definitely a maximum in this region. Our sample of **23** had been separated from the mixture produced by photolysis of 1,1',4,4'-bis(tetramethylene)-2-tetrazene. We have now prepared a more pure sample of **23** by lithium aluminum hydride reduction of **23A**,



and can observe no peak in the 9.9 eV region of the PE spectrum. A large θ conformation of **23** is not appreciably populated at room temperature.

Our latest list of E° and IP_1 values appears in Table I. Figure 1 shows the plot of IP_1 vs. E° for the compounds of Table I (except for **54**, which has distinctly lower IP_1 and E° , and falls off of this plot). Although it cannot be said that there is no correlation, there clearly is not a chemically useful linear correlation between these two quantities. The reasons for a lack of correlation will form the body of this discussion.

Discussion

A. Adiabatic and Vertical Ionizations. On the surface, it would seem that both IP_1 and E° should be measuring the same thing, the energy required to strip an electron from the hydrazine. These quantities are measured in different phases, but good correlation is often seen between them.⁷ An obvious reason for the breakdown in the correlation for tetraalkylhydrazines is the difference in time scale for these two types of oxidation experiments. The PES ionization experiment is extremely rapid, and the position of the first peak maximum (IP_1) is the measure of the free-energy gap between neutral hydrazine and hydrazine radical cation of the same geometry as neutral hydrazine. The rapidity of the PES time scale is made clear by observation of the superposition of PE spectra for both conformations when two conformations are present in significant amounts, as with hexahydropyridazines.²⁻⁴ In contrast, the far slower electrochemical experiment gives E° , the measure of the free energy gap between neutral hydrazine and the relaxed form of the hydrazine radical cation, which are in equilibrium— E° measures the adiabatic neutral-radical ion energy gap in solution. These concepts are shown diagrammatically in Figure 2. It is clearly the adiabatic vapor-phase ion-

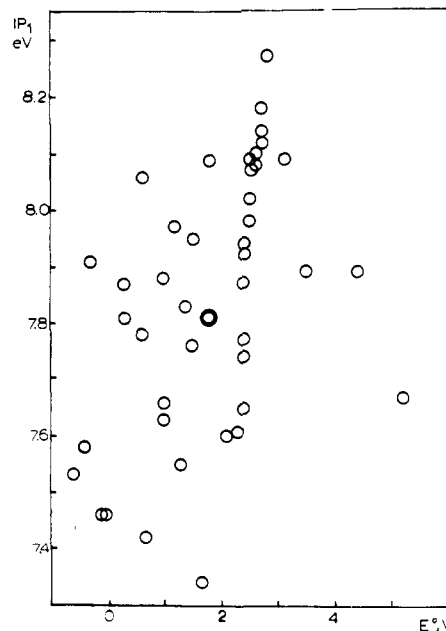


Figure 1. Plot of IP_1 vs. E° for 44 tetraalkylhydrazines.

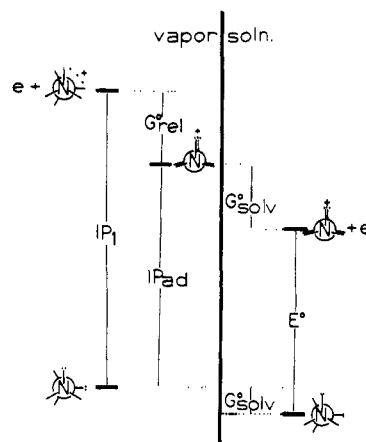


Figure 2. Diagram showing the relation of IP_1 to E° .

ization potential, and not the vertical one, which is required for comparison with E° .⁸ For many types of compounds, such as aromatics, olefins, and oxygen p lone pairs, only small geometrical changes occur upon ionization, and the vertical and adiabatic ionization potential are numerically close; one typically observes a narrow PES peak, showing vibrational fine structure, and the first observed fine-structure maximum is either the adiabatic ionization potential or close to it. Even for alkylamines, however, there is a substantial geometrical change upon ionization (going from tetrahedral to planar geometry at nitrogen). Here the first absorption band is typically broad and featureless (although vibrational fine structure is observed in special cases for which geometrical change is more limited, such as in 1-azamantane⁹ and quinuclidine¹⁰). It is not surprising, then, that PES "first-rise" potentials for amines, such as those reported by Worley and Dewar,¹¹ are a few tenths of an electron volt higher than the adiabatic ionization potentials reported by Watanabe.¹² For hydrazines, not only flattening at nitrogen but N-N bond rotation occurs upon ionization, so that it is quite unlikely that the "first-rise" PES ionization potentials would be close to the adiabatic ionization potential. Indeed, if "first-rise" ionization potentials instead of the vertical IP_1 values are plotted vs. E° , no significant improvement in the linearity of the correlation is observed. We believe that the adiabatic vapor-phase ionization potential for hydrazines

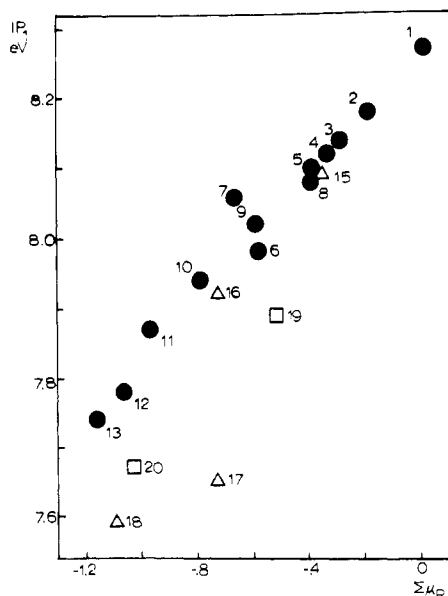


Figure 3. Plot of IP_1 vs. $\Sigma\mu_R$ for acyclic tetraalkylhydrazines. Normal alkyl compounds are shown as \bullet , ones containing isopropyl substituents as Δ , and those with *tert*-butyl substituents as \square .

occurs significantly below the potential for which counts are first observed in the PE spectrum. For tetramethylhydrazine (1), the "first-rise" ionization potential was 7.76 eV, the same as the ionization potential measured by electron impact by Dibeler and co-workers;¹³ we argue that this number is not very close to the adiabatic ionization potential.

B. Influence of Alkyl Group Structure on IP_1 and E° . 1. IP_1 Values of Acyclic Tetraalkylhydrazines. Hydrazines are no exception to the general observation that when a methyl group attached to an atom bearing a lone pair or π orbital is replaced by a larger alkyl group, the ionization potential decreases.^{2,3} It has been frequently noted that although IP_1 gives a fair correlation with the familiar Taft inductive parameter σ^* ,¹⁴ correlations between the IP values of different RX molecules are better. Danby and co-workers^{15a} have defined a new inductive parameter μ_R for use in correlating vapor-phase lone-pair^{15b} ionization potentials using alkyl iodide ionization potentials as the "standard reaction". Both σ^* and μ_R are dimensionless, have a value of zero for $R = \text{methyl}$, and become increasingly more negative for larger alkyl groups. To compare them, we note that 1.95 σ^* gives values essentially identical with μ_R for Me, Et, and *i*-Pr, but that these values are 0.065 and 0.084 less negative for *n*-Pr and *n*-Bu (that is, *n*-Pr and *n*-Bu are more effective at lowering IP_1 than σ^* predicts), while *t*-Bu gives a value 0.070 more negative; these deviations are easily detectable by PES, causing μ_R to give significantly better correlations than σ^* . We show a plot of IP_1 for acyclic hydrazines vs. the sum of the μ_R values for all four alkyl substituents in Figure 3. The *n*-alkyl compounds (solid circles) give a nearly straight line in spite of the fact that the four substituents are not on the same center; the effect of *n*-alkyl for methyl substitution on IP_1 is experimentally nearly additive and linear with $\Sigma\mu_R$. In contrast, the isopropyl compounds (triangles) show almost no deviation for monosubstitution, but substantial downward deviation for 1,1-disubstitution and trisubstitution, and even the monosubstituted *t*-Bu compound shows a large deviation. We suggest that these deviations are caused by the bulk of the α -branched substituents. One might expect flattening at the nitrogens with bulky R groups, which would cause the lone-pair hybrid orbitals to have more p character and hence lower ionization potential, which is the direction of the deviations observed.

We would also like to comment on the remarkable constancy

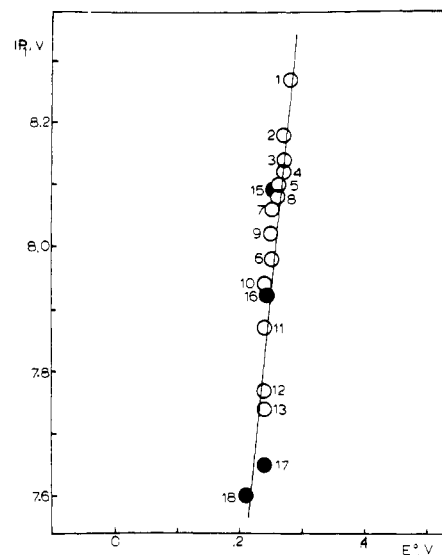


Figure 4. Plot of IP_1 vs. E° for normal alkyl (\circ) and isopropyl (\bullet) tetraalkylhydrazines.

of $\Delta = IP_2 - IP_1$ for acyclic tetraalkylhydrazines, which both we^{2c} and Rademacher³ have interpreted as indicating quite constant θ values, because approximate MO theory predicts Δ to vary nearly linearly with θ with a slope of about 35 meV/deg. Rotation of several degrees about the N-N bond surely cannot be very costly in energy, and changing the size of the α substituents must logically change the equilibrium θ values some. We now believe¹⁶ the explanation must be that the predicted crossover of n_+ and n_- does not actually occur (presumably due to configuration interaction), so that the lone pair-lone pair splitting never drops below the 0.5 eV observed for acyclic hydrazines. This would mean that Δ is in fact quite insensitive to θ near the predicted crossover point (about 83°² or 80.7°³), and that the constancy of observed Δ for acyclic compounds does not actually require them all to mysteriously have exactly the same θ value.

2. IP_1 vs. E° Correlation for Acyclic Hydrazines ($R_1R_1'N_1N_2R_2R_2'$). E° should be affected not only by the "inductive effect" of changing alkyl substituents, but also by strain effects, because neutral hydrazine and radical cation have quite different geometries. If only hydrazines with normal alkyl groups are considered, one should minimize strain energy differences and be able to focus on the "inductive effect". A plot of IP_1 vs. E° for these compounds (shown as Figure 4) shows that an excellent linear correlation is in fact observed, $IP_1 = 5.384 + 10.33E^\circ$ (for 13 compounds, correlation coefficient 0.91, maximum deviation in E° calculated by this equation from the observed E° , 12 mV), which reveals the significant fact that IP_1 is far more sensitive to alkyl group homologation than is E° . Although steric effects are minimized by choosing normal alkyl groups, they are not quite eliminated, for the N(1)-N(2) rotation and flattening at nitrogen which occurs upon electron removal will decrease the R_1-R_1' steric interaction, and substantially increase the R_1-R_2 interaction. Because these hydrazine radical cations are nearly flat (although certainly having large out-of-plane vibrational motions⁵ compared to olefins) and ought to have an N-N bond length close to the C=C bond length for olefins, one should be able to estimate the maximum size of the R_1-R_2 alkyl-alkyl interaction by using an olefin as a model. From equilibration studies on *cis* and *trans* olefins,¹⁷ a *cis* methyl-*n*-alkyl interaction is about 0.23 kcal/mol (10 mV) larger than the methyl-methyl interaction, and the *n*-alkyl-*n*-alkyl interaction is about 0.44 kcal/mol (19 mV) larger. These effects, which would increase E° upon alkyl group homologation and oppose the "inductive"

effect, are expected to be present in our data, but are far too small to account for the IP_1 vs. E° slope of over ten.

When isopropyl groups are substituted for methyl groups (compounds **15–18**), the points in the IP_1 vs. E° plot fall close to the line determined by the n -alkyl substituents (see Figure 4). Although the polyisopropyl-substituted compounds **16–18** deviate noticeably in the IP_1 vs. $\Sigma\mu_R$ plot of Figure 3, the slope in the plot of Figure 5 is so large that this should make little difference. The lack of deviation for **15–18** is not surprising, since the isopropyl–methyl interaction¹⁸ determined by heats of hydrogenation of cis and trans olefins is experimentally no larger than the ethyl–ethyl interaction, presumably because the isopropyl groups can be positioned to minimize R_1 – R_2 alkyl–alkyl interaction. In contrast, *tert*-butyl substitution causes substantial increases in E° (see Figure 5). *tert*-Butyltrimethylhydrazine (**19**) comes 4.5 kcal/mol higher in E° than the line of Figure 4 predicts and 1,2-di-*tert*-butyldimethylhydrazine (**20**) comes 6.8 kcal/mol higher. The increase in E° is presumably at least largely caused by R_1 – R_2 interaction increases in the nearly planar radical cation. For comparison, the cis *tert*-butyl–methyl interaction in the olefin has been measured at 3.9 kcal/mol (0.16 eV).¹⁹ The destabilizing increased R_1 – R_2 steric interaction in the cation must outweigh considerably the stabilizing decrease in R_1 – R_1' interaction.

3. Solvation Effects on Charge Stabilization. The strain energy difference of section 2 should appear in the G°_{rel} (relaxation) term of Figure 2, which shows how IP_1 is related to E° . Another candidate for the high slope of Figure 3 is an effect of ΔG°_{solv} (solvation) between neutral and radical cation. One might suppose that the larger alkyl groups could physically exclude solvent from the region of the highly charged nitrogens, which would decrease $G^\circ_{solv}(H^+)$ and raise E° . If this were the case, we would have expected α -branching (such as going from n -butyl to isopropyl) to cause a significant increase in E° —none is observed. In addition, if exclusion of solvent from the immediate region of the nitrogens were important, we would have expected observable effects in the pattern of E° values observed on going from acetonitrile to the bulkier and less polar methylene chloride—such effects were not observed (see Table II). In contradiction to the above statements, diisobutyldimethylhydrazine (**21**) was 40 mV more difficult to oxidize in solution than the n -butyl analogue **7**, and a differential solvation effect certainly cannot be ruled out here.

Solvation effects are clearly important in ionic reactions such as the one under discussion. Solvation is easing electron removal from a tetraalkylhydrazine by about 6 eV (see below). The formal charge of a hydrazine radical cation is distributed only over the two nitrogens, and in the vapor phase, only the alkyl groups are available for stabilization of this charge. In solution, solvent molecules also participate effectively in charge stabilization. There is substantially less demand upon the alkyl groups for charge delocalization in solution. Decreased response to decreased electronic demand for stabilization has been well documented for transition states in solvolysis reactions, especially by Peters and Brown.²⁰ The domination of solvent effects in altering the order of alcohol acidity in vapor and solution phases was pointed out several years ago by Brauman and Blair.²¹ The solvent effect on E° appears not to be a very specific one, for the same E° ordering is observed in solvents as different in their solvating properties as acetonitrile and methylene chloride. The common feature is a greatly decreased sensitivity of the ease of electron removal to alkyl group homologation in solution compared to the vapor phase.

The far smaller sensitivity of E° than IP_1 to alkyl group homologation has interesting consequences. Parker²² recently discussed the relation of vapor-phase ionization potential to solution-phase oxidation potential, including the problem of relating E° values (determined relative to a reference elec-

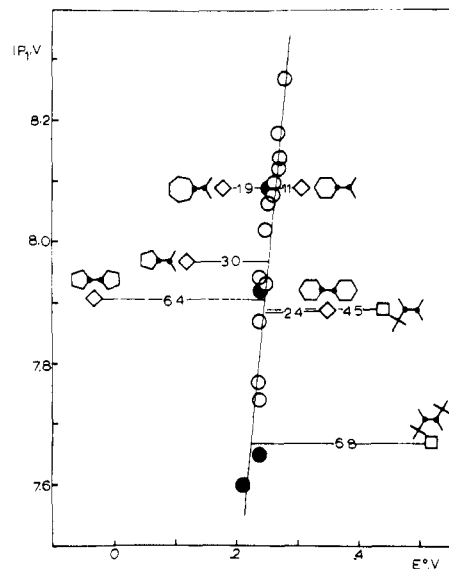
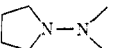
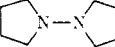
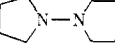
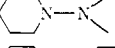
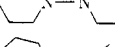
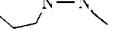


Figure 5. Plot of IP_1 vs. E° , with *tert*-butyl (\square) and 1,1-cycloalkyl (\diamond) hydrazines added to the plot of Figure 4. The numbers are derivations from the n -alkyl line in units of kcal/mol.

trode) to an absolute energy scale. The latter problem was cleverly solved by using alternate aromatic hydrocarbons, in which the orbital energy levels are equally disposed about zero energy. By assuming that ΔG°_{solv} (the difference in energy between the solution and vapor phase) was a constant for these hydrocarbons, he argued that $IP = E^\circ - 0.34 - [\Delta G^\circ_{solv} + \phi]$, in acetonitrile where E° is measured vs. SCE and ϕ is the work function of the electrode, and by comparison with vapor-phase ionization potentials, $[\Delta G^\circ_{solv} + \phi]$ was evaluated as 6.36 eV. The assumption of a constant ΔG°_{solv} energy is at least as reasonable an expectation for our hydrazines as for aromatic compounds, but we do not know IP_{ad} for any hydrazine. As an approximation for the measurement of $[\Delta G^\circ_{solv} + \phi]$ for saturated nitrogen compounds at gold electrodes, we choose to use the diamine 1,4-diazabicyclo[2.2.2]octane (Dabco), for which we measured E° (CH_3CN , vs. SCE, room temp) to be 0.60 V.²³ Because Dabco shows vibrational structure in its first PES peak, the first observed fine structure maximum (7.33^{10c} or 7.23 eV^{10b}) should be a good approximation to IP_{ad} . This gives a value of $[\Delta G^\circ_{solv} + \phi]$ of 6.39 eV, quite close to Parker's value. We would, therefore, use $IP_{ad}(est) = E^\circ + 6.73$ as a reasonable estimation for the relation between vapor phase IP_{ad} and solution E° (making Parker's assumptions). This clearly cannot be correct, however, since $IP_{ad}(est)$ only decreases by 40 mV in going from tetramethylhydrazine (**1**) to tetra- n -propylhydrazine (**13**), although IP_1 decreases by 530 mV. Because of the similar geometries for neutral hydrazine and hydrazine cations for these compounds, it is quite unreasonable to suppose that the difference between the vertical and adiabatic vapor-phase ionization potentials actually decreases by 0.5 eV between **1** and **13**. For this sort of a structural change, E° does not allow prediction of IP_{ad} (vapor); there is a substantial "leveling effect" on the ease of ionization in solution which must also be taken into account. The assumption that ΔG°_{solv} is a constant is almost certainly invalid for tetraalkylhydrazines.

4. Cyclic and Bicyclic Hydrazines. Because the lone pair–lone pair splitting Δ is similar for *N*-aminopyrrolidine, -piperidine, and -homopiperidine-substituted hydrazines to acyclic ones, one would expect that these hydrazines would fall on the same IP_1 vs. E° plot as the acyclic ones, in the absence of strain difference effects. Significant deviations from the line are observed (Figure 5). Incorporation of the N(1) alkyl groups in a pyrrolidine or homopiperidine ring lowers E° , while pi-

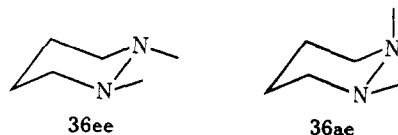
Table III. 1,1-Cycloalkylhydrazine E° Shifts, Compared to n -Alkylhydrazines

Compd		$E^\circ - E^\circ_{\text{ext}}^a$	
		eV	kcal/mol
22		-0.13	-3.0
23		-0.28	-6.3
24		-0.10	-2.3
26		0.05	1.1
27		0.11	2.5
29		-0.08	-1.9

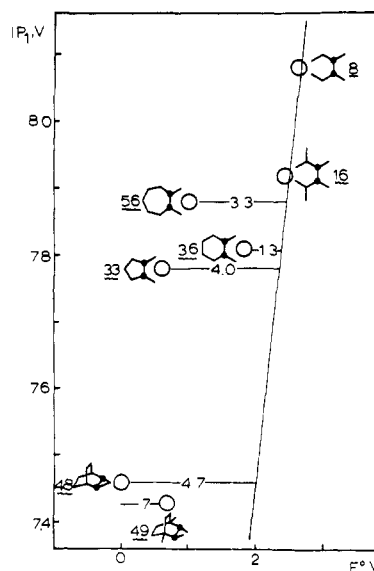
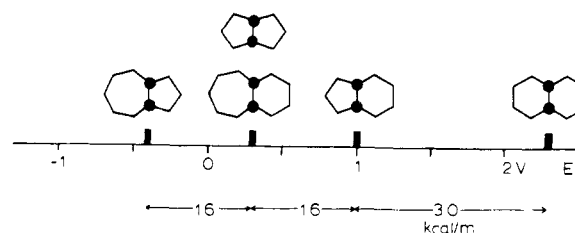
^a $E^\circ_{\text{ext}} = (IP_1 - 5.384)/10.328$, the regression line for normal alkyl hydrazines in an IP_1 vs. E° plot.

peridine rings raise E° . These effects are almost additive, as indicated in Table III. The directions of these changes are the same as those predicted by eclipsing strain changes within the cycloalkyl groups when the flattening at nitrogen caused by electron removal occurs, since the five- and seven-membered ring compounds have considerable eclipsing interaction which is partially relieved by going from sp^3 to sp^2 hybridization at one atom, whereas eclipsing interactions are minimized with all sp^3 centers in a six-membered ring, and are increased by this change.²⁴ The literature data most comparable to ours are rate effects on 1-methyl-1-chlorocycloalkene solvolysis reported by Brown and Borkowski,^{25a} where the relative rates compared to an acyclic model correspond to transition-state energy changes of -2.0, 0.9, and -1.9 kcal/mol for five-, six-, and seven-membered rings, respectively, compared to 6-methyl-6-chloroundecane. This pattern of reactivities is closer to our data than for cycloalkyl tosylate solvolysis^{25b} (lacking the α -methyl group, where the cycloheptyl compound reacts more rapidly than the cyclopentyl one), or for cyclic ketone reduction.^{25c} Another factor which is probably involved is R_1 - R_2 alkyl-alkyl interaction, which ought to be larger as the 1,1-ring size is increased. The sensitivity to $R_1N(1)R_1'$ angle is apparently not very great, but should also influence our data.

For 1,2-cycloalkyl hydrazines the steric requirements of the ring system usually force θ to be changed from the electronically preferred angle near 90° which is seen for acyclic and 1,1-cycloalkyl compounds. The size of the lone pair-lone pair interaction Δ increases, and IP_1 is often lower for large Δ conformations than for small Δ acyclic compounds of comparable substitution. The effect on IP_1 is smaller than the effect on Δ , however, since the average of IP_1 and IP_2 increases as Δ increases.^{2d} Thus, although 1,2-dimethylhexahydropyridazine (36) clearly has a large Δ diequatorial conformation 36ee ($\Delta \approx 2.3$) as its major one, and although IP_2 is clearly resolved for the minor equatorial-axial conformation 36ae, the



IP_1 peaks are not resolved, implying that IP_1 for 36ae comes within about 0.3 eV of that for 36ee. In Figure 6, the IP_1 and E° values for the five-, six-, and seven-membered ring 1,2-dimethylhydrazines 33, 36, and 56 are compared graphically with the regression line for acyclic hydrazines. All these have IP_1 values within 0.11 eV, in spite of the fact that 56 has a Δ

**Figure 6.** Plot of IP_1 vs. E° for 1,2-cycloalkyl and 2,3-diazabicyclo[2.2.2]octylhydrazines. The line represents n -alkyl acyclic hydrazines. Deviations are shown in kcal/mol.**Figure 7.** Comparison of E° values for bicyclo[$m.n.o$] bridgehead hydrazines.

similar in size to that of the acyclic compounds, and 33 and 36 have as large Δ values as any tetraalkylhydrazines (2.3 eV) (although conformations from both with smaller Δ values are also populated). It is apparent that Δ is not the principal factor determining IP_1 or E° . All three have lower E° values than acyclic hydrazines of comparable IP_1 . For acyclic hydrazines, oxidation eclipses both R_1 and R_2 groups. In five- to seven-membered ring 1,2-cycloalkylhydrazines, the ring should cause the R_1, R_2 eclipsing in the cyclic portion of the molecule to be less costly in energy. The decrease in E° is significantly greater for the five- and seven-membered ring compounds 33 and 56 than for the hexahydropyridazine 36. This parallels the pattern of E° changes seen for 1,1-cycloalkylhydrazines, and presumably also is caused by eclipsing interaction changes.

Also included in Figure 6 are 1,2-diisopropyl-1,2-dimethylhydrazine (16) and 2,3-dimethyl-2,3-diazabicyclo[2.2.2]octane (48), which show the effect of bicyclic ring formation. The lowering of IP_1 in comparing 48 with 16 is 0.46 eV (10.1 kcal/mol), and E° is lowered 0.21 V (4.8 kcal/mol). For 48, the effect of decreasing one R_1, R_2 interaction by containing these groups in a ring is augmented by a decrease in nonbonded methyl-bicyclooctane interaction upon oxidation. Introduction of 1,4-dimethyl substituents onto 48 to give 49 decreases bicyclic torsion as expected^{2e} (the 0.36 eV decrease in Δ reflects a decrease in θ of about 14°), but IP_1 is only slightly smaller for 49 than for 48 (0.03 eV). The value for E° of 49 is about 1.6 kcal/mol more positive than that of 48, presumably reflecting the increase in bridgehead methyl- N -methyl eclipsing interaction upon oxidation (the ΔG^\ddagger for nitrogen inversion of 49 is 0.7 kcal/mol greater than that of 48,^{4b} quite close to half of the E° difference).

We compare E° values for some bicyclo[$m.n.o$] bridgehead hydrazines in Figure 7, ignoring the IP_1 differences. Once

Table IV. Tetraalkylhydrazines Prepared by Reductive Alkylation

Compd	Aldehyde (g, mmol)	Hydrazine (g, mmol)	NaBH ₃ CN, g	Workup	Distilled product	
					bp, °C (mm)	Yield, g (%)
2 ^a	aq CH ₂ O (3.5, 50)	Me ₂ NN=CHMe (0.87, 10.1)	1.5	B		(22) ^b
3	aq CH ₂ O (11.3, 161)	Me ₂ NN=CHEt (3.0, 50)	5.04	A	45–50 (20)	0.77 (13)
5 ^a	aq MeCHO (3.3, 30)	Me ₂ NNH ₂ (0.6, 10)	0.95	B		(34) ^b
6	aq CH ₂ O (7.0, 100)	<i>n</i> -Pr ₂ NNH ₂ (23, 20)	2.25	A	48–58 (16)	1.49 (51)
7	EtCHO (11.5, 160)	Me ₂ NNH ₂ (1.16, 20)	3.5	A	70–80 (20)	1.31 (38)
8 ^a	aq CH ₂ O (15.4, 205)	(EtNH) ₂ (3.0, 34)	4.41	A	30–35 (20)	0.51 (13)
9 ^a	CH ₂ CHO (8.8, 200)	MeNHNH ₂ (1.0, 22)	4.16	A	32–33 (20)	0.34 (12)
12	MeCHO (5.52, 120)	<i>n</i> -Bu ₂ NNH ₂ (3.0, 20)	3.7 ^c	A	175–195 (70)	1.90 (47) ^d
13	EtCHO (2.9, 50)	<i>n</i> -Pr ₂ NNH ₂ (1.0, 9)	1.0	A	95–110 (35)	1.02 (25) ^d
14	<i>n</i> -PrCHO (10.8, 150)	(NH ₂) ₂ ·H ₂ O (60, 20)	3.15	A	90–102 (0.5)	2.28 (44) ^d
15	aq CH ₂ O (4, 50)	Me ₂ NN=CMe ₂ (0.58, 10)	1.2	B	82–87 (250)	0.4 (34)
16	aq CH ₂ O (8, 100)	(<i>i</i> -PrNH) ₂ (2.0, 17)	2.14	A	68–72 (50)	0.93 (38)
17	aq CH ₂ O (8, 100)	(<i>i</i> -Pr) ₂ NNH (2.0, 17)	2.14	A	64–70 (20)	1.04 (42)
18	aq CH ₂ O (2, 25)	<i>i</i> -Pr ₂ NN=CMe ₂ (0.78, 5)	0.6	B	75–77 (30)	0.4 (47)
19	aq CH ₂ O (21.8, 290)	<i>t</i> -BuNHNH ₂ ·2HCl (4.0, 32) ^e	6.06	A	35–42 (20)	0.53 (13)
21	<i>i</i> -PrCHO (7.2, 100)	Me ₂ NNH ₂ (1.0, 17)	2.08	A	32 (2.2)	0.61 (21) ^d
22	aq CH ₂ O (11.3, 150)	(CH ₂) ₄ NNH ₂ (2.08, 24)	3.15	A	75–78 (atm)	0.32 (12)
24	(CH ₂ CHO) ₂ (0.63, 7.3)	(CH ₂) ₅ NNH ₂ (0.73, 7.3)	0.28	B	95–105 (12)	0.4 (35)
26	aq CH ₂ O (9, 120)	(CH ₂) ₆ NNH ₂ (2.0, 20)	2.48	A	76–80 (50)	0.94 (37)
27	aq glw ^f (4.0, 10)	(CH ₂) ₅ NNH ₂ (1.0, 10)	0.38	B	105–110 (20)	0.5 (30)
28	aq glw ^f (15, 35)	(CH ₂) ₆ NNH ₂ (4.0, 35)	2.2	A	72–84 (0.4)	1.63 (21)
29	aq CH ₂ O (14.6, 180)	(CH ₂) ₆ NNH ₂ (3.2, 39)	3.78	A	77–79 (22)	1.89 (35)
32	aq CH ₂ O (2.6, 32)	(0.92, 12.2) ^g	0.92 ^c	A		0.90 (44) ^d
40	aq CH ₂ O (10, 125)	(3.55, 25) ^h	4.0 ^c	A	80–85 (25)	1.65 (38)
43	aq MeCHO (5.5, 50)	C ₄ H ₁₀ N ₂ (0.86, 10) ⁱ	1.13 ^c	A	60–63 (15)	0.91 (64)
52	aq glw ^f (4.0, 10)	C ₃ H ₈ N ₂ (0.72, 10) ^j	0.5	B		(32) ^b
55	aq glw ^f (5.49, 13.7)	C ₄ H ₁₀ N ₂ (1.18, 13.7) ⁱ	1.13 ^c	A		(26) ^b
56	aq glw ^f (8.0, 20)	(MeNH) ₂ (1.2, 20)	1.0	A		(27) ^b

^a See ref 28 for another preparation. ^b Isolated by VPC without prior distillation. Yield estimated by peak areas, using weighed internal standard. ^c Using white 83% pure NaBH₃CN. All other preparations used considerably less pure very dark material. ^d Distilled product less pure than usual—VPC indicated only 40–60% purity. ^e 8.5 ml of 15% NaOH (32 mmol) added. ^f 25% aqueous glutaric dialdehyde. ^g 9-Amino-9-azabicyclo[3.3.1]nonane. ^h 3,3,3,6,6-Tetramethylhexahydropyridazine, prepared by hydrogenation of 4.0 g of the azo compound³¹ over 200 mg of 10% Pd/C in 12 ml of acetic acid; NMR (CDCl₃) δ 3.07 (2 H, br s), 1.49 (4 H, s), 1.08 (12 H, s). ⁱ Hexahydropyridazine. ^j Pyrazolidine.

again, the reluctance to form hydrazine radical cations in six-membered ring systems is clear, although for these bridged 1,2-cycloalkyl hydrazines, a seven-membered ring is preferred over a five-membered ring for radical cation formation, in contrast to the monocyclic systems. This presumably reflects a less favorable R₁N(1)N(2) angle in the pyrazolidine containing cations, which show larger nitrogen splitting constants than unstrained hydrazine radical cations.^{5a}

The effects of nonbonded interaction relief upon flattening at nitrogen in lowering *E*^o are sometimes quite large. The *E*^o for 1,2,3,3,6,6-hexamethylhexahydropyridazine (40) is 0.19 V (4.4 kcal/mol) lower than that of 1,2-dimethylhexahydropyridazine (36), and the much smaller changes in *E*^o for the tri- and tetramethyl analogues 37–39 make it likely that relief of 1,3-diaxial methyl-hydrogen interactions in the radical cation is an important factor. The *E*^o value for 9-dimethylamino-9-azabicyclo[3.3.1]octane (32), which has an axial dimethylamino group, is 0.25 V (5.8 kcal/mol) lower in *E*^o than is 1-dimethylaminopiperidine (26), in which the dimethylamino group is doubtless equatorial. The *E*^o difference is surprisingly large, and certainly cannot be entirely attributed to the axial-equatorial strain difference. Our most easily oxidized compound, 54, is 0.25 V lower in *E*^o than 2,3-dimethyl-2,3-diazabicyclo[2.2.2]octane (48), and relief of bicyclooctane-3,3-diethylpyridazine steric interactions upon flattening at nitrogen must be important. Here the 2,3-dialkyl fusion changes from anti (48) to syn (54), and IP₁ is decreased 0.53 eV as well.

Experimental Section

Materials. Our methods of preparing some of the compounds employed have been previously described: 1, 33–39, 44, 46, 48, 50, and 54;¹ 10, 20, and 53;^{5a} 4 and 11;^{2c} 49;^{4e} some in communication form, 15, 18, 24, 27, 52, and 56;²⁶ 47.²⁷

General Method for Reductive Alkylation of Hydrazines. To a mixture of the hydrazine to be alkylated in 25–50 ml of CH₃CN per 10 mmol of hydrazine, several equivalents of the aldehyde to be used per NH hydrogen to be replaced, followed by 0.33 mol of NaBH₃CN per mole of aldehyde, were added. (For cyclization reactions with dialdehydes, 1 mol of aldehyde per mole of 1,1- or 1,2-dialkylhydrazine was employed.) The reaction mixture was stirred at ambient temperature under nitrogen as acetic acid (usually 0.67 mol per mole of aldehyde, but the amount seems not to be critical) was added dropwise in small batches over a period of 1 h. The mixture was stirred for typically an additional 2 h, followed by workup.

Workup A. For higher molecular-weight tetraalkylhydrazines, an excess of 15% NaOH solution was added, the two-phase mixture was extracted with pentane, and the residue, after removal of pentane, was distilled through a Kontes short-path apparatus.

Workup B. For volatile hydrazines, 5–10 ml of concentrated HCl was added dropwise, the acetonitrile was removed by rotary evaporation, the residue was basified and extracted with ether. After drying (Na₂SO₄), the product was isolated by distillation.

Unfortunately, most of our preparations were carried out with one bottle of exceedingly poor, very dark Ventron “sodium cyanoborohydride”, so the amounts of NaBH₃CN used were less than we had believed. Nevertheless, the yields of tetraalkylhydrazine were adequate, usually in the 20–40% range, considering the simplicity of the operations required and the small amounts of each material required. We present the experimental for the compounds prepared by reductive alkylation in Table IV. The 1,2-dialkylhydrazines were prepared by lithium aluminum hydride reduction of the azines.²⁹ Some azines appeared not to be reduced under our conditions.

Several compounds were prepared by refluxing a dialkyl hydrazine with 1 equiv of a succinic anhydride derivative in an aromatic solvent over a Dean-Stark trap, followed by LiAlH₄ reduction of the intermediate bishydrazide in THF, using addition of water, 15% NaOH, and water (1, 1, and 3 ml/g of LiAlH₄, respectively), filtration, and distillation as workup. The scales and yields for these preparations are given in Table V.

All tetraalkylhydrazines were finally purified by VPC on a 15%

Table V. Hydrazines Prepared by LiAlH_4 Reduction of Succinic Anhydride Hydrazides

Compd	Hydrazine (g, mmol)	Solvent, reflux time, h	LiAlH_4 , g (mmol)	Distilled product	
				bp, °C (mm)	Yield, g (%)
23	$(\text{CH}_3)_4\text{NNH}_2$ (2.5, 31)	C_6H_6 , 24	5.6 (150)	75–80 (15)	0.91 (21)
25	$(\text{CH}_3)_6\text{NNH}_2$ (3.53, 31)	$\text{C}_6\text{H}_5\text{CH}_3$, 24	5.0 (135)	64–75 (0.2)	1.65 (32)
30	$(\text{CH}_3)_2\text{NNH}_2$ (9.0, 150)	$(\text{CH}_3)_2\text{C}_6\text{H}_4$, 24	2.0 (54) ^a	130–132 (30)	0.3 (18)
31	$(\text{CH}_3)_2\text{NNH}_2$ (2.04, 34)	C_6H_6 , 72	1.0 (27) ^b	64–70 (2)	0.41 (36)
41	$(\text{CH}_3\text{NH})_2$ (3.31, 55.2)	C_6H_6 , 24	7.3 (193) ^c	mp 35–40	3.66 (69)
42	$(\text{CH}_3\text{NH})_2$ (9.6, 160)	$\text{C}_6\text{H}_4(\text{CH}_3)_2$, 34	11.1 (300) ^d	67–68 (1.3)	7.2 (74)
45	$\text{C}_4\text{H}_{10}\text{N}_2$ (2.54, 29)	C_6H_6 , 24	2.0 (54)	mp 108–111 ^e	1.7 (33)

^a For 2.0 g of the intermediate diketo-30, mp 71–75 °C (from hexane); NMR δ 2.92 (6 H, s), 2.82 (2 H, t), 1.70–1.96 (4 t, m), 1.36–1.57 (4 H, m). ^b For 2.34 g of the intermediate diketo-31, mp 133.5–135.5 °C (from water); NMR (CDCl_3) δ 2.85 (6 H, s), 2.13–2.31 (4 H, m), 1.85–2.02 (2 H, m), 1.20–1.40 (4 H, m). ^c For 6.20 g (31.6 mmol) of the intermediate diketo-41, mp 134–140 °C (from hexane, 7.23 g, 67%); NMR (CDCl_3) δ 3.26 (6 H, s), 2.18 (4 H, m), 1.84 (2 H, m), 1.60–1.0 (4 H, m). ^d For 12.0 g of the intermediate diketo-42, mp 118–120 °C (from hexane), 12.0 g, 38%; NMR (CDCl_3) δ 3.36 (6 H, s), 2.74 (2 H, m), 1.46–1.80 (8 H, m). ^e Purified by sublimation at 70 °C (0.05 mm), followed by crystallization from acetone.

Table VI. ^1H NMR Spectra for Some Tetraalkylhydrazines

Compd	Peak positions in CDCl_3 , δ (no. of H, multiplicity)
2	2.50 (2, q), 2.33 (6, s), 2.27 (3, s), 1.07 (3, t)
3	2.35 (2, t), 2.30 (6, s), 2.24 (3, s), 1.47 (2, m), 0.88 (3, t)
5	2.47 (4, q), 2.33 (6, s), 1.06 (6, t)
6	2.37 (4, br t), 2.29 (6, s), 1.40 (4, br sextet), 0.88 (6, t)
7	2.38 (4, t), 2.28 (6, s), 1.40 (8, m), 0.90 (6, t)
8	2.50 (4, q), 2.27 (6, s), 1.05 (6, t)
9	2.47 (6 q), 2.22 (3, b), 1.05 (9, t)
12	2.48 (4, t), 2.40 (4, q), 1.40 (8, m), 1.01 (6, t), 0.89 (6, t)
13	2.38 (8, t), 1.46 (8, m), 0.87 (12, t)
14	2.38 (8, t), 1.38 (16, m), 0.87 (12, t)
15	2.62 (1, hept), 2.30 (6, s), 2.23 (3, s), 1.05 (6, d)
16	2.66 (2, hept), 2.22 (6, s), 1.01 (12, d)
17	3.12 (2, hept), 2.43 (6, s), 1.02 (d, 12)
18	3.12 (2, hept), 2.70 (1, hept), 2.40 (3, s), 1.05 (12, d), 1.01 (6, d)
19	2.34 (6, s), 2.26 (3, s), 1.05 (9, s)
21	2.26 (6, s), 2.12 (4, d), 1.72 (2, m), 0.90 (12, d)
22	2.62 (4, m), 2.42 (6, s), 1.74 (4, m)
23	2.80 (4, t), 1.80 (4, m)
24	2.70 (8, m), 1.7 and 1.4 (10, 2 overlapping m)
25	2.60–2.94 (8, m), 1.45–1.85 (12, m)
26	2.52 (4, t), 2.31 (6, s), 1.6 and 1.4 (6, 2 overlapping m)
27	2.65 (8, t), 1.6 and 1.4 (10, 2 overlapping m)
28	2.80 (4, m), 2.61 (4, t), 1.16–1.80 (14, m)
29	2.78 (4, m), 2.36 (6, s), 1.56–1.78 (8, m)
30	2.38–2.96 (4, m) 2.32 (6, s) 1.88–2.20 (2, m), 1.24–1.60 (8, m)
31	3.04 (2, br dd, $J = 9.5$ and 6.0 Hz), 2.37–2.63 (2, m), 2.39 (6, s), 1.70–1.95 (4, m), 1.00–1.55 (6, m)
32	3.30 (2, m), 2.44 (6, s), 1.40–2.25 (12, m)
40	2.39 (6, s), 1.40 (4, s), 1.10 (12, s)
41	2.45 (6, s), 2.20–2.70 (4, m), 1.75–1.90 (10, m)
42	2.54–2.72 (4, m), 2.41 (6, s), 2.0–1.3 (10, m)
43	2.83 (4, m), 2.73 (4, q), 1.55 (4, m), 1.05 (6, t)
45	2.79 (4, t, $J = 5.5$ Hz), 1.93–2.53 (4, m), 0.90–1.86 (14, m)
47 ^a	3.42 (1, br s), 3.46 (1, br s), 2.39 (3, s), 1.80–2.25 (2, m), 1.37–1.65 (2, m), 1.10–1.30 (2, m), 1.00 (9, s)
49	2.44 (6, s), 1.3–2.0 (8, m), 0.97 (6, s)
51	1.8–3.4 (8, m), 1.9 (2, q), 1.6 (4, m)
52	2.92 (4, t, $J = 8$ Hz), 2.78 (4, m), 1.98 (2, q, $J = 8$ Hz), 1.71 (6, m)
55	2.66–3.08 (8, m), 1.4–1.95 (10, m)
56	2.88 (4, m), 2.46 (6, s), 1.68 (6, m)

^a In CCl_4 .

XF-1150 on 60–80 mesh Chromosorb W column, except **41** and **45**, which were sublimed for purification. None showed NH or CO bands in the ir, and all gave ^1H NMR spectra consistent with the structures given, which are presented in tabular form in Table VI. The empirical formulas of all were established by high resolution mass spectroscopy.

2-tert-Butyl-3-methyl-2,3-diazanorbornane (47).²⁷ To 1.0 g of 2,3-diazanorbornene (10.4 mmol) in 25 ml of dry THF cooled to –78

°C, 10 ml (12.66 mmol) of a 1.27 M solution of *tert*-butyllithium was added through a septum cap, and after 5 min 0.72 ml of methyl iodide was added by syringe. After the solution had stirred for 30 min, the solution was filtered, evaporated, and concentrated to give 1.5 g of crude **47** (86%), which was purified by VPC.

2,3-Dicarboethoxy-1,4-dimethyl-2,3-diazabicyclo[2.2.2]octane was prepared by catalytic hydrogenation of 3.14 g of crude 2,3-dicarboethoxy-1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-5-ene³³ in 50 ml of absolute ethanol over 350 mg of 10% Pd/C at atmospheric pressure. After filtration, concentration, and distillation, 2.42 g of the product was obtained as an oil, bp 145–155 °C (7 mm); NMR (CDCl_3) δ 4.14 (4 H, q), 1.57 (6 H, s), 1.5–2.3 (4 H, m), 1.25 (6 H, t).

1,2,3,4-Tetramethyl-2,3-diazabicyclo[2.2.2]octane (49) was prepared by addition of the above biscarbamate sample in 25 ml of ether to a stirred mixture of 2.08 g of LiAlH_4 in 100 ml of ether, stirring at ambient temperature for 15 h, and addition of 2 ml of H_2O , 2 ml of 15% NaOH, and 1 ml of H_2O . After filtration, drying (MgSO_4), and solvent removal, distillation gave 0.81 g of an oil, bp 50–60 °C (7 mm), found to be about 90% **49** by VPC.

1,6-Diazabicyclo[4.3.0]decane (51)³⁴ was prepared by refluxing 4.3 g (50 mmol) of hexahydropyridazine, 10.1 g (50 mmol) of 1,3-dibromopropane, 15.23 g (110 mmol) of K_2CO_3 , and 125 ml of ethanol under nitrogen for 17.5 h. Filtration and distillation gave **51** as an oil, 4.89 g (77%), bp 71–74 °C (33 mm).

Electrochemical Data. Cyclic voltammetry data was determined on a Princeton Applied Research 170 instrument. The acetonitrile was Burdick and Jackson “distilled in glass” spectrograde material, containing about 15 ppm water. The data collected were insensitive to added water at many times this concentration. Spectra were run at 5×10^{-5} to 8×10^{-4} M hydrazine concentration, with 0.1 M NaClO_4 (dried over P_2O_5) as supporting electrolyte at a scan rate of 50–60 mV/s. We have found that the lifetime and constancy of readings for SCE electrodes is greatly improved by minimizing the time they are in contact with acetonitrile, and in this work we frequently checked the accuracy of the electrodes used; we attribute the small differences in E° determined in this work from that of Hintz¹ principally to the greater care used in electrode treatment. The E° values reported are $(E_p^{\text{ox}} + E_p^{\text{red}})/2$ values, which are only strictly equal to E° when the peak separation is the theoretical 56 mV. We observed 65–85 mV ΔE_p values for the hydrazines studied here, and are convinced that we have essentially eliminated instrumental broadening, but cannot explain the larger than expected ΔE_p values. The deviations expected in $(E_p^{\text{ox}} + E_p^{\text{red}})/2$ from the true E° are smaller than our reproducibility of ± 10 mV.

Photoelectron Spectroscopy. The PES equipment used, and the data handling techniques, were identical with those of our earlier work.² Our reproducibility for IP_1 seems to be within ± 30 meV.

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Electroinitiated Friedel-Crafts Transalkylations in a Room-Temperature Molten-Salt Medium¹

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Abstract: The electrochemical oxidation of hexamethylbenzene has been studied in a room-temperature molten-salt system, namely a 67:33 mol % aluminum chloride/ethylpyridinium bromide melt and in a 50–50 by volume solution of the melt with benzene. Oxidation of hexamethylbenzene in the melt itself yielded a mixture of alkylated polyphenyl compounds and small amounts of alkylated diphenylmethanes. Preparative oxidations in the melt plus benzene yielded nearly 1 equiv each of pentamethylbenzene and diphenylmethane. The pentamethylbenzene could be oxidized further to yield tetramethylbenzene and more diphenylmethane. Coulometry, cyclic voltammetry, and ring-disk electrode studies were carried out to elucidate a mechanism for the reaction.

In recent years the organic electrochemical literature has been punctuated with reports of aluminum chloride/inorganic chloride molten-salt solvent systems.^{3–8} These investigations were concerned primarily with the stability of electrogenerated intermediates and their acid-base interaction with the solvent rather than electrosynthesis per se. We had hoped to exploit the aprotic, totally anhydrous nature, and variable acid-base properties of these media to do preparative organic electrochemistry. There are, however, two experimental problems associated with these molten salts which preclude their suitability for electrosynthesis: high (for organics) liquidus temperatures and rapid homogeneous reactions with organic substrates. These problems were noted in our study of the

chemical and electrochemical reactions of substituted adamantanes in $AlCl_3/NaCl$ melts.⁷ A recent review of organic reactions in aluminum chloride/inorganic chloride media testifies to the variety of homogeneous transformations undergone in binary and ternary melts at temperatures above 100 °C.⁹ Those compounds which are stable both to the molten salt and its liquidus temperature are, in general, marginally soluble.

Molten-salt systems fluid below 50 °C are not unknown. Half-wave potentials of several organic compounds have been measured in tetrahexylammonium benzoate at room temperature.¹⁰ Several tetraalkylammonium tetraalkylborides have been synthesized¹¹ and the spectroscopic properties of