Bredt's Rule Kinetically Stabilized Nitrogen-Centered Radical Cations and Radicals in the 9-Azabicyclo[3.3.1]nonyl System

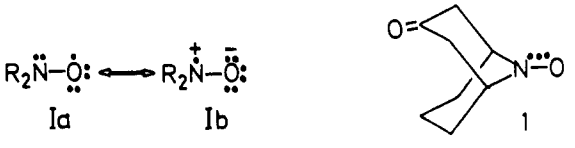
Stephen F. Nelsen,* Carl R. Kessel, and David J. Brien

Contribution from the Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.
Received May 14, 1979

Abstract: Derivatives of 9-azabicyclo[3.3.1]nonane (9-ABN) where the substituent at N_9 is CR_3, NR_2, OR, Cl, NMe_3^+, and carbonyl, and of doubly bonded immonium salts (9-ABN=Y)$^+$, where Y = CRR′, NR′, and O, were studied, along with 9-ABN-substituted *p*-phenylenediamine, 2-tetrazene, and 4-*tert*-butylaniline. 9-*tert*-Butyl-9-ABN is argued to be strongly pyramidal at N_9, and a methodology for estimating pyramidality at nitrogen of amines from PE data is described. Cyclic voltammetry data are reported for these compounds, many of which give stable enough one-electron oxidation or reduction products for $E^{\circ\prime}$ measurement, and PE data are given for the neutral compounds. The oxidized forms may be considered $R_2N^{+}\cdot$ groups stabilized by directly attached X: or Y· N_9 substituents. The relative electron transfer ΔG° values measured cover a range of 87 kcal/mol, depending on N_9 substituent. If σ_I is assumed to properly represent field effects of the substituents, these data allow estimation of the difference in resonance stabilization of the two-atom δ system for the oxidized and reduced forms (ΔRS). ΔRS values obtained (kcal/mol) include 4 (X = *t*-Bu), 8 (C_6H_4-*t*-Bu), 10–14 (OMe), 19 (NMe_2), ca. 20 (O·), ca. 42 (N·-*t*-Bu) and ca. 58 (CH-*t*-Bu). For the only case in which literature comparison is possible, tetraalkylhydrazine radical cations, the above estimate is in good agreement.

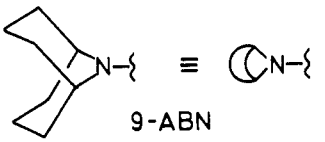
Introduction

For radical ions and radicals formed by electron-transfer reactions, it is particularly important to establish the formal potential, $E^{\circ\prime}$, because $E^{\circ\prime}$ is a thermodynamically significant measure of the ease of electron transfer in solution. The difference in $E^{\circ\prime}$ for two single electron transfer couples measured under the same conditions is the difference in ΔG° for the electron transfers. Cyclic voltammetry (CV) is a convenient method for obtaining $E^{\circ\prime}$ data,[1] but its use requires that the lifetimes of both the oxidized and reduced forms be longer than about 10 ms,[2] which is frequently not the case. Simple alkyl radicals dimerize or undergo hydrogen-atom transfer at near diffusion-controlled rate, although both reactions can be considerably slowed by steric effects.[3] Thermodynamic stabilization of a radical, as in allyl and benzyl radicals, does not provide long radical lifetimes. The combination reaction becomes considerably slower in heteroatomic systems where only weak bonds are formed in dimerization. An example particularly pertinent to this work is the intensively studied[4] nitroxide system I, in which the diamagnetic dimer is in equilibrium with

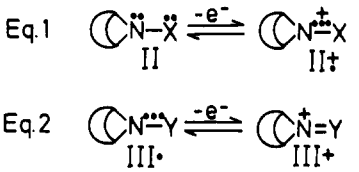


the monomeric form in solution. Nitroxides are delocalized species, as indicated in resonance forms Ia,b. We will employ the "three-electron π bond" notation used in structure **1** to represent such species with a single structure. Irreversible nitroxide disappearance is quite rapid if there is a sterically accessible hydrogen at carbon attached to nitrogen, as hydrogen-atom disproportionation to nitrone and hydroxylamine remains rapid (a second-order rate constant of greater than 10^3 mol/L·s for diethyl nitroxide; the reaction proceeds by rearrangement of the unstable dimer[5]). Dupeyre and Rassat[6] showed in 1966 that a Bredt's rule effect, requiring twist at the C=N bond of the nitrone disproportionation product, effectively eliminates rapid disproportionation, and renders norpseudopelletierine-*N*-oxyl **1** both long lived in solution and isolable (as the solid diamagnetic dimer).

In this work we employed Bredt's rule kinetic stabilization for species having electron-deficient p orbitals at trisubstituted nitrogen atoms to generate a variety of radical ions and radicals containing such an atom for which $E^{\circ\prime}$ data are measurable.[7] We have used the 9-azabicyclo[3.3.1]nonyl (9-ABN) group



(abbreviated as shown for convenience[8]) as a dialkylamino group which is not very different electronically from a dimethylamino group, but provides the kinetic stabilization necessary for $E^{\circ\prime}$ measurement. The examples studied may be divided into two series based upon charge of the paramagnetic form, as outlined in eq 1 (we studied X = CR_3, NR_2,



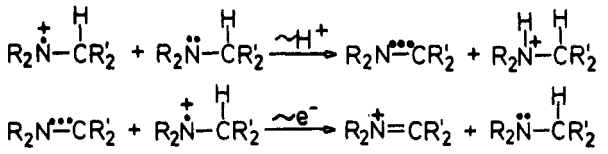
OMe, Cl, NMe_3^+) and 2 (Y = CRR″, NR, O). In simplest terms, $II^{+}\cdot$ is an amine radical cation stabilized by a neutral X· group, while III^+ is a Y· stabilized amine radical cation.

Preparation and Results

9-Alkyl-9-ABN Derivatives. We wrote eq 1 with a lone-pair-bearing heteroatom substituted at the ABN nitrogen, and a trialkylamine lacks a lone pair at X for stabilization of an odd electron at N in the radical cation. An alkylamine would not be depicted as three-electron π-bonded species $II^{+}\cdot$, but as having a half-occupied nitrogen p orbital, with the nitrogen bearing three alkyl groups. Nevertheless, an alkyl group is not as different electronically from a lone-pair-bearing heteroatom as such valence-bond structures would suggest. An alkyl group σ bond combination orbital of the proper symmetry and orientation for interaction with a p orbital exists, and provides hyperconjugative stabilization for an electron-deficient p or-

0002-7863/80/1502-0702$01.00/0

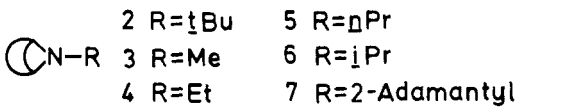
Scheme I



bital in a manner qualitatively similar to (although less effectively than) a heteroatom lone pair.[9]

Simple alkylamines give totally irreversible CV curves.[10] The problem is probably not combination; radical ion combination reactions are far less rapid than those for comparably substituted neutral radicals because of charge repulsion. Product studies have shown that immonium salt and protonated amine are formed, making the reaction observed a formal hydrogen atom transfer disproportionation. Because amine radical cations become long lived in strong enough acid,[10,11] it seems clear that the proton and electron are transferred sequentially, as outlined in Scheme I.

The *N*-alkyl ABN derivatives **2–7** were prepared by standard methods (see Experimental Section) and studied by CV.

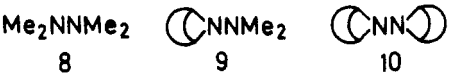


Deprotonation α to nitrogen is clearly the only problem in measuring trialkylamine $E^{\circ\prime}$ values, because **2** (lacking Bredt's rule unprotected α hydrogens) shows a completely reversible CV curve, even at low scan rates. Oxidation of **2** with tris(*p*-bromophenyl)amine cation hexafluoroantimonate gives solutions in which the ESR spectrum of $\mathbf{2}^{+\bullet}$ persists for over 1 h.[7b] In contrast, **3–7**, which have C_α–H bonds unprotected by the Bredt's rule effect, all gave totally irreversible CV curves, even at low temperature and fast scan rates (−60 °C, 20 V/s), indicating cation radical lifetimes under 10 ms. Even the steric hindrance provided by the 2-adamantyl group does not make deprotonation slow on the CV time scale.

We note that it is the deprotonation to form the three-electron π-bonded α-amino radical which is being kinetically destabilized in $\mathbf{2}^{+\bullet}$. ESR studies have shown that there is significantly more spin density at C than at N in unconstrained α-amino radicals[12] (using Fischer's method[13] for spin-density estimation gives about a quarter of the spin delocalized to N[14]). Twist about the N⋯C bond would be expected to be considerably less costly in energy than twisting about the $^{+}$N=C bond of a nitrone or an immonium salt; yet the deprotonation of $\mathbf{2}^{+\bullet}$ remains conveniently slow. The C_α–H bond lying in the nodal plane of the p orbital appears to effectively preclude interaction at the transition state.

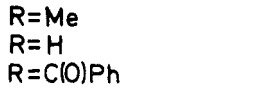
Photoelectron (PE) spectra of **2–7** provide a vapor-phase vertical measure of the case of electron removal from these compounds, for comparison with electrochemically derived adiabatic solution values. The IP_1 and CV data for **2–7** are summarized in Table I. As indicated, we found the peak potentials for the irreversible oxidations rather unreproducible. Although a careful enough electrode preparation sequence could presumably have been worked out to give reproducible data in a single sequence of experiments, this was not seriously attempted. Peak potentials are notoriously sensitive to electrode surface, and their position is thus influenced by kinetic factors which have little direct connection with compound structure.

N-Heteroatom Substituted 9-ABN Derivatives (II, II$^{+\bullet}$). Tetraalkylhydrazine radical cations do not require Bredt's rule C_α–H protection to show reversible CV curves. They typically last for hours in dilute solution.[15] In contrast, the second electron transfer to give the hydrazine dication (a dialkylated azo compound) is completely irreversible for CV for **8, 9,** and a host of other examples. Bredt's rule protection is successful



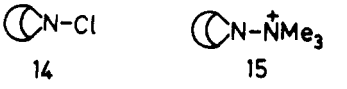
at kinetically stabilizing the dication, for the second oxidation wave for **10** is totally reversible even at slow scan rates, requiring a dication lifetime of seconds, even in the presence of excess neutral hydrazine. In contrast to unprotected compounds, $\mathbf{10}^{+\bullet}PF_6^-$ is isolable and indefinitely storable as the solid, which was shown by its magnetic moment to be completely paramagnetic;[7a] an X-ray crystal structure provided the final proof that the solid is $\mathbf{10}^{+\bullet}PF_6^-$.[16] We have not been able to obtain the NMR spectrum of $\mathbf{10}^{2+}$, despite several tries. Although rapid decoloration of $\mathbf{10}^{+\bullet}$ solutions occurs with NO_2PF_6, a complex and uncharacterized mixture of products is all that we have observed after oxidation at room temperature, and solubility difficulties have prevented our doing the oxidation at very low temperature.

We had a more difficult time preparing 9-alkoxy-9-ABN derivatives than we had hoped. We observed no 9-*tert*-butoxy-9-ABN formation from reactions in which either 9-ABN-9-yl, *tert*-butoxy or 9-ABN-oxyl, *tert*-butyl radical pairs were generated. We next turned to preparing the methoxy compound **11** by alkylation of hydroxylamine **12,** prepared by hydrolysis of the 9-ABN–benzoyl peroxide reaction[17] product **13.** Electron-transfer problems apparently prevent clean S_N2



reactions for hydroxylamine salts. Following the lead provided by Surzur and co-workers,[18] phase-transfer reaction of **12** using dimethyl sulfate as the methylating agent (following the conditions recommended for methyl ether formation[19]) gave **11.** Unfortunately, the $\mathbf{11}^{+\bullet}$ lifetime is so short that only irreversible CV curves were observed for **11.**

The *N*-chloro amine **14** shows reversible electrochemistry at platinum. We have used gold electrodes for most of this work because tetraalkylhydrazines are known to show significantly faster electron transfers at gold than at platinum or glassy carbon,[20] and we wanted to have as reversible CV curves as possible for more accurate measurement of $E^{\circ\prime}$. Both **14** and **15** have $E^{\circ\prime}$ values so high that the acetonitrile–gold electro-



chemistry near +1.5 V[21] interferes with the process of interest, requiring a switch to a platinum working electrode. Methylation of **9** gave $\mathbf{15}^{+\bullet}$, providing an ABN derivative with a really strong inductively electron withdrawing substituent. Although $\mathbf{15}^{2+\bullet}$ has a short lifetime, its rereduction wave was observed

Table I. CV and PE Data for *N*-Alkyl-ABN Derivatives

compd	IP_1, eV	E_p^{ox}, V[a]
2	7.30	rev[b]
3	7.84	0.76
4	7.76	0.77
5	7.71	0.71
6	7.68	0 68
7		0.77

[a] At 200 mV/s scan rate, in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, vs. SCE. [b] See Table II.

Table II. CV and PE Data for 9-Substituted 9-ABN Derivatives and Some Dimethylamine Analogues

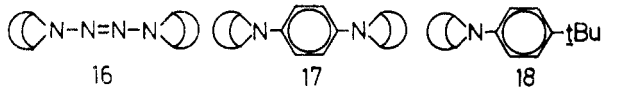
compd	$E_1^{\circ\prime}$ [a] (ΔE_{pp})[b]	$E_2^{\circ\prime}$ [a] (ΔE_{pp})[b]	IP, eV
2	0.63 (71)	unobsd	7.30
8	0.33 (86)	irrev	8.27, 8.81[c]
9	0.11 (62)	irrev	7.53, 8.42, 9.5-9.6
10	−0.01 (62)	1.18 (70)	6.94, 9.07
11	E_p^{ox} 0.73		7.79
14	1.49 (82)[d]	unobsd	8.55
15	2.0 (300)[d,e]	unobsd	
16	0.40 (72)	1.35 (91)	7.07, 8.54, 9.09
17	0.02 (68)	0.60 (78)	
18	0.65 (77)	irrev	6.94, 8.64, 9.23
19	0.46 (60)	irrev	7.71, 9.32, 9.80[c]
20	0.12 (65)	0.69 (64)	6.75[f]
21	0.72 (62)	irrev	7.72, 8.80, 9.55[g]
32	0.58 (92)[h]	unobsd	7.39, 9.45

[a] In V vs. SCE, in acetonitrile containing 0.1 M tetrabutylammonium perchlorate at a gold electrode. [b] $E_p^{ox} - E_p^{red}$ in mV at a 0.2 V/s scan rate. [c] From ref 15b. [d] As *a* but at a platinum electrode. [e] At a 5 V/s scan rate. [f] Nakato, Y.; Ozabii, M.; Egawa, A.; Tsubomura, H. *Chem. Phys. Lett.* **1971**, 615. [g] Determined by V. E. Peacock. [h] At a 0.05 V/s scan rate.

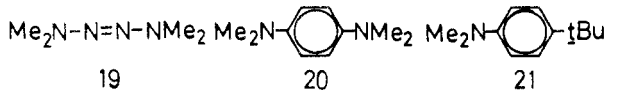
at rapid scan rates, allowing $E^{\circ\prime}$ to be estimated (with considerably less accuracy than for our other cases because of the rather large peak potential separation at the scan rates required).

In contrast to reversibility for the **14** and **15**$^+$ oxidations, 9-acyl-9-ABN derivatives exhibit totally irreversible oxidation waves at quite high potentials (the peak potential for 9-formyl-9-ABN was +2.06 at a 0.2 V/s scan rate). The decomposition pathways remain unknown, and thermodynamic data are not available from these results.

We also studied **16–18,** to provide quantitative comparison of 9-ABN-substituted compounds with dimethylamino-substituted compounds **19–21** for some systems in which Bredt's



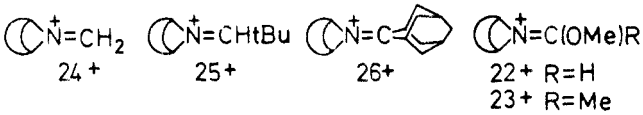
16 17 18



19 20 21

rule stabilization is not necessary for $E^{\circ\prime}$ determination. The second oxidation wave is reversible for **16,** and the Bredt's rule protection is necessary for this result, since **19** and other unprotected 2-tetrazenes have totally irreversible second oxidations. Both oxidations are reversible for **17** and **20.** The electrochemical and PE data for **16–21** are compared in Table II with those for the other compounds discussed in this section.

Immonium Derivatives (III•, III$^+$). The *C*-alkoxyimmonium salts **22**$^+$ and **23**$^+$ were prepared by alkylation of the corresponding amides. Neither showed any reversibility in its CV curves (see Table III), despite the Bredt's rule protection of the NC_α–H bonds. The carbon unsubstituted, monoalkyl, and dialkyl immonium salts **24–26** were prepared by a literature



24+ 25+ 26+ 22+ R=H 23+ R=Me

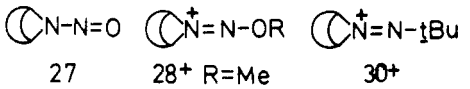
method.[22] Reduction of **24**$^+$ was electrochemically irreversible at all scan rates, which is not surprising because the α-amino radical **24**• is not sterically hindered and will probably dimerize at a nearly diffusion-controlled rate. In contrast, **25**$^+$ and **26**$^+$, which give more hindered α-amino radicals, both show reversible one-electron reduction CV curves, allowing $E^{\circ\prime}$ measurement.

Table III. Electrochemical Data for 9-ABN Immonium Salt Derivatives

Y	compd	$E^{\circ\prime}$ [a] (ΔE_{pp}[b])[SR[c]]	E_p^{red} [a] [SR[c]]
CHOMe	**22**$^+$	irrev	−1.87 [0.2]
OMeOMe	**23**$^+$	irrev	−1.93 [0.2]
=CH_2	**24**$^+$	irrev	−0.95 [0.5]
=CH-*t*-Bu	**25**$^+$	−1.54 (90) [5]	
2-adamantylidine	**26**$^+$	−1.77 (83) [0.2]	
=NOMe	**28**$^+$	−0.67 (87) [1.0]	
=NOEt	**29**$^+$	−0.69 (79) [1.0]	
=N-*t*-Bu	**30**$^+$	−0.63 (67) [0.2]	
=O	**37**$^+$	+0.58 (92) [0.05]	

[a] For a 2×10^{-3} M solution in acetonitrile containing 0.1 M *n*-Bu_4NClO_4; reported in V vs. SCE. [b] $E_p^{ox} - E_p^{red}$ in mV. [c] Scan rate in V/s.

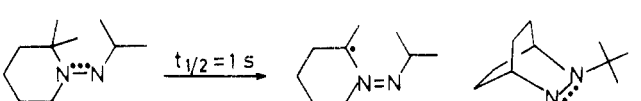
Nitrosamine **27** is a convenient starting material for III (Y = NR) salts. The 2-alkyoxy-1,1-dialkyldiazenium salts[23] **28**$^+$ and **29**$^+$ were prepared by alkylation of **27.** In contrast to the



27 28+ R=Me 29+ R=Et 30+

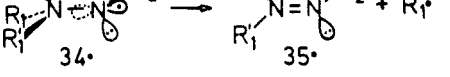
III (Y = CHOMe) case **23**$^+$, both **28**$^+$ and **29**$^+$ give radicals which are long lived enough to show partially reversible CV curves at scan rates of ca. 1 V/s (estimated radical lifetimes of 0.1–1 s), allowing measurement of $E^{\circ\prime}$. The ESR spectrum of **28•,** generated electrochemically in the ESR cavity, showed a broadened triplet of triplets for the two nitrogens (a(N) = 13.2, 10.2 G) with a g factor of 2.0042. The methyl splitting was not resolved. The unalkylated nitroso compound **27** showed only an irreversible reduction wave at $E_p^{red} = -2.64$ at a 0.2 V/s scan rate. No reduction wave was observed out to solvent breakdown at −2.8 V for 9-formyl-9-ABN.

Although *N*-nitroso compounds are well known to easily deprotonate α to nitrogen, the Bredt's rule effect clearly inhibits this process for **27.** The trialkyldiazenium salt **30**$^+$ $O_2CF_3^-$ was prepared conveniently by *tert*-butyllithium addition to **27,** followed by trifluoroacetic anhydride addition in 24% yield (44%, based on recovered nitrosamine). The CV of **30**$^+$ is completely reversible at a 10 mV/s scan rate, so the lifetime of **30•** is estimated to exceed 20 s, significantly longer than that of **31•,** found by Ingold and co-workers[24] to have a



31• 32• 33•

lifetime of about 1 s, and to give the products expected from the N, C cleavage product **32•.** They postulated that the much shorter lifetime for **31** than for Bredt's rule protected bicyclic hydrazyl **33•,** which persists for months,[26] was caused by the requirement for twisting about the N···N bond to allow overlap of odd electron density at N_2 with the N_1C_α bond (see **34•** → **35•**). Such twisting cannot occur for **33•.** This postulate

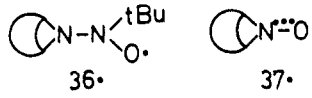


34• 35•

is also consistent with a longer lifetime for **30•,** in which great NN twisting is sterically inhibited, than for **31•,** in which twisting is sterically encouraged, and in which a tertiary alkyl

radical instead of a secondary one can be lost.

The ESR spectrum of **30•**, generated electrochemically or by reduction with sodium naphthalenide, differed from that of **28•** in that the two nitrogen splittings were not resolved (a(2N) = ca. 11.3 G), and the g factor was lower (2.0030). As with **33•** and related trialkylhydrazyl radicals, oxygen reacts rapidly with **30•**. If degassing of the sample is inadequate, reduction of 30^+ is observed to give a different radical with a higher g factor, showing only one nitrogen splitting of 18.2 G, which we attribute to the hydrazyloxy radical **36•** by analogy with previous work.[25]



36• **37•**

Nitroxide **37•** (III• (Y = O)) has been previously isolated,[6,26] and in this case the radical is the most easily handled form. The oxonium salt $37^+PF_6^-$ is easily generated by reaction of the nitroxide with nitrosyl hexafluorophosphate, but decomposes inconveniently rapidly in solution for purification, and we have not characterized it completely.

Discussion

Pyramidality at Nitrogen for 2. When the 9-ABN substituent is large, such as the *tert*-butyl group of **2**, the nitrogen will flatten to accommodate this large group, and this flattening causes rehybridization of the lone-pair electrons, affecting the properties of the nitrogen atom. Wiseman and co-workers[27] have noted that the ^{13}C NMR and UV spectra and basicity of the 3-keto analogue of **2** are noticeably affected compared to those for less bulky 9-alkyl substituents (the 3-keto analogues of **3–5**) and even suggested that the nitrogen might be flat. This is a very important point for us, since great rehybridization at the 9-ABN nitrogen of **2** would clearly cause problems in comparing its $E^{o\prime}$ value with those for 9-ABN derivatives with less bulky substituents. We suggest that the evidence for great flattening at nitrogen which Wiseman and co-workers cited is rather ambiguous. The large upfield shift that they observed for the methylene carbons would be minimized if the nitrogen flattened. The UV spectral effect of a higher energy charge transfer lone pair, σ conjugated C=O band could be caused either by nitrogen flattening or by ring flattening. The decreased basicity might be at least partially a solvation effect.

We believe that the amount of flattening at N in **2** compared with other 9-alkyl compounds can be profitably considered by comparison of their PE spectra. Since flattening at nitrogen is accompanied by an increase in the p character of the lone-pair orbital, IP_1 should be lowered by such flattening. IP_1 is also lowered by increasing the size of an alkyl group. The effect of changing alkyl group size on IP is quite regular, and can be quantitated by using the "inductive" parameter μ^* developed by Danby and co-workers,[28] which is based on IP values for alkyl halides and alcohols, where rehybridization does not accompany alkyl group homologation. A plot of IP_v vs. μ^* for **3–6** has a slope of 0.86 and a correlation coefficient of 0.999, establishing that the Danby relationship holds for this group of tertiary alkylamines. The *tert*-butyl compound **2** deviates 0.31 eV to lower IP_1 in the plot (Figure 1). We suggest that this IP_1 deviation allows an estimation of the amount of flattening at nitrogen which is present in **2**. The value of IP_1 for tripropylamine is 7.92 eV,[29] and tripropylamine probably has a very similar amount of flattening to that of trimethylamine, for which β has been determined to be 51.8° by electron diffraction and 51.0° by microwave spectroscopy.[31] β is the angle one CN bond makes with the plane of nitrogen and the other attached substituents. 1-Azamanxane (**38**)[32] provides a trialkylamine with alkyl groups of about the same size which is known to be almost completely flat at nitrogen from PE[33] and vapor-phase UV spectroscopy[34] studies. IP_1 for **38** is 7.05 eV,[29]

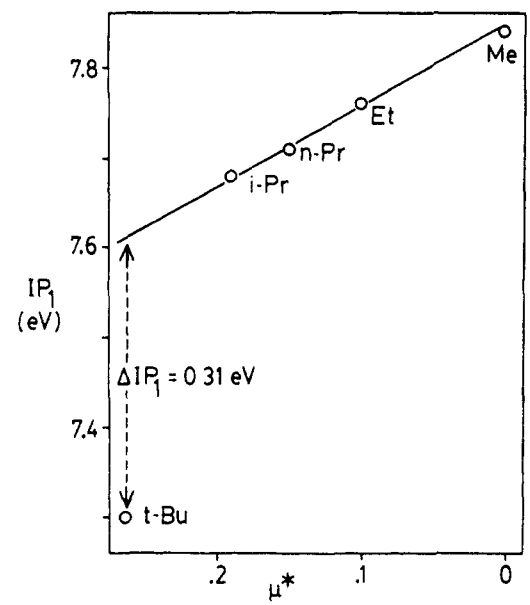
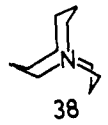


Figure 1. Plot of IP_1 vs. μ^* for 9-alkyl-9-ABN derivatives.



38

giving ΔIP_1 for going from a nearly tetrahedral to a nearly planar nitrogen of −0.87 eV.

To determine the expected shape of the IP_1 vs. β curve for a trialkylamine, we have employed MINDO/3 calculations[35] on trimethylamine. The methyl groups were idealized (d(C–H) = 1.119 Å, all angles tetrahedral), and IP_1 was calculated for six values of β ranging from 3 to 55°, allowing the methyl groups to rotate and the CN bond length to adjust to minimize the total energy at each point. The results of these calculations are presented graphically in Figure 2. It is seen that the major drop in IP_1 occurs in the first stages of flattening (decrease of β from a near-tetrahedral value). At β = 51.4° (the average of the experimental values[30,31]) the MINDO/3 IP_1 for Me_2N is calculated to be 8.66 eV, in good agreement with the experimental value of 8.53 eV.[29] Although ΔIP_1 (β = 51.4 → 0°) is calculated by MINDO/3 to be only 0.30 eV, far less than the experimental values quoted above, we will use the *shape* of the MINDO/3 curve in Figure 2 to estimate β for **2**. The experimental ΔIP_1 for **2** is 0.31 eV; so we take the flattening to be 0.31/0.87 or 36% of the way down the IP_1 scale of Figure 2, corresponding to a β of 45° for **2**. This value is admittedly only an estimate, but rather large ΔIP_1 value errors have a small effect on the estimated β. For instance, a 33% error in the pyramidal to flat αIP_1 estimate, using only 0.58 instead of the 0.87 eV observed, would cause only a 3° change in the β estimated. The amount of flattening at N is rather small, but the chemical consequences of this flattening on the barrier to nitrogen inversion, pK_a, and the like may well be large, in the same manner as predicted by MINDO/3 for ΔIP_1; chemical properties are probably far more linear with the fractional p character of the lone-pair orbital than they are with β (a plot of IP_1 vs. f_p has a very similar shape to that of IP_1 vs. β).

The result of little flattening for **2** does not seem particularly surprising to us, because a little flattening at nitrogen will start to relieve the 1,3-diaxial *tert*-butyl–H interaction and the 9-ABN six-membered rings are known[16] to be substantially flattened; so this interaction will be smaller than it would be

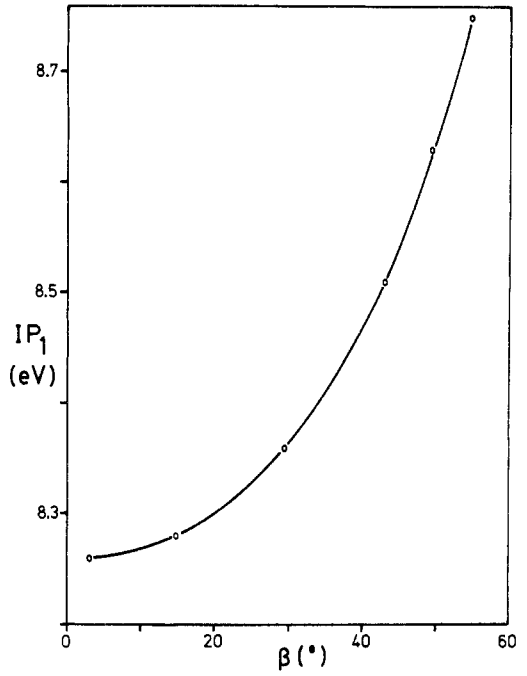


Figure 2. Plot of calculated IP_1 vs. β for trimethylamine, employing the MINDO/3 method.

in an ordinary piperidine ring. One might have hoped that DNMR studies of the barrier heights for nitrogen inversion would help determine the amount of steric interaction with the ring hydrogens, but this has not proven fruitful. Although the methyl compound **3** has a ^{13}C NMR barrier height of 8.1 kcal/mol at −90 °C, and 9-NH_2-9-ABN 9.1 at −90 °C,[36] accurate barriers have not been measured for other 9-ABN derivatives. Although broadening of the proper resonances for slowing down nitrogen inversion was detected for **4, 6,** and **9,** "frozen" spectra were not obtained,[37] making even these barriers unavailable.

Comparison of 9-ABN with Me_2N. Data are available (Table II) for direct 9-ABN for Me_2N substitution effects in 2-tetrazenes (**16** vs. **19**), *p*-phenylenediamines (**17** vs. **20**), *tert*-butylanilines (**18** vs. **21**), and hydrazines (**8, 9,** and **10**). In all cases substitution of the layer 9-ABN alkyl groups lowers both IP and $E^{\circ\prime}$. IP_1 is a vapor-phase measurement which is much more sensitive to alkyl group size change than is $E^{\circ\prime}$. Considerable study of tetraalkylhydrazine data led us to conclude that, in the absence of other effects, $\Delta E^{\circ\prime}/\Delta IP_1$ is experimentally about 0.15 for acetonitrile (it must be remembered that solvation differences affect $E^{\circ\prime}$, and solvation differences between 9-ABN and Me_2N are likely). The first three systems have the nitrogen conjugated with an unsaturation, and presumably will have the nitrogens somewhat flattened compared to amines or hydrazines. They show quite comparable behavior for the alkyl-group change: 2-tetrazenes, $\Delta E^{\circ\prime}$ (**19** − **16**) = 0.06 V, $\Delta E^{\circ\prime}/\Delta IP_1$ = 0.094; *p*-phenylenediamines, $\Delta E^{\circ\prime}$ (**20** − **17**) = 0.10 V, IP_1 not available for **17** because of volatility problems; anilines, $\Delta E^{\circ\prime}$ (**21** − **18**) = 0.07 (for a monosubstitution), $\Delta E^{\circ\prime}/\Delta IP_1$ = 0.090. The $E^{\circ\prime}$ change for the hydrazine examples is significantly larger, 0.22 V between **9** and **8** and 0.12 V between **10** and **9**. We attribute these larger $\Delta E^{\circ\prime}$ values in the hydrazines to larger strain differences in these compounds.[38]

The principal conclusion reached by comparing **8–10** and **16–21** is that changing Me_2N– for 9-ABN has a rather minor effect on $E^{\circ\prime}$, both because $E^{\circ\prime}$ is inherently less sensitive to alkyl-group change than is IP_1 and because there are opposing effects on $E^{\circ\prime}$ when the nitrogen flattens upon electron removal. Using 9-ABN instead of dimethylamino will not change

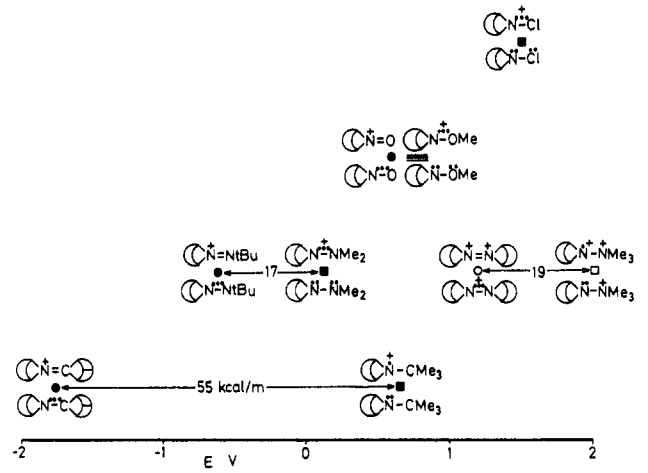


Figure 3. Display of $E^{\circ\prime}$ values for 9-ABN derivatives. Filled circles are II–$II^{+\cdot}$ examples, filled squares $III^{\cdot}$–III^{+} examples, and the open symbols +–2+ examples. The horizontal position is determined by $E^{\circ\prime}$, and the vertical one by the atom attached to N_9.

the $E^{\circ\prime}$ values observed very much, but does allow the $E^{\circ\prime}$ measurements to be made; kinetic stability problems preclude use of dimethylamino for most of the entries in Tables II and III.

Comparison of $E^{\circ\prime}$ Values. The $E^{\circ\prime}$ values of Tables II and III are relative free energy differences between the reduced and oxidized forms of 9-ABN with a variety of third substituents at nitrogen. They cover a range from −1.77 to +2.0 V, or 87 kcal/mol. Some examples are displayed in Figure 3, where the horizontal position shows the $E^{\circ\prime}$ value and the vertical position indicates the atom attached to N_9 (C, N, O, Cl). The filled circles are $III^{\cdot}$–III^{+} equilibria, which increase in $E^{\circ\prime}$ in the order C, NO, O, reflecting the electronegativity of the attached atom. The filled squares are II–$II^{+\cdot}$ equilibria, for which $E^{\circ\prime}$ does not change regularly with electronegativity. The difference in $E^{\circ\prime}$ between the II–$II^{+\cdot}$ and $III^{\cdot}$–III^{+} equilibria is quite dependent upon the N_9 substituent; 55 kcal/mol for C, 17 for N, and significantly less for 0 (where $E^{\circ\prime}$ has not been accurately measured for the II–$II^{+\cdot}$ example). We suggest that the principal reason for the less positive $E^{\circ\prime}$ value for 9-dimethylamino-9-ABN (**9**) than for 9-*tert*-butyl-9-ABN (**2**) is the greater resonance stabilization of $R_2N^{+\cdot}$ by a dimethylamino group than by a *tert*-butyl group. Although $E^{\circ\prime}$(**2**) − $E^{\circ\prime}$(**9**) = 0.52 V or 12.0 kcal/mol, we suggest that this energy difference is smaller than the difference in resonance stabilization, because this factor is not the only one affecting $E^{\circ\prime}$. The HOMO energy is clearly a significant factor in determining $E^{\circ\prime}$. PE spectroscopy provides a convenient experimental measure of the HOMO energy of the reduced form, because the first vertical ionization potential, IP_1, is a vapor-phase measure of the ease of removing an electron to give the cation of the same geometry as the neutral material. Because the IP_1 of **9** is somewhat higher than that of **2**, $E^{\circ\prime}$(**2**) − $E^{\circ\prime}$(**9**) will slightly underestimate the resonance stabilization difference. Another factor making $\Delta E^{\circ\prime}$ different from the stabilization difference is the difference in relaxation energy for these compounds. $E^{\circ\prime}$ is an adiabatic measurement, but IP_1 is a vertical one. More energy is released upon allowing the nitrogen to flatten upon electron removal for **2** than for **9**, because the larger *tert*-butyl group strains the neutral form of **2** more than that of **9** is strained, also causing $\Delta E^{\circ\prime}$ to be smaller than the stabilization difference.

Because a variable amount of resonance energy is present and affecting the IP_1 values in our series of compounds, we have used substituent constants to analyze our data. Physical organic chemists have correlated equilibrium and rate data with substituent constants ever since Hammett conceived this

Table IV

compd	substituent[a]	$E^{\circ\prime}$, V[b]	σ_I[c]	ΔRS, kcal/mol[d]
15$^+$	$-{}^+NMe_3$	2.0	0.86	[0][e]
14	-Cl	1.49	0.47	[0][e]
11	-OMe	(~0.75 ± 0.05)[f]	0.27-0.34	(~10-14)[f]
2	-*t*-Bu	0.63	−0.07	4
9	$-NMe_2$	0.11	+0.06	19
18	$-C_6H_4$-*t*-Bu	0.65	+0.10	8
25·	-ĊH-*t*-Bu	−1.54	[0.05-0.15][g]	57-60[g]
30·	-Ṅ-*t*-Bu	−0.63	[0.20-0.30][g]	41-44[g]
37·	-Ȯ	+0.59	[0.40-0.50][g]	19-22[g]

[a] The substituent on R_2N^+· in the oxidized form. [b] From Tables II and III. [c] A consistent set from the compilation of values by Exner, ref 43. [d] See text for an explanation. [e] Assumed to be zero; see text. [f] $E^{\circ\prime}$ not measured; an estimate from E_p^{ox} is employed. [g] Estimated; see text.

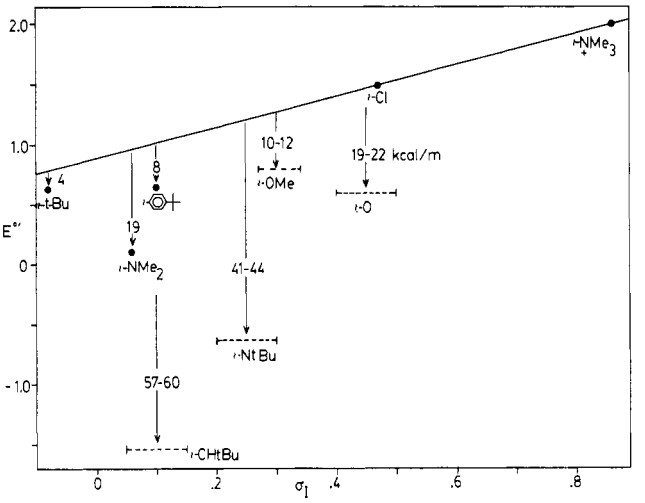
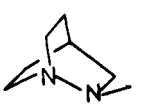


Figure 4. Plot of $E^{\circ\prime}$ vs. σ_I. The substituents attached to N_9 of 9-ABN are shown. The vertical deviations (kcal/mol) from a line through the points for **14** and **15** are also shown.

method of analysis.[40] The $E^{\circ\prime}$ values of 9-ABN derivatives are very sensitive to substituent, as expected. A plot of $E^{\circ\prime}$ vs. σ_p for Me_3N^+, Cl, *t*-Bu, and NMe_2 is a reasonably straight line ($r = 0.96$) and conversion to a log (K/K_0) basis for the vertical axis to the slope has the usual significance for a Hammett plot yields a ρ value of −16.9. It is clear, however, that Hammett σ values cannot be used for this series of compounds with any theoretical justification, because of the large resonance effect of having the substituent directly attached to a single charge bearing atom. A great deal of effort has gone into separating field (also called inductive) from resonance stabilization and steric effects.[41] We shall discuss such an analysis of these data by ignoring the steric differences that we are well aware are present in our compounds, suggesting that steric effects are minor in this series compared to field and resonance effects. There seems to be general agreement[42] that the σ_I parameter[41,43] is a reasonably good representation of the field effect for various substituents. One might therefore hope that a plot of $E^{\circ\prime}$ vs σ_I would give a straight line with a positive slope if resonance effects were unimportant, and that cases with significant resonance effects would show deviations from this line to less positive E°. $E^{\circ\prime}$ and σ_I values employed[43] appear in Table IV, and a plot of these data appears as Figure 4. The trimethylammonium substituent is that traditionally chosen as having no resonance stabilization in separations of field and resonance effects.[41,42,44] For lack of a better way to proceed, we shall also assume that the resonance stabilization of R_2N^+· by Cl is unimportant. There is a considerable electonegativity difference between N and Cl and a mismatch in orbital size, which we believe makes this a reasonable assumption; to the extent that it is not, all of the deviations discussed below should be increased proportionately. We therefore will consider vertical deviations from the line through the NMe_3^+ and Cl points in Figure 4 to be measures of resonance stabilization differences for R_2N^+· and R_2N: by the attached substituents. Values of this vertical deviation (kcal/mol) are called ΔRS, and are listed in Table IV. A value of 19 kcal/mol for the resonance stabilization difference in the hydrazine radical cation case seems quite reasonable to us. As pointed out from a different perspective at the beginning of the discussion, this resonance stabilization difference must be greater than 12 kcal/mol. The best previous estimate for this number comes from oxidation potential increases when hydrazine radical cations are forced to be twisted and hence lose resonance stabilization.[45] From E_p^{ox} for **39**, which has the cation radical so twisted that it is



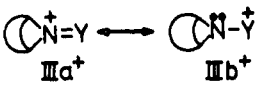
39

too short lived for $E^{\circ\prime}$ measurement, we estimated the resonance stabilization of a hydrazine radical cation to be above 15 kcal/mol, in excellent agreement with $\Delta RS(NMe_2)$ in Table IV. Although $E^{\circ\prime}$ was not accurately measured for the methoxy compound **11** because of the short lifetime of **11**$^+$·, it is probably positive of the observed E_p^{ox} value of 0.71, and 0.75 + 0.05 is a reasonable estimate. Literature σ_I estimates for OMe vary between 0.27 and 0.34,[43] yielding an estimate for ΔRS(OMe) in the range 10–14 kcal/mol. A smaller ΔRS(OMe) than $\Delta RS(NMe_2)$ is certainly to be expected because a hydroxylamine radical cation three electron δ bond should not be as resonance stabilized as the more symmetrical hydrazine radical cation case. We note that the $\Delta RS[R_2N^+{\cdot}X - R_2N{:}X]$ order given by this analysis, *t*-Bu < C_6H_4-*t*-Bu < OMe < NMe_2, is that expected.

Turning to III–III$^+$ equilibria it is interesting to compare the effects of methoxy for *tert*-butyl substitution again. In the hydrazyl radical–diazenium cation equilibrium, $E^{\circ\prime}$ is almost unaffected by this substitution: $E^{\circ\prime}$(**30**·–**30**$^+$) − $E^{\circ\prime}$(**28**·–**28**$^+$) = +0.04 V (0.6 kcal/mol). A significantly larger effect is seen for the α-amino radical–immonium cation equilibrium. $E^{\circ\prime}$ can only be estimated for the methoxy example there, but, if electron transfer remains rapid, as we expect, replacement of *tert*-butyl by methoxy makes electron removal significantly easier; $E^{\circ\prime}$(**25**·–**25**$^+$) − $E^{\circ\prime}$(**22**·–**22**$^+$) > 0.33 V (7.6 kcal/mol). Similarly, replacement of hydrogen by alkyl as a substituent on the α carbon of the immonium salt has a substantial effect on $E^{\circ\prime}$. $E^{\circ\prime}$ for the $=CH_2$ compound **24**$^+$ is probably somewhat negative of the −0.95 V E_p^{red} observed, but $E^{\circ\prime}$ for the dialkyl example **26**$^+$ is 0.23 V (5.3 kcal/mol) negative of the monoalkyl example **25**$^+$. A large substituent effect on $E^{\circ\prime}$ and E_p^{red} values for immonium salts has been previously reported by Andrieux and Savéant.[46] We note that the direction of the methoxy for *tert*-butyl replacement effect on $E^{\circ\prime}$ is the opposite for the amine examples **11** vs. **2**. A steric effect tending to lower $E^{\circ\prime}$(**2**) relative to $E^{\circ\prime}$(**11**) will contribute to this result, but so will the 0.49 eV lower IP_1 for **2** than for **11**. Because the inductive and resonance contributions for a methoxy substituent are opposite in sign and rather large, it is not trivial to predict the effect of methoxy for alkyl substitution on a given equilibrium.

It would be possible to fit III·–III$^+$ examples into the same framework as used for II–II$^+$· examples, if σ_I were known for radical substituents; **25**$^+$ may be formally considered to be $(R_2N{-})^+$· stabilized by [–CH-*t*-Bu]·, and so forth. We suggest that σ_I for the radical substituents may be estimated to a useful accuracy. Measured σ_I values are rather insensitive to alkyl

substitution (σ_I(Me) = 0.05; σ_I(*t*-Bu) = −0.07), but there is a definite positive increment in σ_I for rehybridization from sp^3 to sp^2 for the atom of attachment ($\sigma_I(C_6H_5)$ = +0.10; $\sigma_I(CHCH_2)$ = +0.06 to 0.09). Since a radical at carbon is effectively sp^2 hybridized (sweeping aside the *tert*-butyl radical controversy[47]) we shall employ σ_I([-CH-*t*-Bu]·) as 0.10 ± 0.05, and for similar reasons use σ_I([-N-*t*-Bu]·) as 0.25 ± 0.05 and σ_I([-O]·) as 0.45 ± 0.05. Use of these σ_I ranges gives estimates for RS([R_2N=CH-*t*-Bu]$^+$), RS([R_3N=N-*t*-Bu]$^+$), and RS([R_2N=O]$^+$) of about 58, 42, and 20 kcal/mol, respectively. It can be seen from Figure 4 that these ΔRS values are quite insensitive to the value of σ_I employed. They are principally determined by $\Delta E^{\circ\prime}$, and σ_i gives a relatively small correction. It is certainly reasonable that π stabilizations of R_2N^+=Y would decrease in this order, because resonance structure IIIb$^+$ is obviously less favorable relative to IIIa$^+$ as



IIIa$^+$ IIIb$^+$

Y becomes more electronegative. This analysis gave a 58 kcal/mol σ stabilization difference for a dialkylimmonium cation-α-amino radical pair. The rotational barrier in $(H_2N{=}CH_2)^+$ has been recently calculated to be 42 kcal/mol,[48] but we are unaware of experimental measurements. As shown above, substitution of alkyls for hydrogen at carbon substantially raises ΔRS in an immonium salt-α-amino radical electron transfer equilibrium.

We have obviously made several assumptions in estimating ΔRS from $E^{\circ\prime}$ data by employing σ_I. The major justification for this type of treatment is the plausible ΔRS([R_2NMR_2]$^+$·) value thus obtained. An important practical purpose of a theoretical analysis at any level of sophistication is to make testable predictions. Because one would need to break up the resonance stabilization represented by ΔRS for rotation about an axially disymmetric [$R_2N{\cdots}X$]$^+$ or [$R_2N{=}Y$]$^+$ bond, the true ΔRS should be close to the difference in rotational barriers for the oxidized and reduced forms. For the unsymmetrical substituents of Table IV, then, our admittedly crude analysis leads to the prediction of rotational barriers. These barriers are, in principle, measurable, although we are not aware that any of them have been determined yet. We suggest that our data provide a useful estimate of the magnitude of such barriers which should help in designing experiments to measure them, but judgment on the validity of the numbers obtained must wait experimental measurement of some of these barriers. We hope that a more sophisticated analysis of thermodynamic data like those presented here will be possible in the future.

Conclusions

The 9-ABN group results in remarkable kinetic stability for radicals and radical ions which contain it. Although its substitution for a dimethylamino group does not result in a large decrease in $E^{\circ\prime}$ for electron transfer in cases for which measurement can be made for both groups, $E^{\circ\prime}$ can be measured for a far wider range of 9-ABN-substituted compounds, and data are presented which cover a range of 87 kcal/mol. Although 9-*tert*-butyl-9-ABN is clearly strained and flattened at nitrogen relative to the 9-methyl compound, PE spectroscopy indicates that the nitrogen is substantially pyramidal. It is suggested that the fractional p character of the lone-pair orbital is an important determinant of amino nitrogen reactivity, and a methodology for estimating this for amines from PE measurements is given. Assuming that σ_I values have the significance Taft and others have attributed to them, the $E^{\circ\prime}$ values give differences in resonance stabilization for $R_2N{:}X$ and $R_2N^+{\cdot}X$. The order determined is that expected and the magnitude for the largest ΔRS substituent examined, $-NMe_2$, is consistent with previous estimates. Similar analysis of III·-III$^+$ equilibria gives ΔRS values for $R_2N{\cdots}Y$-($R_2N{=}Y$)$^+$ pairs. It is pointed out that ΔRS values may be interpreted as differences in activation energies for rotation (except for steric factors) in examples of proper symmetry.

Experimental Section

The preparations employed for **3, 10, 16,** and **27** have been reported previously,[16] as has that for **9**.[15a] ^{1}H NMR spectra were recorded on a JEOL JMN-MH-100 instrument, carbon spectra on a JEOL FX-60 instrument, IR spectra on a Perkin-Elmer 267 instrument, and mass spectra on an AEI MS-902 instrument. A page showing the 100-MHz ^{1}H NMR, IR, and low-resolution mass spectrum of each previously uncharacterized compound (no MS for the salts) is available in the Ph.D. Thesis of C.R.K.[49]

9-*tert*-Butyl-9-azabicyclo[3.3.1]nonane (2). A solution of 1.32 g of 85% KOH in 15 mL of di(ethylene glycol) was prepared by gentle heating. After cooling, 1.0 g (5.13 mmol) of the 3-keto compound (prepared by the method of Wiseman[27]) and 1.00 g (20 mmol) of hydrazine hydrate were heated to 140 °C in a Wood's metal bath for 1.2 h and then heated to 230 °C over 1 h, during which time a small amount of liquid distilled through a 4-in. Vigreux column and distillation head attached to the reaction flask. The mixture was heated at 230 °C for an additional 3 h and cooled to room temperature, and 20 mL of water was added to the combined distillate and reaction mixture. After extraction with three 20-mL portions of ether, the combined organic layers were washed with 20 mL of water, dried over $MgSO_4$, and concentrated to 0.65 g (70%) of **5** as a crude yellow oil. Purification by preparative VPC (15% XF-1150 on Chromosorb W) gave **5** as a clear liquid:[30] ^{1}H NMR ($CDCl_3$) δ 3.29 (m, 2 H), 1.4-2.2 (m, 12 H), 1.15 (s, 9 H); IR (CCl_4) no NH or C=O.

9-Ethyl-9-azabicyclo[3.3.1]nonane (4). Ethyl fluorosulfonate (0.80 g, 6.2 mmol) was added via syringe to a stirred 0 °C solution of 0.78 g (6.2 mmol) of freshly sublimed anhydrous 9-azabicyclo[3.3.1]-nonane[16] in 10 mL of methylene chloride. After 1 h at 0 °C, the solution was allowed to warm to room temperature as it stirred for 12 h. After concentration, dissolution of the residue in 50 mL of water, basicification with NaOH pellets, and extraction with 3 × 25 mL of ether, the combined organic layers were dried ($MgSO_4$) and concentrated to a yellowish oil (>95% **2** by NMR), 0.84 g (89%):[50] ^{1}H NMR ($CDCl_3$) δ 2.80 (br s, 2 H), 2.70 (q, J = 7 Hz, 2 H), 2.2-1.2 (m, 12 H), 1.04 (t, J = 7 Hz, 3 H); IR (CCl_4) no NH.

9-Propyl-9-azabicyclo[3.3.1]nonane (5). The reductive alkylation procedure of Borch[51] was employed. A mixture of 0.82 g (5.1 mmol) of 9-azabicyclo[3.3.1]nonane hydrochloride,[16] 15 mL of methanol, 0.11 g (1.7 mmol) of 85% KOH pellets, and 2.35 g (40.5 mmol) of propionaldehyde was stirred while a solution of 0.74 g (11.8 mmol) of $NaBH_3CN$ in methanol was added over 10 min. After 15 min, 4 drops of glacial acetic acid was added, and the mixture was stirred for 72 h at ambient temperature. After acidifying with concentrated HCl, removal of solvent, dissolution in 30 mL of H_2O, and washing with 2 × 25 mL of ether, the solution was made basic with NaOH pellets and extracted with 3 × 25 mL of ether. Drying ($MgSO_4$) and concentration gave an oil: bp (15 mm) 98-100 °C; 494 g (58%);[50] ^{1}H NMR ($CDCl_3$) δ 2.82 (br s, 2 H), 2.62 (m, 2 H), 2.2-1.2 (m, 12 H), 0.90 (m, 5 H); IR (CCl_4) no NH.

9-Isopropyl-9-azabicyclo[3.3.1]nonane (6). The reductive alkylation procedure of Borch[51] was employed, as for **5**, 1.01 g of 9-azabicyclo[3.3.1]nonane hydrochloride giving 0.71 g (68%) of **4** as a clear oil:[50] ^{1}H NMR ($CDCl_3$) δ 3.10 (m, 3 H), 1.3-2.2 (m, 12 H), 1.05 (d, J = 7 Hz, 6 H); IR (CCl_4) no NH or C=O.

2-Adamantamine. The reductive alkylation procedure of Borch et al.[51] on 3.76 g (25.1 mmol) of 2-adamantanone gave 2.62 g (69%) of 2-adamantamine[50] as a white solid.

9-(2-Adamantyl)-9-azabicyclo[3.3.1]nonan-3-one. A mixture of cycloocta-2,7-dienone[52] (1.5 g, 12.3 mmol), 2-adamantamine (1.86 g, 12.3 mmol), and methanol (11 mL) was stirred at room temperature for 5 days. Filtration, concentration, and trituration of the residue with methanol gave 1.87 g of a white solid, mp 133.5-135 °C.[50] An additional 0.36 g was obtained from the residual methanol upon cooling to −78 °C (total yield 2.23 g, 66%): ^{1}H NMR ($CDCl_3$) δ 3.59 (m, 2 H), 2.85 (br s, 1 H), 2.57 (d of d, J = 7, 15 Hz, 2 H), 2.26 (br s, 1 H), 1.4-2.6 (m, 21 H); IR (CCl_4) no NH, 1700 cm^{-1} (C=O).

9-(2-Adamantyl)-9-azabicyclo[3.3.1]nonane (7). Wolff-Kishner reduction of 2.12 g (7.77 mmol) of the ketone gave 1.86 g (92%) of the product as a white solid: mp 126.5-130 °C;[50] ^{1}H NMR ($CDCl_3$) δ 3.00 (m, 3 H), 1.2-2.2 (m, 26 H); IR (CCl_4) no NH or C=O.

9-Hydroxy-9-azabicyclo[3.3.1]nonane (12) was prepared by the method of Gambarjan[17a] as modified by Denny.[17b] A solution of 9-ABN (2.25 g, 18 mmol) in 10 mL of ether was added to 3.88 g (16 mmol) of benzoyl peroxide in 50 mL of refluxing ether. After 36 h of reflux, the mixture was cooled to room temperature and stirred for 12 h. After filtration of the precipitated benzoic acid, the filtrate was dried over $MgSO_4$ and concentrated to a white solid (crude **13**). The solid was dissolved in 10 mL of ether and added to a sodium ethoxide solution prepared from 0.8 g of sodium and 40 mL of absolute ethanol over 0.5 h, and the pink, gelatinous mixture allowed to stand for 24 h, when 70 mL of water was added. The aqueous layer was extracted with 3 × 50 mL of ether and the extracts were combined with the organic layer and dried over $MgSO_4$. Concentration and recrystallization from acetonitrile gave 0.81 g (36%) of **12** as white needles: mp 154–157 °C;[50] ^{1}H NMR ($CDCl_3$) δ 7.6–8.7 (br, 1 H), 3.20 (br s, 2 H), 2.1–2.6 (m, 2 H), 1.1–2.1 (m, 10 H); IR 3000–3400 cm^{-1} (OH).

9-Methoxy-9-azabicyclo[3.3.1]nonane (11). A mixture of 2 mL of 50% aqueous NaOH, 11 mg of tetra-*n*-butylammonium iodide, 0.402 g (2.85 mmol) of hydroxylamine **12**, and 5 mL of ether was stirred vigorously for 30 min, and 0.38 mL (4.0 mmol) of dimethyl sulfate was added dropwise by syringe. After the mixture was stirred vigorously for 6 h, water was added to dissolve the solids formed and the aqueous layer was extracted with 5 × 5 mL of ether. The combined organic layers were dried over Na_2SO_4, solvent was removed by distillation through a short Vigreux column, and the last traces of ether were removed under reduced pressure to give a yellow, semisolid residue (0.11 g, 26%). Purification by VPC (15% XF-1150 on Chromosorb W 60/80) gave a white solid: mp 53.5–55 °C;[50] ^{1}H NMR ($CDCl_3$) δ 2.76 (br s, 2 H), 2.53 (s, 3 H), 1.8–2.2 (m, 6 H), 1.4–1.7 (m, 6 H); IR no NH or CH.

9-Trimethylammonium-9-azabicyclo[3.3.1]nonane Tetrafluoroborate ($15^+BF_4^-$). Trimethyloxonium fluoroborate (0.24 g, 1.62 mmol) was added to 0.268 g (1.60 mmol) of 9-dimethylamino-9-ABN (**14**) in 3 mL of methylene chloride. After the mixture was stirred for 18 h, concentration gave a pink solid. Slow addition of ethyl acetate to a hot acetone solution caused very thin, colorless flakes of $15^+BF_4^-$ to precipitate; mp 223–224 °C[53] dec; ^{1}H NMR (acetone-d_6) δ 4.22 (br s, 2 H), 3.64 (s, 9 H), 1.6–2.4 (m, 12 H); IR no NH.

1,4-Bis(3′-keto-9′azabicyclo[3.3.1]non-9′-yl)benzene. A mixture of 1.0 g of cycloocta-2,7-dienone, 0.45 g of *p*-phenylenediamine, and 25 mL of methanol was stirred under nitrogen for 5 days. Concentration gave 0.90 g of a solid which was crystallized from acetone to give 0.50 g (30%) of the bis adduct as pink plates: mp 264–265 °C;[52] NMR ($CDCl_3$) δ 7.0 (s, 4 H), 4.4 (br s, 4 H), 1.5–2.8 (m, 20 H); IR (Nujol mull) cm^{-1} 1695 (C=O), 1510, 1450, 825.

1,4-Bis(9′-azabicyclo[3.3.1]non-9′-yl)benzene (17). Reduction of 1.53 g (4.3 mmol) of the above diketo compound using 13 mL of di(ethylene glycol), 1.15 g (17 mmol) of 85% KOH, and 0.87 g (17.4 mmol) of hydrazine hydrate using the procedure employed for **2** gave 0.84 g (60%) of **17** as a white solid: mp 96–97.5 °C;[50] NMR ($CDCl_3$) δ 3.8 (s, 4 H), 3.4 (s, 4 H), 1.9–2.0 (m, 12 H), 1.4 (m, 12 H); IR (Nujol mull) cm^{-1} 1510, 1460, 1370, 825.

9-(4-*tert*-Butylphenyl)-9-azabicyclo[3.3.1]nonan-3-one. *p-tert*-Butylaniline (2.44 g, 16.3 mmol) was added to a solution of 2.0 g (16.4 mmol) of 1,7-cyclooctadienone in 50 mL of methanol, and solvent was removed under reduced pressure after 70 h. The solid residue was recrystallized from methanol to give the bis Michael adduct as a white solid (2.4 g, 54%): mp 126.5–127 °C;[50] ^{1}H NMR ($CDCl_3$) δ 7.36, 6.92 (AA′BB′, 4 H), 4.44 (br s, 2 H), 2.70 (d of d, J = 7, 16 Hz, 2 H), 2.36 (d, J = 16 Hz, 2 H), 1.3–2.0 (m, 6 H), 1.32 (s, 9 H); IR 1704 cm^{-1} (CO), no NH.

9-(4-*tert*-Butylphenyl)-9-azabicyclo[3.3.1]nonane (18). Wolff-Kishner reduction of 1.0 g (3.69 mmol) of the 3-keto compound with 2.0 g (40 mmol) of hydrazine hydrate, 2.3 g of 85% KOH, and 25 mL of di(ethylene glycol) gave a 60% yield of **18** after crystallization from methanol: mp 115–116 °C;[50] ^{1}H NMR ($CDCl_3$) δ 7.30, 6.84 (AA′BB′, 4 H), 4.04 (br s, 2 H), 1.5–2.3 (m, 12 H), 1.39 (s, 9 H); IR no NH or CO.

9-Formyl-9-azabicyclo[3.3.1]nonane. A mixture of freshly distilled acetic anhydride (20 mL, 0.21 mol) and 97% formic acid (10 mL, 0.26 mol) was cooled in an ice-salt bath and stirred for 20 min. Anhydrous 9-ABN (0.90 g, 7.2 mmol) was added in small portions, and the solution allowed to warm to room temperature. After 48 h, the mixture was neutralized with NaOH and extracted with 3 × 50 mL of chloroform, and the organic layers were washed with 2 × 25 mL of 10% Na_2CO_3, dried over $MgSO_4$, and concentrated to 0.946 g (86%) of a yellowish oil. Distillation (bp 87 °C, 0.7 mm) gave a white solid: mp 47–54 °C;[54] ^{1}H NMR ($CDCl_3$) δ 8.15 (br s, 1 H), 4.56 (br s, 1 H), 3.72 (br s, 1 H), 1.4–2.4 (m, 12 H); IR 1680 cm^{-1} (CO), no NH.

***O*-Methyl-9-formyl-9-azabicyclo[3.3.1]nonanium Tetrafluoroborate ($22^+BF_4^-$).** Trimethyloxonium tetrafluoroborate (0.175 g, 1.18 mmol) was added to 0.181 g (1.18 mmol) of 9-formyl-9-ABN in 5 mL of CH_2Cl_2. After 5 h of stirring at room temperature, concentration and recrystallization from ethyl acetate gave $22^+BF_4^-$ as a white solid (0.22 g, 73%): mp 173–175 °C;[53] ^{1}H NMR ($CDCl_3$) δ 8.57 (s, 1 H), 4.55 (br s, 1 H), 4.45 (s, 3 H), 4.32 (br s, 1 H), 1.4–2.4 (m, 12 H); IR ($CDCl_3$) 1695 cm^{-1} ($^+$N=C).

***O*-Methyl-9-acetyl-9-azabicyclo[3.3.1]nonanium Fluorosulfonate ($23^+FSO_3^-$).** Crude 9-acetyl-9-azabicyclo[3.3.1]nonane was prepared by adding 1.2 g (15 mmol) of acetyl chloride to a solution of 1.40 g (8.67 mmol) of the amine hydrochloride in 25 mL of pyridine, stirring for 18 h, and pouring the red-brown solution into 50 mL of H_2O. The solution was extracted with 3 × 50 mL of CH_2Cl_2, dried over Na_2SO_4, and concentrated. Elution from an alumina column gave a yellow oil: ^{1}H NMR ($CDCl_3$) δ 4.76 (br s, 1 H), 3.92 (br s, 1 H), 2.06 (s, 3 H), 2.1–1.2 (m, 12 H). This oil was methylated by stirring with 1 equiv of methyl fluorosulfonate in CH_2Cl_2 (1 h at 0 °C; 2 h at room temperature). Solvent removal and precipitation from $CHCl_3$ with Et_2O gave a white powder, 0.60 g (72%). Recrystallization from acetone-ethyl acetate gave $22^+FSO_3^-$: mp 210–212 °C;[53] ^{1}H NMR ($CDCl_3$) δ 4.68 (br s, 1 H), 4.26 (br s, 1 H), 4.18 (s, 3 H), 2.57 (s, 3 H), 1.5–2.2 (m, 12 H); IR 1640 cm^{-1} ($^+$N=C).

9-Methyl-9-azabicyclo[3.3.1]nonane *N*-Oxide. Following the general procedure of Craig,[54] a solution of 85% *m*-chloroperbenzoic acid (1.48 g, 7.29 mmol) in 30 mL of $CHCl_3$ was added to a solution of **3** (1.01 g, 7.27 mmol) in 5 mL of chloroform at 0 °C. After stirring at room temperature for 4 h, removal of solvent gave a white solid residue, which was taken up in $CHCl_3$ and chromatographed on a 40 × 2 cm column of basic alumina. Elution with $CHCl_3$ gave a small amount of amine, and 3:1 $CHCl_3$–MeOH gave an extremely hygroscopic white solid, recrystallized from acetone–hexane to give white needles of the *N*-oxide hydrate, mp 71–72 °C. Drying under vacuum over 36 h at 70 °C gave 0.73 g (65%) of the anhydrous *N*-oxide: mp 214–216 °C dec;[50] ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 3 H), 2.9–3.4 (m, 4 H), 1.4–2.5 (m, 12 H); IR ($CHCl_3$) 1435 cm^{-1} (N→O).

9-Methylene-9-azabicyclo[3.3.1]nonanium Tetrafluoroborate ($24^+BF_4^-$). The general procedure of Potier[22] was employed. Trifluoroacetic anhydride (0.46 mL, 3.26 mmol) was added slowly to a 0 °C solution of the *N*-oxide (0.50 g, 3.23 mmol) in 25 mL of CH_2Cl_2. The colorless solution was allowed to warm to room temperature, and solvent removed, giving 1.08 g of a yellow oil containing a 4:1 mixture of immonium salt and amine trifluoroacetic acid salt, to which was slowly added 0.478 g (2.95 mmol) of HBF_4·Et_2O. After addition of 2 mL of ether and stirring of the suspension for 15 min, filtration gave 0.44 g of white solid. Two recrystallizations from benzene–$CHCl_3$ gave $12^+BF_4^-$ as colorless needles: mp 254 °C[52] dec; ^{1}H NMR ($CDCl_3$) δ 8.04 (s, 2 H), 4.52 (m, 2 H), 1.4–2.6 (m, 12 H); IR (Nujol) cm^{-1} 3160 (vinyl H), 1680 ($^+$N=C).

9-Neopentyl-9-azabicyclo[3.3.1]nonane. The 3-keto compound was prepared by adding 3.11 g (35.7 mmol) of neopentylamine to 4.36 g (35.7 mmol) of cycloocta-2,7-dienone[52] in 15 mL of methanol. After the mixture was stirred at room temperature for 3 days, concentration followed by sublimation gave the crude ketone as an oily, yellow solid (5.54 g, 74%): ^{1}H NMR ($CDCl_3$) δ 3.19 (br s, 2 H), 2.64 (d of d, J = 15, 6 Hz), 2.32 (s, 2 H), 2.18 (d, J = 15 Hz, 2 H), 2.1–1.3 (m, 6 H), 0.91 (s, 9 H). A mixture of 5.0 g (23.9 mmol) of this crude ketone, 75 mL of di(ethylene glycol), 6.83 g of 85% KOH, and 5.07 g (101 mmol) of hydrazine hydrate was heated to 140 °C for 1 h in a 250-mL flask equipped with a 4-in. Vigreux column and a distillation head. The temperature was raised to 235 °C over 1.5 h and held at 235 °C for 5 h. After cooling, the mixture was poured into 100 mL of H_2O and extracted with 4 × 75 mL of pentane, and the combined organic layer was dried and concentrated to a yellowish oil (4.55 g, 98%) in which no impurities were observed by NMR:[50] ^{1}H NMR ($CDCl_3$) δ 2.60 (br s, 2 H), 2.23 (s, 2 H), 2.1–1.2 (m, 12 H), 0.82 (s, 9 H).

9-Neopentyl-9-azabicyclo[3.3.1]nonane *N*-Oxide. Preparation just as for the *N*-methyl compound starting with 4.0 g (20.5 mmol) of the neopentylamine gave the anhydrous *N*-oxide as an oil, 3.68 g (87%):[50] ^{1}H NMR ($CDCl_3$) δ 3.46 (br s, 2 H), 3.26 (s, 2 H), 3.2–2.8 (m, 2 H), 2.4–1.0 (m, 10 H), 1.26 (s, 9 H).

9-Neopentylidine-9-azabicyclo[3.3.1]nonanium Tetrafluoroborate

($25^+BF_4^-$). Trifluoroacetic anhydride (2.39 g, 11.3 mmol) was added slowly to 2.38 g (11.3 mmol) of the *N*-oxide in 15 mL of CH_2Cl_2. After the mixture was stirred for 1.5 h, 2.42 g (11.5 mmol) of HBF_4·Et_2O was added in one portion, the mixture was stirred for 1 h, and the solvent was removed. Crystallization from ethyl acetate gave (in low recovery) 0.62 g (20%) of $13^+BF_4^-$ as white plates:[53] ^1H NMR ($CDCl_3$) δ 8.56 (s, 1 H), 4.76 (br s, 1 H), 4.42 (br s, 1 H), 2.6–1.4 (m, 12 H), 1.48 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 180.8, 63.9, 53.9, 33.3, 28.8, 28.4, 24.8, 15.5.

9-(2-Adamantyl)-9-azabicyclo[3.3.1]nonane *N*-Oxide. This was prepared just as for the *N*-methyl compound from 0.70 g (2.7 mmol) of **7**, giving 0.16 g of recovered amine and 0.54 g of nonhygroscopic *N*-oxide (94% based on recovered starting material) after chromatography: mp 181–183 °C;[50] ^1H NMR ($CDCl_3$) δ 3.85 (br s, 3 H), 2.8–3.3 (m, 4 H), 2.44 (br s, 2 H), 1.4–2.4 (m, 20 H); IR (CCl_4) 1450 cm^{-1} (N → O).

9-Adamantylidine-9-azabicyclo[3.3.1]nonanium Tetrafluoroborate ($26^+BF_4^-$). Preparation was as for $13^+BF_4^-$, starting with 0.47 g (1.7 mmol) of the *N*-oxide. After solvent removal, NMR indicated the crude solid to be a 55:45 mixture of $14^+BF_4^-$ and amine fluoroboric acid salt. The immonium salt was separated by fractional crystallization from MeOH–Et_2O: mp >330 °C[53] dec; ^1H NMR ($CDCl_3$) δ 3.64 (br s, 2 H), 1.6–2.5 (m, 26 H).

***O*-Methyl-9-nitroso-9-azabicyclo[3.3.1]nonanium Fluorosultonate** ($28^+FSO_3^-$). Freshly distilled methyl fluorosulfonate (0.89 g, 7.8 mmol) in 5 mL of methylene chloride was added to 1.2 g (7.8 mmol) of **7** in 10 mL of methylene chloride at 0 °C. After the mixture was stirred for 10 min and warmed to room temperature, solvent removal gave 2.54 g of crude yellow solid. Recrystallization from $CHCl_3$–benzene gave 1.42 g (68%) of $8^+FSO_3^-$: mp 154–155 °C; ^1H NMR ($CDCl_3$) δ 5.54 (m, 1 H), 4.90 (s, 3 H), 4.50 (m, 1 H), 2.4 and 1.8 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 1.89 (t), 31.5 (t), 32.7 (t), 59.6 (d), 65.6 (d), 70.0 (q); IR ($CHCl_3$) cm^{-1} 1290 (N=N), 1070 (SO_2).

***O*-Ethyl-9-nitroso-9-azabicyclo[3.3.1]nonanium fluorosulfonate** ($29^+FSO_3^-$) was prepared similarly to the methyl salt, using ethyl fluorosulfonate. Drying the crude solid under high vacuum gave a white solid, mp 125–135 °C. We did not succeed in recrystallizing this material, which was characterized only by its NMR spectrum: ^1H NMR ($CDCl_3$) δ 5.52 (br s, 1 H), 5.24 (q, J = 7 Hz, 2 H), 4.88 (br s, 1 H), 2.8–1.8 (m, 12 H), 1.64 (t, J = 7 Hz, 3 H).

1,1-(1,5-Cyclooctyl)-2-*tert*-butyldiazenium Trifluoroacetate ($30^+CF_3CO_2^-$). A solution of *tert*-butyllithium (7.4 mL, 13 mmol of 1.75 M solution in pentane) was added over a 10-min period to 2.0 g (13 mmol) of nitrosamine **27** in 100 mL of anhydrous THF at 0 °C. The red solution was stirred for 30 min at 0 °C, 1.94 mL (13 mmol) of trifluoroacetic anhydride was added via syringe, and the orange solution was stirred at 0 °C for 6 h. The residue after solvent removal was triturated with 125 mL of ethyl acetate and filtered. Concentration of the filtrate gave a red, oily residue which was precipitated by addition of 50 mL of ether. Filtration gave $30^+CF_3CO_2^-$ as a tan solid (0.96 g, 24%), which was recrystallized from ethyl acetate–ether to give white plates, mp 160.0–160.5 °C.[53] Chromatography of the filtrate on a 35 × 2.5 cm column of alumina (chloroform elution) gave 0.923 g (46%) of recovered nitrosamine: ^1H NMR ($CDCl_3$) δ 5.69 (br s, 1 H), 4.70 (br s, 1 H), 2.0–2.8 (m, 12 H), 1.76 (s, 9 H); ^{13}C NMR (CD_3CN, Me_4Si) δ 80.2 (d), 73.0 (d), 71.8 (s), 35.1 (t), 34.8 (t), 27.9 (q), 19.0 (t).

9-Oxyl-9-azabicyclo[3.3.1]nonane (37·) was prepared by chloroperbenzoic acid oxidation of the amine in ether,[26] giving a red oil having the ESR spectrum of **6**.[55]

9-Oxo-9-azabicyclo[3.3.1]nonanium hexafluorophosphate ($37^+PF_6^-$) was prepared by adding an equimolar amount of $NO^+PF_6^-$ to a solution of 0.145 g (1.04 mmol of **6**·) in 5 mL of methylene chloride. The color changed from red to yellow over a 10-min period, and gas was evolved. After stirring at 25 °C for 1.5 h, the solution was concentrated to about half its volume and cooled to −15 °C, and 5 mL of hexane was added, giving 0.187 g (63%) of a solid believed to be 6^+PF_6. Solutions in $CDCl_3$ decompose with gas evolution. We did not succeed in purifying this material, or the tetrafluoroborate salt, prepared similarly using $NO^+PF_6^-$.

Electrochemistry. All cyclic voltammetry was run at ambient temperature (22 ± 1 °C) at 2 × 10^{-3} M concentration of substrate in Burdick and Jackson "distilled in glass" acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (Eastman, recrystallized from 1:1 H_2O–EtOH and dried in vacuo). The gold electrode employed was constructed from a 3.0-mm gold rod force fit into a Teflon support tube and mounted coaxially in the cell. Final polishing used aqueous suspensions of Fischer polishing alumina (3, 1, and 0.1 μm in that order) on a polishing cloth mounted on a polishing wheel. A freshly polished electrode was used directly in most cases. For the methyl-substituted hydrazines **8** and **9**, however, large peak-to-peak CV separations were found, and additional pretreatment was employed. The polished electrode was soaked for 60 s in chromic acid and 60 s in hot concentrated HCl and thoroughly rinsed with distilled water. This pretreatment was successful in reducing $E_p^{ox} - E_p^{red}$ to a near-theoretical value. A standard three-electrode CV cell was employed. The counterelectrode was a 1-in. length of platinum wire, coiled. The reference electrode was a Corning ceramic junction SCE which was isolated from the main compartment by a cracked glass bead. Voltammograms were recorded on an apparatus consisting of a Princeton Applied Research (PAR) 173 potentiostat/galvanostat, a PAR 179 digital coulometer, and a PAR 175 universal programmer. Scans under 1 V/s were recorded on a Houston Instruments Omnigraphic 2060 X-Y recorder, and those at 1 V/s and faster photographed from a Tektronix 5000 storage oscilloscope.

ESR spectra were recorded on a Varian E-15 spectrometer. The details of sample preparation, as well as photographs of the spectra, appear in the thesis.[49]

PE spectra were determined on a Varian IEE-15 electron spectrometer, operating in the UV mode, and were internally calibrated with the argon 15.759-eV line. The ionization potentials reported are vertical IPs measured at the maxima of Gaussian curves used to fit the digitized data employing program GFIT, written by Dennis Lichtenberger, and calculated on the Madison Academic Computing Center Univac 1110.

Acknowledgment. We thank the National Science Foundation for support of this work, both through individual grants and the major instrument program. We thank the Graduate School of the University of Wisconsin for a fellowship to C.R.K. We thank Professor J. W. Taylor for providing a MINDO/3 program and Professor P. R. Certain and W. C. Hollinsed for converting it to the Harris/7 computer.

References and Notes

(1) For general discussions of cyclic voltammetry, see: Cauquis, G.; Parker, V. D. "Organic Electrochemistry", Baizer M. M., Ed.; Marcel Dekker: New York, 1973; p 115. Fry, A. J. "Synthetic Organic Electrochemistry"; Harper and Row: New York, 1973.
(2) Breslow and co-workers have shown that reversibility in electron transfer can be detected in considerably shorter lived intermediates by use of ac polarographic techniques: Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976,** *98* 4222. Breslow, R.; Goodin, R. *Ibid.* **1976,** *98,* 6076. Breslow, R.; Grant, J. L. *Ibid.* **1977,** *99,* 7745. Trapping experiments (Breslow, R.; Drury, R. F. *Ibid.* **1974,** *96,* 4702, and references cited therein) have shown that the medium in which very short-lived species are formed is quite different from that of the bulk solution, described as a sheath of supporting electrolyte. This would seem to make comparison with formal potentials derived under less forcing conditions (in which equilibration between the oxidized and reduced forms in the bulk solution is attained) difficult. Perhaps this factor is important in causing the disturbing difference between the Breslow pK_a of toluene (54) and that recently estimated by Bordwell (42): Algrin, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978,** *43,* 5024.
(3) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976,** *9,* 13.
(4) (a) Forrester, A. R.; Hay, J. M.; Thomsen, R. H. "Organic Chemistry of Stable Free Radicals"; Academic Press: New York, 1968; pp 180–246. (b) Berhmes, L. J., Ed. "Spin Labelling"; Academic Press: New York, 1976.
(5) Adamic, K.; Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971,** *93,* 902.
(6) Dupeyre, R. M.; Rassat, A. *J. Am. Chem. Soc.* **1966,** *88,* 3180.
(7) For preliminary communications of portions of this work, see: (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977,** *99,* 2392; (b) *J. Chem. Soc., Chem. Commun.* **1977,** 490.
(8) We follow Brown's use of the symbol and acronym 9-BBN for 9-borabicyclo[3.3.1]nonane derivatives: Brown, H. C.; Knights, E. E.; Coleman, R. A. *J. Am. Chem. Soc.* **1969,** *91,* 2144.
(9) See: Krucic, P. J.; Bingham, R. C. *J. Am. Chem. Soc.* **1976,** *98,* 230, for leading references to the idea that "α-methyl substituents may be regarded as pseudo-electron-pair substituents".
(10) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978,** *78,* 243.
(11) Kelly, R. P.; Lindsay Smith, J. R. *J. Chem. Soc., Chem. Commun.* **1978,** 320.
(12) Wood, D. E.; Lloyd, R. V. *J. Chem. Phys.* **1970,** *52,* 3840.
(13) Fischer, H. *Z. Naturforsch. A* **1965,** *20,* 428.
(14) Nelsen, S. F. In "Free Radicals", Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 528.
(15) (a) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976,** *98,* 5269. (b) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *Ibid.* **1978,** *100,*

7017.
(16) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978,** *100,* 7876.
(17) (a) Gambarjan, S.; Ciatlician, O. *Chem. Ber.* **1927,** *60,* 390. (b) Denny, D. B.; Denny, D. Z. *J. Am. Chem. Soc.* **1960,** *82,* 1389.
(18) Fiesia, E.; Nouguier, R.; Surzur, J.-M. *Tetrahedron Lett.* **1979,** 197.
(19) Merz, A. *Angew. Chem., Int. Ed. Engl.* **1973,** *12,* 846.
(20) Kinlen, P. J.; Evans, D. H.; Nelsen, S. F. *J. Electroanal. Chem.* **1979,** *97,* 265.
(21) Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1968,** *40,* 1978.
(22) Ahoud, A.; Cave, A.; Kan-Fan, C.; Husson, H.; Rostolan, J.; Potier, P. *J. Am. Chem. Soc.* **1968,** *90,* 5622.
(23) For a review, see: Hunig, S. *Helv. Chim. Acta* **1971,** *53,* 1721.
(24) Kaloa, R. A.; Linazzi, L.; Lindsay, D.; Ingold, K. J. *J. Am. Chem. Soc.* **1975,** *97,* 6762.
(25) (a) Nelsen, S. F.; Landis, R. T., II. *J. Am. Chem. Soc.* **1973,** *95,* 6454; (b) *Ibid.* **1974,** *96,* 1788.
(26) (a) Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973,** *95,* 6395. (b) Depeyre, R. M.; Rassat, A. *Tetrahedron Lett.* **1975,** 1839.
(27) Wiseman, J. R.; Krabbenhoft, H. O.; Lee, R. E. *J. Org. Chem.* **1977,** *42,* 629.
(28) Cocksey, B. J.; Elgand, D. H.; Danby, W. *J. Chem. Soc. B* **1971,** 790. We employ $\mu^*(R) = 0.512_8\mu_R$, simply rescaling to make $\mu^*(Et) = -0.10$, so that these "inductive" parameter values have the same numerical significance as Taft σ^* values.
(29) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976,** *98,* 311.
(30) Beagley, R.; Hewitt, T. G. *Trans. Faraday Soc.* **1968,** *64,* 2561.
(31) Wollrab, J. E.; Laurie, V. W. *J. Chem. Phys.* **1969,** *51,* 1580.
(32) (a) Leonard, N. J.; Coll J. C. *J. Am. Chem. Soc.* **1970,** *92,* 6685. (b) Coll, J. C.; Crist, D. R.; Barrio, M.d.C.G.; Leonard, N. J. *Ibid.* **1972,** *94,* 7092.
(33) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975,** *97,* 4136.
(34) Halpern, A. M. *J. Am. Chem. Soc.* **1974,** *96,* 7655.
(35) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975,** *97,* 1285.
(36) Nelsen, S. F.; Wesiman, G. R.; Clennan, E. L.; Peacock, V. E. *J. Am. Chem. Soc.* **1976,** *98,* 6393.
(37) Clennan, E. L.; Hollinsed, W. C., unpublished results.
(38) As previously discussed,[15b] for tetraalkylhydrazines $E^{o\prime}$ (correlation) = $0.15IP_1 - 0.910_5$ gives a reasonably consistent estimation of the $E^{o\prime}$ expected for a tetraalkylhydrazine of a given IP_1 if the change in strain energy introduced upon undergoing the geometry change associated with electron loss were the same as in tetramethylhydrazine. Strain differences may be estimated by deviations from this line. The observed $E^{o\prime}$ for **9** is 0.11 V (2.5 kcal/mol) less positive than the correlation line predicts, which we attribute to relief of the axial NMe_2 interaction present in neutral **9** in the flattened radical cation. $IP_1(\mathbf{8} - \mathbf{9})$ is 0.74 eV, but $IP_1(\mathbf{9} - \mathbf{10})$ is only 80% as large at 0.59 eV, presumably due to the saturation effect.[39] $\Delta E^{o\prime}(\mathbf{10} - \mathbf{9})$ is not 80% that of $(\mathbf{9} - \mathbf{8})$. The difference of 0.05_8 V (1.3 kcal/mol) represents, we suggest, strain introduced by forcing the α-CH groups close together in $\mathbf{10}^{+\bullet}$. X-ray work[16] shows that this H–H distance decreases from 1.90 Å in **10** to 1.79 Å in $\mathbf{10}^{+\bullet}$. A similar decrease in $C_\alpha H$–Me distance will occur in $\mathbf{9}^{+\bullet}$, but the strain energy introduced will be smaller because the methyl groups can rotate to minimize the interaction. Both axial strain relief (lowering $E^{o\prime}$) and eclipsing effects (raising $E^{o\prime}$) are decreased in the conjugated systems previously discussed, which are flatter at nitrogen in the neutral form.
(39) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974,** *96,* 2392.
(40) For a recent collection of reviews see: "Correlation Analysis in Chemistry", Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978.
(41) For a review of this area which still remains important, see: Taft, R. W. In "Steric Effects in Organic Chemistry", Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.
(42) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968,** *90,* 4328.
(43) For the most recent detailed listing of σ_I and other Hammett parameters, see: Exner, O. In ref 35, pp 439–540.
(44) For dissenting views on $(Me_3N–)^+$ having no resonance effect, see: Charton, M. *J. Org. Chem.* **1971,** *36,* 266, and references cited therein.
(45) Nelsen, S. F.; Kessel, C. R.; Brace, H. N. *J. Am. Chem. Soc.* **1979,** *101,* 1979.
(46) (a) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1970,** *26,* 223. (b) *Ibid.* **1970,** *28,* 446.
(47) See: Griller, D.; Ingold, K. J.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978,** *100,* 6750, and references cited therein.
(48) Kollman, P.; McKelvey, J.; Gund, P. *J. Am. Chem. Soc.* **1975,** *97,* 1640.
(49) Kessel, C. R. Ph.D. Thesis, University of Wisconsin, 1979.
(50) Molecular formula established by high-resolution mass spectroscopy (AEI MS 902).
(51) (a) Borch, R. F.; Bernstein, M. O.: Durst, H. D. *J. Am. Chem. Soc.* **1971,** *93,* 2897. (b) Borch, R. F. *Org. Synth.* **1972,** *52,* 124.
(52) Garbisch, E. W., Jr. *J. Org. Chem.* **1965,** *30,* 2109.
(53) Empirical formula established by an acceptable C, H, N analysis (Spang Microanalytical Laboratories, Eagle Harbor, Mich.).
(54) Craig, J. C.; Purushothaman, K. K. *J. Org. Chem.* **1970,** *35,* 1721.
(55) Rey, P.; McConnell, H. M. *J. Am. Chem. Soc.* **1977,** *99,* 1637.

Cycloaddition Reaction of Some Representative 1-Cyclopropyl-1,3-butadienes with Tetracyanoethylene and Reaction of the Resultant Vinylcyclobutanes. An Easy Vinylcyclobutane–Cyclohexene Rearrangement[1a,2]

Fumio Kataoka, Nobujiro Shimizu,[1b] and Shinya Nishida*

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060, Japan. *Received May 14, 1979*

Abstract: In the reaction with TCNE, (*Z*)-1-cyclopropyl-1,3-butadiene (**1b**) as well as several 1,1-disubstituted 1,3-butadienes (**1c–f**) yielded vinylcyclobutane **2** as the major product particularly in a polar solvent, whereas the *E* isomer **1a** gave the cyclohexene **3** exclusively. The resultant vinylcyclobutanes, except for **2f,** isomerized easily to **3**. The most reactive of all was **2c** while **2b** was the least reactive. The isomerization of **2c** in acetonitrile in the presence of **1a** yielded virtually no cross product **3a,** supporting the intramolecular nature of the transformation. Since the intermediate was trapped by *p*-toluenethiol, the rearrangement will most probably be stepwise. The solvent effects and the substituent effects on the rate of the reaction indicate that the ionic mechanism is operating. In contrast, **2f** did not rearrange at all, but, especially at elevated temperatures, it split into the two fragments, i.e., methylenemalononitrile and **4f.** The lack of effect of solvent polarity on the rate suggests that the fragmentation would be a diradical stepwise process. In the reaction of other vinylcyclobutanes, also, the fragmentation became appreciable at elevated temperatures in solvents of low polarity. The extent of the fragmentation depends upon the substituent(s) at the terminal carbon of the vinyl group.

1,1-Disubstituted 1,3-butadienes are known to react with tetracyanoethylene (TCNE) preferentially in a [2 + 2] manner.[3] This is most probably due to the fact that the substituents sharply diminish the rate of the concerted [2 + 4] cycloaddition as the cisoid conformation of the diene[4] becomes difficult to attain. In contrast, however, we observed some time ago that 1,1-dicyclopropyl-1,3-butadiene (**1c**) produced a significant amount of the Diels–Alder adduct[5] in a polar solvent in a somewhat prolonged reaction time. Eventually, we unraveled the discrepancy by finding out that the primary product of the reaction was a vinylcyclobutane **2c,** but it easily isomerized to the cyclohexene **3c** under the reaction conditions.[2]

The vinylcyclobutane–cyclohexene rearrangement is known to occur at elevated temperatures and the diradical mechanism

0002-7863/80/1502-0711$01.00/0