

# The Diazenium Cation-Hydrazyl Equilibrium. Three-Electron-Two-Center $\pi$ Systems

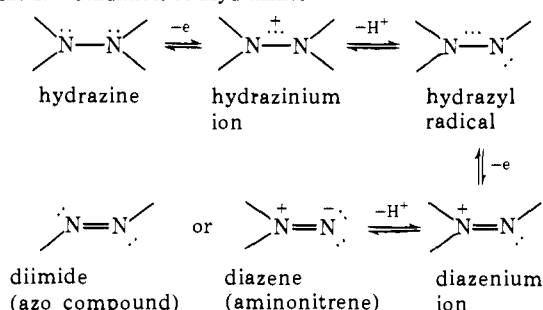
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**Abstract:** The preparation of bicyclic examples of six-, five-, and four-membered ring diazenium tetrafluoroborate salts and 1,2-di-*tert*-butyl-1-allyldiazenium tetrafluoroborate is described, and the electrochemical reduction of these salts in acetonitrile is studied. The compounds without easily abstractable hydrogens on carbon attached to nitrogen give much stabler hydrazyls (one-electron reduction products) than those having abstractable hydrogens. Trialkylhydrazyl diazenium ion  $E_{1/2}$  values are significantly negative (over 0.7 V) of tetraalkylhydrazine-hydrazinium radical cation  $E_{1/2}$  values. The second oxidation wave of tetraalkylhydrazines is postulated to give very unstable dications. The esr spectra of five trialkylhydrazyl radicals (all lacking abstractable hydrogens) and of their air oxidation products, which include amino nitroxides and dialkyl nitroxides derived by N-N bond cleavage, are reported.

A generalized sequence of intermediates for hydrazine oxidations is shown in Scheme I. Ex-

Scheme I. Oxidation of Hydrazines



amples of all the compounds shown (except the diazenes,<sup>1</sup> which are very reactive) have been known for years,<sup>2</sup> but the reactions leading to them have received little mechanistic study, because complex sequences of electron and proton transfers are usually involved to obtain stable products. It has been clear that aryl substituents stabilize the intermediates on the first line of Scheme I (the most impressive example being DPPH,<sup>3</sup> which not only does not dimerize, but is quite unreactive toward oxygen, a property shown by very few classes of free radicals), making these intermediates easier to study. Since the special properties of both hydrazinium radical cations and hydrazyl radicals must be greatly influenced by the rather unusual three-electron-two-orbital bonding present, study of examples without electron-delocalizing substituents, which must "dilute" the unusual bonding, would be preferable. The discovery that tetraalkylhydrazinium ions are rather stable<sup>4</sup> allowed structure-reactivity studies of the first equilibrium in Scheme I, using nmr for determination of the equilibrium conformations of the hydrazines,<sup>5</sup>

(1) For a review, see D. M. Lemal in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, pp 345-403.

(2) (a) C. G. Overberger, J. P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press, New York, N. Y., 1966; (b) S. Hunig, *Helv. Chim. Acta*, **54**, 1721 (1971).

(3) For a review, see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Stable Free Radicals," Academic Press, New York, N. Y., 1968, pp 137-166.

(4) (a) S. F. Nelsen, *J. Amer. Chem. Soc.*, **88**, 5666 (1966); (b) W. H. Bruning, C. J. Michejda, and D. J. Romans, *Chem. Commun.*, 11 (1967).

(5) See S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 3138 (1972), and references therein.

esr for the hydrazinium radical cations,<sup>6</sup> and electrochemical studies to probe the structural influence upon the equilibrium.<sup>7</sup> In this paper, we turn our attention to the third equilibrium, the hydrazyl radical-diazenium ion equilibrium.

Diazenium ions are the most familiar species of this pair, for the 1,1-dimethyl species was isolated 16 years ago by McBride and Kruse,<sup>8</sup> and interesting studies of Diels-Alder reactions of this species were carried out.<sup>9</sup> More recently, *N*-dimethylaminoaziridine formation has been observed with strained olefins.<sup>9c</sup> The esr spectra of hydrazyl radicals lacking strongly electron-withdrawing substituents have been the subject of a number of recent reports, including those on the parent<sup>10</sup> (on zeolite), 1,1-dialkyl (in solid matrices<sup>11</sup> and in solution<sup>12</sup>), and trialkyl (in solution<sup>13</sup>).<sup>13a</sup> Electrochemical data on hydrazyl-diazenium ion equilibria have also been reported for arylated species.<sup>14</sup>

## Results

Our study of trialkylhydrazyl radical-diazenium ion equilibria has relied heavily on the fact that trialkyl-diazenium ions are isolable as air-stable tetrafluoroborate salts.<sup>15</sup> We used the reaction generalized below to prepare  $1^+$ - $7^+$  (although it should be admitted that the samples of  $5^+$  and  $6^+$  employed were not analytically

(6) (a) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **92**, 6212 (1970); **93**, 7104 (1971); (b) S. F. Nelsen, G. R. Weisman, P. V. Hintz, D. Olp, and M. R. Fahey, *J. Amer. Chem. Soc.*, in press.

(7) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 7108 (1972).

(8) W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).

(9) (a) W. H. Urry, P. Szeesi, C. Ikoku, and D. W. Moore, *J. Amer. Chem. Soc.*, **86**, 2224 (1964); (b) G. Cauquis and M. Genies, *Tetrahedron Lett.*, 4677 (1971); (c) W. H. Urry, Z. L. F. Gabriel, J. C. Duggan, and S. S. Tseng, *J. Amer. Chem. Soc.*, **95**, 4338 (1973).

(10) R. Fantechi and G. A. Helcké, *J. Chem. Soc., Faraday Trans. 2*, **68**, 924 (1972).

(11) D. E. Wood, C. A. Wood, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 9278 (1972).

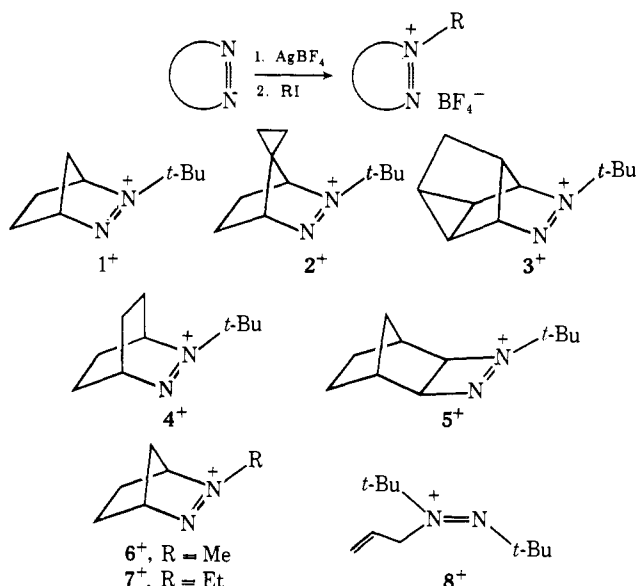
(12) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973). We thank Professor Ingold for communication of his results prior to publication.

(13) S. F. Nelsen and R. T. Landis, *J. Amer. Chem. Soc.*, **95**, 6454 (1973).

(13a) NOTE ADDED IN PROOF. Trisilylated hydrazyls have recently been reported by R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **95**, 7897 (1973).

(14) G. Cauquis and M. Genies, *Tetrahedron Lett.*, 2903, 3405 (1970).

(15) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 2719 (1973).



pure). The most notable feature of this reaction is the fact that the yield is fairly high when R is *tert*-butyl, meaning that relatively little elimination to isobutylene is occurring, in contrast to the reaction of *tert*-butyl cation-like intermediates with most nucleophiles. It seems reasonable that a silver tetrafluoroborate-azo compound complex (analogous to the isolable cuprous halide-azo complexes) is an intermediate. The nmr spectra of the salts obtained indicated that they were  $1^+$ – $7^+$ . We observed *tert*-butyl absorptions in the range  $\delta$  1.59–1.67, and bridgehead hydrogens in the range  $\delta$  5.72–6.20, both showing considerable downfield shifts compared to the neutral azo compounds, and the other proton absorptions were less shifted, but easily assigned to the expected simple alkylation products. Additional evidence for the structures lies in the fact that the same hydrazyls were generated by reduction of  $1^+$  and  $4^+$  as by hydrogen abstraction from **1-H** and **4-H** (see below). We have thus far been unsuccessful at obtaining tri-*tert*-butyldiazenium fluoroborate by *tert*-butylation of azoisobutane, but remain unconvinced that the reaction fails (solids which are apparently not very stable were obtained, but we failed in purifying them). Our acyclic trialkylhydrazyl, **8**, was made by oxidation of the trialkylhydrazine with silver tetrafluoroborate. Its nmr spectrum is consistent with the structure shown.

Cyclic voltammetry (cv) experiments demonstrated that  $1^+$ – $4^+$  underwent electrochemically reversible one-electron reduction in acetonitrile, and that the hydrazyls thus formed are stable on a time scale of tens of seconds because the reoxidation wave remained large even at slow scan rates (down to 10–20 mV/sec). Coulometric experiments verified the cv result of a one-electron reduction for  $1^+$  and  $4^+$ . The four-ring salt  $5^+$  gave a rather less stable hydrazyl, since at slower scan rates the reoxidation wave became increasingly smaller, and was nearly indiscernible at a scan rate of 60 mV/sec. The hydrazyls from  $6^+$  to  $8^+$ , all of which had abstractable hydrogens on a carbon attached to nitrogen, were all unstable, for no reoxidation wave could be discerned at slow scan rate. The *N*-ethyl compound  $7^+$  gave a substantially stabler hydrazyl than the *N*-methyl compound  $6^+$ , because the reoxidation wave was easily observable at a 100 mV/sec

scan rate for the former, but completely unobservable for the latter at 360 mV/sec. The reoxidation wave for the acyclic hydrazyl, **8**, became vanishingly small at scan rates below 200 mV/sec. The  $E_{1/2}$  values (calculated as the potential midway between the oxidation and reduction peaks) are summarized in Table I. For

Table I.  $E_{1/2}$  Values for Trialkyldiazenium Salt Reductions

Compd	$E_{1/2}$ , V <sup>a</sup>	Scan rate, mV/sec	$\Delta E_p$ , mV
$1^+$	-0.72	46	63
$2^+$	-0.73	15	72
$3^+$	-0.71	12	59
$4^+$	-0.79	120	73
$5^+$	-0.51	360	70
$6^+$	Irrev ( $E_p = -0.56$ )	360	
$7^+$	-0.70	100	78
$8^+$	-0.53	240	100

<sup>a</sup> Vs. sce, in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, at a platinum bead electrode.

purposes of comparison, we also examined the electrochemically reversible one-electron oxidation of the structurally related tetraalkylhydrazines<sup>7</sup> **9**–**13**, and summarize the results in Table II. An interesting

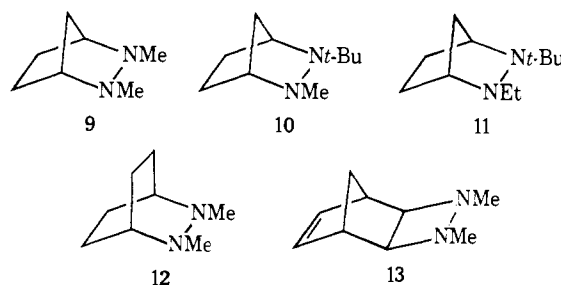


Table II.  $E_{1/2}$  Values for Some Tetraalkylhydrazine Oxidations

Compd	$E_{1/2}$ , V <sup>a</sup>	Scan rate, mV/sec	$\Delta E_p$ , mV
<b>9</b>	-0.10 <sup>b</sup>	54	80
<b>10</b>	+0.17	30	60
<b>11</b>	-0.19	120	80
<b>12</b>	+0.00 <sup>b</sup>	62	70
<b>13</b>	+0.26	50	57

<sup>a</sup> Vs. sce, in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, at a gold bead electrode. <sup>b</sup> Taken from ref 7.

feature of the cv spectra of tetraalkylhydrazines which we have not reported previously is that in addition to the reversible hydrazine-hydrazinium ion wave, there is a second oxidation wave at higher potential than the first one, which is totally irreversible, but of comparable height to the first wave. Coulometry gave  $n = 2$  for oxidation at 1.2 V. For **11**, this wave had a peak potential at 1.0 V vs. sce (340 mV/sec). In a scan from 0 to +1.8 and back to -1.8 V, an irreversible reduction wave appears at -0.6 V. This reduction wave is apparently due to a product formed at the +1.0 V wave, since it is not present unless the electrode is first taken to >+1.0 V.

We also briefly investigated the reduction of  $1^+$  and  $4^+$  in water. In acidic and neutral buffer solutions, the

reduction wave was observed, but no reoxidation wave. Coulometry demonstrated  $n = 2$  for  $4^+$  at pH 3. We believe it is clear that the hydrazyl is being rapidly protonated to the hydrazinium cation under these conditions, and that since this species is being generated at an electrode which is far cathodic of its reduction potential, it is immediately reduced to the hydrazine, resulting in an overall two-electron reduction. At high enough pH values, the rate of protonation can be decreased, until a reoxidation wave becomes visible at attainable scan rates. Although quantitative studies of the lifetime of  $1\cdot$  and  $4\cdot$  before protonation have not been carried out, and such studies would be rather difficult to carry out quantitatively,<sup>16</sup> we suggest that the necessity of going to such large scan rates and high pH values to observe reoxidation requires an extremely high protonation rate for the hydrazyl. A problem with the use of very high pH buffers is that the foot of reduction wave for the sodium ion begins to interfere with the reduction wave, especially for  $4^+$ . The use of tetramethylammonium hydroxide as base eliminated this problem. Our data for aqueous systems appear in Table III.

**Table III.** Comparison of  $E_{1/2}$  Values for Trialkyldiazonium Salt Reduction in Acetonitrile and Water

Compd	Solvent	$E_{1/2}$ (obsd); V	Scan rate, mV/ sec	$\Delta E_p$ , mV
$1^+$	CH <sub>3</sub> CN (TBAP)	-0.72	46	63
$1^+$	DMF (TEAP)	-0.63	200	70 <sup>a</sup>
$1^+$	H <sub>2</sub> O (pH 13)	-0.74	1,000	86
$1^+$	H <sub>2</sub> O (pH 12)	-0.76	5,000	104
$1^+$	H <sub>2</sub> O (pH 10)	-0.80	5,000	129
$4^+$	CH <sub>3</sub> CN (TBAP)	-0.79	120	73
$4^+$	H <sub>2</sub> O (pH 12)	-0.77	28,000	200
$4^+$	10% Me <sub>4</sub> NOH-H <sub>2</sub> O	-0.81	4,000	90

<sup>a</sup>  $E_p = -2.16$  for a broad wave showing no reoxidation wave under these conditions.

The problem with measurement of  $E_{1/2}$  values for trialkylhydrazine oxidation is somewhat similar to that for reduction in water, in that proton transfer effectively removes the product. In this case, proton loss gives the hydrazyl at an electrode which is far anodic of its  $E_{1/2}$  for oxidation to the diazenium ion. Oxidation of  $1\text{-H}$  and  $4\text{-H}$  was observed to give a distended, irreversible wave even in acetonitrile, presumably because the hydrazine is basic enough to deprotonate the hydrazinium cation. Scanning to negative potentials after oxidation demonstrated the formation of diazenium ion. By lowering the pH in water, one would expect to reach a point where rereduction of the hydrazinium cation radical would effectively compete with deprotonation, but at low pH values the majority of the hydrazine becomes protonated, and electroinactive. In a sample of  $4\text{-H-}4\text{H}_2^+$  generated by coulometric reduction of  $4^+$  in pH 3 buffer, the cv spectrum showed a tiny (<5% of the current expected if none of the  $4\text{-H}$  present had been protonated) oxidation peak near +0.16, but this oxidation was still not reversible, and may or may not actually correspond to  $4\text{-H}$  oxidation.

(16) For a discussion of some of the problems involved in cv studies for evaluation of rate constants, see R. S. Nickolson and I. Shain, *Anal. Chem.*, **36**, 722 (1964).

**Table IV.** ESR Spectra of Bicyclic Hydrazyls (gauss)

Compd	$a(N)$	$a(N')$	Other splittings	$g$
1·	11.03	10.25	Unresolved	2.0035
2·		10.5 (av)	Unresolved	
3·		11.0 (av)	Unresolved	
4·	11.44	10.61	3.00 (2 H), 2.13 (2 H), 0.97 (2 H), 0.37 (3 H)	2.0035
5·	10.72	10.72	17.38 (1 H), 7.37 (1 H)	2.0033

A fact which particularly surprised us about the reduction of the diazenium salts was the impressive reluctance of the hydrazyls to accept a second electron. In fact, both  $1^+$  and  $4^+$  showed no second reduction wave beyond the diazenium-hydrazyl wave out to  $-2.4$  V in acetonitrile. The implication of these results for the acidity of the trialkylhydrazines has been discussed previously.<sup>17</sup> Surprisingly, the second reduction wave was easily accessible in DMF, appearing as a peak with no reoxidation wave at  $E_p = -2.16$  (see Table III). The solvent effect on both reduction waves of  $1^+$  is noted to be quite substantial.

The esr spectra of the hydrazyls  $1\cdot$ ,  $4\cdot$ , and  $5\cdot$  were obtained from samples prepared by hydrogen abstraction from the related hydrazines, using photolysis of di-*tert*-butyl peroxide to generate the abstracting radicals. For the "stable" hydrazyls  $1\text{-}4\cdot$ , we found it more convenient to obtain the desired concentration by complete reduction of the diazenium salt in acetonitrile followed by transferring (in the absence of air) to esr tubes and sealing. The final concentration of hydrazyl could be easily adjusted either by varying the amount of the air-stable salt used, or by dilution with degassed solvent. The hydrazyl could also be extracted into pentane, and it was found that for  $4\cdot$ , the spectra in acetonitrile and pentane were not distinguishable. We were unable to obtain sufficient resolution for analysis of the proton hyperfine splittings for any of the bicyclo[2.2.1]heptyl hydrazyls, although for  $1\cdot$ , sufficient resolution was present to ascertain that the two nitrogen splittings were different. We had better resolution for  $4\cdot$ , although the centers of all five major multiplets were seriously overlapped. The spectrum is fit only fairly well by the splittings quoted in Table IV, in which the ratios for the pairs of hydrogen splittings are set at the ratio for the nitrogen splittings. Although it is doubtful that the reported splittings are better than  $\pm 0.2$  G, it is clear that there is a pair of larger triplets and a pair of smaller triplets.

By monitoring the esr signal in completely reduced samples of  $1\cdot$  and  $4\cdot$ , we found that the former decays fairly slowly, requiring about 12 hr at room temperature for complete disappearance. The products of this decomposition have been discussed.<sup>13,15</sup> In contrast, the signal from  $4\cdot$  was indefinitely stable; the signal has remained detectable for 3 months when the tube was stored at room temperature and not protected from ambient light. Neither  $1\cdot$  nor  $4\cdot$  gave any evidence for reversible dimerization to the related tetrazane, as has been reported for bicyclic nitroxides<sup>18</sup> and less hindered hydrazyls.<sup>19</sup>

(17) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 5422 (1973).

(18) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7166 (1972); **95**, 6390 (1973).

(19) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6404 (1973).

We were unable to observe the esr spectra of the hydrazyls containing nonbridgehead hydrogens on carbons bound to nitrogen (**6**–**8**·), even using *intra muros* reduction in the esr cavity. Although we suspect that attempts at lower temperatures would probably be successful in the case of **7**·, from its cv behavior, there is no doubt that these hydrazyls are far less stable than **1**–**4**·.

The “stable” hydrazyls **1**–**4**· disappeared rapidly in the presence of air, as ascertained both by cv and the disappearance of their esr spectra. A new radical appeared, which was characterized by a single large (20.65–21.1 G) nitrogen splitting, and a larger *g* factor (see **1-O**·, **2-O**·, **4-O**· in Table V). These species were

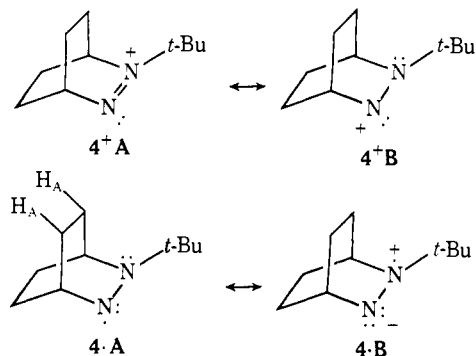
**Table V.** ESR Spectra of Reaction Products Derived from Bicyclic Hydrazyls with Air (gauss)

Compd	<i>a</i> (N)	Other splittings	<i>g</i>
<b>1-O</b> ·	20.65	4.24 (1 H), 2.85 (1 H), 6.08 (1 H)	2.0060
<b>2-O</b> ·	21.1	2.91 (2 H)	2.0061
<b>4-O</b> ·	20.95	1.60 (1 N), 3.98 (1 H), 0.90 (2 H)	2.0065
<b>14-O</b> ·	14.9	2.7 (1 H), 0.8 (4 H)	2.0065
<b>15-O</b> ·	14.5	2.5 (1 H), 0.7 (4 H)	2.0065

also observed instead of the hydrazyls during *intra muros* reduction of **1**<sup>+</sup> and **4**<sup>+</sup> using an oxygen bubbler instead of the customary argon one. The radical producing these spectra was not very stable, however, and in a few minutes its esr spectrum was no longer observed. In the presence of a large excess of air, a second oxygen-derived species was observed, which had the nitrogen splitting and *g* factor characteristic of a dialkyl nitroxide (see Table V, species identified as **14-O**· and **15-O**·).

## Discussion

The similarity of the bridgehead hydrogen chemical shifts found for the bicyclic diazenium ions **1**<sup>+</sup>–**7**<sup>+</sup> ( $\Delta\delta$  in the range 0.25 to 0 for all seven compounds) requires a substantial decrease in charge density at both nitrogens compared to neutral compounds, implying that the azaimmonium and aminozenium structures **4**<sup>+</sup>**A** and **4**<sup>+</sup>**B** are both important contributors, and



that a two-electron–two-center  $\pi$  bond is present. The near equality of the nitrogen esr splittings for hydrazyls **1**–**5**· (the smaller splitting was 93% the size of the larger for **1**· and **4**·, and even closer to 100% for **5**·) suggests importance of both **4****A** and **4****B** in contributing to the hydrazyl structure. The situation is not simple in quantitative terms, however, since *a*(N) is known to be sensitive to the degree of s orbital hy-

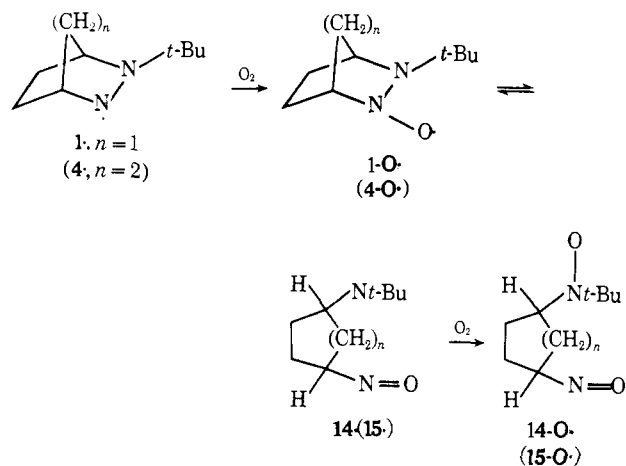
bridization of the spin-bearing orbitals. Nonplanarity even in acyclic hydrazyls is suggested by the fact that the trisubstituted nitrogen of 1,1-dialkylhydrazyls has been shown to give the larger splitting,<sup>19</sup> which is the opposite of the result calculated by MO methods,<sup>10,11</sup> although the calculations do not agree on the question of planarity. We believe it is clear that such calculations are not yet sufficiently reliable to probe this problem effectively. For **4**·, the hydrogen splittings occur in four pairs, and the two larger ones are of the appropriate size to be assigned to *a*(H<sub>A</sub>) and *a*(H<sub>A</sub>′) for **4****A**–**4****B**, suggesting rapid inversion or near planarity at N<sub>3</sub>. We therefore suggest that this hydrazyl is best described as possessing an approximately sp<sup>2</sup> hybridized “lone pair” on N<sub>2</sub>, with a  $\pi$  bond containing three electrons centered upon N<sub>2</sub> and N<sub>3</sub>, as is implied by **4****A** ↔ **4****B**. For **5**·, although any difference in the nitrogen splittings must be very small, single proton splittings of 17.4 and 7.4 G were observed. We argue these can only be reasonably assigned to the four-ring bridgehead hydrogens  $\beta$  to the nitrogen spin-bearing orbitals. The substantial difference in size requires a substantial difference in direction for the spin-bearing orbitals at nitrogen. We submit that this difference most likely arises from increased nonplanarity at the trisubstituted nitrogen, which is most likely to arise for steric reasons—the *tert*-butyl group of **5**· should have a more serious interaction with the syn hydrogen on the one-bridge in **5**· than should the *tert*-butyl groups of **1**· or **4**· with syn hydrogens in these molecules.

The bicyclo[2.2.2]hydrazyl has been shown to be stable toward dimerization or self-disproportionation at room temperature, and persists indefinitely in solution in the absence of air.<sup>13</sup> Its rapid reaction with atmospheric oxygen demonstrates an important contrast with the behavior of aryl-stabilized hydrazyls such as DPPH. We assign the first species observed by esr when trialkylhydrazyls are reacted with oxygen to the related amino nitroxides **1-O**·, **2-O**·, and **4-O**· on the basis of the similarity of the esr spectra observed to those generated by spin trapping<sup>20</sup> of amino radicals with nitroso-*tert*-butane<sup>21</sup> (for *N*-piperidinyl *tert*-butyl nitroxide, *a*(N) = 18.8, *a*(N′) = 0.88). We were unable to observe the smaller nitrogen splitting for **1-O**· or **2-O**·, but since the geometry of these bicyclic amino nitroxides is rather different from those of the acyclic examples quoted, we do not find this alarming. We presume without proof that the amino nitroxides are formed in the most obvious fashion, by oxygen addition to the hydrazyl to yield an R<sub>2</sub>NO<sub>2</sub>· intermediate, which is trapped by R<sub>2</sub>N· to give an unstable R<sub>2</sub>NO<sub>2</sub>NR<sub>2</sub> species, which cleaves the central bond. Conversion of other N-centered radicals to nitroxides by air is well precedented.<sup>22</sup> The amino nitroxide radicals are substantially less stable than the hydrazyl radicals, and their esr spectra decay in a few hours. For the only cases studied much, a second species with the splittings characteristic of a dialkyl nitroxide appears if large amounts of oxygen were present, and we suggest that the reaction pathway shown in Scheme II is most

(20) For a discussion of spin trapping, see E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

(21) O. E. Edwards, D. H. Paskovich, and A. F. Reddoch, *Can. J. Chem.*, **51**, 978 (1973).

(22) S. F. Nelsen in “Free Radicals,” Vol. 2, J. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 21.

**Scheme II.** Radicals Derived by Reaction of Trialkylhydrazyls with Oxygen

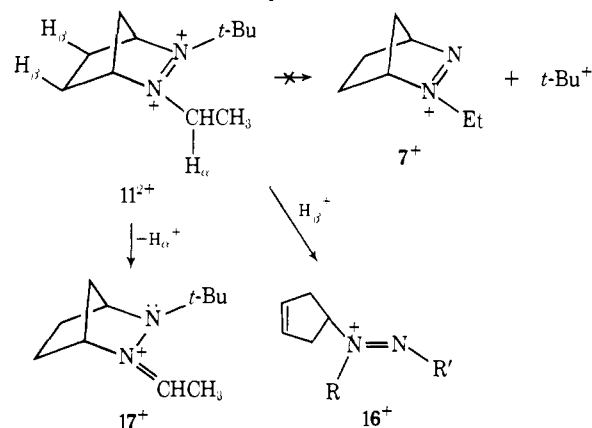
likely. The similarity of the splittings for the species identified as  $15\text{-O}\cdot$  (Table V) with those reported for *tert*-butyl cyclohexyl nitroxide<sup>23</sup> ( $a(\text{N}) = 14.5$ ,  $a(1\text{ H}) = 1.52$ ,  $a(4\text{ H}) = 0.67$ ,  $a(2\text{ H}) = 0.97$ ) lends support to Scheme II. Because amino nitroxides have three connected atoms bearing five orbitals containing nine electrons, destabilizing interactions are expected to be a driving force for the reaction  $1\text{-O}\cdot \rightarrow 14\cdot$  ( $4\text{-O}\cdot \rightarrow 15\cdot$ ), which is the reverse of spin trapping. In the presence of enough oxygen, nitroxide formation should compete with hydrogen abstractions, and allow observation of the dialkyl nitroxide  $14\text{-O}\cdot$  ( $15\text{-O}\cdot$ ); we have no evidence as to whether the dialkyl nitroxides observed actually are the secondary nitroso compounds, as shown, or not.

One of the most significant results of this study is that for acyclic as well as four-, five-, and six-ring compounds, the oxidation potential for the hydrazyl is substantially cathodic of ("easier than") that of the neutral hydrazine. If  $E_{1/2}$  values of the model hydrazines **13** and **10** are used as approximations for  $E_{1/2}$  values of the four- and five-ring trialkylhydrazines **5-H** and **1-H**, respectively,  $\Delta E_{1/2}$  values of 0.77 and 0.90 V are calculated. (We argue that the former number is too small because the mono-*tert*-butyl compound would be a better model, and that both are too small because  $\text{N-CH}_3$  compounds should oxidize slightly anodic of  $\text{N-H}$  compounds. We do not believe the changes would be larger than +0.2 V, in any event.) These numbers correspond to about 16 and 20 kcal/mol in the energy units usually employed by organic chemists. It is 20 kcal/mol more difficult to force a single antibonding electron into the two-electron-two-center  $\pi$  bond of  $1^+$  than it is to add an electron to the three-electron-two-center  $\pi$  system of ( $1\text{-H}^+$ ). Approaching the equilibrium from the other side, it is 20 kcal/mol "harder" to remove an electron from the hydrazine **1-H** to give the hydrazinium ion, with its three-electron bond, than it is to remove the antibonding electron from **1**.

Another manifestation of the ease of removing an electron from a two-center-three-electron  $\pi$  bond is seen in the accessibility of the second oxidation of

(23) Th. A. J. W. Wajer, A. Mackor, and Th. J. DeBoer, *Recl. Trav. Chim. Pays-Bas.*, **70**, 568 (1971). They also observed  $a(2\text{ H}) = 0.97$  for two of the  $\delta$  hydrogens in the cyclohexyl group. Our spectra were ill-resolved, and presumably we missed the outer lines; our observed splitting is between the two splittings we presumably did not resolve.

tetraalkylhydrazines in spite of the fact the immediate product is presumably a two-center dication. Although the second oxidation wave showed no rereduction wave, indicating a rapid following reaction and showing that  $E_{1/2}$  is actually anodic of the 1.0-V peak potential observed,  $E_p$  only shifts 30 mV for each power of ten increase in the rate of the following reaction, and huge shifts will not occur if the rate of the following reaction is limited by diffusion. We suggest, then, that  $E_{1/2}$  ( $11^+$ ,  $11^{2+}$ ) -  $E_{1/2}$  (**11**,  $11^+$ ) falls in the range 1–1.5 V, and probably at the lower end of this range. This difference is remarkably small considering the electrostatic problem in  $11^{2+}$ . A product formed at the second wave undergoes irreversible reduction at  $-0.53$  V. This establishes that de-*tert*-butylation to  $7^+$  does not occur, and is consistent with formation of the acyclic diazenium ion  $16^+$ , although the electrochemical properties of the deprotonation product from the ethylmethylene,  $17^+$ , remain unknown (see Scheme III).

**Scheme III.** Possible Decomposition of  $11^{2+}$ 

## Experimental Section

A Princeton Applied Research Model 1170 Electrochemistry system was used for all coulometry and some cv experiments, and other cv experiments used an instrument built by John Buschek of this department, to plans designed by Professor D. H. Evans. A standard cell was used, with a platinum coil counter electrode, a Sargent-Welch sce reference electrode with a cracked glass bead connection to the cell, and a platinum bead working electrode. Coulometric experiments used a mercury pool working electrode. The solvent used was acetonitrile (Burdick and Jackson "distilled in glass") containing 0.1 M tetrabutylammonium perchlorate (Matheson Coleman and Bell, recrystallized from ethanol-water at 50°). Buffer solutions used:<sup>24</sup> pH 3, 100 ml of 0.1 M KH<sub>2</sub>PO<sub>4</sub> and 46.6 ml of 0.1 M HCl; pH 10, 50 ml of 0.05 M NaHCO<sub>3</sub> and 10.7 ml of 0.1 M NaOH; pH 12, 50 ml of 0.05 M Na<sub>2</sub>HPO<sub>4</sub> and 26.9 ml of 0.1 M NaOH; pH 13, 25 ml of 0.2 M KCl and 66 ml of 0.2 M NaOH.

Esr spectra were recorded on Varian E.15 equipment, and  $g$  factors were determined *vs.* an  $f$  center in the quartz temperature insert which came at  $g = 2.0006$ . A 2500-W Hanovia lamp was used for photolytic generation of radicals.

**3-*tert*-Butyl-2,3-diazanoborn-2-ene tetrafluoroborate (1)** was prepared by addition of 2.36 g (8.3 mmol) of *tert*-butyl iodide in 10 ml of methylene chloride to a solution of 500 mg (5.2 mmol) of 2,3-diazanoborn-2-ene<sup>25</sup> and 2.5 g (12.8 mmol) of silver fluoroborate (stored under vacuum over P<sub>2</sub>O<sub>5</sub>) in 60 ml of methylene chloride. After stirring for 3 hr the solution was filtered, the volume reduced, and **1** precipitated as a white solid by addition of ether; yield, 0.93 g (75%). After several reprecipitations from methylene chloride-ether, an analytical sample, mp 208–209° dec,

(24) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 49th ed, Chemical Rubber Co., Cleveland, Ohio, 1968, pp 1-79.

(25) P. G. Gassmann and K. T. Mansfield, *Org. Syn.*, **49**, 1 (1969).

was obtained; nmr (DMSO-*d*<sub>6</sub>) 1.41 (br d, *J* = 10 Hz, 2 H), 1.67 (s, 9 H), 2.11 (br s, 2 H), 2.31 (br d, *J* = 10 Hz, 2 H), 5.95 (br s, 1 H), 6.20 (br s, 1 H); ir (CH<sub>2</sub>Cl<sub>2</sub>) 3.26, 3.35, 7.09, 7.27, 9.48. *Anal.* Calcd for C<sub>9</sub>H<sub>17</sub>N<sub>3</sub>BF<sub>4</sub>: C, 45.03; H, 7.14; N, 11.71. Found: C, 45.01; H, 7.22; N, 11.79.

**3-*tert*-Butyl-2,3-diaza-7,7-spirocyclopropyl-norborn-2-ene tetrafluoroborate (2)** was prepared from the analogous azo compound<sup>20,28</sup> by the method used for **1** in 68% yield: mp 164–167° dec; nmr (DMSO-*d*<sub>6</sub>) 0.75 (br s, 4 H), 1.42 (m, 1 H), 1.59 (s, 9 H), 2.01 (br s, 1 H), 2.41 (m, 1 H), 3.22 (br s, 1 H), 5.72 (br s, 1 H), 5.82 (br s, 1 H). *Anal.* Calcd for C<sub>11</sub>H<sub>19</sub>N<sub>3</sub>BF<sub>4</sub>: C, 49.60; H, 7.20; N, 10.53. Found: C, 49.51; H, 7.09; N, 10.59.

**8-*tert*-Butyl-8,9-diazadetracycl-2-ene tetrafluoroborate (3)** was obtained from the azo compound<sup>21,27</sup> in 54% yield: mp 181–183° dec; nmr (DMSO-*d*<sub>6</sub>) 1.67 (s, 9 H), 2.12 (br s, 2 H), 2.42 (br s, 3 H), 3.12 (br s, 1 H), 5.88 (br s, 1 H), 6.04 (br s, 1 H). *Anal.* Calcd for C<sub>11</sub>H<sub>17</sub>N<sub>3</sub>BF<sub>4</sub>: C, 50.03; H, 6.49; N, 10.61. Found: C, 50.10; H, 6.34; N, 10.66.

**3-*tert*-Butyl-2,3-diazabicyclo[2.2.2]oct-2-ene tetrafluoroborate (4)** was prepared from the analogous azo compound<sup>21,28</sup> by the method used for **1** in 62% yield: mp 243–245° dec; nmr (DMSO-*d*<sub>6</sub>) 1.61 (br d, *J* = 8 Hz, 4 H), 1.77 (s, 9 H), 2.27 (br d, *J* = 8 Hz, 4 H), 5.99 (br s, 2 H). *Anal.* Calcd for C<sub>10</sub>H<sub>19</sub>N<sub>3</sub>BF<sub>4</sub>: C, 47.27; H, 7.54; N, 11.03. Found: C, 47.29; H, 7.45; N, 11.08.

**4-*tert*-Butyl-3,4-diazatricyclo[4.2.1.0<sup>2,3</sup>]nona-3,7-diene tetrafluoroborate (5)** was obtained from the azo compound<sup>21,29</sup> in impure form in 15% yield; mp 118–120° dec; partial nmr (DMSO-*d*<sub>6</sub>) 1.72 (s, *t*-Bu), 5.78 (br s, 2 H?); several impurities were apparent, but we were unable to remove them. *Anal.* Calcd for C<sub>11</sub>H<sub>17</sub>N<sub>3</sub>BF<sub>4</sub>: C, 50.03; H, 6.49; N, 10.61. Found: C, 48.86; H, 6.30; N, 10.19.

**3-Methyl-2,3-diazanorborn-2-ene tetrafluoroborate (6)** was pre-

pared from the azo compound using methyl iodide: mp 181–183° dec. The sample was brown and not analytically pure, but the nmr indicated that **6** was the major component: nmr (DMSO-*d*<sub>6</sub>) (br s, 1 H), 5.75 (br s, 1 H), 4.57 (s, 3 H), 1.3–2.6 (complex).

**3-Ethyl-2,3-diazanorborn-2-ene tetrafluoroborate (7)** was prepared from the azo compound using ethyl iodide: mp 66–67° dec; nmr (D<sub>2</sub>O, vs. DSS) 5.82 (br s, 1 H), 5.63 (br s, 1 H), 4.72 (quant, *J* = 7 Hz, 2 H), 2.6–1.3 (complex, 6 H), 1.52 (t, *J* = 7 Hz, 3 H). *Anal.* Calcd for C<sub>8</sub>H<sub>13</sub>N<sub>3</sub>BF<sub>4</sub>: C, 39.66; H, 6.18; N, 13.21. Found: C, 39.86; H, 6.13; N, 13.22.

**1-Allyl-1,2-di-*tert*-butyldiazonium Tetrafluoroborate (8)**. A mixture of 12.9 g (89.6 mmol) of freshly prepared 1,2-di-*tert*-butylhydrazine<sup>30</sup> and 18.1 g (89.6 mmol) of trimethylene dibromide was refluxed in 150 ml of ethanol containing 30 g of potassium carbonate for 19 hr, filtered, and distilled. A fraction boiling at 91–94° (110 mm), 4.6 g, proved to have the nmr spectrum expected for 1-allyl-1,2-di-*tert*-butylhydrazine: 1.01 and 1.02 (2 s, *t*-Bu), 3.3–3.55 (complex, CH<sub>2</sub>), and 4.9–5.3 and 5.6–6.1 (complex, CH=CH<sub>2</sub>). A solution of 0.66 g (3.59 mmol) of this material in 25 ml of methylene chloride was treated with 1.42 g (7.18 mmol) of silver fluoride causing rapid deposition of a silver mirror. After stirring for 15 min, filtration and washing with 10 ml of methylene chloride, the filtrate was diluted to 125 ml with ether, and cooled in Dry Ice. Filtration gave 200 mg (20%) of gray crude **8**, which was crystallized several times from chloroform-ether, to give 80 mg of white solid mp 100–104°; nmr (CDCl<sub>3</sub>) 1.70 and 1.75 (2s, *t*-Bu), 5.52 (complex, 3 H), 6.0 (m, 1 H). *Anal.* Calcd for C<sub>11</sub>H<sub>23</sub>N<sub>3</sub>BF<sub>4</sub>: C, 48.19; H, 8.58; N, 10.37. Found: C, 48.55; H, 8.66; N, 10.36.

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## Steric Effects at C-7 of Bicyclo[2.2.1]hept-2-enes. Thermodynamic and Kinetic Probes<sup>1</sup>

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**Abstract:** Thermodynamic and kinetic probes for the relative steric factors at C-7 of norbornenes, taken collectively, indicate that the etheno bridge is less hindering than the ethano bridge. The difference is relatively small. Among pairs of syn-anti isomers of 7,7-dialkoxynorbornenes that were equilibrated, the largest free energy difference (370 cal mol<sup>-1</sup> at 54°) was that separating the 7-methoxy-7-(2-pentoxy) pair.

**B**icyclo[2.2.1]heptanes and -heptenes<sup>2</sup> have been studied very extensively and intensively because the comparative rigidity of those systems removes some of the uncertainties about geometry that are common to conformationally mobile systems. For example, norbornene systems have figured prominently in studies of homoallylic participation and skeletal rearrangements<sup>3</sup> and of the stereochemistries of addition and elimination.<sup>4,5</sup>

(1) Presented in part at 55th Annual Conference of the Chemical Institute of Canada, June 5, 1972.

(2) Referred to subsequently by their trivial names, norbornanes and norbornenes, respectively.

(3) P. D. Bartlett, "Nonclassical Ions, Reprints and Commentary," W. A. Benjamin, New York, N. Y., 1965.

In spite of the breadth and depth of investigations into the chemistry of norbornyl systems, one important aspect has received little attention. Steric effects at C-7 of norbornenes, arising from interactions of C-7 substituents with the ethano and etheno bridges, were not well understood when this work was undertaken. Two measurements, based on equilibrated systems, were recorded in the literature. Sauers<sup>6</sup> reported that epimerization of 7-carbomethoxynorbornenes by methoxide in methanol at 65° gave a mixture in which the

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