Pyramidal Geometry around the Radical-Center Carbon Atom of Some 2-Norbornyl-Type Radicals as Studied by Electron Spin Resonance

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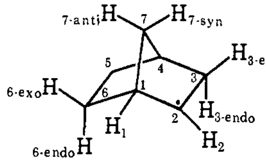
Abstract: Some 2-norbornyl-type radicals are generated in aqueous solution with a rapid flow technique and examined with esr. Based on the hyperfine splitting constants of protons bonding to the radical-center carbon atom (15–21 G), and of 3-endo protons (21–26 G), this type of radicals is concluded to have a pyramidal radical-center carbon atom with the C_2–H bond tilting in the endo direction. The dependence of hyperfine splitting constants of H_1, H_2, and $H_{3\text{-endo}}$ on the 3-exo substituent shows that the geometry around C_2 becomes more pyramidal with the increase of the electronegativity of the substituent. Electronic and steric factors governing the geometry of the trigonal carbon and the stereoselectivity of these radicals are discussed.

It has been concluded that the methyl radical is planar or nearly so by analysis of the electronic spectrum,[1] the electron spin resonance (esr) spectrum,[2] and the infrared spectrum.[3] Recent *ab initio* SCF-MO calculations of the methyl radical[4] show that the planar minimum is very flat; the bending (keeping the C_{3v} symmetry of CH_3) of a C–H bond out of the plane defined by the remaining two C–H bonds to 14.5 and to 29.4° results in destabilization of only 0.13 and 0.81 kcal/mol, respectively.[4a] This implies the possibility of a pyramidal geometry around a radical-center carbon atom of some substituted alkyl radicals.

Recent extensive esr studies[5–9] on the geometry of substituted alkyl radicals and their isoelectronics revealed that the radical-center carbon atom of a substituted alkyl radical, $\cdot CRR'R''$, has a tendency to have a pyramidal geometry in the following cases: (1) the bond angle R–C–R′ is strained to a value smaller than 120° (by a small-membered ring), (2) one or more of the substituents bonding to the radical-center carbon is more electronegative than carbon, and (3) one or more of the substituents has π-type lone-pair electrons which can delocalize onto the odd electron π orbital on the carbon atom. The former two factors result in a decrease of the s character in the hybrid orbitals extending from the radical-center atom to the atoms forming the strained ring[10] or to the electronegative substituents[10–13] and some extra s character accumulates in the odd electron orbital of the radical-center atom. Thus these two factors give a pyramidal tendency to the radical-center atom. The third factor is easy to explain. The delocalization of the π-type lone-pair electrons of the substituent(s) onto the odd electron orbital on the radical-center atom gives the carbanion-like character (pyramidal) to the radical-center atom.

The bond angle C_1–C_2–C_3 of a 2-norbornyl-type radical would be nearly equal to the corresponding angle of norbornane which is reported as 104.3°,[14] and it is expected that this radical has a pyramidal radical-center carbon atom. Fujimoto and Fukui[15] proposed that the radical-center carbon of 2-norbornyl radical has a shallow pyramidal structure with the C_2–H bond bent in the endo direction and that the stereoselectivity of this radical in radical-transfer reactions is basically controlled by the frontier orbital, the odd electron orbital in this case. Esr studies of 2-norbornyl and related radicals[16–18] showed that these radicals have a pyramidal radical-center carbon atom with the C_2–H or C_2–OH bond bent toward the endo direction in the estimated range of 8–30° depending on substituents.



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[1] G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

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[18] R. Marx and L. Bonazzola, *Mol. Phys.*, **19**, 899 (1970).

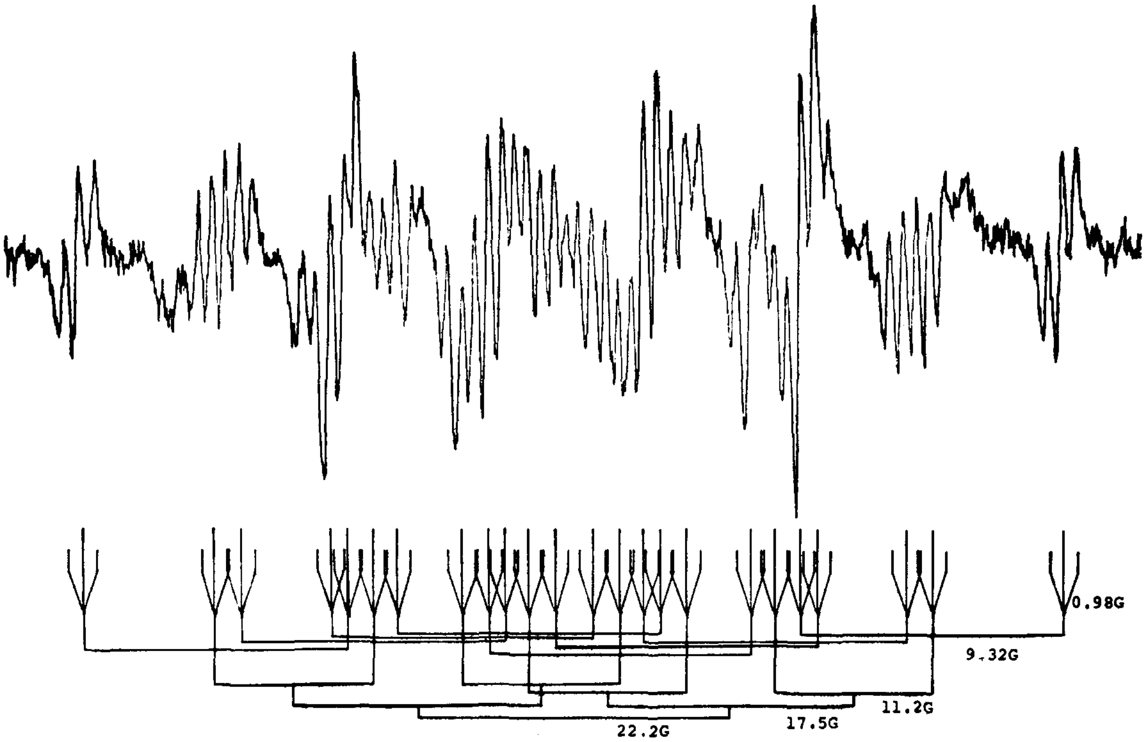
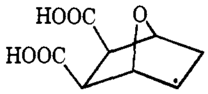


Figure 1. Esr spectrum of radical 7.

In the preceding paper,[16] the radical-center carbon atom of the *exo*-3-hydroxy-*exo*-*cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-yl radical (**2**) is shown to be



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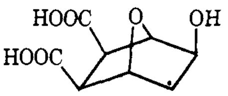

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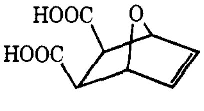
more pyramidal than that of the *exo*-*cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-yl radical (**1**). This result suggests that substituents bonded to C_3 (β substituents) give effects on the nonplanarity of the radical-center carbon atom, C_2. To examine these effects we studied, with esr, structures of some substituted 2-norbornyl radicals generated by radical addition to *exo*-*cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-ene (**3**) and to *endo*-*cis*-5,6-dicarboxybicyclo[2.2.1]hept-2-ene (**4**) or by hydrogen abstraction from *exo*-*cis*-2,3-dicarboxy-7-oxabicyclo[2.2.1]heptane (**5**) and from *endo*-*cis*-2,3-dicarboxybicyclo[2.2.1]heptane (**6**).



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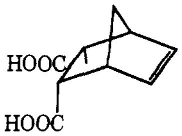

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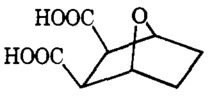

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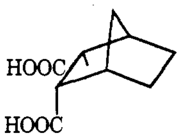

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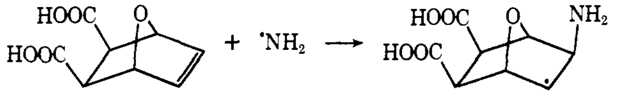
Results

Amino Radical Adduct to 3. When olefin **3** is allowed to react with the amino radical generated from the reaction between hydroxyamine and titanous ion[19] in the esr cavity, the esr spectrum shown in Figure 1 was observed. This spectrum is analyzed as three sets of doublets (22.2, 17.5, and 11.2 G) split further into a 1:1:1 triplet of 9.32 G and a 1:2:1 triplet of 0.98 G. The 1:1:1 triplet with a fairly large hyperfine splitting constant (hfsc) shows that this radical has a nitrogen nucleus near the radical-center atom. Addition of a radical to a norbornene-type olefin occurs entirely or preferentially to the exo side.[20] Thus the observed radical is identified as *exo*-3-amino-*exo*-*cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-yl radical (**7**) formed as follows.

$$NH_2OH + Ti^{3+} \longrightarrow {}^{\cdot}NH_2 + Ti^{4+} + OH^-$$



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The assignment of 9.32 G to the nitrogen nucleus is clear. Three doublets of 22.2, 17.5, and 11.2 G are assigned respectively to $H_{3\text{-endo}}$, H_2, and H_1 based on the comparison of these values with those of **1** and **2**. The assignment of the hfsc of 0.98 G (two protons) is not clear, but this hfsc should be assigned to two protons among H_4, H_5, H_6, and two amino protons.

If the amino group is protonated, protons in the ammonium group should either not give a resolvable hyperfine splitting because of rapid proton exchange with water, or give a 1:3:3:1 quartet splitting due to the rapid rotation around the C–N bond. Then the two protons responsible for the 0.98-G triplet

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[19] J. Dewing, G. F. Longster, T. Myatt, and R. F. Todd, *Chem. Commun.*, 391 (1965).

[20] D. I. Davies and S. J. Cristol, *Advan. Free-Radical Chem.*, 1, 155 (1965).

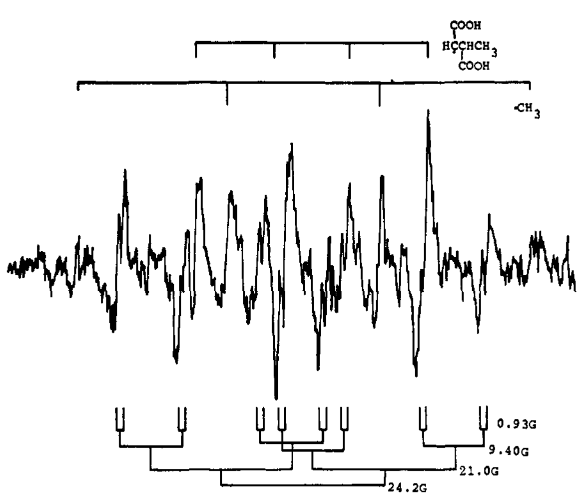


Figure 2. Esr spectrum of radical **8**.

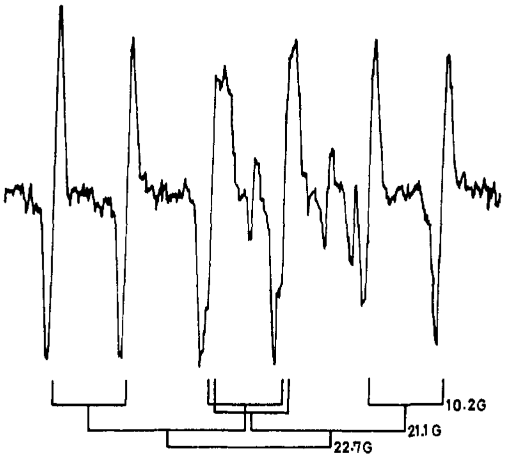


Figure 3. Esr spectrum of radical **9**.

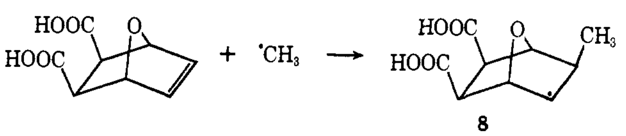
should be assigned to two protons among H_4, $H_{5\text{-endo}}$, and $H_{6\text{-endo}}$. However, splitting due to H_4 or $H_{5\text{-endo}}$ has not been resolved in other 2-norbornyl-type radicals. Thus we tentatively assume that the amino group in this radical is not protonated and one or both of the amino protons have a hfsc of 0.98 G, although the pH of the solution is *ca.* 1.

Adduct of Methyl Radical to 3. The methyl radical generated from the reduction of peroxyacetic acid or *tert*-butyl hydroperoxide with titanous ion adds to **3** resulting in *exo*-3-methyl-*exo*-*cis*-5,6-dicarboxy-7-oxabicyclo[2.2.1]hept-2-yl radical (**8**), which gave the esr spectrum shown in Figure 2. The spectrum shows coexistence of methyl radical and the adduct of methyl radical to maleic acid which was present as an impurity in **3**. The absorptions of radical **8** are analyzed as four sets of doublets of 24.2, 21.0, 9.40, and 0.93 G with the *g* factor of 2.0025. From the comparison of these hfsc's with those of radicals **1**, **2**, and **7**, hfsc's of 24.2, 21.0, 9.40, and 0.93 G are assigned respectively to $H_{3\text{-endo}}$, H_2, H_1, and $H_{6\text{-endo}}$.

$$CH_3C(O)O_2H \xrightarrow{Ti^{3+}} (CH_3C(O)O\cdot) \longrightarrow \cdot CH_3 + CO_2$$

or

$$(CH_3)_3CO_2H \xrightarrow{Ti^{3+}} ((CH_3)_3CO\cdot) \longrightarrow \cdot CH_3 + (CH_3)_2CO$$



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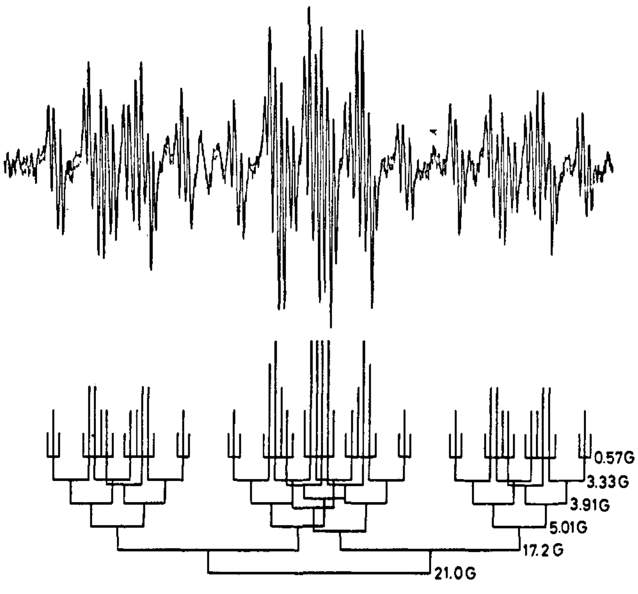
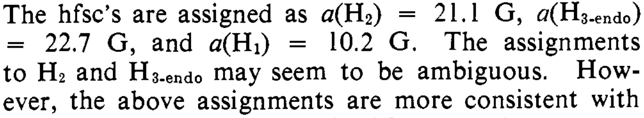


Figure 4. Esr spectrum of radical **10**.

Adduct of the Thiyl Radical from Thioglycolic Acid to 3. In a preceding paper,[21] it was shown that hydroxy radical formed from the reaction between H_2O_2 and Ti^{3+} abstracts the thiol hydrogen atom from thioglycolic acid resulting in the thiyl radical $\cdot SCH_2CO_2H$, which readily adds to an olefin. Thus the radical observed during the mixing of H_2O_2, Ti^{3+}, thioglycolic acid, and olefin **3** (Figure 3) is assigned to radical **9**.

$$HSCH_2COOH + \cdot OH \longrightarrow \cdot SCH_2COOH + H_2O$$



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The spectrum of **9** consists of three sets of doublets (22.7, 21.1, and 10.2 G) with the *g* factor of 2.0025. The hfsc's are assigned as $a(H_2) = 21.1$ G, $a(H_{3\text{-endo}}) = 22.7$ G, and $a(H_1) = 10.2$ G. The assignments to H_2 and $H_{3\text{-endo}}$ may seem to be ambiguous. However, the above assignments are more consistent with those of all other radicals derived from **3** and **5**.

Adduct of Hydroxyl Radical to 4. When titanium trichloride is allowed to react in the esr cavity with hydrogen peroxide in the presence of **4**, the esr spectrum shown in Figure 4 was observed. The spectrum is analyzed as five sets of doublets (21.0, 17.2, 5.01, 3.91, and 3.33 G) split further into a 1:2:1 triplet of 0.57 G. The *g* factor was 2.0024. The largest two of the hfsc's (21.0 and 17.2 G) of this radical are similar to those of radical **2** (22.0 and 15.2 G) and the former is assigned to *exo*-3-hydroxy-*endo*-*cis*-5,6-dicar-

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(21) T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Amer. Chem. Soc.*, 93, 908 (1971).

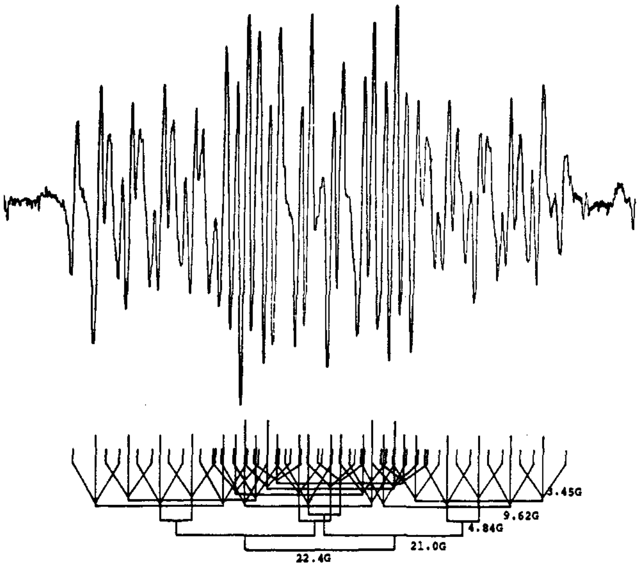
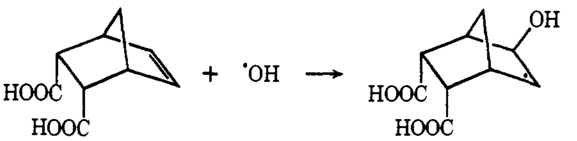


Figure 5. Esr spectrum of radical **11**.



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boxybicyclo[2.2.1]hept-2-yl radical (**10**). The comparison of $a(H_2)$ and $a(H_{3\text{-endo}})$ of radical **2** (15.2 and 22.0 G, respectively) with those of radical **1** (20.9 and 25.5 G, respectively) reported in the preceding paper[16] suggests that the substitution of 3-exo hydrogen atom of a 2-norbornyl-type radical with hydroxy group decreases both hfsc's of H_2 and $H_{3\text{-endo}}$. The hfsc's of H_2 and $H_{3\text{-endo}}$ of 2-norbonyl radical are reported to be 20.8 and 25.8 G, respectively.[17,18] The hsfc's of H_2 and $H_{3\text{-endo}}$ of **10** are expected to be less than these values if carboxy groups bonding to C_5 and C_6 do not have much effect. The largest two hfsc's of **10** are thus assigned as $a(H_2)$ = 17.2 G and $a(H_{3\text{-endo}})$ = 21.0 G. Assignments of hfsc's of 5.01, 3.91, 3.33, and 0.57 G are difficult. Values of $a(H_1)$ and $a(H_{6\text{-exo}})$ of substituted 2-norbornyl radicals are in the ranges of 6.0–8.3 G and 4.7–15.1 G, respectively.[17,18] Some 2-norbornyl radicals[17] as well as bicyclo[2.2.1]heptane-2,3-semidiones[22] have a large hfsc due to $H_{7\text{-anti}}$. Thus the observed hfsc's of 5.01, 3.91, and 3.33 G seem to arise from each proton among H_1, $H_{6\text{-exo}}$, and $H_{7\text{-anti}}$. The resolved smallest hfsc of 0.57 G (two protons) is tentatively assigned to $H_{7\text{-syn}}$ and the proton of the hydroxy substituent.

Adduct of Amino Radical to 4. Amino radical added to olefin **4** resulting in the radical which gave the spectrum of Figure 5. The *g* factor of the radical was 2.0025. The hyperfine structure of the spectrum is analyzed as three sets of doublets (22.4, 21.0, and 4.84 G) split further into a 1:1:1 triplet of 9.62 G and into a 1:2:1 triplet of 3.45 G. The existence of the 1:1:1 triplet due to a nitrogen nucleus as well as the similarity of hfsc's of protons of this radical to those of radicals **7** and **10** is consistent with *exo*-3-amino-*endo*-*cis*-5,6-dicarboxybicyclo[2.2.1]hept-2-yl radical (**11**). Assignments of the largest three hfsc's

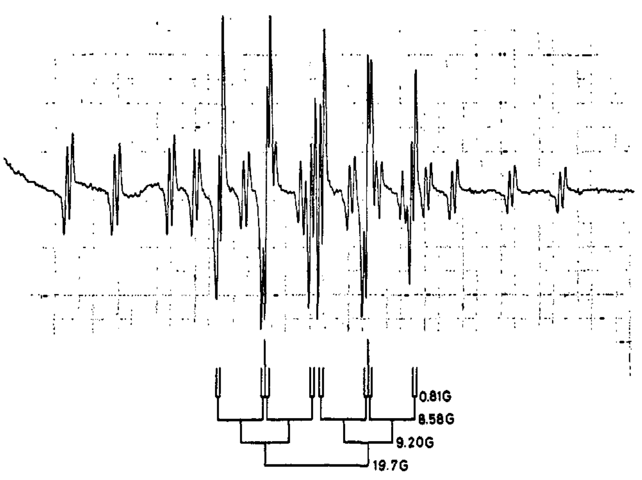
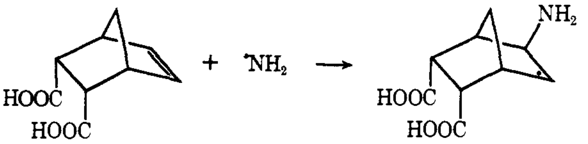


Figure 6. Esr spectrum of radical **12**.



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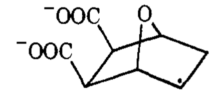
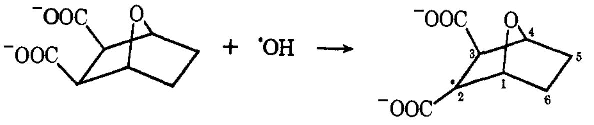
are straightforward: $a(H_2)$ = 21.0, $a(H_{3\text{-endo}})$ = 22.4, and $a(N)$ = 9.62 G. The remaining hfsc's, 4.84 and 3.45 G (two protons), probably arise from each proton among H_1, $H_{6\text{-exo}}$, and $H_{7\text{-anti}}$.

Hydrogen Abstraction from 5. The spectrum in Figure 6 was observed during mixing of a slightly basic (pH 8) aqueous solution of a mixture of **5** and hydrogen peroxide and a slightly basic (pH 8) aqueous solution of a mixture of **5**, titanous chloride, and EDTA. This spectrum shows existence of two radical species. The spectrum of one species consists of five sets of doublets (40.1, 25.4, 20.4, 9.5, and 1.0 G). These hfsc's are quite similar to those of radical **1**, and this species is identified as



The remaining absorptions are analyzed as four sets of doublets (19.7, 9.20, 8.58, and 0.81 G). The *g* factor of this radical was 2.0033, which shows the existence of a carboxy group neighboring to the radical-center carbon.[23] The hydroxy radical is known to be electrophilic and it is expected that the hydroxy radical abstracts the hydrogen atom from the carbon atom to which the carboxylate group is bonding. Thus the other radical is assigned to **12**. The hfsc of 19.7 G



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is assigned to $H_{3\text{-endo}}$. The smallest resolved hfsc of 0.81 G is similar to values of $a(H_{6\text{-endo}})$ of radicals **1**, **2**, **7**, and **8** and is assigned to $H_{6\text{-endo}}$. The remain-

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[22] G. A. Russell and K. Y. Chang, *ibid.*, 87, 4381 (1965).

[23] R. O. C. Norman and R. J. Pritchett, *Chem. Ind.* (*London*), 2040 (1965).

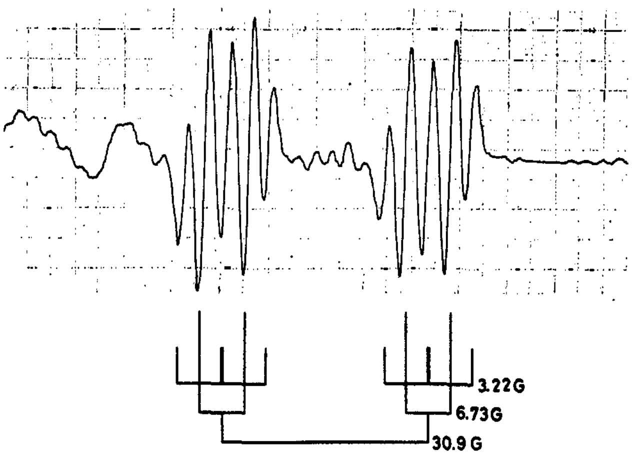
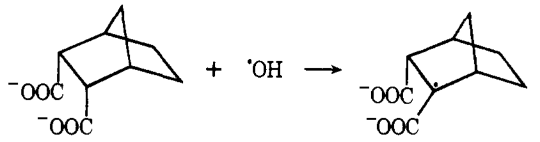


Figure 7. Esr spectrum of radical **13**.

ing hfsc's, 9.20 and 8.58 G, should be assigned to each proton among H_1 and $H_{6\text{-exo}}$.

Hydrogen Abstraction from 6. Figure 7 shows the esr spectrum observed during the reaction between hydroxy radical and **6** in a slightly basic aqueous solution (pH 8). The g factor was 2.0033. The analysis of the hyperfine splitting pattern is straightforward: two sets of doublets (30.9 and 6.73 G) split further into a 1:2:1 triplet of 3.22 G. This radical is assigned to radical **13** formed by hydrogen abstraction from C_2



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of the anion of **6**. The hfsc of 30.9 G is assigned to $H_{3\text{-exo}}$. Two protons with the hfsc of 3.22 G and a proton with 6.73 G may be assigned to each proton among H_1, $H_{6\text{-exo}}$, and $H_{7\text{-anti}}$.

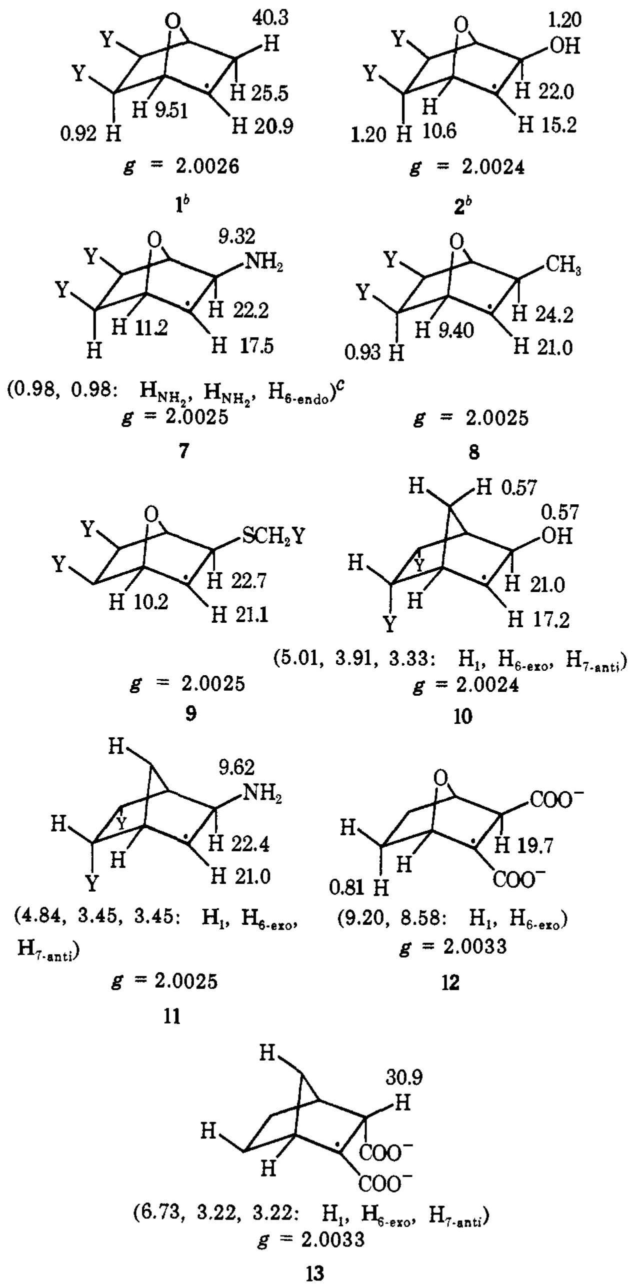
Table I summarizes the observed g factors and hfsc's of the radicals with their assignments.

Discussion

Pyramidal Geometry around the Radical-Center Carbon Atom. Electron diffraction data of norbornane were shown[14] to be consistent with the structure in which the $C_1C_2C_3$ plane bisects the bond angle of $H_{3\text{-exo}}\text{–}C_3\text{–}H_{3\text{-endo}}$. This structure around C_3 is assumed to be held for substituted bicyclo[2.2.1]hept-2-yl and 7-oxabicyclo[2.2.1]hept-2-yl radicals. If the radical-center carbon had a planar structure and the odd electron orbital on C_2 were perpendicular to this plane, $a(H_{3\text{-exo}})$ would be approximately equal to $a(H_{3\text{-endo}})$. However, the experimental results in Table I show that $a(H_{3\text{-exo}})$ is far larger than $a(H_{3\text{-endo}})$, which is consistent with the pyramidal geometry around C_2 with a bending of the C_2–H bond toward the endo direction.

The values of the α-proton hfsc of **1**, **8**, **9**, and **11** are around 21 G, which may seem reasonable as for an α-proton hfsc of a planar carbon radical. Some open-chain secondary radicals have an α-proton hfsc of this magnitude.[5a] However, the bond angle $C_1\text{–}C_2\text{–}C_3$ of the radicals under discussion would be around 104° and s character in the hybrid orbitals extending from C_2 to C_1 and C_3 would be less than one-third. If the geometry around C_2 were planar, extra s character would flow into the hybrid orbital of C_2 directing to H_2. Then the exchange interaction between the odd electron on C_2 and the C_2–H σ electrons would increase resulting in a more negative Q_α, McConnell's constant for the α proton, than −24 G.[24,25] The cyclopentadienyl radical seems to show this effect. The cyclopentadienyl radical should be planar or nearly so and the angle between two C–C bonds is 108°. The proton hfsc of this radical is reported to be 5.60

Table I. Observed Hfsc's of Substituted 2-Norbornyl Radicals[a]



g = 2.0026
1[b]

g = 2.0024
2[b]

(0.98, 0.98: H_{NH_2}, H_{NH_2}, $H_{6\text{-endo}}$)[c]
g = 2.0025
7

g = 2.0025
8

g = 2.0025
9

(5.01, 3.91, 3.33: H_1, $H_{6\text{-exo}}$, $H_{7\text{-anti}}$)
g = 2.0024
10

(4.84, 3.45, 3.45: H_1, $H_{6\text{-exo}}$, $H_{7\text{-anti}}$)
g = 2.0025
11

(9.20, 8.58: H_1, $H_{6\text{-exo}}$)
g = 2.0033
12

(6.73, 3.22, 3.22: H_1, $H_{6\text{-exo}}$, $H_{7\text{-anti}}$)
g = 2.0033
13

[a] In units of gauss. In this table Y designates COOH. [b] From ref 16. [c] Each number in the parentheses represents a hfsc of a proton. Protons with suffix show the probable assignment of the hfsc's.

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(24) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 1489 (1962).

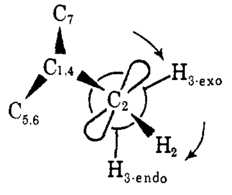
(25) J. Higuchi, *ibid.*, 39, 3455 (1963).

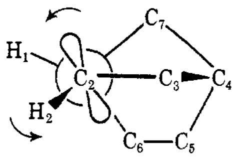
G^{26} and 6.06 G^{27} which corresponds to $Q_\alpha = (-)28$–30 G. If the 2-norbornyl-type radicals were assumed to have a planar radical center, the geometry around the trigonal carbon of these radicals would be similar to that of cyclopentadienyl radical. Then Q_α for the former radicals would be around (−)29 G. If 10% of the odd electron is assumed to be delocalized from C_2, $a(H_2)$ may be around (−)26 G, which is larger than the observed values. If the C_2–H bond bends out of the $C_1C_2C_3$ plane, the s content of the hybrid orbital of C_2 directing to H_2 will decrease accompanied with the decrease of the σ–π spin-polarization interaction. This effect as well as the delocalization of the odd electron onto C_2–H σ orbitals will decrease the absolute value of $a(H_2)$. Thus the values of $a(H_2)$ ranging from (−)15 to (−)21 G are not inconsistent with a shallow pyramidal geometry around the radical-center carbon atom.

The pronounced effect of a β substituent (the 3-exo substituent as well as the substitution of the bridging methylene group with an oxygen atom) in reducing $a(H_2)$ from 21 to 15 G also supports the pyramidal geometry around the radical-center carbon atom. The decrease of 6 G in $a(H_2)$ would correspond to a decrease of 0.20–0.25 in the odd electron density on C_2 (using Q_α = 24–30 G), if the radical-center carbon atom of all the radicals under discussion was assumed to be planar. Such a large change seems unlikely, but if the substitution changes the departure of the radical from planarity, a much larger effect on $a(H_2)$ is expected.

Figure 8 shows a plot of $a(H_{3\text{-endo}})$ and $a(H_1)$ against $a(H_2)$. Plots for 7-oxabicyclo[2.2.1]hept-2-yl radicals indicate that the decreases of hfsc's of H_2 and $H_{3\text{-endo}}$ are accompanied with an increase of the hfsc of H_1. This is inconsistent with an explanation that the decrease in $a(H_2)$ and $a(H_{3\text{-endo}})$ is due to the decrease of the odd electron density on C_2.

The bending of the C_2–H bond in the endo direction results in tilting of the odd electron orbital on C_2





in the exo direction as well as some expansion of the exo-side lobe of the orbital due to some increase of the s nature of the orbital. As the C_2–H bond bends, the overlap of the odd electron orbital with the C_3–$H_{3\text{-exo}}$ σ orbital(s) gets larger and that with the C_3–$H_{3\text{-endo}}$ σ orbital(s) decreases. Thus $a(H_{3\text{-exo}})$ is larger than $a(H_{3\text{-endo}})$ in this structure. Accompanying the tilting of the C_2–H bond the overlap between the C_1–H σ orbitals and the odd electron orbital on C_2 also increases, resulting in the increase of $a(H_1)$. In the pyramidal geometry the absolute value of $a(H_2)$ would decrease[28] as mentioned earlier. Thus plots for 7-oxabicyclo[2.2.1]hept-2-yl radicals show that the dependence of $a(H_2)$ and $a(H_{3\text{-endo}})$ on the 3-exo substituent is mainly due to the change of the pyramidality around C_2,[30] and that the smaller value of $a(H_2)$ of a substituted 7-oxabicyclo[2.2.1]hept-2-yl radical shows a more pyramidal geometry around the radical-center carbon atom.

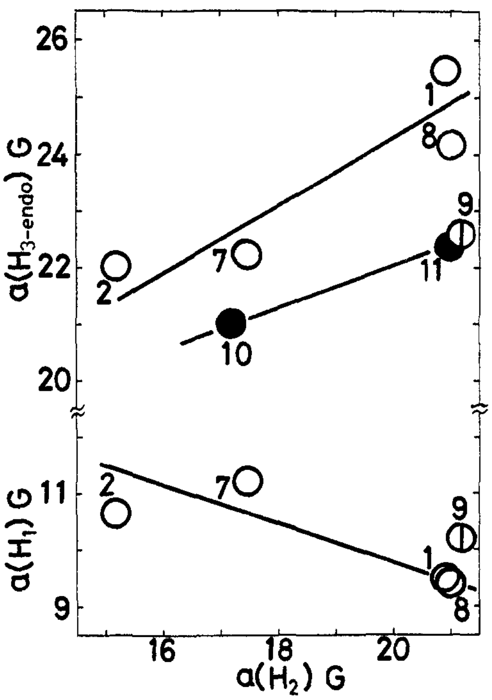
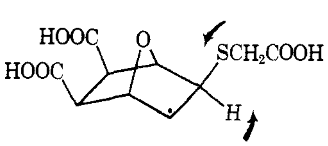


Figure 8. Plots of $a(H_{3\text{-endo}})$ and $a(H_1)$ against $a(H_2)$. The number at each plot designates a radical as in Table I: (○) substituted 7-oxabicyclo[2.2.1]hept-2-yl radicals; (●) bicyclo[2.2.1]hept-2-yl radicals.

The plot of $a(H_{3\text{-endo}})$ of radical **9** deviates from the other plots in Figure 8. Hfsc's of β protons of alkyl radicals with a β-thiyl substituent are known to be abnormally smaller than those of other radicals,[21,31] which has been attributed to an asymmetrical bridging of the thiyl group.[31] We propose that the somewhat smaller value of $a(H_{3\text{-endo}})$ of **9** than those of other radicals is due to the bending of the C_3–$H_{3\text{-endo}}$ bond in the opposite direction to C_2 accompanying the slight asymmetrical bridging of the thiyl group toward C_2.



The relation between $a(H_{3\text{-endo}})$ and $a(H_2)$ of bicyclo-[2.2.1]hept-2-yl radicals (Figure 8) is similar to that for 7-oxabicyclo[2.2.1]hept-2-yl radicals. This relation is also expected to arise mainly from the difference in the nonplanarity around the radical-center carbon atom, although we cannot confirm this by examining the relation between $a(H_1)$ and $a(H_2)$.

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(26) S. Ohnishi and I. Nitta, *ibid.*, 39, 2848 (1963).

(27) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, 47, 79, (1973).

(28) All the values of $a(H_2)$ in Table I are assumed to be negative. Dobbs, Gilbert, and Norman[6] found a monotonic relation between J_{CH} of $R'RCH_2$ and $a(H_\alpha)$ of $R'R\dot{C}H$. Randić and Stefanović[29] calculated the s:p hybridization ratio of the hybrid orbital of C_2 bonding to H_2 in norbornane to be 2.758, which corresponded to J_{CH} of *ca.* 128 Hz. Only if $a(H_2)$ is assumed to be negative the observed values of $a(H_2)$ and the estimated value of J_{CH} fit well with the J_{CH}–$a(H_\alpha)$ relation.

(29) M. Randić and D. Stefanović, *J. Chem. Soc. B*, 423 (1968).

(30) It is assumed that the 3-exo substituent does not have much effects on the angles between the C_1–H bond and the $C_1C_2C_3$ plane and between the C_3–$H_{3\text{-endo}}$ bond and the plane of $C_1C_2C_3$.

(31) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

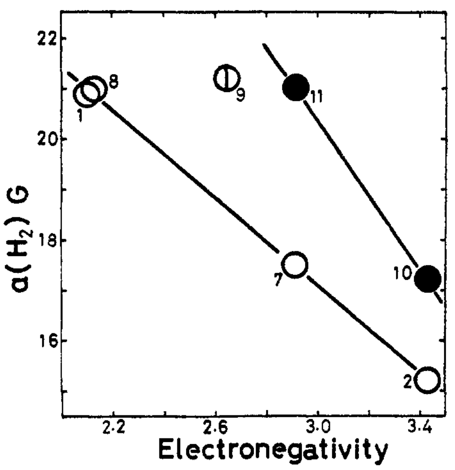

Figure 9. Plots of $a(H_2)$ against the group electronegativity of the 3-exo substituent. The number at each plot (○ and ●) has the same significance as in Figure 8.

Figure 9 shows the relation between the observed hfsc's of H_2 and electronegativities[32] of 3-exo substituents. A more electronegative substituent at the 3-exo position of a 7-oxabicyclo[2.2.1]hept-2-yl radical results in a smaller value of $a(H_2)$, that is, a more pyramidal geometry around the radical-center carbon atom. A similar behavior for substituted bicyclo-[2.2.1]hept-2-yl radicals is also shown in Figure 9. An electronegative substituent at the 3-exo position increases the effective electronegativity of C_3 (inductive effect). The increase of the electronegativity of the atom bonding to the radical-center carbon atom is known to induce the departure of the radical from planarity.[11,12]

Figure 9 shows that the adduct of hydroxy or amino radical to **3** has $a(H_2)$ a few gauss smaller than that of the corresponding adduct to **4**. We propose the former adduct radical has a more pyramidal radical-center carbon than the latter. The substitution of the bridging methylene group with an oxygen atom increases the effective electronegativity of C_1, which is expected to distort the radical center to a somewhat more pyramidal geometry. The substitution of the methylene to an oxygen would slightly shorten the distance between C_1 and C_4 accompanied with the narrowing of the bond angle of C_1–C_2–C_3, which is also favorable to a more pyramidal geometry of the radical-center atom as mentioned earlier.

This model, however, does not predict the direction in which H_2 moves. If the C_2–H bond tilted toward the exo direction in a pyramidal geometry, this bond would eclipse more with the C_1–H bond. The bending of the C_2–H bond in the endo direction would release the repulsive energy due to the partial eclipsing between C_2–H and C_1–H bonds at the planar geometry. Thus we propose that one of factors governing the direction of the bending of the C_2–H bond would be this "tortional effect" arising from the unsymmetrical staggering of the hydrogen atoms at C_1 and C_2 of the norbornane ring.[33,34]

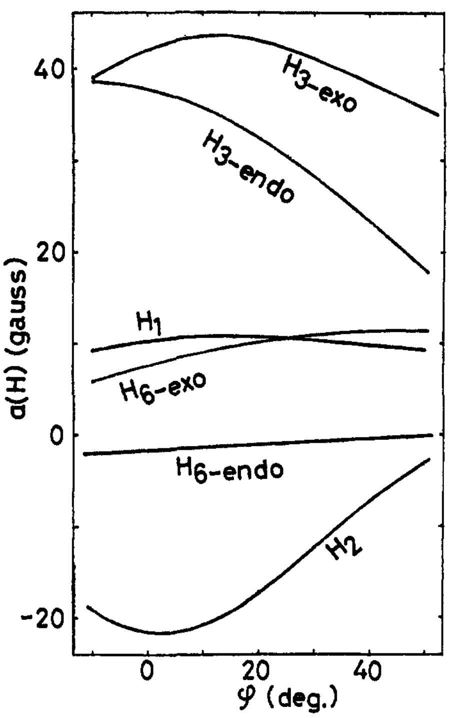

Figure 10. Dependence of calculated hfsc's of protons in 7-oxabicyclo[2.2.1]hept-2-yl radical on φ.

INDO-UHF[35] calculations (*vide infra*) of the 7-oxabicyclo[2.2.1]hept-2-yl radical show that even at the planar geometry of the radical center the odd electron orbital on C_2 is slightly tilting in the same direction in which the odd electron orbital tilts when the C_2–H bond bends toward the endo direction. This may suggest the existence of some electronic factors which stabilize the geometry with the C_2–H bond tilting in the endo direction, although we cannot clarify such a mechanism.

The plot for **9**, the radical with the 3-exo thiyl group, deviates from the other plots. This deviation suggests the asymmetrical bridging interaction between the sulfur atom and the odd electron orbital has the effect of distorting the structure around the radical-center carbon to a less pyramidal geometry than the structure expected from the electronegativity of the thiyl group.

Estimation of Geometry around the Radical Center. To elucidate the geometry around the radical-center carbon atom, proton hfsc's of the 7-oxabicyclo[2.2.1]-hept-2-yl radical were calculated with the unrestricted SCF-MO method with INDO approximations.[35] The carbon skelton and the configurations of the hydrogen atoms except H_2 of the radical are assumed to be the same as norbornane determined by electron diffraction studies,[14] in which the $C_1C_2C_3$ plane bisects the bond angle $H_{3\text{-exo}}$–C_3–$H_{3\text{-endo}}$. The bond length of C_1–O_7 (and C_4–O_7) is assumed to be 1.45 Å.[36] Figure 10 shows dependence of calculated hfsc's of protons on the angle (φ) between the C_2–H bond and the $C_1C_2C_3$

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(32) (a) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955); (b) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

(33) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967).

(34) P. D. Bartlett, G. N. Ficks, F. C. Haupt, and R. Helzeson, *Accounts Chem. Res.*, **3**, 177 (1970).

(35) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

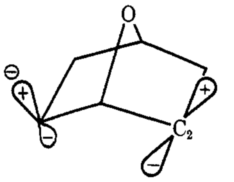
(36) The bond length of C_1–C_7 of norbornane (1.558 Å)[14] is nearly equal to the average of C–C bond lengths[37] in cyclopropane and cyclobutane. Thus the average length of the C–O bonds in ethylene oxide and oxetane, 1.45 Å,[37] was adopted for the C–O bond length in 7-oxabicyclo[2.2.1]hept-2-yl radical.

(37) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

plane (a positive value of φ corresponds to a bending of the C_2–H bond in the endo direction). Absolute values of hfsc's of H_4, $H_{5\text{-endo}}$, and $H_{5\text{-exo}}$ are calculated to be less than 0.7 G at φ in the range of $-10 \sim 50°$, and their hfsc's are not shown in Figure 10.

Some feature of φ dependence of calculated hfsc's can be explained as follows. When C_2 has a very shallow pyramidal geometry ($0 \leqq \varphi \leqq 15°$), the odd electron orbital on C_2 is almost pure p orbital. Thus $a(H_{3\text{-exo}})$ increases with the increase of φ which results in the decrease of the dihedral angle between the odd electron orbital on C_2 and the C_3–$H_{3\text{-exo}}$ bond. At more pyramidal geometries ($\varphi > 15°$), the s nature of the odd electron orbital increases with the increase of φ, which decreases the overlap between the odd electron orbital and the pseudo-π orbital consisting of C_3–$H_{3\text{-exo}}$ and C_3–$H_{3\text{-endo}}$ σ orbitals.[17] Thus the increase of φ is accompanied with the decrease of $a(H_{3\text{-endo}})$ and $a(H_{3\text{-exo}})$.

The hfsc of H_2 becomes less negative as φ deviates from 0°. This is due to the increase of the odd electron delocalization onto the C_2–H σ orbitals and to the decrease of the spin polarization in the C_2–H bond accompanying the bending of the C_2–H bond out of the $C_1C_2C_3$ plane.[38] The shape of the calculated odd electron orbital reveals that the hfsc of $H_{6\text{-exo}}$ originates from the direct (through-space) odd electron delocalization onto the C_6–$H_{6\text{-exo}}$ σ-antibonding orbital. The tilting of the odd electron orbital on C_3 (*i.e.*, the increase of φ) increases the (rear-lobe) overlap between the odd electron orbital and the C_6–$H_{6\text{-exo}}$ σ orbital(s), thus resulting in the increase of $a(H_{6\text{-exo}})$.



The ratio of calculated $a(H_{3\text{-endo}})$ to $a(H_{3\text{-exo}})$ decreases monotonically as φ increases. The observed ratio of $a(H_{3\text{-endo}})$ to $a(H_{3\text{-exo}})$ of radical **1**, 0.633, fits with the calculated ratio of 7-oxabicyclo[2.2.1]hept-2-yl radical at $\varphi \simeq 34°$. The observed value of $a(H_2) = (-)20.9$ G of radical **1** fits with the calculated value at $\varphi \simeq 10°$ in Figure 10. The calculated potential minimum of the 7-oxabicyclo[2.2.1]hept-2-yl radical was found at $\varphi \simeq 20°$. Thus the nonplanarity angle φ of radical **1** is roughly estimated to be in the range of 5–40°.

It is interesting to estimate the angle φ of radical **2**, the radical with the most pyramidal radical-center carbon atom in Table I. The value of 22.0 G of $a(H_{3\text{-endo}})$ corresponds to $\varphi \simeq 42°$ in Figure 10, that is, φ of **2** is about 8° larger than that of **1** estimated by the same method. The absolute value of the α-proton hfsc of **2** is 5.5 G smaller than that of **1**. In the $a(H_2)$–φ plot in Figure 10 this decrease corresponds to the increase of 10–17° in φ. Thus the nonplanarity angle φ of radical **2** is roughly estimated to be 5–20° larger than that of radical **1**.

Stereoselectivity of 2-Norbornyl-Type Radicals. The INDO[39] calculation at $\varphi = 34°$ shows that the odd electron orbital on C_2 consists of 4.3% s and 96% p orbitals with the expansion of the orbital lobe toward the exo direction. This exo-side expansion of the orbital would favor a radical-transfer reaction at the exo side over that at the endo side.[15] Accompanying the bending of the C_2–H bond in the endo direction, the axis of the odd electron orbital tilts in the exo side. The axis of the calculated odd electron orbital at $\varphi = 34°$ deviates *ca.* 25° from the line perpendicular to the $C_1C_2C_3$ plane. In this structure 5- and 6-endo hydrogens would exert more steric hindrance for an approach of a transfer reagent from the endo side[40] than expected for the planar geometry. The "torsional effect,"[34] the effect of the extra barrier arising from the eclipsing of the C_2–H bond to the C_1–H bond at or near the transition state during the radical transfer from the endo side, would be also larger than that expected for the planar geometry around C_2.

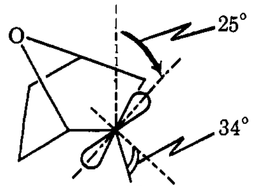


Table II. Reagents and Their Concentrations in the Solutions

Radical	Temp,[a] °C	Reagents and their concentrations Solution A (concn, *M*)	Solution B (concn, *M*)
1	40	**5** (1), H_2O_2 (0.02)	**5** (1), $TiCl_3$ (0.01) H_2SO_4 (0.1)
2	*b*	**3** (0.09), H_2O_2 (0.06)	**3** (0.09), $TiCl_3$ (0.007) H_2SO_4 (0.07)
7	*b*	**3** (0.1), $NH_2OH \cdot HCl$ (1)	**3** (0.1), $TiCl_3$ (0.01) H_2SO_4 (0.1)
8	30	**3** (0.2), CH_3CO_3H (0.2)	**3** (0.2), $TiCl_3$ (0.01) H_2SO_4 (0.1)
8	30	**3** (0.2), $(CH_3)_3CO_2H$ (0.3)	**3** (0.2), $TiCl_3$ (0.01) H_2SO_4 (0.1)
9	*b*	**3** (0.1), H_2O_2 (0.05)	**3** (0.1), $TiCl_3$ (0.01) H_2SO_4 (0.1) $HSCH_2CO_2H$ (0.2)
10	*b*	**4** (0.09), H_2O_2 (0.06)	**4** (0.09), $TiCl_3$ (0.007) H_2SO_4 (0.07)
11	*b*	**4** (0.09) $NH_2OH \cdot HCl$ (1)	**4** (0.09), $TiCl_3$ (0.01) H_2SO_4 (0.1)
12	*b*	**5** (1), NaOH (2) H_2O_2 (0.05), H_2SO_4[c]	**5** (1), NaOH (2), $TlCl_3$ (0.03), EDTA (0.06), K_2CO_3[c]
13	*b*	**6** (1), NaOH (2) H_2O_2 (0.05), H_2SO_4[c]	**6** (1), NaOH (2), $TlCl_3$ (0.04), EDTA (0.08), K_2CO_3[c]

[a] The temperature of both solutions. [b] Room temperature (15–25°). [c] This reagent was added to adjust the pH of the solution to 8.

Experimental Section

Materials. 7-Oxabicyclo[2.2.1]hept-2-ene-*exo-cis*-5,6-dicarboxylic anhydride was prepared from freshly distilled furan and maleic anhydride in dry ether according to the method of Diels, Alder, and Naujoks.[41] The adduct was hydrolyzed to 7-oxabi-

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[38] *Cf.* Figure 1 of ref 4b.

[39] D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968).

[40] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, 4, 382 (1958).

[41] O. Diels, K. Alder, and E. Naujoks, *Chem. Ber.*, 62, 557 (1929); R. B. Woodward and H. Bear, *J. Amer. Chem. Soc.*, 70, 1161 (1948).

cyclo[2.2.1]hept-2-ene-*exo-cis*-5,6-dicarboxylic acid (**3**) by dissolving it in warm water (40–60°), and was used immediately for esr measurements. The oxygen-bridged olefinic acid anhydride was hydrogenated in acetone with 5% Pd/charcoal catalyst[42] and then hydrolyzed into diacid **5** by dissolving it in hot water.

Bicyclo[2.2.1]hept-2-ene-*endo-cis*-5,6-dicarboxylic anhydride and its diacid, **4**, were prepared according to the procedure of Fieser.[43] Bicyclo[2.2.1]heptane-*endo-cis*-5,6-dicarboxylic acid was prepared from the anhydride of **4** by hydrogenation with 5% Pd/charcoal catalyst in ethyl acetate followed by hydrolysis in boiling water.

The following reagents were obtained commercially from Nakarai Chemicals Ltd. and Wako Pure Chem. Ind. and used without further purification: 20% $TiCl_3$ aqueous solution, 30% H_2O_2 aqueous solution, hydroxylamine hydrochloride, 9% peroxyacetic acid in acetic acid, *tert*-butyl hydroperoxide, and thioglycolic acid.

Generation of Radicals. For the generation and the esr measurement of the radicals, the Dixon–Norman[44] type rapid flow technique was used. Two aqueous solutions (A and B) flew into the mixing chamber and then into the sample cell in the esr cavity. The reagents and their concentrations in both solutions are summarized in Table II. When the solubility of the substrate was insufficient the solution was heated to increase the solubility.

Esr Measurement. The esr spectra were obtained with a JEOL 3BSX spectrometer with 100-kHz modulation. The flow system consists of a JEOL JES-SM-1 mixing chamber, a JES-LC-01 capillary-type aqueous sample cell. Hyperfine coupling constants and *g* factors were determined relative to the hfsc of ^{14}N (13.07 G) and the *g* factor (2.00559) of potassium peroxylaminedisulfonate in aqueous solution filled in a capillary which was attached to the sample cell. The reported *g* factors were corrected to second order with respect to the hyperfine interactions.

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(42) O. Diels and Olsen, *J. Prakt. Chem.*, **156**, 302 (1940).

(43) L. F. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1964, Chapter 15.

(44) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. X. Reactions of Some Alkylamino Radicals in Solution[1,2]

J. R. Roberts[3] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9. Received September 29, 1972

Abstract: Dimethylamino, diethylamino, and diisopropylamino radicals have been generated in the cavity of an epr spectrometer by photolysis of the appropriate tetraalkyltetrazenes and by photolysis of di-*tert*-butyl peroxide in the presence of the dialkylaminodiethoxyphosphines. The second-order decay of dimethylamino and diethylamino occurs at the diffusion controlled limit, $(2 \pm 1) \times 10^9\ M^{-1}\ \text{sec}^{-1}$. The decay of diisopropylamino is second order at temperatures below ambient ($k^2_{\text{epr}} \approx 1.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$) and first order above. For radicals generated from the tetrazene, the first-order process is rather slow and represents thermal decomposition of an intermediate which is probably the cis tetrazene. For radicals generated from the phosphine the first-order process is quite rapid and probably corresponds to a true unimolecular reaction of diisopropylamino radicals, except when the solvent is a good hydrogen donor. 2,2,6,6-Tetramethylpiperidyl radicals were generated from the tetrazene. The decay is first order in hydrocarbon solvents. The variation in the rate constants for decay with hydrocarbon structure, the rate constants in perdeuterated solvents, and product studies show that this reaction is usually a hydrogen abstraction from the solvent. The tetramethylpiperidyl radical is more reactive in abstractions than are peroxy radicals. Tetramethylpiperidyl ($a_N = 14.66$ G, $g = 2.0048$ in isopentane at 27°) reacts rapidly with oxygen and is converted to the corresponding nitroxide ($a_N = 15.3$ G, $g = 2.0064$ at $-100°$). With ^{17}O labeled oxygen this nitroxide has $a(^{17}O) = 19.35$ G.

Studies of the chemistry of dialkylamino radicals in solution have generally been confined to the dimethylamino radical which has been generated by the thermolysis or photolysis of tetramethyl-2-tetrazene.

$$Me_2NN{=}NNMe_2 \xrightarrow[h\nu]{\text{heat}} 2Me_2N\cdot + N_2$$

In the absence of any other reactant the principal products appear to arise from the combination and disproportionation of the dimethylamino radicals.[4,5]

$$2Me_2N\cdot \longrightarrow Me_2NNMe_2$$

$$2Me_2N\cdot \longrightarrow Me_2NH + (CH_2{=}NMe) \longrightarrow \text{trimer and polymer}$$

Some hydrogen abstraction from the tetrazene, leading to induced decomposition, may also occur.[4,6,7] Dimethylamino radicals appear to add to styrene[8] and to α-methylstyrene[9,10] but not to simple olefins[7,9] or to aromatic systems.[9,11,12] They abstract benzylic (and other activated) hydrogens "feebly" at elevated temperatures,[7–9,12,13] and the relative reactivities of some substrates have been determined.[7,13] However, they do not readily abstract benzylic hydrogens at room temperature which is a bit surprising since the

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