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## Electron Spin Resonance of Alkyl Radicals from Bicyclobutanes

*Sir:*

Considerable interest in the chemical and physical properties of the $C_4H_6$ hydrocarbon bicyclobutane has been aroused by its highly strained configuration[1] and interesting structural[2] and bonding possibilities.[3] We wish to report on electron spin resonance (esr) studies of the $C_4H_5$ free radical derived from bicyclobutane in solution. Although bicyclobutane undergoes facile free-radical addition across the 1,3 bond,[4] the $C_4H_5$ radical can be generated by hydrogen abstraction with *t*-butoxy radical.[5]

Previous studies showed that photochemically generated *t*-butoxy radicals from di-*t*-butyl peroxide can be employed to produce alkyl radicals from a variety of

$$(CH_3)CO\cdot + RH \longrightarrow R\cdot + (CH_3)_3COH \qquad (1)$$
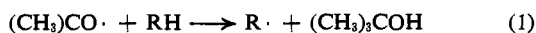
hydrocarbons directly in the cavity of the spectrometer.[7] An intense and well-resolved esr spectrum (Figure 1)
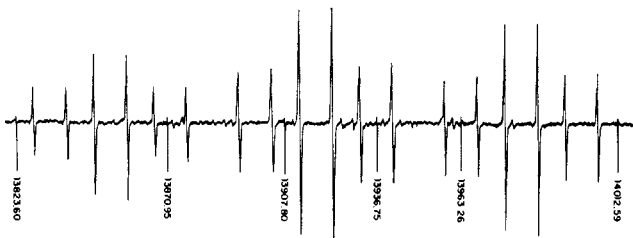


Figure 1. The esr spectrum of cyclobutenyl radical I from bicyclobutane at −90°. The proton nmr field markers are in kcps.

was obtained when a dilute solution (*ca.* 10% v/v) of di-*t*-butyl peroxide in the binary system consisting of equal volumes of bicyclobutane and cyclopropane[8] was irradiated at −90° in the esr cavity. The identical spectrum was obtained when *cyclobutene* was treated under these conditions with *t*-butoxy radicals. We identify

(1) K. B. Wiberg, *Record Chem. Progr.*, 26, 143 (1965); K. B. Wiberg, G. M. Lampman, R. P. Ciula, P. S. Connor, P. Scherfler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965).

(2) M. D. Harmony and K. Cox, *J. Am. Chem. Soc.*, 88, 5049 (1966).

(3) M. Pomerantz and E. W. Abrahamson, *ibid.*, 88, 3970 (1966).

(4) E. P. Blanchard, Jr., and A. Cairncross, *ibid.*, 88, 487 (1966).

(5) *t*-Butoxyl is generally the radical of preference for hydrogen abstraction even from alkenes.[6]

(6) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, 83, 3877 (1961); J. K. Kochi, *ibid.*, 84, 774 (1962).

(7) P. J. Krusic and J. K. Kochi, *ibid.*, 90, 7155 (1968).

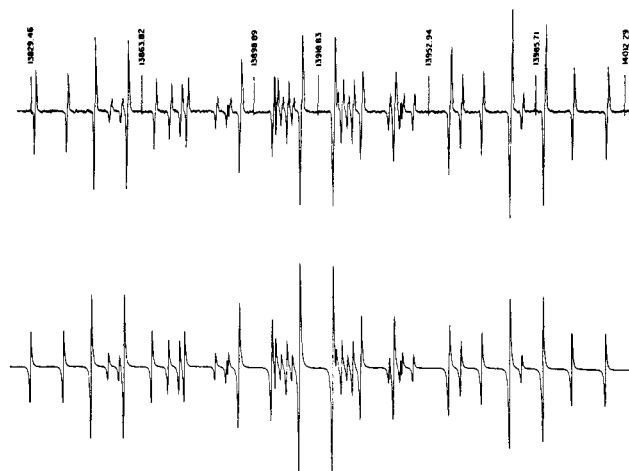(8) Cyclopropane and ethane are used as inert solvents in these experiments.



Figure 2. The esr spectrum obtained from bicyclobutane at −170°. The minor components of the spectrum are associated with the radical species II. The computer-simulated superposition of the two spectra is shown below.

the paramagnetic species as the cyclobutenyl radical I. The hyperfine coupling constants obtained for I are: $a_{H_1}$ = 2.41 G (doublet), $a_{H_2}$ = 15.20 G (triplet), $a_{H_3}$ = 4.45 G (triplet). Fessenden[9] has recently reported
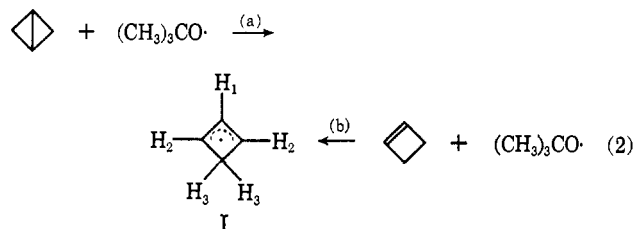


that the magnitude of the coupling constant for the central hydrogen ($H_1$) in allylic moieties decreases with the internal angle. Our value for the cyclobutenyl radical is consistent with this trend. The coupling constant for $H_2$ is comparable to that obtained for analogous alicyclic and acyclic allylic radicals.[9,10] Interestingly, the small value found for $H_3$ confirms Whiffen's prediction based on molecular orbital theory.[11]

At temperatures below approximately −100°, the esr spectrum consisted of additional lines due to a second paramagnetic species II (Figure 2) with a slightly larger *g* value ($\Delta g$ = 0.00012). Its importance increased as the temperature was lowered to −170°. Such low temperatures could be achieved without crystallization with the ternary system consisting of equal volumes of bicyclobutane, cyclopropane, and ethane.[8] The spectrum of 24 lines was readily analyzed into a doublet ($a_{H\alpha}$ = 12.64 G) of triplets ($a_{Hb'}$ = 4.40 G) further split into two doublets of 7.85 and 0.81 G due to *endo* and *exo* hydrogens. A unique assignment for the latter pair cannot be made rigorously at this juncture (*vide infra*). The most reasonable structure for II is given in Figure 3.

(9) R. W. Fessenden, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9, 1968, Abstract No. ORGN-85.

(10) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, 90, 7157 (1968); unpublished results.

(11) D. H. Whiffen, *Mol. Phys.*, 6, 224 (1963). See also W. T. Dixon, *Chem. Commun.*, 559 (1969).
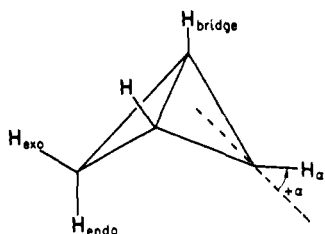
Figure 3. The bicyclobutyl radical II.

The above coupling constants are quite remarkable and reflect the unusual geometry and electronic structure of the radical. The small magnitude of the $\beta$ coupling due to the bridgehead protons (4.40 G) indicates that these protons are close to the nodal plane of the spin-containing p orbital as dictated by the constrained geometry of II. A similar situation arises in the cyclopropylcarbinyl radical.[12] Secondly, the splitting of one of the $\gamma$-methylene protons is extraordinarily large (7.85 G) compared to typical values of less than 1 G for alkyl radicals generally.

The coupling of the $\alpha$ proton (12.64 G) is intermediate between the values found for typical alkyl radicals (21–23 G) and the very abnormal $\alpha$ coupling found for cyclopropyl[13] ($a_\alpha$ = 6.51 G). The variations in the $\alpha$-coupling constants can be related to deviations from planarity at the radical site.[14] The strong angular dependence of the $\alpha$-coupling constant in bicyclobutyl radical is predicted by INDO molecular orbital calculations (Figure 4).[15] The experimental data best fit the theoretical model with $\alpha$ = +15°. The alternative choice with $\alpha$ = −15° also corresponds to a higher calculated energy. We are thus led to the interesting conclusion that $a_{endo}$ is greater than $a_{exo}$, contrary to the empirical W-plan formulation.[16]

Radical species II is no doubt generated by direct abstraction of one of the methylene hydrogens by $t$-butoxy radicals. Intramolecular rearrangement of II to the more stable allylic species I is facile but not instantaneous, since a relatively slight lowering of the temperature (from −90 to −120°) retards the following rearrangement (eq 3).[17] Interestingly, we could obtain no evidence of either the tertiary bicyclobutyl radical III derived by removal of the bridgehead hydro-

$$\text{(3)}$$

tain no evidence of either the tertiary bicyclobutyl radical III derived by removal of the bridgehead hydro-

$$+ \quad (CH_3)_3CO\cdot \quad \longrightarrow \quad \cdot + \quad (CH_3)_3COH \quad \text{(4)}$$

III
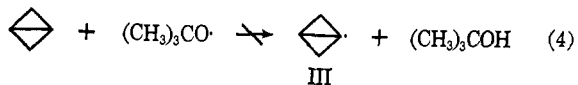
(12) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 1877, 1879 (1969).

(13) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(14) (a) R. W. Fessenden and R. H. Schuler, *ibid.*, **43**, 2704 (1965); (b) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967); (c) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968); (d) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 3938 (1969).

(15) (a) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968). (b) We wish to thank the Quantum Chemistry Program Exchange, Indiana University, for a copy of this program. (c) The structural parameters were those reported by K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).

(16) (a) G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 87 ff. (b) Deuterium-labeling studies are under way in order to establish these assignments unambiguously.

(17) Equation 3 is analogous to the facile ring opening in the cyclopropylcarbinyl radical (*cf.* ref 10).
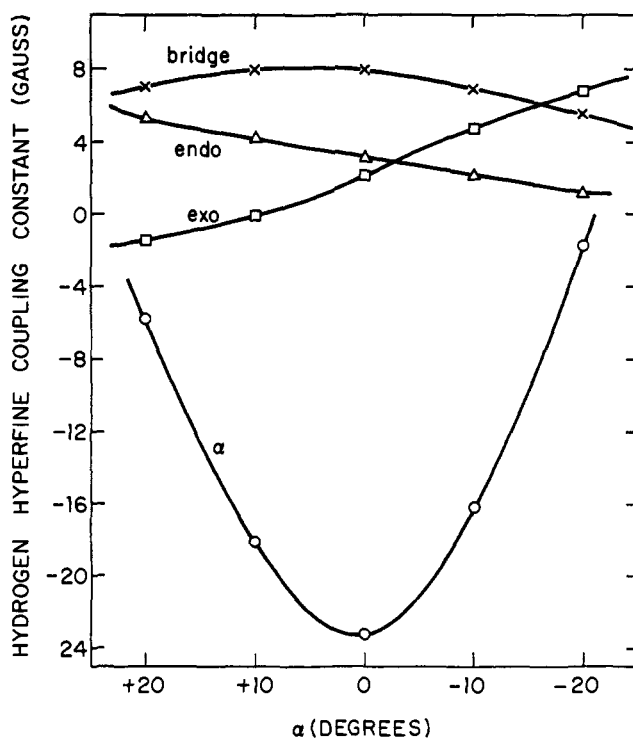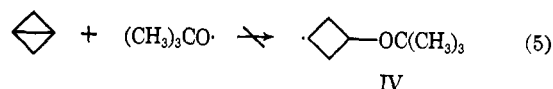
Figure 4. Hydrogen hyperfine coupling constants for bicyclobutyl radical II by INDO molecular orbital calculations.

gen (eq 4) or the cyclobutyl derivative IV derived by addition of $t$-butoxy radical to bicyclobutane[18] (eq 5).

$$+ \quad (CH_3)_3CO\cdot \quad \longrightarrow \quad \cdot \langle\rangle\text{—}OC(CH_3)_3 \quad \text{(5)}$$

IV

The abstraction of one of the methylene hydrogens of bicyclobutane by $t$-butoxy radical to afford II is in contrast with the unreactivity of cyclopropane under equivalent conditions.[8] Judging from the strong esr spectrum obtainable from bicyclobutane,[19] we conclude that the bonding in the methylene groups is different[3] in these two molecules.

The formation of cyclobutenyl radicals related to I is not restricted to bicyclobutane, since the analog[4] 3-methylbicyclo[1.1.0]butane-1-carbonitrile (V) in cyclopropane solution affords the cyclobutenyl radical VI on reaction with $t$-butoxy radical. No other paramagnetic species was detected at −110°. We were

$$CH_3\text{—}\langle\rangle\text{—}CN \quad + \quad (CH_3)_3CO\cdot \quad \longrightarrow \quad CH_3\text{—}\langle\rangle\text{—}CN$$

V

VI
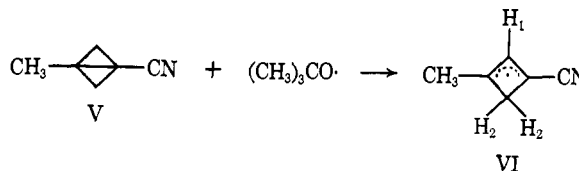
unable to examine the esr spectrum at lower temperatures because of crystallization. The pertinent coupling constants are: $a_{H_1}$ = 1.79 G (doublet); $a_{H_2}$ = 3.65 G (triplet); $a_{CH_3}$ = 13.70 G (quartet); and $a_N$ =

(18) The esr spectrum of cyclobutyl has been reported in ref 13 and 7.

(19) (a) In our work with various hydrocarbons we have been able to judge qualitatively the facility of reaction 1 by the intensity of the esr signals. Quantitative kinetic studies are in progress. (b) Furthermore, in the analog V it is also the methylene rather than the methyl hydrogen which is preferentially abstracted by $t$-butoxy radical, although in methylcyclopropane the opposite pertains.[12]

2.73 G (1:1:1 triplet). Interestingly, the radical species VI is also obtained when 3-methylcyclobutene-1-carbonitrile (VII) is subjected to *t*-butoxy radicals, indicating that the tertiary allylic hydrogen in VII is much
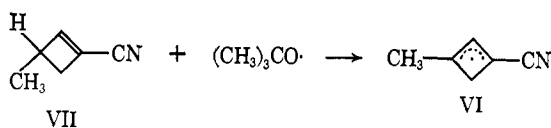


more reactive toward homolytic abstraction than the two secondary allylic hydrogens.

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## Hydrogen-Bridged Silicon–Rhenium Bonds. A Diphenylsilane Complex of Rhenium Carbonyl

*Sir:*

The role of hydrogen as a bridging group between two transition metals is now well established as, for example, in the molecules $C_5H_5(CO)_2Mo(H)(P(CH_3)_2)$-$Mo(CO)_2C_5H_5$[1] and $(OC)_4Mn(H)(P(C_6H_5)_2)Mn(CO)_4$[2] and in various polynuclear carbonyl hydrides of manganese and rhenium.[3] Hydrogen bridges between a main group element and a transition metal have heretofore been encountered only for boron, as in the compounds $HMn_3(CO)_{10}(BH_3)_2$,[4] $[(CH_3)_4N][Cr(CO)_4B_3H_8]$,[5] and $[(C_6H_5)_3P]_2CuBH_4$.[6] We now report such a mixed hydrogen bridge involving silicon as the main group element.

The first compound of this new class is $(C_6H_5)_2$-$SiH_2Re_2(CO)_8$, prepared by ultraviolet irradiation of a benzene solution of $Re_2(CO)_{10}$ and $(C_6H_5)_2SiH_2$ at room temperature under a nitrogen atmosphere. After removal of solvent and unreacted starting materials under vacuum, the residual solid was crystallized three times from *n*-hexane to afford colorless, moderately air-stable crystals of the product,[7] mp 168–169°. The mass spectrum established that 12 hydrogen atoms were present in the molecule. The nmr spectrum (taken on a $CCl_4$ solution, in which, rather surprisingly, the com-

pound is stable for long periods) exhibited a peak at $\tau$ 19.56 of about one-fifth the intensity of the phenyl protons. Further investigation by infrared and nmr (*vide infra*) suggested that a transition metal hydride of novel type was involved, and a single-crystal X-ray diffraction study was undertaken to establish the structure more rigorously.

The complex was found to crystallize in the orthorhombic space group Pbcn with eight molecules per unit cell. Three-dimensional intensity data were collected on a PAILRED automated diffractometer, and the structure was solved by conventional methods. At the present state of refinement the $R$ factor is 5.7% for 1300 unique above-background reflections. All non-hydrogen atoms have been located and anisotropic temperature factors assigned to the rhenium and silicon atoms. The molecular structure is shown in Figure 1, in which the unique pair of hydrogen atoms has been placed in the conspicuously vacant sixth coordination site of each rhenium. This inference is strongly supported by spectroscopic evidence mentioned later. If the hydrogen atoms are placed in the Re–Si–Re plane, with a Re–H distance of 1.68 Å[8] at right angles to the Re–Re bond, the Si–H distance is 1.57 Å, not unreasonable in comparison with the value of 1.48 Å found in $SiH_4$,[9] and certainly consistent with a bridging rather than a terminal hydrogen. It is of interest that the molecular symmetry is 2 mm ($C_{2v}$), although none is required crystallographically; there are no significant deviations from it.

The infrared spectrum of $(C_6H_5)_2SiH_2Re_2(CO)_8$ showed carbonyl stretching bands (with relative intensities) at 2110 (3.2), 2075 (6.7), 2021 (7.7), 2015 (10), 2000 (7.2), 1995 (4.5), and 1977 (7.9) cm$^{-1}$ (cyclohexane). The over-all band pattern resembled that of $(C_6H_5)_2GeFe_2(CO)_8$,[10] suggesting a similar geometry for the heavy-atom framework in both molecules. The possibility that one or more bands in the carbonyl region was due to $\nu$(Re–H) was excluded by examining the infrared spectrum of $(C_6H_5)_2SiD_2Re_2(CO)_8$.[11] The spectra of the two compounds were almost identical except for minor changes ($\leq 3$ cm$^{-1}$) in some of the carbonyl stretching bands; this effect is due to altered mixing of $\nu$(CO) with an unobserved H or D mode.[12] In particular, the 1600–1200-cm$^{-1}$ region, where terminal $\nu$(Re–D) would be expected, was unchanged.

The mass spectrum of $(C_6H_5)_2SiH_2Re_2(CO)_8$ provides further evidence for bridging hydrogens. As noted above, the molecular ion of the compound was observed, and a comparison of ion intensities with the theoretical multiplet pattern[13] established that there is no appreciable hydrogen loss from the molecular ion.[14]

(1) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965); R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).
(2) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 4323 (1967); R. G. Hayter, *ibid.*, **86**, 823 (1964).
(3) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *ibid.*, **90**, 7135 (1968); H. D. Kaesz, R. Bau, and M. R. Churchill, *ibid.*, **89**, 2775 (1967); J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, **89**, 1759 (1967); H. D. Kaesz, V. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid.*, **91**, 1021 (1969); A. P. Ginsberg and M. K. Hawkes, *ibid.*, **90**, 5930 (1968).
(4) H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *ibid.*, **87**, 2753 (1965).
(5) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).
(6) S. J. Lippard and K. M. Melmed, *ibid.*, **6**, 2223 (1967).
(7) *Anal.* Calcd for $C_{20}H_{12}O_8Re_2Si$: C, 30.77; H, 1.55; Si, 3.60. Found: C, 30.67; H, 1.77; Si, 3.68.

(8) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).
(9) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, England, 1962, p 696.
(10) E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Am. Chem. Soc.*, **90**, 3587 (1968).
(11) This compound was prepared by the same method using $(C_6H_5)_2$-$SiD_2$. Carbonyl stretching bands (with relative intensities) are observed at 2110 (3.0), 2076 (6.4), 2018 (8.8) sh, 2016 (10), 1998 (7.9), 1995 (5.2), and 1975 (7.4) cm$^{-1}$ in cyclohexane solution.
(12) Shifts in $\nu$(CO) upon deuteration have previously been observed; *cf.* the analysis by P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967), and references cited.
(13) The computed multiplet pattern is (nominal mass, relative abundance): 778 (28.8); 779 (8.1); 780 (100); 781 (27.6); 782 (91.0); 783 (24.2); 784 (7.0); 785 (0.8); 786 (0.1). Peaks at 776 or 777 would indicate hydrogen loss.