insertion to give **7**; and (c) azetine **7** (path B) should undergo cyclobutene-type ring opening[5] to 1-phenyl-2-azabutadiene (**8**; *vide infra*) much more rapidly than retro 2 + 2 cleavage to styrene and HCN. A clue to what we believe is the true mechanism was obtained by examining the products of thermal decomposition (480°) of 2-phenyl-3,3-dimethyl-2*H*-azirine (**4c**). In this reaction, along with styrene (15%), benzonitrile (8%), and acetonitrile,[6] was isolated a product (46%) of longer retention time. The new material exhibited pmr signals at δ 7.27–7.90 (5 H), 8.18 (1 H), 4.69 (1 H), 4.49 (1 H), and 2.00 (3 H) ppm. On the basis of this, mass spectral (M⁺ = m/e 145) and ir (intense band at 1644 cm⁻¹) data, it was assigned structure **8c**. The assignment was confirmed by hydrolysis of **8c** in aqueous mineral acid to benzaldehyde and acetone.

Subjection of **8c** to the azirine pyrolysis conditions gave styrene and acetonitrile, and this provided the key to the mechanism; we infer that the **7** → **8** reaction is *reversible*. Such reversibility is consistent with the recent demonstration that cyclobutene is thermally accessible from butadiene.[7] It also allows **7c** and **8c** to be intermediates in the pyrolysis of **4c** without requiring $k_2 > k_1$ and allows **8** to be formed directly by

Scheme III

$$4 \longrightarrow 6 \longrightarrow 8 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} 7 \overset{k_2}{\longrightarrow} 5 + CH_3CN$$
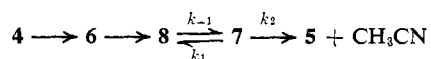
1,4 hydrogen transfer[4] from **6**. In addition, we have independently prepared 3-phenyl-2,3-dimethyl-2*H*-azirine[8] (**9**, Scheme II) and subjected it to the pyrolysis conditions. This material rearranges only to indole **2** ($R_1 = R_3 = CH_3$). The lack of detectable styrene formation rigorously rules out the operation of path A in the decomposition of **4c**.

Thermal decomposition of either **4c** or **8c** at somewhat higher temperature (540°) resulted in the disappearance of **8c** and formation of a new product, identified as 3-methyldihydroisoquinoline[9a,b] (**10**). Thermolysis of **4a** at 580° gave the parent 3,4-dihydroisoquinoline (**11**). This provides evidence that, although the conversion of

10, R = CH₃
11, R = H
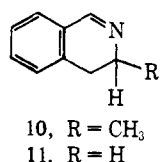
8a to styrene or polymer occurs rapidly enough during the 565° pyrolysis of **4a** to preclude its isolation, the imine is in fact an intermediate in this reaction as well.

We cannot rule out the occurrence of C–H insertion in intermediate **6**, but the observation of 1,4 hydrogen transfer in analogous vinylcarbenes[4,10] indicates that

(5) L. A. Paquette, J. J. Wynratt, and R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1763 (1970).

(6) Acetonitrile was found to be somewhat unstable to the reaction conditions; although its yield is therefore uncertain, sufficient material was obtained for identification.

(7) L. M. Stephenson, R. V. Gemmer, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 8620 (1972).

(8) Prepared by the method of (a) R. F. Parcell, *Chem. Ind. (London)*, 1396 (1963); see also (b) N. J. Leonard and B. Zwanenburg, *J. Amer. Chem. Soc.*, **89**, 4456 (1967).

(9) (a) V. M. Potapov, V. M. Dem'yanovick, L. D. Solov'eva, and A. P. Terent'ev, *Dokl. Akad. Nauk SSSR*, **185**, 614 (1969); (b) U. P. Basu and B. Bhattacharya, *J. Org. Chem.*, **32**, 4108 (1967); (c) S. Ikegami and S. Yamada, *Chem. Pharm. Bull.*, **14**, 1389 (1966).

(10) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Amer. Chem. Soc.*, **95**, 5680 (1973).

our results are best accommodated by the modified mechanism outlined in Scheme III.[11] With regard to the variable mode of azirine thermal decompositions,[1] we suggest that the presence of a stabilizing group (such as phenyl) at C-2 tends to induce the formation of products formed from C–C cleavage,[12] whereas its location at C-3 (*cf.* compounds **1a–1e**) results in products formed by initial rupture of the inherently weaker C–N bond. We believe that product formation reflects true bond-cleavage preferences because no imine analogous to **8** is apparently formed in the thermolysis of **1a**. However, confirmation of that inference awaits experiments (such as those carried out in the analogous cyclopropene system[10]) designed to directly determine the rate-determining step in azirine pyrolysis.

(11) In solution photochemical studies,[2] a nitrile ylide structure is most often written for **6**. While it is quite possible that such a structure is most reasonable for the C–C cleavage intermediate formed in solution, the general avoidance of charge-separated structures in the gas phase and the distinctive chemical behavior of **6** suggest that it is best thought of here as an iminocarbene.

(12) Both pathways outlined in Scheme I are consistent with this picture; apparently the carbene-stabilizing phthalimido group induces the *subsequent* step in **1d–1g** to be C–C cleavage leading to **3**, while in **1a–1c**, the "nitrene" nitrogen attacks the phenyl ring in a second step to give **2**.

(13) Camille and Henry Dreyfus Teacher–Scholar Grant Awardee, 1970–1975.

Larry A. Wendling, Robert G. Bergman*[13]
Contribution No. 4778, Gates and Crellin
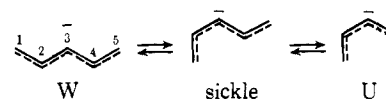*Laboratories of Chemistry*
California Institute of Technology
Pasadena, California 91109
Received October 12, 1973

Direct Observation of Acyclic Pentadienyllithium Conformational Isomers by Carbon-13 Magnetic Resonance Spectroscopy

Sir:

Pentadienyl anions could exist in three planar conformations, W, sickle, and U. Previous attempts to
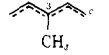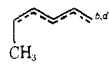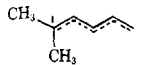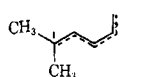

W   sickle   U

detect more than one conformer of pentadienyl anions in low temperature pmr spectra failed in all but one case, 2-methylpentadienyllithium, in which two conformers were observed in the pmr spectrum at −20° but no conformational assignment could be made.[1] However, by comparison of pmr spectra of acyclic pentadienyllithiums to those of rigid sickle and U-shaped analogs, it was concluded that a proton–proton coupling constant, J_{23},[2] of ~12 Hz corresponded to a trans conformation and a coupling constant of ~6.5 Hz corresponded to a cis conformation of an inner bond of a pentadienyl anion.[1] On this basis acyclic pentadienyllithiums in ethers[1,3] and acyclic pentadienyl-

(1) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

(2) Subscripts refer to protons bound to the corresponding numbered carbon atoms of the pentadienyl anions.

(3) S. Brenner and J. Klein, *Isr. J. Chem.*, **7**, 735 (1969).

Table I. Cmr Chemical Shifts of Pentadienyllithiums[a]

	T, deg	C_1	C_2	C_3	C_4	C_5
[b,c]	−41	66.2	143.8	86.9		
CH₃ [c]	−37	63.4	144.4	91.6		
CH₃ [b,d]	−37	85.7	137.3	81.4	143.6	56.7
CH₃ [b,d]	−37	89.2	139.6	83.8	142.9	51.5
CH₃ / CH₃	−37	94.7	133.1	81.9	142.7	50.8
CH₃ / CH₃	−37	101.2	126.4	77.2	138.2	49.2

[a] In ppm downfield from external TMS in acetone-d_6. Samples 2–3 M in THF–hexane were prepared by the method of H. H. Freedman described in ref 6. Data were collected at 25.2 MHz on a Varian XL-100-15 spectrometer equipped with a Digilab Model FTS-NMR-3 Fourier transform accessory. [b] Peak assignments were made in part from an off-resonance decoupled spectrum. [c] See ref 8. [d] Assignments of C_1 and C_3 were made from the spectrum at 80° of a sample partially deuterated at C_3.

potassiums in ammonia[4] are W. The U was predicted to be more stable by MO theory.[5] However, there must be at least small amounts of sickle and U in some pentadienyllithiums because their hydrolyses produce some cis-1,3-pentadienes,[6] and the sigmatropic [1,6] hydrogen shifts observed in certain alkylpentadienyllithiums require U conformations.[7]

For detection of pentadienyl anion conformations proton-decoupled cmr spectroscopy is attractive because it lacks the extensive coupling and dynamic changes due to slow rotation about the C_1–C_2 and C_4–C_5 bonds which complicate the corresponding pmr spectra. ^{13}C chemical shifts for specific conformations of some pentadienyllithiums at low temperature in THF–hexane are listed in Table I.[8] Comparison of cis- and trans-1-methylpentadienyllithium to pentadienyllithium reveals that methyl substitution at C_1 shifts C_1 downfield by >19 ppm and C_5 upfield by >9 ppm and indicates qualitatively that the methyl group shifts charge density from C_1 to C_5 in the anion. The other carbon which bears high charge density, C_3, shifts upfield much less than C_5.

(4) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **86**, 807 (1967); G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *ibid.*, **88**, 1377 (1969); H. Kloosterziel and J. A. A. van Drunen, *ibid.*, **89**, 270 (1970); H. Kloosterziel and J. A. A. van Drunen, *ibid.*, **89**, 368 (1970).

(5) R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

(6) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(7) R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **92**, 6345 (1970).

(8) The chemical shift data in Table I for pentadienyllithium differ substantially from values reported earlier[9] because (i) the chemical shifts are temperature dependent and (ii) remeasurement of the chemical shifts of the same pentadienyllithium sample used in ref 9 has given revised values (R. B. Bates, personal communication) which differ from ours at ∼35° (C_1 71.1 ppm, C_2 142.2, C_3 82.3) by ≤2.6 ppm when converted to our referencing system. Our data for 3-methylpentadienyllithium agree with the previously published data[9] to ≤3.0 ppm. The differences which remain between the results from the two laboratories are most likely due to subtle but significant differences in temperature and sample composition.

(9) R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Amer. Chem. Soc.*, **95**, 926 (1973).

The major component of a mixture of cis- and trans-1-methylpentadienyllithium is cis-W (cis-1-methyl, W conformation) according to its −30° pmr spectrum in which $J_{12} = 9.5$ Hz,[10] $J_{23} = 11.5$ Hz, and $J_{34} = 12.0$ Hz. In the cmr spectrum at −37° a set of five peaks assigned to cis-W accounts for 65% of the mixture as measured by peak heights. We assign another set of five peaks (21% of the mixture) to a secondary component and at least eight small peaks to two minor conformers (6–8% each). At +40° all of the 1-methylpentadienyllithium peaks in the spectrum are broad but at +80° there are only ten sharp peaks due to a 62:38 mixture of cis and trans isomers. The corresponding pmr spectrum at +70° also shows cis and trans isomers which are both predominantly W according to proton–proton coupling constants of 11–12 Hz across their inner bonds, but our pmr spectrum does not permit determination of whether cis or trans predominates. Because of the sizable amount of trans-W present at +80°, we assign it tentatively to the secondary set of peaks in the −37° cmr spectrum. If W is the predominant form of both cis and trans isomers, the minor (6–8%) components of the mixture observed by cmr at −37° are the sickles below, because higher charge density at C_5 than at C_1 gives C_3–C_4 more double bond character than C_2–C_3 and consequently rotation about C_3–C_4 becomes slow on the nmr time scale at higher temperature than rotation about C_2–C_3.
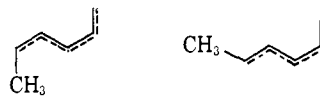
At −37° two conformers are apparent in the cmr spectrum of 1,1-dimethylpentadienyllithium. The major one (80%) must be W because $J_{23} = 11.0$ Hz and $J_{34} = 12.5$ Hz in its −30° pmr spectrum. The minor one must be the sickle shown in Table I for reasons identical with those given for the sickles of 1-methylpentadienyllithium.

The major conformer of pentadienyllithium is W according to its pmr spectra.[1] At −41° its cmr spectrum contains the three W peaks (>90% of the mixture) listed in Table I and peaks of a minor conformer at 76.7 and 136.8 ppm, which merge with the W peaks at ≤35°. Although the sickle should have five cmr peaks and the U only three, we hesitate to call the minor conformer U because more than one small peak could be hidden by the larger peaks or by spectral noise.

3-Methylpentadienyllithium has only three unsaturated carbon peaks in its cmr spectra from +40 to −80°, and, unlike all other compounds in Table I, its chemical shifts are nearly independent of temperature. Protonation produces 91% (E)-3-methyl-1,3-pentadiene. Therefore only the W conformation of 3-methylpentadienyllithium is detected by cmr.
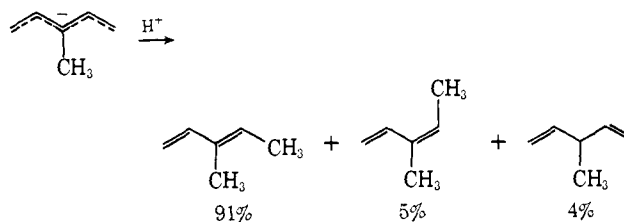
(10) Normally J_{12} (cis) = 7.5–9.5 Hz and J_{12} (trans) = 15–16 Hz.[1]

In conclusion, cmr spectroscopy provides a simple way to observe conformations of acyclic pentadienyl anions and can be used in conjunction with coupling data from pmr spectroscopy to assign their structures. The principal conformations of pentadienyllithiums are W with substantial amounts of sickle present in certain cases.

Warren T. Ford,* Martin Newcomb

*The Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801*

## Competitive Bromination of B-Isopropyl-9-borabicyclo[3.3.1]nonane. The Remarkable Selectivity and Enhanced Reactivity of the α Hydrogen in B-sec-Alkyl-9-borabicyclo[3.3.1]nonanes

Sir:
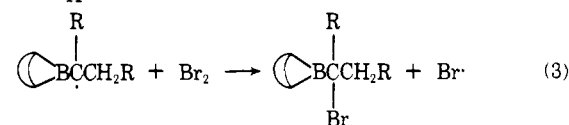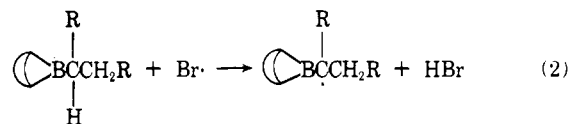
Competitive bromination of B-isopropyl-9-borabicyclo[3.3.1]nonane (B-i-Pr-9-BBN) reveals that the α hydrogen of the isopropyl group is 5.5 times as reactive as the highly activated tertiary hydrogen of cumene. Consequently, the boron moiety activates the α position to an even greater extent than the phenyl group. The α-hydrogen atoms at the bridgehead are not substituted competitively. This feature makes it possible to synthesize and isolate the α-bromoalkyl derivatives and to utilize them in synthesis. Thus treatment of 2-bromo-2-propyl-9-BBN with water results in a carbon–boron migration with the formation of a new bicyclic boron derivative. Alternatively, the α-bromo compound is readily converted by treatment with methyllithium at −78° into B-t-Bu-9-BBN.

Recently, B-sec-alkyl-9-borabicyclo[3.3.1]nonanes have been shown to undergo a dark reaction with bromine to afford the corresponding secondary alkyl bromides (eq 1).[1] Although the reaction provides a
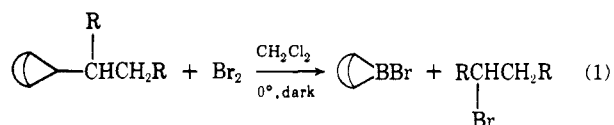

highly convenient procedure for the anti-Markovnikov hydrobromination of internal olefins, the mechanistic implications are of special interest.

It was proposed that the reaction does not involve direct rupture of the carbon–boron bond by the bromine molecule but proceeds instead through a highly selective free radical substitution of the α position of the sec-alkyl group (eq 2, 3). Protonolysis of the inter-


mediate by the hydrogen bromide affords the final product (eq 4).
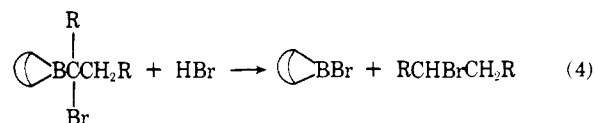
Yields in the neighborhood of 90% were realized. This suggests that the α position of the alkyl group must be exceptionally activated to achieve such a selective substitution at this position.[2] This conclusion has now been tested by examining the competitive bromination of B-i-Pr-9-BBN and cumene. Treatment of an equimolar solution of 9-BBN (1), cumene (2), and cyclohexane in methylene chloride with bromine at 0° revealed that the relative reactivity of 1/2 is 5.5, as shown by glpc analysis for residual 1 and 2. No substitution of the cyclohexane occurs.

If we utilize the literature value of 120 for the relative reactivities of cumene and isobutane[3] (3), this results in a relative reactivity of the tertiary hydrogen in B-i-Pr-9-BBN to isobutane of 660. Clearly, the acti-

	1	2	3
Rel react	660	120	1.00
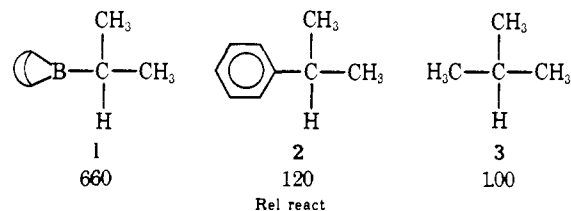
vation toward attack by bromine atoms of the tertiary position provided by the 9-BBN moiety in 1 exceeds that provided by the phenyl group in 2.

This remarkable activation can be attributed to stabilization of the free radical produced in the hydrogen abstraction step (eq 2) by the interaction of the odd electron with the vacant p orbital of the boron atom. Attack on the other two α positions (bridgehead) of the 9-BBN moiety is apparently much less facile because in these positions the odd electron would necessarily occupy an orbital which is orthogonal to the vacant p orbital on boron.

By carrying out the bromination of 1 in methylene chloride with continuous removal of hydrogen bromide under the vacuum afforded by a water aspirator,[4] it was possible to avoid the protonolysis (eq 4) and achieve

(1) C. F. Lane and H. C. Brown, *J. Organometal. Chem.*, **26**, C51 (1971).

(2) Qualitative evidence, in part conflicting, that the α position in boron derivatives may be activated toward attack by bromine atoms has been reported by several investigators: D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron*, **25**, 1557 (1969); J. Grotewold, E. A. Lissi, and J. J. Scaiano, *J. Organometal. Chem.*, **19**, 431 (1969); C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **92**, 7212 (1970). It was also noted that a boron substituent serves to stabilize an organic radical in free radical additions to vinylborinates: D. S. Matteson, *ibid.*, **82**, 4228 (1960).

(3) G. A. Russell and D. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963).

(4) H. C. Brown and Y. Yamamoto, *J. Amer. Chem. Soc.*, **93**, 2796 (1971).