

without ketonization through $14 \rightarrow 15$ and $14 \rightarrow 17$. This prompted us to reexamine the decompositions of deuterated analogs of **14** (Table II).⁷ These data indicate that the direct cleavage, $14 \rightarrow 15$, is not important, but that the loss of the ethyl radical occurs only after rearrangement¹³ and ketonization, $14 \rightarrow 16 \rightarrow 18$. The decompositions of **18** are similar to those of ionized 2-butanone.

It is well established that normal (higher energy) ions of the next higher enolic homolog **6** rearrange specifically to **1** with the transfer of a γ -H atom.²⁻⁴ Metastable ion evidence, such as the formation of $C_4H_7O^+$, $C_3H_6O^+$, and $C_2H_5O^+$ from $CH_3CH_2CH_2C(OD)=CH_2$,⁺, again indicates that ketonization can occur prior to decomposition of these low energy ions; six-membered ring rearrangements are favored over the five- and four-membered analogs. It appears that much of the "scrambling" of H and D atoms observed in the low-energy spectra of ketones^{6,14} can be accounted for through similar H transfers to specific active sites.^{7,15}

(13) Note when five-membered ring rearrangements are possible ($14 \rightarrow 16$, $16 \rightarrow 18$) that the four-membered analogs ($1 \rightarrow 2$, $1 \rightarrow 9$) are almost completely eliminated in the metastable transitions; the latter rearrangements actually become more competitive in the higher energy normal ions in contrast to previous observations that scrambling decreases with increasing ion internal energy.^{6,14}

(14) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).

(15) Helpful discussions with S. H. Bauer, R. Kornfeld, I. Howe, and H. D. R. Schuddemage, and the financial support of the Army Research Office, Durham, are gratefully acknowledged.

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1,6-Sigmatropic Hydrogen Shifts in Pentadienyl Anions. Relative Stabilities of Pentadienyl Anions

Sir:

We wish to report high-yield equilibrations of pentadienyl anions in several systems, and that these reactions are intramolecular, thermal antarafacial, and photochemical suprafacial 1,6-sigmatropic rearrangements in accordance with the Woodward-Hoffmann rules.¹

In the course of preparing 1,1-dimethylpentadienyllithium (I) from 5-methyl-1,4-pentadiene² with *n*-butyllithium in THF-hexane,³ a partial rearrangement of I to II at 40° was detected by nmr.⁴ To confirm the

(1) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965). (b) J. Klein, S. Gily, and D. Kost (*J. Org. Chem.*, **35**, 1281 (1970)) have noted migration of the pentadienyl anion system in long aliphatic chains. They suggest without isotopic labeling experiments that the isomerizations are intramolecular, and (incorrectly) that a minimum of 14 carbons in a chain is necessary for reaction. (c) Taken in part from the Ph.D. Theses of D. E. Potter (1969) and W. H. Deines (1970). For a preliminary report, see Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN 144.

(2) Purchased from the Chemical Samples Co.

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

(4) For nmr parameters of pentadienyllithiums, see R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *ibid.*, 205 (1967). For anions like II with one alkyl group at the end of the pentadienyl system, the two species differing in the configuration of this alkyl group were generally visible in the nmr; the percentages in Figure 1 include both stereoisomers. The relative amounts of these stereoisomers and the rotation barriers in these pentadienyllithiums will be discussed in a later publication.

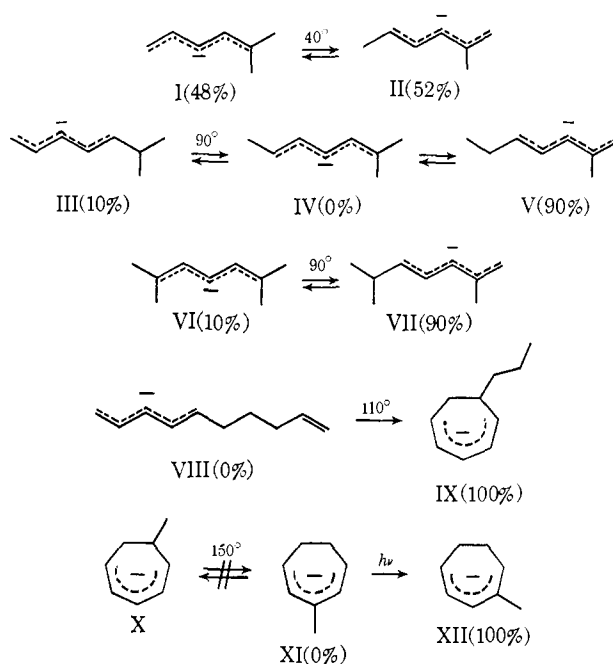


Figure 1. Isomerized pentadienyl anions with equilibrium concentrations in parentheses.

identity of II and to show that equilibrium had been reached, II was synthesized at 20° from 2-methyl-1,4-hexadiene,⁵ and on warming to 40° gave a I-II mixture of the same composition. Other equilibrated systems included III-IV-V (approached from III,⁶ IV,⁷ and V⁸), VI-VII (approached from VI² only), and VIII-IX (approached from VIII² only). This last case presumably involves three sigmatropic rearrangements to 1-propylheptatrienyl anion, which rapidly electrocyclicizes to IX.⁹

To determine whether these isomerizations are intramolecular, 6-methyl-5-hepten-2-one was pentadeuterated by four exchanges in basic D_2O , converted⁷ to 2-methyl-5,7,7,7-tetradeuterio-2,5-heptadiene, and thence to tetradeuterated IV. After heating to 90° for 30 min, the equilibrated anions were protonated. The absence of deuterium scrambling, shown by mass spectrometry, indicated the intramolecularity of the isomerizations. A second test, consisting of heating a 1:1 mixture of undeuterated and tetradeuterated IV, also showed no scrambling of deuterium.

If these thermal isomerizations involve concerted 1,6-hydrogen shifts, the Woodward-Hoffmann rules predict that they will occur *antarafacially via* a helical all-cisoid transition state (Figure 2).^{1a,b} This cannot be conveniently tested with cyclohexadienyl anions due to their tendency to aromatize,³ so we employed the cyclo-

(5) Prepared in 20% yield from 5-methyl-5-hexen-3-ol² by acetylation, pyrolysis, and preparative glpc, and characterized by nmr and mass spectral analysis. This synthesis gives the cis/trans isomers in a 29/71 ratio; the mixture was used in the preparation of II.

(6) *trans*-6-Methyl-1,4-heptadiene was obtained as the major by-product in the synthesis of 6,6-dimethyl-1,4-cyclohexadiene³ from 1,3-cyclohexanedione by the sequence methylation, lithium aluminum hydride reduction, acetylation, acetate pyrolysis, and preparative glpc.

(7) 2-Methyl-2,5-heptadiene was prepared from 6-methyl-5-hepten-2-one by lithium aluminum hydride reduction, acetylation, acetate pyrolysis, and preparative glpc.

(8) IV rearranges quantitatively to V in 4 hr at 35°; on heating further to 90° for 1 hr, the equilibrium mixture of III and V is observed.

(9) (a) R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969); (b) K. Kloosterziel and J. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1984 (1969).

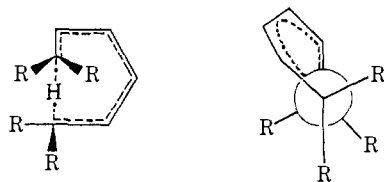


Figure 2. Two views of the thermal transition state.

heptadienyl anions X^{9a} and XI.¹⁰ Heating solutions of these anions to 150° for 30 min gave no change; above this temperature, gradual decomposition occurred which did not appear to involve anion equilibration. To check that the geometry of this system permitted *suprafacial* 1,6-hydrogen shifts, anions X and XI were irradiated in quartz at 0° using a high-pressure mercury lamp. After 1 week of irradiation, X was virtually unchanged, but XI had been quantitatively converted into a new anion, XII, presumably via a photochemical *suprafacial* hydrogen shift. These stereochemical results are consistent with the Woodward–Hoffmann rules.

Although other factors are certainly involved, the relative rates of the thermal isomerizations observed thus far correlate well with the number of alkyl substituents in the positions bearing R's in Figure 2. The slowing effect of an alkyl substituent is considerably greater than the statistical factor expected due to the decrease of one in the number of hydrogens available to migrate, and is presumably due to nonbonded steric interactions in the transition state. Observed activation energies are: I → II, 18 kcal/mol (no R's); IV → V, 20 kcal/mol (one R); III → V and VI → VIII, 26 kcal/mol (two R's on same carbon); and VIII → IX, 27 kcal/mol (two R's on different carbons). Presumably with three or four R's, the reaction will be slower still.

The relative thermodynamic stabilities of four sets of thermally equilibrated pentadienyl anions are shown by the percentages in Figure 1. The results can be rationalized as follows: VIII is >3 kcal/mol less stable than IX (and the other acyclic anions in the equilibrium) because of the extra carbon–carbon σ bond in VIII; I, IV, and VI are the least stable anions in their respective sets because of their greater degree of alkyl substitution on carbons 1, 3, and 5 of the pentadienyl system, which bear nearly all of the negative charge; V is favored over III by 1.6 kcal/mol largely because of nonbonded steric interactions due to a trisubstituted sp³-hybridized carbon in the latter (this same factor favors VI over VII, but is outweighed by the previous factor in this case).

These thermal rearrangements should increase considerably the utility of acyclic pentadienyl anions in synthesis. By keeping the temperature low, they can be avoided. On heating, equilibration occurs, sometimes quantitatively (e.g., IV → V at 35°, and VIII → IX).

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(10) Prepared in 24% yield from cycloheptadienyllithium^{9a} by treatment with methyl iodide, preparative gpc purification, and the addition of butyllithium in THF–hexane.

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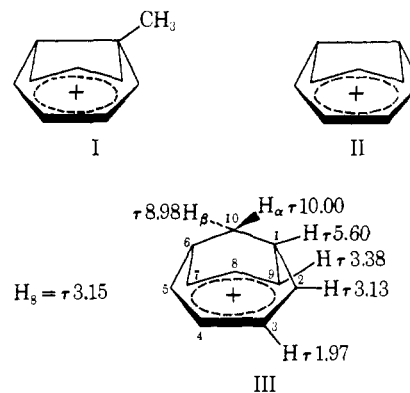
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The Bicyclo[4.3.1]deca-2,4,7-trienyl Cation. A Homoconjugative Protonation Route to a 1,4-Bishomotropylium Ion¹

Sir:

The study of polyhomotropylium ions has received increased interest in the past few years.² The first reported bishomotropylium ions, I^{2d} and II,^{2e} showed some evidence for ring current, but this aromatic character was largely deduced from the observed charge delocalization. During our attempts to prepare by more conventional methods the more informative bicyclo[4.3.1] skeleton, we discovered a protonation reaction which we have successfully applied to the preparation of III, a 1,4-bishomotropylium ion.³ III contains two methylene hydrogens which lie over the face of the potentially aromatic ring system, thus offering a means of observing the shielding effects of a ring current.



The prototype of the reaction used to generate III was first observed in the protonation of bicyclo[4.2.1]-nona-2,4,7-triene (IV),⁴ which was extracted from a

Table I. Coupling Constants for Ion V

J	1,2	2,3	3,4	4,5	5,6 _{exo}	5,6 _{endo}	$\frac{ 6_{exo,-}}{6_{endo} }$	1,7	2,4
Hz	9	9	9	9	8	0	16	6	Small

(1) Research supported in part by the National Science Foundation.
(2) (a) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (b) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967); (c) J. C. Baborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); (d) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 2146 (1970); (e) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4454 (1970); (f) Schröder has recently reported the methoxymercuration of VI and has considered a bishomotropylium ion intermediate: H. P. Löffler and G. Schröder, *Tetrahedron Lett.*, 2119 (1970). Subsequent to the submission of this communication, Professor Schröder informed us of similar results from the protonation of bicyclo[4.2.2]deca-2,4,7,9-tetraene.

(3) This nomenclature is defined in ref 2a, p 147.

(4) (a) W. Grimme, *Chem. Ber.*, **100**, 113 (1967); (b) L. G. Cannell, *Tetrahedron Lett.*, **48**, 5967 (1966).