equilibrium concentration of 1_{aa}. At higher temperatures the height of the first peak grows relative to the second owing to the conversion of some 1_{ee} to 1_{aa} near the electrode during the experiment. At lower scan rates (longer experiments) even more 1_{aa} is formed and the height of the first peak increases. This reaction occurs in the solution within a thin (of the order of 1 μm) diffusion layer adjacent to the electrode surface. Thus in our model the rate and equilibrium constants are those of the solution species rather than adsorbed molecules. The dependence of relative peak height on temperature and scan rate is illustrated in Figure 1. In the digital simulations the relative peak height is governed by the interrelated parameters K and $k_{ee\rightarrow aa} + k_{aa\rightarrow ee}$. Since K was obtained from the low-temperature data, the rate constants could be calculated from the simulation parameters for the higher temperature data. The results are summarized in Table I.

The internal consistency of the data and the good agreement with earlier reports of K and $\Delta G^{\ddagger}$ lend credence to our model in which 1_{aa} is the more easily reduced conformer and conformational interconversion occurs in solution near the electrode surface. Thus, 1,2-dibromides appear to be another class of compounds in which the electrode reaction occurs preferentially via a given conformer. Other examples are currently being investigated.

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Two Conformations of the Pentadienyl Radical[1]

Sir:

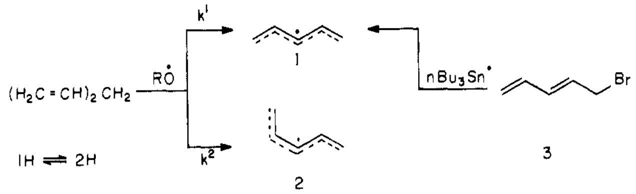
Pentadienyl is the simplest acyclic hydrocarbon radical having five conjugated π electrons. This has made pentadienyl the subject of numerous theoretical studies[2-11] but, prior to the present work, it had not been observed. We have now identified pentadienyl by EPR spectroscopy and we find that, when it is generated by hydrogen atom abstraction from 1,4-pentadiene, it can exist in two distinct conformations, a possibility overlooked in the theoretical treatments. The conformers are not in equilibrium with one another; instead the relative concentrations of the two conformers are determined by kinetic factors.

Photolysis of a mixture of 1,4-pentadiene and di-*tert*-butyl peroxide, either neat or in a variety of hydrocarbon solvents, at ambient temperatures in the cavity of a Varian E-104 EPR spectrometer gave a spectrum which we assign to pentadienyl in the *E,E* conformation, **1**. Apart from a minor variation in one of the hyperfine splittings (hfs, see Table I) the spectrum was unchanged from 100 °C to ca. −60 °C. However, when the solution was photolyzed at −60 °C or below, a new spectrum appeared and became predominant at temperatures below ca. −120 °C. This new spectrum, which we assign to pentadienyl in the *E,Z* conformation, **2**, had the same overall width and the same g factor as **1** but showed hfs by 7 nonequivalent hydrogen atoms. Since **2** predominates at low temperatures,[12] we must conclude that, *if* **1** and **2** are in equilibrium, not only is **2** more stable than **1**, which would be surprising, but also the barrier to interconversion of **1** and **2** must be rather small.

Table I. EPR Parameters for **1** and **2** Recorded at a Microwave Power Level of 0.4 mW

1 at −40 °C, $a^{\mathrm{H}a-c}$	**2** at −160 °C, $a^{\mathrm{H}a-c}$
11.58	3.08,[e] 9.69
3.32 (**2H**)[d]	3.62,[f] 10.12
9.62 (**2H**)	8.48, 14.38
10.40 (**2H**)	9.18

[a] $g = 2.00264 \pm 0.00002$. [b] a^{H} in Gauss. [c] $\partial a^{\mathrm{H}}/\partial T \leqslant \pm 0.3$ mG/K unless otherwise noted. [d] Assigned to H_2 and H_4. $\partial a^{\mathrm{H}}/\partial T = 1.3$ mG/K (from 33 to −170 °C). [e] Assigned to H_2 or H_4. $\partial a^{\mathrm{H}}/\partial T = 1.5$ mG/K (from −91 to −170 °C). [f] Assigned to H_2 or H_4. $\partial a^{\mathrm{H}}/\partial T = 2.7$ mG/K (from −91 to −170 °C).



The simplest way to check whether **1** and **2** are in equilibrium is to generate pentadienyl from a precursor whose geometry would constrain it to yield *only* **1** or **2** initially. This was accomplished by abstraction of bromine from *trans*-bromopenta-2,4-diene,[13] **3**. The pentadienyl radicals which were produced in this way existed *solely* in conformation **1** at temperatures from 180 to −130 °C. This proves that, when **1** and **2** were generated from 1,4-pentadiene at low temperatures, they were not in equilibrium. Their relative concentrations must therefore have been determined either by their relative rates of destruction or(and) by their relative rates of formation. The former possibility can be virtually ruled out since **1** and **2** are destroyed by diffusion-controlled radical–radical reactions, which will occur at the same rate.[14] It must, therefore, be concluded that **2** is formed more readily than **1** at low temperatures. Let us designate all those conformations of 1,4-pentadiene[15] which yield **1** as **1H** and those that yield **2** as **2H**. The more facile formation of **2** at low temperatures could come about because the [**2H**]/[**1H**] ratio increases as the temperature is lowered and/or because the rate constant for H-atom abstraction from **2H**, k^2, decreases less rapidly with temperature than the rate constant for abstraction from **1H**, k^1. Unfortunately, it is not possible to determine which factor is the more important because, at each temperature, the relative amounts of **2** and **1** depend on the ratio of the products of the conformer concentration and the rate constant for their reaction with *tert*-butoxy, i.e., $[2]/[1] = k^2[2\mathrm{H}]/k^1[1\mathrm{H}]$.[16]

Models suggest that the transition state for H-atom abstraction from **2H** is sterically less crowded than that for abstraction from **1H**. For this reason, an alkoxy radical which is less bulky than *tert*-butoxy might be expected to yield relatively more **1** and less **2** than does *tert*-butoxy at the same temperature. This was indeed found to be the case using ethoxy radicals generated by photolysis of diethyl peroxide. In the temperature

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range studied (−80 to −120 °C) ethoxy always gave relatively less **2** than did *tert*-butoxy: the data could be represented by $1.6\,([\mathbf{1}]/[\mathbf{2}])_{t\text{-BuO}\cdot} \approx ([\mathbf{1}]/[\mathbf{2}])_{\text{EtO}\cdot}$.

The relative thermodynamic stabilities of **1** and **2** and the barrier to their interconversion could not be determined.[17] However, the fairly large positive temperature coefficients for a^{H_2} and a^{H_4} in both **1** and **2** suggests that there is an appreciable degree of torsional motion about the C_2–C_3 and C_3–C_4 bonds in both conformers. That is, additional positive spin will reach these hydrogens as the vinyl group to which they are attached is twisted out of the radical plane, because hyperconjugation to the partly occupied C_3 $2p_z$ orbital will improve. A similar phenomenon has been observed in the allyl radical[18] and, in fact, $\partial a^{\mathrm{H}_2}/\partial T$ for allyl is of similar magnitude to $\partial a^{\mathrm{H}_2}/\partial T$ and $\partial a^{\mathrm{H}_4}/\partial T$ for pentadienyl.

Additional experimental work and the results of INDO molecular orbital calculations on pentadienyl and on a variety of substituted pentadienyl radicals will be reported in a full paper.

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where $\theta = 2.303RT$ kcal/mol.
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Derivatives of Heteropolyanions. 1. Organic Derivatives of $W_{12}SiO_{40}^{4-}$, $W_{12}PO_{40}^{3-}$, and $Mo_{12}SiO_{40}^{4-}$

Sir:

This communication reports the facile preparation of organic derivatives of the Keggin-type (Figure 1) heteropolyanions $W_{12}SiO_{40}^{4-}$, $W_{12}PO_{40}^{3-}$, and $Mo_{12}SiO_{40}^{4-}$. The few previous reports[1,2] of organic derivatives of heteropolyanions were restricted to organoheteropolymolybdates such as $(RP)_2Mo_5O_{21}^{6-}$, $(RAs)_2Mo_6O_{26}^{6-}$, and $(RAs)_4Mo_{12}O_{46}^{4-}$ in which the structure permits bonding of an organic group to a surface heteroatom (phosphorus or arsenic) of the parent anion. No organic derivatives of Keggin-type anions, in which the heteroatom is buried in the middle of the structure, have been reported, nor have any heteropolyanion derivatives been described which contain a carbon–*metal* bond. Such species promise to be attractive models for solution studies of metal carbon bonds in a metal-oxide-like environment.

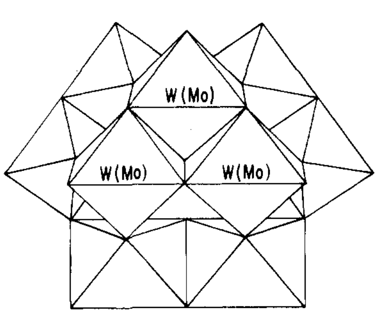

Figure 1. The Keggin structure, shared by $W_{12}SiO_{40}^{4-}$, $W_{12}PO_{40}^{3-}$, $Mo_{12}SiO_{40}^{4-}$, and many other heteropolyanions. It consists of four sets of three metal-centered octahedra symmetrically located around a central tetrahedrally coordinated heteroatom. This perspective does not show the heteroatom or all the octahedra but was chosen to permit better correlation with Figure 2 and 3. For a better depiction and description of the Keggin structure as a whole see ref 14.

Organometal and organometalloidal halides including $RSnCl_3$, $RSiCl_3$, $RGeCl_3$, $RAsCl_2$, and $C_5H_5TiCl_3$ were reacted with the "unsaturated" Keggin fragments $W_{11}SiO_{39}^{8-}$, $W_{11}PO_{39}^{7-}$, or $Mo_{11}SiO_{39}^{8-}$. The latter were prepared either in a prior separate step or in situ by standard techniques.[3] In each case heteropolyanions which contained the corresponding RM group were formed. These were precipitated as trimethylammonium or tetramethylammonium salts, recrystallized from water and characterized by elemental analysis and by infrared and NMR spectroscopy. NMR integration of the substituent protons relative to those of the alkylammonium cations served as a further check on composition.

Three structurally different classes of derivatives were encountered.

Class I. This includes 12-tungstosilicate and 12-molybdosilicate derivatives such as $CH_3SnW_{11}SiO_{39}^{5-}$ $C_6H_5SnW_{11}SiO_{39}^{5-}$, $C_2H_5SnMo_{11}SiO_{39}^{5-}$, $C_3H_5SnW_{11}SiO_{39}^{5-}$, $HOC(O)CH_2CH_2SnW_{11}SiO_{39}^{5-}$, $C_2H_5GeW_{11}SiO_{39}^{5-}$, and $C_6H_5AsW_{11}SiO_{39}^{4-}$. In addition, it includes both monosubstituted and disubstituted 12-tungstophosphate derivatives such as $CH_3SnW_{11}PO_{39}^{4-}$ and $C_6H_5SnW_{11}PO_{39}^{4-}$ (formed at pH 5) and $(CH_3Sn)_2W_{10}PO_{38}^{5-}$ and $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$ (formed at pH 7). In all of these derivatives the replacement of a tungsten- or molybdenum-oxygen moiety by an RM group is one for one.[4] The infrared spectra of the products are exceedingly similar to those of the corresponding salts of the parent heteropolyanions in the 1100–700-cm^{-1} region. This strongly suggests that the Keggin structure is retained, with the organic substituents at the unshared, terminal vertices of octahedrally coordinated tin, germanium, or arsenic atoms.

The ^{31}P NMR spectrum[5] of $C_6H_5SnW_{11}PO_{39}^{4-}$ exhibits only one resonance in D_2O, at −12.2 ppm from external H_3PO_4. The ^{31}P NMR spectrum of $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$ exhibits at least four resonances, at −8 to −9.2 ppm. All of these signals exhibit $^2J_{^{31}P-^{117}Sn^{119}Sn}$ of 16–20 Hz. These spectra are consistent with the single isomer possible for $C_6H_5SnW_{11}PO_{39}^{4-}$ and the maximum five geometric isomers possible for $(C_6H_5Sn)_2W_{10}PO_{38}^{5-}$ based on the Keggin structure. If isomerization of the Keggin skeleton had occurred,[6] more isomers would be possible for both the mono- and disubstituted derivatives although, of course, all possible isomers might not be formed or be separately observable.

Class II. Reaction of $RSiCl_3$ ($R = C_2H_5$, C_6H_5, $NC(CH_2)_3$, C_3H_5) with $W_{11}SiO_{39}^{8-}$ in unbuffered aqueous solution gives

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