the carbenoid carbon is seen to possess the remarkable facility to move in either direction on the surface of the π system.

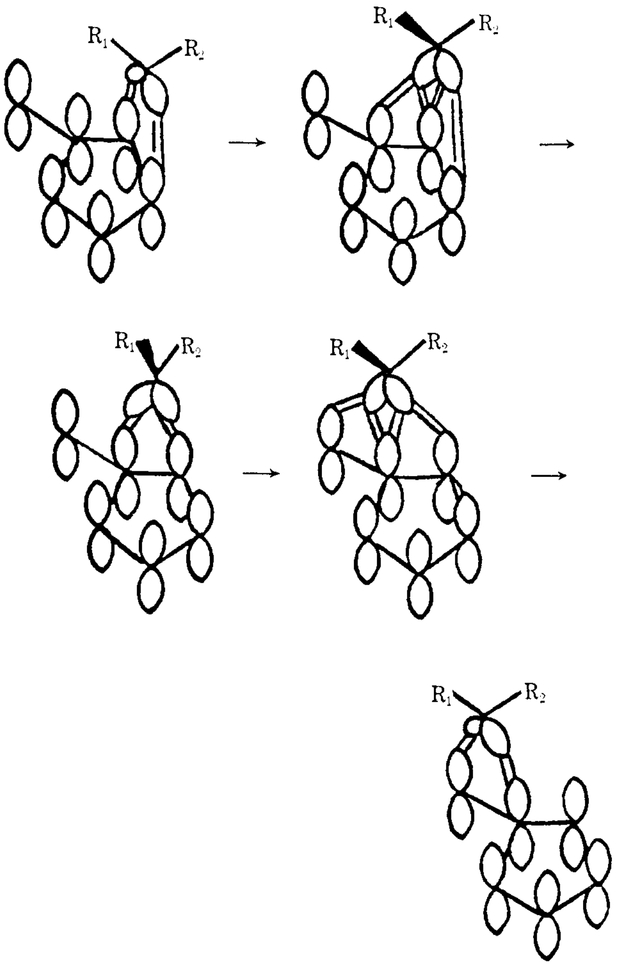
Further evidence on the nature of the walk process derived from the reaction stereochemistry. Irradiation of bicyclic diene **3** was found to afford two stereoisomers, **4a** and **4b**. Proton assignments were made on the basis of spin decoupling and analysis of spin coupling. Most interesting was the chemical shifts of protons at C-4 and C-7. The synthesis and study of model compounds spiro[2.4]-4,6-heptadiene (**10**) with H-4 and H-7 at τ 4.05 and 1-phenylspiro[2.4]-4,6-heptadiene[5] (**11**) with H-4 at τ 4.26 and H-7 at τ 3.96 revealed shielding of the *syn* protons and deshielding of the *anti* protons of the C-1 phenyl group in this system. Thus, in the case of **4a** and **4b**, the isomer with the high-field H-4 was assigned *syn* stereochemistry of **4a** and the compound with the low-field H-4 was given the *anti* configuration of **4b**.

Photolysis runs beginning with the *trans*-diphenyl bicyclic diene **3** were found to give a predominance (73:27, *syn*:*anti*) of the *syn*-spiro product **4a**. However, this was due to secondary photolysis[6] as seen from runs made at lower conversions where the *anti*-stereoisomer **4b** began to predominate (30:70, *syn*:*anti*). Very facile spiroheptadiene stereoisomerization made extrapolation to zero time difficult.

This stereochemical preference in which the *endo*-phenyl group in **3** becomes *anti* in the spiro-product **4** suggests that the walk rearrangement occurs by a slither[3] process in which the diradical species in Chart I are convenient for inspecting points along the reaction coordinate but do not represent actual intermediates of finite lifetime. For example, the biradical species **7** and **8** as well as **12** and **13** are species we have previously suggested as being involved in the di-π-methane rearrangement.[1,7] However, even there the evidence was against these being discrete species.[1] Very recently an example of the conversion of a 2-methylenebicyclo-[3.1.0]-3-hexene[8] to a spiro diene has been reported and species similar to those depicted in Chart I have been considered.

A reasonable view is that the rearrangement involves a divalent carbon "slithering" along the π system in the direction of the exocyclic methylene (note Scheme I) or in the reverse direction.

Scheme I. Orbitals Involved in the Slither Process



Finally, we note that conversion of **2** to **5** provides the first real test of the reactivity of a methylene analog of a 4,4-disubstituted cyclohexadienone. Previously, we found[9] that 1-methylene-4,4-diphenylcyclohexadiene rearranged very inefficiently ($\Phi = 0.10$) compared with the dienone analog ($\Phi = 0.85$).[10] However, in the analog **1**, phenyl migration intervened in place of the usual dienone-like type A rearrangement. In the present case of 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**2**), no phenyl migration is possible, and a type A transformation, equivalent here to a di-π-methane rearrangement, is enforced. However, this is exceptionally inefficient ($\Phi = 0.0030$) when compared with the higher efficiency of the usual di-π-methane rearrangements (*i.e.*, $\Phi = 0.080$).[7] The efficiency difference is striking and seems to correlate with the low 3,5-bond order in the excited state of **2** relative to the acyclic systems (0.00 *vs.* 0.50 bond orders). Most remarkably, the 3,5 interaction (see Chart II for numbering) in the $\pi-\pi^*$ excited state initially becomes slightly antibonding as this 3,5 overlap begins but then becomes more favorable with further increase in overlap. Hence, the di-π-methane rearrangement is inhibited appreciably both in theory and in fact by cyclic conjugation as in the 1-methylene-4,4-disubstituted 2,5-cyclohexadiene system.

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[9] Unpublished results of H. E. Zimmerman and P. Hackett.

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Rate of Water Exchange from Hydrated Magnesium Ion

Sir:

A direct measurement of the water exchange rate from Mg^{2+} at room temperature has been made possible

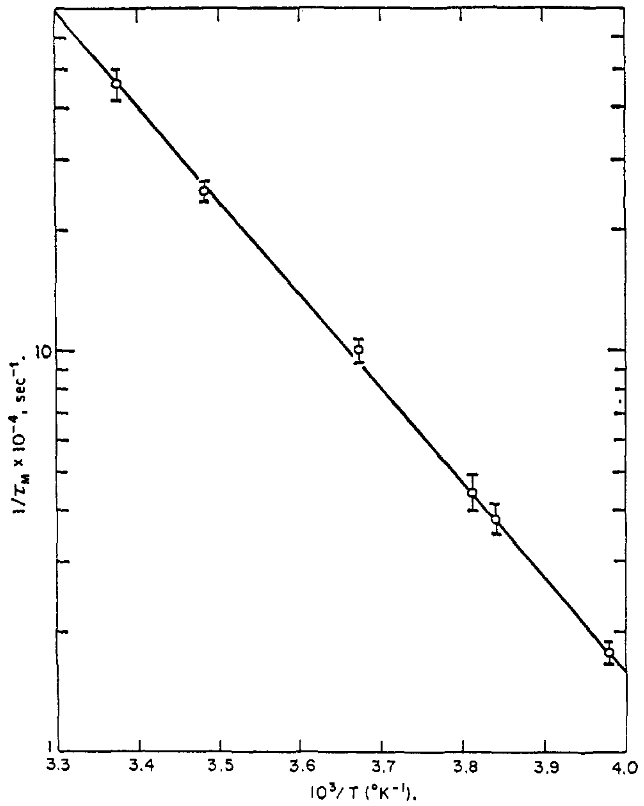

Figure 1. Rate of water exchange *vs.* reciprocal of absolute temperature. Composition of solution was 1.30 g of H_2O enriched to 20% in oxygen-17, 1.00 g of $Mg(ClO_4)_2$ (anhydrous), and 0.30 g of $Mn(ClO_4)_2 \cdot 6H_2O$.

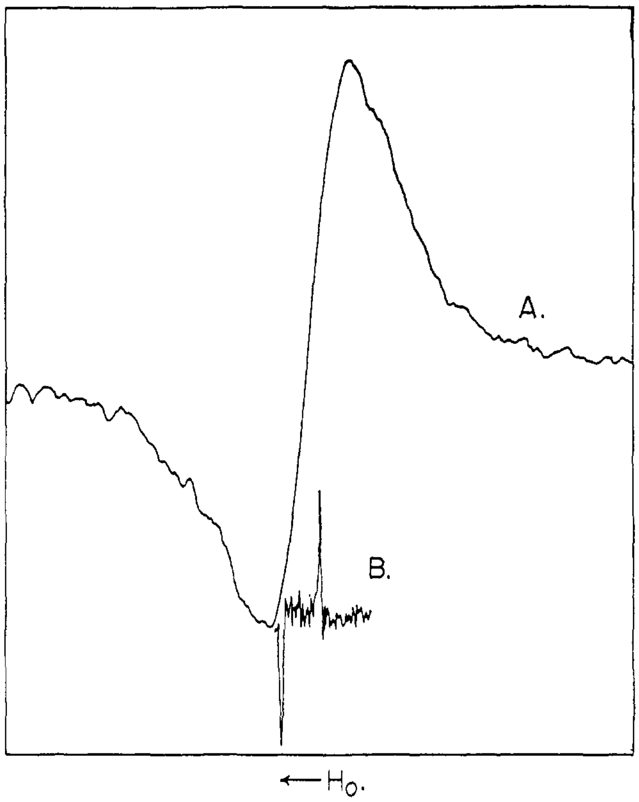

Figure 2. (A) Oxygen-17 nmr spectrum of the waters in first coordination sphere of Mg^{2+} at −22°. Spectrum is the average of 25 scans. (B) Pure water sample run at a later time on side-band mode to calibrate the scale. Distance between side bands is 1591.2 Hz.

by observation of the oxygen-17 nmr signal of the waters in the first coordination sphere of Mg^{2+} ion. Interference from the bulk water resonance was avoided by addition of sufficient Mn^{2+} to broaden the bulk water resonance to at least ten times that of the bound water signal. Under these conditions the general two-site exchange equation[1] can be shown to reduce to

$$\delta\omega = \frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{\tau_M} \tag{1}$$

where $\delta\omega$ is $\sqrt{3}/2$ times the peak-to-peak width of the derivative curve measured in radians/sec, T_2 is the transverse relaxation time, $1/T_{2M}$ is the first-order relaxation rate constant of the ^{17}O in the first coordination sphere of Mg^{2+} ion, and $1/\tau_M$ is the first-order rate constant for exchange of a particular water molecule from the first coordination sphere of Mg^{2+} into the bulk solvent. The $1/T_{2M}$ term has been shown by Connick and Wüthrich[2] to be nearly the same as that of ^{17}O in pure water, which is many orders of magnitude smaller than the observed line widths. Therefore the observed relaxation rate of the bound waters can be associated directly with the rate of water exchange.

The results of a temperature study from −22 to +23° are shown in Figure 1. A representative spectrum is shown in Figure 2. The apparent first-order constant k of the reaction

$$Mg(H_2O)_6^{2+} + H_2O^* \rightleftharpoons Mg(H_2O)_5H_2O^{*2+} + H_2O$$

is defined by

$$\text{rate} = 6k[Mg(H_2O)_6^{2+}]$$

where the coordination number is assumed to be 6. The value of k is found to be 5.3×10^5 sec^{-1} at 25° with an enthalpy and entropy of activation of 10.2 kcal/mol and 2 eu, respectively.

Approximate values of the rate of exchange of water molecules from the first coordination sphere of Mg^{2+} ion have been determined previously by various methods. Sonic relaxation and temperature-jump techniques[3-6] are incapable of measuring reactions where no net chemical change takes place, such as water exchange. However, an estimate of the water exchange rate can be obtained by measuring the rate at which a water molecule is replaced by some other ligand in the first coordination sphere, if it is assumed that the rate is primarily controlled by the difficulty of removing the water. The first-order rate constant for the entry of various divalent anions into the first coordination sphere of Mg^{2+} from the second at room temperature has been measured to be 1×10^5 sec^{-1} [3]

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[1] T. J. Swift and G. P. Weinberger, *J. Amer. Chem. Soc.*, **90**, 2023 (1968), eq 2. (In term C a plus sign has been omitted between T_{2A}^{-1} and the remainder of the expression.)

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Proton magnetic resonance techniques[7,8] are capable of measuring the rate of exchange directly but the resonance of the bound protons is resolved from that of the bulk protons only at temperatures below −60°. Rate data have been obtained only for mixed water–acetone solvents which give an extrapolated room temperature k of *ca.* 4-6 $\times$ 10^6 $\sec^{-1}$.[7] Possible solvent effects and the large interval of extrapolation to room temperature make a direct comparison with the present results dubious.

The magnitude of the difference between the present result and the sound absorption and temperature jump data is not surprising. Differences of the same relative size have been noted previously for transition metal ions.[9] The rate constant for water exchange would be expected to be ${}^4/_3$ that of the rate constant for a ligand entering the first coordination sphere if it is assumed that only molecules on the faces of a first sphere octahedron of waters can enter a vacated site. The fact that the observed water rate is much greater than ${}^4/_3$ the ligand rate may be an indication of the extent to which water is electrostatically and/or sterically favored over the other ligands studied in competing for a vacated coordination site.

In principle one could determine from the intensity of the bound water signal the number of waters coordinated to magnesium ion in the first coordination sphere. No such attempt was made because of experimental errors, which were large enough to render meaningless any such results. Within experimental accuracy no chemical shift was observed between the first coordination sphere waters and pure water.

Acknowledgment. This work was performed under the auspices of the United States Atomic Energy Commission, AEC Contract No. W-7405-eng-48.

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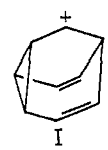
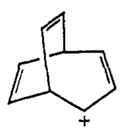
Direct Observation of the Degenerate 9-Methyl-9-barbaralyl Cation[1]

Sir:

The 9-barbaralyl cation (I) has previously been studied solvolytically,[2a-e] as well as under other conditions for short life,[2c,3a] usually in connection with attempts to investigate the bicyclo[3.2.2]nonatrienyl cation (II), a potentially "antibicycloaromatic" species.[3a,b] Earlier attempts to directly observe cations I and II have been reported as unsuccessful.[2d,e] We now wish to report the successful generation and direct observation of the 9-methyl-9-barbaralyl cation (III), a partially degenerate derivative of I. Ion I has also been successfully generated in super acid media and its observation is reported in a following communication.[4]

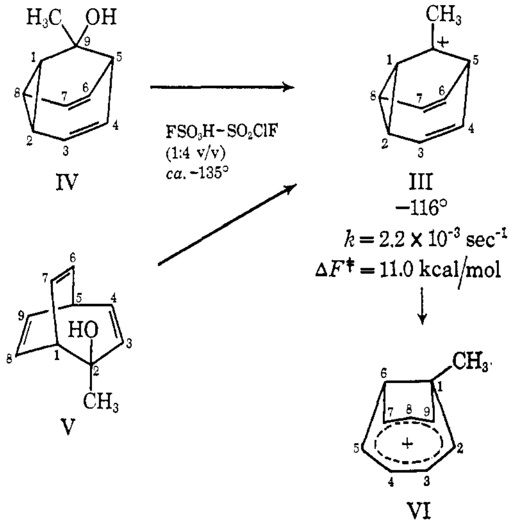


I



II

Ion III was prepared by extraction of either 9-methyltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-ol (IV)[5] or 2-methylbicyclo[3.2.2]nona-3,6,8-trien-2-ol (V)[6] from a CD_2Cl_2 solution into a mixture of FSO_3H-SO_2ClF (1:4 v/v) at *ca.* −135° and was observed by nmr in the temperature range −135 to −115°. At −116° ion III rearranged exclusively to the 1-methylbicyclo[4.3.0]nonatrienyl cation (VI), which was previously demonstrated to be a 1,4-bishomotropylium ion.[5] The structure 9-methyl-9-barbaralyl cation is assigned to ion III on the basis of its nmr data, compared to those of protonated barbaralone (VII),[7] protonated bicyclo[3.2.2]nona-3,6,8-trien-2-one (XII),[7] and dimethylcyclopropylcarbinyl cation (IX).[8] At −135° the nmr of III (Figure 1a) shows six different groups of protons, in the approximate ratio 3:1:1:2:2:2, with the chemical shifts τ 7.06, 5.23, 4.79, 4.20, 4.07, and 3.82, respectively. The $\Delta\tau_{X-IX}$ ($\tau_X - \tau_{IX}$) values observed for the bisected cation IX compared to dimethylcyclopropylcarbinol (X)[8] are *ca.* 2.9 for the α proton, *ca.* 3.5 for the β protons, and 1.46 for the *trans*-methyl group. These values, compared to the corresponding $\Delta\tau_{IV-III}$ values, indicate that III contains the structural element IX. As in protonated barbaralone (VII), the charge in III is not significantly delocalized onto the olefinic carbons



(1)

[1] Research supported in part by the National Science Foundation.

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[7] Either barbaralone[2d] or bicyclo[3.2.2]nona-3,6,8-trien-2-one[3a] was extracted from deuteriochloroform solutions into FSO_3H at −78°. Internal standard $CHCl_3$, τ 2.73.

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