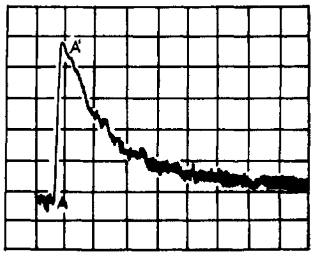

Figure 1. Absorbance change at 440 nm as a function of time in 0.1 M Ni(2,3,2-tet)$^{2+}$ at 23°: initial absorbance (A) 0.41; vertical scale, 1% absorbance change/division; horizontal scale, 0.2 μsec/division.

dymium laser[3] and the concentration of the square-planar form was monitored by the absorption at 440 nm; the result is shown in Figure 1. There was a rapid 5% rise (AA′) in the concentration of the square-planar species followed by a return almost to the original level, with a relaxation time of about 0.3 μsec. The difference in the equilibrium absorbance before and after irradiation is due to the slight temperature rise in the system (~0.15°).

The relaxation time was independent of the concentration over the range 0.05–0.2 M but varied (0.3–0.09 μsec) with temperature (12–58°). The effect was observed at other monitoring wavelengths within the 440-nm band of the square-planar form and also when D_2O was used as solvent. D_2O is transparent at 1.06 μm whereas H_2O is not; this shows that the effect does not occur through absorption by the solvent. No absorbance changes were observed for nickel(II) chloride solutions in the absence of 2,3,2-tet; effects such as cavitation can therefore be ruled out as a possible cause of the observed transients. Since the complex absorbs at the laser wavelength ($\epsilon_{1.06}$ ~2.0 M^{-1} cm^{-1}), the absorption being attributed to the electronic transition ($^3T_{2g} \leftarrow {}^3A_{2g}$) of the trans-octahedral form,[4,5] we conclude that the observed effect in Figure 1 is due to a photochemical displacement of equilibrium 1 followed by rapid restoration of equilibrium (*i.e.*, chemical relaxation).

The interpretation of the relaxation time τ depends on the assumed mechanism for the configurational change. It is likely that this proceeds in two stages (L denotes 2,3,2-tet)

$$\mathrm{NiL^{2+}} + \mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NiL(H_2O)^{2+}} \tag{2}$$

$$\mathrm{NiL(H_2O)^{2+}} + \mathrm{H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{NiL(H_2O)_2{}^{2+}} \tag{3}$$

as proposed for the octahedral–tetrahedral interconversion in cobalt(II) complexes.[6] $\mathrm{NiL(H_2O)_2{}^{2+}}$ is a high-spin species whereas $\mathrm{NiL^{2+}}$ is a low-spin species.[2,4,5] Considerations of the stereochemistry and the extent of d-orbital perturbation expected to be caused by the water ligand[7] indicate that the pentacoordinated intermediate is also likely to be a high-spin species, so that step 2, involving a change of spin, is likely to be rate controlling.[8] On the basis of this mechanism and making the steady-state approximation for $\mathrm{NiL(H_2O)^{2+}}$, the following expression for the relaxation time τ may be derived[6]

$$\tau^{-1} = k_1[\mathrm{H_2O}] + k_{-1}k_{-2}/k_2[\mathrm{H_2O}] \tag{4}$$

$$= k_1[\mathrm{H_2O}](1 + K) \tag{5}$$

where $K = [\mathrm{NiL^{2+}}]/[\mathrm{NiL(H_2O)_2{}^{2+}}]$. Using the values[9] $K = 0.16$, $[\mathrm{H_2O}] = 55\ M$, $\tau = 0.28$ μsec, all at 23°, the value of k_1 at 23° is $(5.6 \pm 0.3) \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$. The activation parameters associated with k_1 were calculated from a least-squares plot of ln (k_1/T) *vs.* $1/T$: $\Delta H^{\ddagger} = 20 \pm 2$ kJ mol^{-1}; $\Delta S^{\ddagger} = -48.6 \pm 5$ J mol^{-1} K^{-1}; the errors quoted are twice the standard deviations. We have also observed similar effects in aqueous solutions of the Ni(II) complex with triethylenetetramine (trien), a homolog of 2,3,2-tet. The relaxation times were about a factor of 2 slower than in the 2,3,2-tet system.

Finally it may be noted that the transition, $^3T_{2g} \leftarrow {}^3A_{2g}$, which we believe to be responsible for the absorption of the laser radiation, is symmetry forbidden. It is therefore observable only on account of the simultaneous excitation of a molecular vibration of the correct symmetry, a point which may be relevant to a discussion of the photophysical processes involved in the rearrangement of the excited octahedral species, with the expulsion of two H_2O ligands, to the square-planar form. The enthalpy change[9] for equilibrium 1, 20 kJ mol^{-1}, confirms that the energy required to bring about photodissociation of the water molecules is less than that available at the laser wavelength (113 kJ mol^{-1}).

Acknowledgment. This work was supported by a grant from the Science Research Council. R. J. thanks the Ministry of Education (N. I.) for the award of a studentship.

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(8) We acknowledge valuable discussions with Dr. S. M. Nelson on this point.

(9) K values were estimated from spectral measurements using a value of 61 M^{-1} cm^{-1} for the extinction coefficient of $\mathrm{NiL^{2+}}$ at 440 nm, measured in aqueous solution saturated with $\mathrm{NaClO_4}$.[4] A value of $\Delta H° = 20 \pm 1$ kJ mol^{-1} for equilibrium 1 was calculated from the temperature variation of K.

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Nuclear Magnetic Resonance Paramagnetic Shift Reagents. The Use of Internal Protons as Standards for Structural Determinations. A Method for Determination of Complexation Equilibrium Constants

Sir:

Rare-earth paramagnetic and diamagnetic nmr shift reagents[1,2] have recently received widespread attention. Structural assignments have generally been made[1–3]

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(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971).

(3) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); G. N. La Mar, W. DeW. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964); G. N. La Mar, *ibid.*, **43**, 1085 (1965); B. R. McGarvey, *ibid.*, **53**, 86 (1970); R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970); the exact form is unimportant to the present discussion.

according to $\delta_{\max}{}^i = C_i(3\cos^2\theta_i - 1)/R_i{}^3$ or by plotting the observed shift, $\Delta_{\text{obsd}}{}^i$, *vs.* the mole ratio of *total* shift reagent to *total* substrate (E_t/S_t).[4,5] The "observed" shift at $E_t/S_t = 1$, often obtained by extrapolation from data at lower E_t/S_t, has been taken as a standard.[5,6] These procedures generally do not allow comparisons of different substrates because of difficulty in determining $\delta_{\max}{}^i$, θ_i, and R_i, because of experimentally nonlinear $\Delta_{\text{obsd}}{}^i$ *vs.* E_t/S_t plots at both low[5,7] and high[4,8] E_t/S_t, and because of differences in equilibria, geometry,[6] and substrate concentrations.[9] The use of $\Delta_{\text{obsd}}{}^i$ at $E/_tS_t = 1$ could be misleading, since the data[4] clearly show that such extrapolated values can be $\gg \Delta_{\max}{}^i$.

Preliminary results are reported for two useful and important observations. (1) If a suitably chosen model compound is used, the structural features of an unknown compound can be assigned by using internal "standard" protons (here acetoxy). (2) Plotting $1/\Delta_{\text{obsd}}{}^i$ *vs.* S_t (holding E_t constant) gives a straight line from which $\Delta_{\max}{}^i$ ($= \delta_{\max}{}^i - \delta_0{}^i$) and K, the equilibrium constant, can be obtained. This work was done with europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione), Eu(fod)$_3$, a superior shift reagent recently reported by Rondeau and Sievers.[4,10]

The complexation equilibrium of substrate with shift reagent is fast on the nmr time scale.[2,11] Therefore, the observed chemical shift, $\delta_{\text{obsd}}{}^i$, must be the result of a weighted average,[12] $\delta_{\text{obsd}}{}^i = [\delta_0{}^i(\text{S}) + \delta_{\max}{}^i(\text{ES})]/S_t$, where $\delta_0{}^i$ is the original chemical shift (no reagent), $\delta_{\max}{}^i$ the resonance when complexed to reagent E, and (S) and (ES) the moles (molar concentrations) of uncomplexed and complexed substrate. Using material balance equations, one obtains eq 1, where E is the concentration of uncomplexed shift reagent.[12a] This predicts the slope for $\Delta_{\text{obsd}}{}^i$ *vs.* E_t/S_t is *not* constant as previously assumed[5,6] and should show curvature at low E_t/S_t where E/E_t varies, and at high E_t/S_t, where $E/E_t \rightarrow 1$ and the slope $\rightarrow 0$. This is in accord with published data.[4,5,7,8]

$$\Delta_{\text{obsd}}{}^i = \delta_{\text{obsd}}{}^i - \delta_0{}^i = \Delta_{\max}{}^i(1 - E/E_t)E_t/S_t \quad (1)$$

For two protons i and j in the same molecule, dividing $\Delta_{\text{obsd}}{}^i$ by $\Delta_{\text{obsd}}{}^j$ gives $\Delta_{\text{obsd}}{}^i = (\Delta_{\max}{}^i/\Delta_{\max}{}^j)\Delta_{\text{obsd}}{}^j$. Plots of $\Delta_{\text{obsd}}{}^i$ *vs.* $\Delta_{\text{obsd}}{}^j$ give excellent *straight* lines (correlation coefficients >0.9995, intercepts <|2.0| Hz) independent of substrate or reagent concentrations, which allow analyses of mixtures of compounds—a difficult task with the previous methods. The $\Delta_{\max}{}^{\text{Ac}}/\Delta_{\max}{}^j$ slopes are given in Table I for several vinyl acetates[10] of general structures I and II. The data clearly show that a given geometrical arrangement, *e.g.*, vinyl hydrogens "cis" to the acetoxy group, gives a characteristic slope, probably because $\Delta_{\max}{}^{\text{Ac}}$ and the complex conformational distributions remain nearly the same for the series. Isomers **7** and **8** (as a 1:1.5 inseparable mixture) were assigned unequivocally by this method. This illustrates the utility and reliability of this method (without directly requiring estimates of θ_i and R_i).[13]

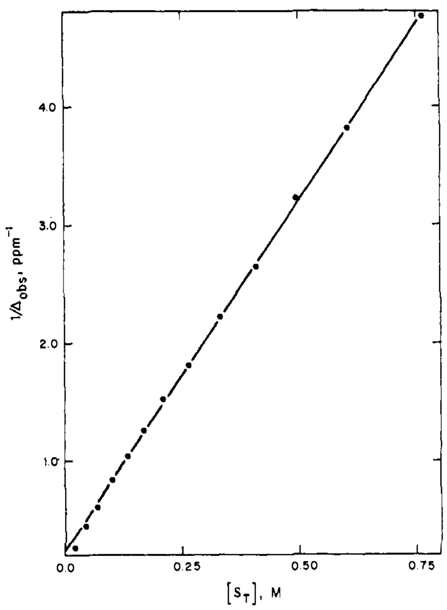
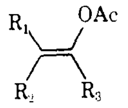
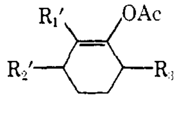


Figure 1. Plot of $1/\Delta_{\text{obsd}}$ *vs.* S_t for acetoxy protons of allyl acetate [Eu(fod)$_3$] = 0.0101 *M*.



I



II

Table I. Characteristic $\Delta_{\max}{}^{\text{Ac}}/\Delta_{\max}{}^j$ for Vinyl Acetates I and II[a,b,d]

Compd	R$_1$	R$_2$	R$_3$
1	H, 1.55	H, 2.63	CH$_3$, 1.71
2[c]	CH$_3$, 2.36	H, 2.48	CH$_3$, 1.77
3	H, 1.58	CH$_3$, 5.25	CH$_3$, 1.64
4[c]	H, 1.46	H, 2.54	CH$_2$CH$_3$, 1.60, 3.53
5	H, 1.38	CH$_3$, 5.20	*c*-Pr
6	CH$_3$, 2.11	H, 2.21	*c*-Pr
7[c]	*c*-Pr	H, 1.92	*c*-Pr
8[c]	H, 1.34	*c*-Pr	*c*-Pr
9	H′, 1.53	H′, 5.49	H′, 1.38
10[c]	CH$_3$′, 2.13	H′	H′, 1.38
11[c]	H′, 1.40	H′	CH$_3$′, 2.33

[a] *c*-Pr = cyclopropyl. [b] Duplicate runs show reproducibilities better than 4%. [c] Data obtained for mixtures: **2** + **4**, **7** + **8**, **10** + **11**. [d] Reference 10.

In principle, the method can be used with any functional group that contains nmr nuclei which are not

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(6) H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971).

(7) B. L. Shapiro, *et al.*, *J. Amer. Chem. Soc.*, **93**, 3281 (1971).

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(9) K. K. Anderson and J. J. Uebel, *ibid.*, 5253 (1970).

(10) Eu(fod)$_3$ (Norell Chemical Co.) was used as a 0.2–0.5 *M* solution in CCl$_4$ (accurately known for the equilibrium experiments) and measured with a syringe. Except for "spectro" quality isopropyl alcohol, all compounds were purified by preparative glc. Vinyl acetates were prepared by acid-catalyzed exchange of the corresponding ketones with isopropenyl acetate. Spectra were obtained with a Varian A60-A spectrometer.

(11) G. H. Wahl, Jr., and Max R. Peterson, Jr., *Chem. Commun.*, 1167 (1970).

(12) E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91**, 7274 (1969).

(12a) Note Added in Proof. Equation 1 is of the form previously derived for charge-transfer complexes (R. C. Foster and C. A. Fyfe, *Progr. Nucl. Magn. Spectrosc.*, **4**, 1 (1969)). This treatment has not been previously applied to shift reagent complexations. The author thanks Professor M. Robert Willcott, University of Houston, for pointing out this similarity.

(13) The 10-methyls for cholesteryl and 3-β-cholestanyl acetates have $\Delta_{\max}{}^{\text{Ac}}/\Delta_{\max}{}^{\text{Me}}$ of 7.00 and 6.80, respectively.

"important" to the molecular structure: -COCH$_3$, -OCH$_3$, -OSO$_2$CH$_3$, -COH, -NCOCH$_3$, -OCOPh, etc.

At high S_t/E_t, where $S \approx S_t$, the approximation $K \approx (E_t - E)/S_tE$ was used to obtain eq 2. Plots of

$$(\Delta_{obsd}{}^i)^{-1} = (\Delta_{max}{}^iE_t)^{-1}S_t + (\Delta_{max}{}^iE_tK)^{-1} \qquad (2)$$

$1/\Delta_{obsd}$ *vs.* S_t give straight lines (Figure 1) from which the slopes and intercepts give $\Delta_{max}{}^i$ and K. The K values at ambient probe temperature (32 ± 1°) for isopropyl alcohol, tetrahydrofuran, 2-butanone, isopropenyl acetate, and allyl acetate are 97 ± 8, 57 ± 3, 32 ± 3, 27 ± 3, and 26 ± 3 l. mol^{-1}, respectively. The relative ordering is consistent with that estimated qualitatively by competition experiments.[6] The calculated $\Delta_{max}{}^i$ are consistent with the $\Delta_{max}{}^i/\Delta_{max}{}^j$ slopes, *e.g.*, Δ_{max} for the 2- and 3-methylenes of tetrahydrofuran are calculated to be 1948 and 793 Hz; ratio 2.46. The plot of $\Delta_{obsd}{}^{2\text{-H}}$ *vs.* $\Delta_{obsd}{}^{3\text{-H}}$ gives slope 2.40.

This analysis allows convenient estimations of Δ_{max} and K.[13a] Both are necessary for meaningful comparisons of vastly different substrates. The pseudocontact shift equation[1-3] (above) properly requires $\delta_{max}{}^i$, not some arbitrarily selected $\delta_{obsd}{}^i$.

Acknowledgment. The author thanks Professor Robert G. Bergman for his generous encouragement of this work and his commitment of partial financial support from National Institutes of Health Grant No. AM-AI-13554, and Professor John D. Roberts for his stimulating discussions and helpful suggestions.

[13a] NOTE ADDED IN PROOF. After submission of this report, a communication reported the use of S_t *vs.* $1/\Delta_{obsd}$ to calculate Δ_{max} and K for propylamine and neopentyl alcohol using the less soluble Eu(dpm)$_3$ reagent (I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Commun.*, 1281 (1971)).

[14] National Science Foundation Predoctoral Fellow, 1968–1971.

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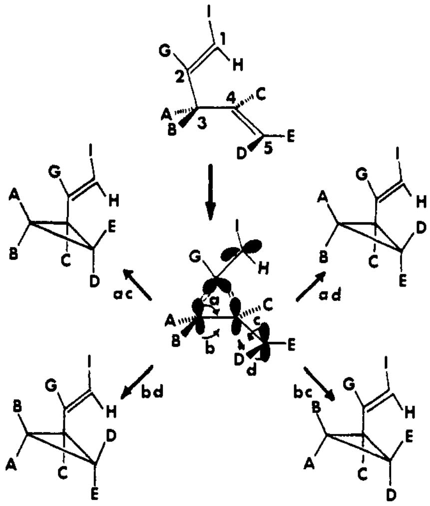
The Stereochemistry of Excited State Atom Reorganization Processes. Di-π-methane Rearrangement

Sir:

The photochemical di-π-methane rearrangement of di-π-methanes to π-cyclopropanes has become one of the more general excited state atom reorganization reactions.[1] A large effort has been directed recently at determining how structures and electronic properties of the di-π-methanes influence the direction, multiplicity, and efficiency of this process.[1,2] Another interesting, yet less studied,[3] facet of this excited state process is its stereochemistry, *i.e.*, whether the process is a concerted one and, if so, which of the manifold of transition-state orbital geometries is of lowest energy. In addition, the question of whether or not the preferred stereochemical pathways are influenced by structure and multiplicity of the di-π-methanes seems important.

Initial considerations of the stereochemistry of this process include expectations based upon the variety of possible mechanisms for the conversion of di-π-methanes to π-cyclopropanes. For example, the four concerted reaction pathways, which correspond to π migration from C-3 to C-4 in concert with C-3–C-5 disrotatory ring closure, syn (pathway ac in Chart I) or anti (bd) to the migrating moiety, or conrotatory closure with retention (ad) or inversion (bc) at C-3, lead to stereochemically distinct π-cyclopropanes, when starting with an appropriately substituted di-π-methane in which free rotation about the C-3–C-4 bond is restricted. On the other hand, nonconcerted processes are expected to display a manifold of stereochemical outcomes depending on the degree of nonsimultaneity of bond formation and cleavage. In the course of our studies, we have prepared model 1,4-dienes, having necessary substituents and structures to reflect favored pathways in the vinylcyclopropanes produced. We would like to report some of our initial results from studies on one of these, 1-phenyl-3-methyl-3-(*cis*-1-propenyl)cyclohex-1-ene (**1**),[6] which indicate that anti-disrotatory C-3–C-5 ring closure is preferred.

Chart I. Di-π-methane Concerted Pathways



Direct irradiation of **1** in hexane resulted in formation of a complex mixture from which two major products were separated. The spectral and analytical data indicated that both the major I (37.8%) and minor II (24.3%)[7] photoproducts are isomeric with the starting diene and have structures in which the propenyl group is retained and the styryl is lost, as in the propenylbicyclo[3.1.0]hexanes (**2**-**5**).

In order to distinguish between these possibilities, degradation of the minor direct irradiation photo-

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[1] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

[2] (a) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259, 6267 (1970); (b) H. E. Zimmerman and A. Baum, *ibid.*, **93**, 3646 (1971).

[3] The stereochemistry of the benzovinyl version of this rearrangement has been investigated by Zimmerman[4] and Swenton[5] who found pathways involving anti-dirotatory closure (path bd in Chart I) to be preferred.

[4] (a) H. E. Zimmerman and G. Samuelson, *J. Amer. Chem. Soc.*, **91** 5307 (1969); (b) H. E. Zimmerman and G. Epling, *ibid.*, **92**, 1411 (1970).

[5] J. S. Swenton, A. L. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970).

[6] (a) Full details of the synthetic and degradative sequences used in this work will be given in our full paper. All new compounds gave satisfactory quantitative analyses. (b) The spectral properties (ir, absence of absorption in the 9.8–12.5-μ region) and known stereoselectivity of the Wittig reaction support the assignment of cis stereochemistry to our starting diene **1**.

[7] Separation was accomplished using glc on a 12 ft × $^1/_4$ in. column of 2% SE-30 on Chromosorb P (acid washed) at 210°; yields are based on unrecovered starting material.