A proton-decoupled, natural abundance cmr spectrum of **1** in DMSO-d_6 was run at 50°. All but the carbonyl carbon signals were found and the chemical shifts assigned (Table II). Analysis of the quinoline

Table II. Cmr Data for **1**[a]

Carbon	Chemical shift[b]	Relative peak height (Natural abundance[c])/ (^{13}C-enriched[d])
2	156.8	
3	145.4[e]	
5	50.2	97/150
6	129.7	
7	131.4[f]	
8	127.9	
9	128.4	
10	127.5	
11	129.0	
12	130.2[f]	
13	149.9[e]	
14	96.7	113/90
15	147.9[e]	
16	119.0	
17	65.4	100/100
18	7.8	77/63
19	30.6	103/87
20	72.4	52/55

[a] Determined on a JEOL PFT-100 nmr spectrometer at 25.1 MHz; 16K data points (time domain) over 5000 Hz were used with 3.2 and 5.0 sec pulse repetition rates and 90° pulses. [b] Relative to external TMS: $\delta^{DMSO} = \delta^{TMS} + 39.6$ ppm. [c] Ca. 0.1 M. [d] Ca. 0.03 M. [e] These three assignments could be interchanged. [f] These two assignments may be interchanged.

and α-pyridone nuclei was based on the shift data of quinoline,[17] α-pyridone,[18] and its N-methyl derivative[18] and application of proper substituent effects.[19] The methines of the benzene half of the quinoline moiety were assigned in the order in which they appear in quinoline itself, the methine of the pyridine half being 5 ppm upfield of the corresponding quinoline carbon resonance. Carbons 2 and 6 are displaced downfield by 7 and 10 ppm, respectively, from their normal quinoline resonances in agreement with shift differences evaluated from a methylated quinoline model.[17] The small shift difference (0.8 ppm) between C-16 of **1** and C-3 of α-pyridone and the downfield shift of C-15 fit the known effect of alkylation of the α- and β-carbons of conjugated ketones.[19b] There being only one methyl group and one quaternary carbon and each methylene unit being surrounded by a different environment, all nonaromatic carbons of camptothecin are unique.

[1-^{13}C]Tryptamine was synthesized from [^{13}C]KCN and thereby [5-^{13}C]-**5a** and **5b** were obtained by procedures analogous to those reported by Battersby and coworkers.[10,12b] The resulting labeled **5b** contained ≧84 atom % ^{13}C as shown by mass spectrometric analysis, being labeled solely at C-5 (cmr, δ 40.9). Intact plants (206 g) were wick-fed [5-^{13}C]-**5a** (38 mg) over a 2-day period and then maintained under growth lamps[20] at 27° for an additional 17 days during Decem-

(17) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley, New York, N. Y., 1972.
(18) U. Vogli and W. von Philipsborn, *Org. Magn. Resonance*, **5**, 551 (1973).
(19) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley, New York, N. Y., 1972.
(20) Westinghouse Plant-Gro F40.

ber, 1973. Standard isolation techniques were used to obtain chromatographically pure **1** (20 mg) from the whole plants. The proton noise-decoupled cmr spectra of natural-abundance and "enriched" **1** were determined under as closely identical conditions as possible to obtain comparable S/N ratios and peak heights for the relevant carbons. The normalized peak heights of six of the carbons of **1** (Table II) were compared, particular significance being given to the C-5 and C-17 methylenes. It could be seen that, as anticipated from consideration of the lactam hypothesis, *only* C-5 of **1** had been labeled by the biosynthetic incorporation of [5-^{13}C]-**5a**. The signal enhancement of C-5, corresponding to *ca.* 55% increase over natural abundance (C-5 compared to C-17), represents a specific incorporation of *ca.* 1.6%, quite in line with the specific incorporation of 1.3–1.8% of radioactively labeled **5a**.

It is noteworthy that from the results of our biosynthetic study of **1**, it appears that there are two closely related pathways for indole alkaloid biosynthesis among higher plants. Both pathways involve the utilization of only one epimer of a common key intermediate, **4**, yet both epimers of **4** are produced by *C. acuminata*[21] and *C. roseus*.[9] An intriguing question arises from these and other observations herein; are some steps of biosynthetic pathways to secondary natural products more the result of chemical reactivity under optimal conditions and less the outcome of stereoselective, enzymatic control? Similar views have been expressed recently by Scott and Wei[22] for the Vinca alkaloids.

(21) Shown by a cold-trap experiment in which the two epimers of **5** were added to the plant material from a feeding experiment with [3,6-^{3}H$_3$]loganin. Under the isolation conditions, **4b** was converted to **5b**. The reisolated **5a** contained 0.01% of the total radioactivity fed and **5b**, 0.03%.
(22) A. I. Scott and C. C. Wei, *J. Amer. Chem. Soc.*, **94**, 8264 (1972).

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Dipolar Relaxation in Shift Reagents as a Solution Structural Probe

Sir:

The basis for effecting meaningful solution structural determinations using proton nmr shifts due to lanthanide shift reagents,[1] SR's, is the assumed magnetic axial symmetry which permits the analysis of the dipolar

(1) R. E. Sievens, Ed., "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York, N. Y., 1973.

shifts using only the axial geometric factor,[2] $(3 \cos^2 \theta - 1)r^{-3}$. The apparent success of such structural determinations was initially suspect[3] in view of the highly rhombic symmetry reflected in both single-crystal X-ray structural[3,4] and susceptibility anisotropy[5] studies. However, recent papers[6] have produced satisfactory theoretical rationalizations for effective axial symmetry based on averaging to zero of the rhombic component of the anisotropy by either substrate ligand rotation and/or ligand exchange. For the case of heteronuclei, ^{13}C, ^{31}P, the comparable importance of contact[7] and dipolar contributions to the shifts undermines any quantitative use of the shift ratios.

We have recently advocated[8] the use of the relaxation reagents, Gd(dpm)$_3$[9] and Gd(fod)$_3$,[9] for inducing line width or relaxation rates which, due to their r^{-6} dependence,[10] can be successfully interpreted in terms of solution structures for both protons and ^{13}C nmr. We selected[8] Gd^{3+}, since it exhibits negligible magnetic anisotropy. Although dipolar relaxation equations for axially anisotropic complexes[11] have been derived and utilized in the analysis of line width effects due to shift reagents,[12,13] the validity of assuming effective axial symmetry, as in the case of dipolar shifts, has not yet been established.

We wish to demonstrate here that the shift-reagent-induced relative line widths fail to reflect the true geometry if axial symmetry is assumed, and suggest a probable origin for these discrepancies. Hence the commonly used Sternlicht relaxation equations[11] do not appear to be applicable to the lanthanide shift reagents.

For proton i experiencing dipolar relaxation in ligand, S, undergoing rapid chemical exchange between free and coordinated forms, the Sternlicht equations yield[11]

$$\pi\delta_i = T_{1i}^{-1} = T_{2i}^{-1} = f_i Br_i^{-6}[g_{av}^2 + g_{||}^2 \cos^2 \theta_i + g_\perp \sin^2 \theta_i], \quad (1)$$

where δ_i is the line width, in hertz, f_i is the fraction of ligand coordinated, $B = \beta^2\gamma^2 S(S + 1)$, r is the metal-proton vector, and θ is the angle between this vector and the unique magnetic axis. If effective axial symmetry is assumed, the known structural data for the rigid SR–S complex[3,4,8] yield for the o-H and p-H

(2) J. P. Jesson in "NMR in Paramagnetic Molecules: Principles and Applications," G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N. Y., 1973, pp 1–52.

(3) W. D. Horrocks, Jr., J. P. Sipe, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

(4) R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972); D. S. Dyer, J. A. Cunningham, J. J. Brooks, R. E. Sievers, and R. E. Rondean, ref. 2, pp 21–51.

(5) W. D. Horrocks, Jr., and J. P. Sipe, III, *Science*, **177**, 994 (1972).

(6) J. M. Briggs, G. P. Moss, E. W. Randall, and K. D. Sales, *J. Chem. Soc., Chem. Commun.*, 1180 (1972); J. M. Briggs, F. A. Hart, G. P. Moss, G. W. Randall, K. D. Sales, and M. L. Staniforth, ref 2, pp 197–227; W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **96**, 3022 (1974).

(7) M. Hirayama, E. Edagawa, and Y. Hanyu, *J. Chem. Soc., Chem. Commun.*, 1343 (1972); R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *ibid.*, 636 (1972).

(8) G. N. La Mar and J. W. Faller, *J. Amer. Chem. Soc.*, **95**, 3817 (1973).

(9) Dpm = dipivaloylmethane; fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadione.

(10) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

(11) H. Sternlicht, *J. Chem. Phys.*, **42**, 2250 (1965).

(12) J. Reuben and J. S. Leigh, *J. Amer. Chem. Soc.*, **94**, 2789 (1972).

(13) E. Nieboer, D. Gast, J. S. Cohen, B. Furie, and A. N. Schechler, Proceedings 10th Rare Earth Research Conference, Carefree, Ariz., April 30–May 3, 1973, pp 763–769.

line width ratio

$$\frac{\delta_o}{\delta_p} = \frac{r_o^{-6}[g_{av}^2 + 0.67g_{||}^2 + 0.33g_\perp^2]}{r_p^{-6}[g_{av}^2 + g_{||}^2]} \quad (2)$$

This latter relation requires that for all SR's which cause upfield shifts, $(g_\perp^2 > g_{||}^2)$, $(\delta_o/\delta_p) > (r_o^{-6}/r_p^{-6})$, while for all downfield shift reagents $(g_\perp^2 < g_{||}^2)$, $(\delta_o/\delta_p) < (r_o^{-6}/r_p^{-6})$. In the case of Gd^{3+}, which has $g_{||} = g_\perp$, eq 2 predicts $\delta_o/\delta_p = r_o^{-6}/r_p^{-6}$; this equality has been confirmed[8] experimentally. If effective axial symmetry is valid, eq 2 predicts[14] that δ_o/δ_p for upfield SR's (Ho(dpm)$_3$, Dy(dpm)$_3$, Dy(dpm)$_3$, Tb(dpm)$_3$)[15] exceeds δ_o/δ_p for Gd(dpm)$_3$, while δ_o/δ_p for downfield SR's (Er(dpm)$_3$, Tm(dpm)$_3$) will be less than δ_o/δ_p for Gd-(dpm)$_3$.

We have measured the induced proton line width for 3,5-lutidine in the presence of the lanthamide reagent Ln(dpm), with Ln = Er, Ho, Dy, Tb, and Tm, which induce sufficient relaxation to permit accurate determination of line widths. The line width increased monotonically with increased SR concentration, and the line width ratios were found to be independent of the [SR]/[S] ratio in the range of 0.05–0.25, suggesting that chemical exchange contributes negligibly to the averaged line width.[16] The data in Table I give the

Table I. Relative Line Widths and Shifts for 3,5-Lutidine in the Presence of Lanthanide Reagents[a]

	Downfield SR $(g_{||} > g_\perp)$ Tm(dpm)$_3$	$(g_{||} = g_\perp)$ Gd(dpm)$_3$	Upfield SR $(g_{||} < g_\perp)$ Ho(dpm)$_3$
Line width ratio			
o-H/p-H	13.3 ± 1.2	29.1 ± 2.8[b]	16.4 ± 1.8
Shift ratios[c]			
m-CH$_3$/o-H	0.210	b	0.202
p-H/o-H	0.295	b	0.285

[a] Data at 35°, in CDCl$_3$ solution, with shifts referenced to La-(dpm) complex under similar conditions. [b] Determined in the presence of Eu(dpm)$_3$, as described in ref 8; no shifts due to Gd-(dpm)$_3$ alone were observed. [c] The m-CH$_3$ shift ratio was obtained as a function of rotational angle and then averaged. Computations based on using an average angle and distance yielded a ratio which was too large by 7%.

observed line width ratio δ_o/δ_p, corrected for diamagnetic contribution and outer-sphere relaxation,[8] for a typical upfield SR, Ho(dpm)$_3$, and downfield SR, Tm(dpm)$_3$, as well as for Gd(dpm)$_3$. The Gd(dpm)$_3$ line widths were determined by the method described earlier.[8] Also included in the table are the observed shift ratios, which are quantitatively consistent with the axial geometric factor.[15]

The line width ratio data for the SR's in the table are clearly inconsistent with a dipolar relaxation mechanism described by eq 1. Hence structures determined from such line width ratios are invalid. The δ_o/δ_p for the various SR's all differed with values gen-

(14) Changes in the r_o^{-6}/r_p^{-6} ratio due to decreases in the Ln–N distance are relatively small, <10% on reducing it from 2.65 Å (a reasonable maximum) to 2.50 Å (a reasonable minimum). Hence the observed deviations must arise from effects other than simple changes in bond distances. In our calculations, a value of 2.60 Å was employed.

(15) W. D. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

(16) The near linearity of δ with [SR]/[S] also suggests negligible chemical exchange effects at 35°. However, only T, data will yield true relaxation rates independent of chemical exchange.

erally considerably less than observed for Gd(dpm)$_3$. It may be noted that the relative r_i calculated from $\langle\delta_i\rangle^{1/6}$ for Gd(dpm)$_3$, 0.57, 0.55, and 0.96, for δ_p/δ_o, δ_m/δ_o, and δ_m/δ_p, agree reasonably well with predictions from X-ray data,[4,5] whose values are 0.53, 0.54, and 1.02, respectively.

It is evident from our results that analysis of relative line widths due to shift reagents can lead to very serious errors in estimated distance ratios. This work points out the hazards of relying on structural information deduced from line widths arising from *shift* reagents. The suggested absence of exchange broadening effects for Er(dpm)$_3$ therefore indicates that the observed linewidth ratios reflect nonaxial magnetic anisotropy.

Preliminary considerations suggest that this contrast in behavior with respect to effective axial symmetry noted for the line width and shift data should not have been unexpected. The dipolar shift equation contains only odd powers of trigonometric functions of the azimuthal angle[2]; such odd functions can be averaged to zero *via* rotations as discussed elsewhere. Dipolar relaxation, on the other hand, is made up of sums of squares of matrix elements of the dipolar Hamiltonian,[17] such that even powers of these trigonometric functions will appear; such functions cannot be averaged to zero. Hence relaxation rates may be expected to reflect rhombic anisotropy under conditions where such effects vanish for dipolar shifts.

Work is in progress to define more clearly nuclear relaxation, both proton and heteronuclei,[18] in the presence of lanthanide ions. The possibility of obtaining information of the rhombic anisotropy from the experimental line width data is being explored.

(17) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 11.

(18) J. W. Faller and G. N. La Mar, *Tetrahedron Lett.*, 699 (1974).

(19) Fellow of the Alfred P. Sloan Foundation.

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## Comparative β-Hydride Eliminations from η^1-Vinyliridium(I) and -rhodium(I) Complexes

Sir:

β-Elimination and readdition of metal hydride has been shown[1] to be responsible for the formation of rearranged organic products of certain reactions involving transition metal alkyls. η^1-Vinylmetal complexes also occur as intermediates in several metal-assisted organic transformations and we have observed that such complexes can undergo two different types of β-hydride elimination sequences.

η^1-Vinylic derivatives of Ir(I) or Rh(I) can be prepared by reaction of metal(I) halide complexes and the corresponding lithium reagent[2-5] (reaction 1). Thermol-

(1) For example, see C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971), and references cited therein.

(2) J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, **94**, 6226 (1972).

$$\text{(1)}$$
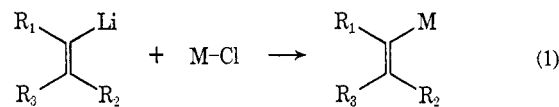
1, R$_1$ = R$_3$ = CH$_3$; R$_2$ = H; M = *trans*-L$_2$Ir(CO)

2, R$_1$ = R$_2$ = CH$_3$; R$_3$ = H; M = *trans*-L$_2$Ir(CO)

3, R$_1$ = R$_3$ = H; R$_2$ = CH$_3$; M = *trans*-L$_2$Ir(CO)

4, R$_1$ = R$_2$ = CH$_3$; R$_3$ = H; M = *trans*-L$_2$Rh(CO)

5, R$_1$ = R$_2$ = CH$_3$; R$_3$ = H; M = L$_3$Rh

L = PPh$_3$

ysis products of **1–5** depend on the (C=C) stereochemistry of the trisubstituted vinylic moiety and on the position of attachment of alkyl groups to the double bond. For **1**, a β-vinylic H cis to Ir is present; metal hydride and alkyne are formed. For **2**, **4**, and **5** (which have no cis-β-vinylic H) elimination of β-allylic H occurs to generate, *via* an η^2-allene complex, η^3-crotyl species **6**.[6] For **1**, in which both types of β-H are present, no η^3-crotyl complex is formed. Thus, the trend for competitive rates of β-H elimination is cis β-vinylic H > β-allylic H. If neither type of β-H is present (**3**), only intramolecular oxidative addition of a C–H bond of coordinated L occurs[2] to yield, ultimately, olefin. In no case were the products of elimination of trans β-vinylic H, γ-allylic H, or α-vinylic H observed.

A typical synthesis and thermolysis sequence occurred as follows. Compound **2** was prepared by stirring a suspension of 312 mg of L$_2$Ir(CO)Cl (0.4 mmol) with a slight excess of *trans*-2-lithio-2-butene[7] in ether, under argon, at −30° for 0.5 hr and then at room temperature for 0.5 hr.[8] The yellow suspension of L$_2$Ir(CO)Cl slowly dissolved and the solution became orange. Ethanol (10 ml) was added and the reaction mixture was filtered and then concentrated by partial removal of solvents *in vacuo*. Golden yellow crystals of **2** were formed and were recovered by filtration, washed copiously with ethanol, and dried *in vacuo* (ν_{CO} 1935 cm^{-1} (Nujol); nmr (C$_6$D$_6$): δ 1.45 (m, 6), 6.50 (m, 1), and complex absorption for PPh$_3$ (30)).[9,10] A solution of **2** in C$_6$D$_6$ was heated to 90° in a sealed tube for 8 hr during which time it slowly isomerized to **6** (reaction 2). At no time could nmr signals attributable to free or η^2-coordinated organic ligands be detected.

Complexes **1** and **3** were prepared in the same way and were spectrally comparable with **2**. In contrast with the decomposition behavior of **2**, **1** in C$_6$D$_6$ rapidly underwent cis β-vinylic H elimination to yield 2-butyne at room temperature (reaction 2). Vinylic complexes **1** and **2** all underwent β-H elimination slowly compared with their *n*-octyl analog[11] which has not yet been

(3) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

(4) M. D. Rausch and G. A. Moser, *Inorg. Chem.*, **13**, 11 (1974).

(5) We were unable to prepare **1** by direct reaction of 2-butyne with HIr(CO)L$_3$.

(6) C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 850 (1971).

(7) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

(8) Ether was distilled under argon from sodium benzophenone ketyl. This was made possible by admixing 10% tetraglyme with the ether.

(9) Satisfactory elemental analyses were obtained.

(10) The stereochemistry of the lithium reagent was checked by vpc determination (6 ft × 0.25 in. column packed with 5% Carbowax 20 M on 60/80 Chromosorb P) of the bromide products from reaction with 1,2-dibromoethane. Protonation of **2** (in C$_6$D$_6$) with dilute HCl yielded *trans*-2-butene as the sole organic product. (C=C) Stereochemistry is therefore maintained in the vinylation of the metal.

(11) J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, **96**, 2276 (1974).