Using a Lanthanide Shift Reagent

D. Scott Wilbur [1]

Medical Radioisotope Research, INC-3, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545
Received October 25, 1983

The use of a lanthanide shift reagent, Eu(fod)₃, to aid in the structural assignments of some chloroazepine-2,5-diones is described. The chloroazepine-2,5-diones, synthesized via the Schmidt reactions of chloro-1,4-benzoquinones, could not readily have their structures assigned by other spectroscopic methods. Correlations of plotted lanthanide induced shifts in pmr studies demonstrated that there was a large positional dependence on the magnitude of induced shifts. The large difference in the magnitude of induced shifts made it possible to assign protons and methyl substituents to specific positions on the azepine ring, thus assigning the structure of the compound.

Introduction.

Schmidt reactions of 1,4-benzoquinones result in ring expansion, forming the seven-membered ring heterocyclic products, azepine-2,5-diones (Scheme I) [2-4]. The insertion of nitrogen in this reaction can potentially lead to a mixture of up to four different products. Indeed, the

Scheme I
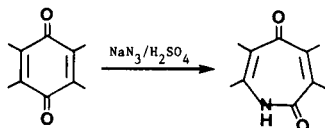
Schmidt reaction of 2-methoxy-5-methyl-1,4-benzoquinone yielded three of the four possible regioisomeric products [5]. The possibility of having two or more structurally similar compounds in a reaction necessitates that each reaction be examined for mixtures of products, and each product have it's structure carefully assigned. The products obtained from the first reported examples of Schmidt reactions of 1,4-benzoquinones were assigned structures based on their proton nmr spectra [2,3]. However, this method proved to be inadequate as it led to misassignments due to long-range ¹H-¹H (cross carbonyl) coupling [6] observed in some spectra. Reinvestigation of the reported structures were carried out using gas chromatographic analyses of the products obtained from degradation of the azepine-2,5-diones with base [7]. While this method worked well for simple alkyl-substituted azepinediones, it might be expected to yield ambiguous results when other substituents are present. Furthermore, this method of structural analysis suffers from the fact that some of the product must be destroyed. Other investigations have relied on conversions of the azepine-2,5-diones to different compounds for structural assignments [8-11].

Studies of the synthetic utility of the Schmidt reactions of chloroquinones produced a number of new azepine-2,5-diones, which could not readily have their structures assigned via the methods previously described. A desire to evaluate the regiochemistry of the products obtained in a non-destructive, unambiguous manner led to an investigation of the use of a lanthanide shift reagent, Eu(fod)₃, for this purpose. The results of that investigation are described here.

Results and Discussion.

Several new azepine-2,5-diones containing chlorine substituents were synthesized via the Schmidt reactions to the corresponding chloro-1,4-benzoquinones (Table I). The reactions of the chlorine substituted quinones were slower than those reported for quinones containing only alkyl substituents. While alkyl substituted benzoquinones undergo a vigorous reaction at 0°, monochloro-1,4-benzoquinones required up to 16 hours at room temperature, and dichloro-1,4-benzoquinones required up to seven days at room temperature [12]. Trichloro- and tetrachloro-1,4-benzoquinones were found to be non-reactive at room temperature even after 30 days [13].

Table I

Chloroazepine-2,5-diones Synthesized *via* Schmidt Reactions
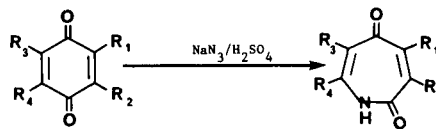
Compound	R₁	R₂	R₃	R₄	Yield, % Crude (Recrystallized)
1	Cl	H	CH₃	H	81 (69)
2	Cl	H	CH₃	CH₃	85 (76)
3	CH₃	H	CH₃	Cl	84 (73)
4	Cl	H	CH₃	Cl	65 (56)
5	Cl	CH₃	CH₃	Cl	87 (74)
6	CH₃	Cl	CH₃	Cl	87 (67)

The crude reaction products were examined by proton and carbon nmr for possible mixtures. Only one regioisomeric product was obtained in each reaction examined. Preliminary structural assignments were made by applying the generally accepted rule that the reactions occur at the least hindered, most basic carbonyl, with the most substituted vinyl carbon undergoing the migration [14]. Evaluation of the most probable reaction pathway could be accomplished by considering the steric environment of the two carbonyls of the quinone precursors for 2, 3, and 4. However, preliminary assignments of the structures of 1 and 5 required that the basicities of the two carbonyls of the quinone precursors be evaluated. Fortunately, the basicities of the carbonyls can be assessed by ^{13}C nmr [15]. The ^{13}C nmr chemical shifts indicated that the most basic carbonyls were the ones which did not contain a chlorine in the adjacent α-vinyl position. Compound 6 could not be evaluated in this manner.

Routine spectral analyses of the products were not definitive [16]. While the spectra were consistent with the preliminary structural assignments, conclusive evidence to rule out all of the other possible regioisomeric products could not be obtained. To assist in the spectral assignments of the chloroazepinediones, the previously reported [3] dimethyl-, trimethyl-, and tetramethylazepine-2,5-diones, 7-9, were synthesized. These compounds were chosen as their structures had been unequivocally determined [7], and they afforded examples of three different substitution patterns.
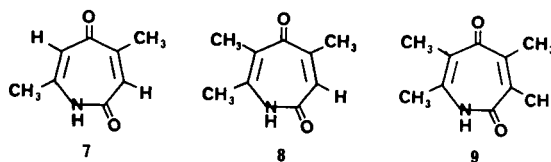
The desire to gain more information from proton nmr data led to the use of Eu(fod)$_3$, a lanthanide shift reagent (LSR) [17]. Initial studies with 7, 8, and 9 demonstrated that there was a remarkable position dependence for the lanthanide induced shifts (LIS) in these compounds. All of the induced shifts were observed to be downfield from the original resonances. Evaluation of the LIS data was best accomplished by plotting the change in chemical shift ($\Delta\delta$) for the substituents on the vinyl carbons, versus the stoichiometry of the added Eu(fod)$_3$ [18]. The resulting graphs are shown in Figures 1-3 for compounds 7-9, respectively. To differentiate the four substituent positions, they were arbitrarily assigned as substituents (a) through (d) as shown below. The proton on the nitrogen was not plotted as it was not observable during most of the experiments.
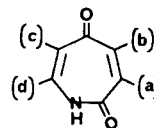
Assignments of the plotted induced shifts were possible through a combination of initial proton chemical shifts, in-

Table II

Physical and Spectral Data for Azepine-2,5-diones

	Mp (°C)	IR (nujol, cm⁻¹)	MS (%)	Elemental Analysis Calcd.	Found
1	216-218, reported 214-215 [a]	3210, 3108, 3070, 2990, 1669, 1622, 1590	173 (21) 171 (60)		
2	211.5-213	3202, 3060, 1690, 1681, 1618, 1590	187 (15) 185 (47)	C, 51.77 H, 4.34	C, 51.70 H, 4.33
3	249.5-251	3202, 3145, 3055, 1669, 1617, 1585	187 (15) 185 (44)	C, 51.77 H, 4.34	C, 51.62 H, 4.20
4	224-226 (dec)	3190, 3120, 3040, 1659, 1624, 1608, 1563	207 (9) 205 (12)	C, 40.81 H, 2.45	C, 40.72 H, 2.58
5	217-218	3195, 3060, 1650, 1594, 1576	221 (7) 219 (10)	C, 43.67 H, 3.21	C, 43.67 H, 3.24
6	230-231.5	3210, 3030, 1668, 1600	221 (13) 219 (21)	C, 43.67 H, 3.21	C, 43.47 H, 3.05
7	219-221, reported 216-217 [b]	3215, 3140, 3075, 3000, 1683, 1654, 1648, 1614			
8	199.5-201, reported 194-196 [b]	3217, 3155, 3108, 3075, 1681, 1629, 1600			
9	213.5-215, reported 214-215 [b]	3190, 3120, 2080, 1670, 1629, 1624, 1616			

[a] Rf [28]. [b] Ref [2].

tegration, coupling with other protons (Table III), and correlations with the other plotted LIS. The correlations between the graphs (Figures 1-3) were made by comparing the magnitude of the LIS for a particular substituent position. Discussions of how the assignments were made are given in the following text.

Table III

NMR Data for Azepine-2,5-diones

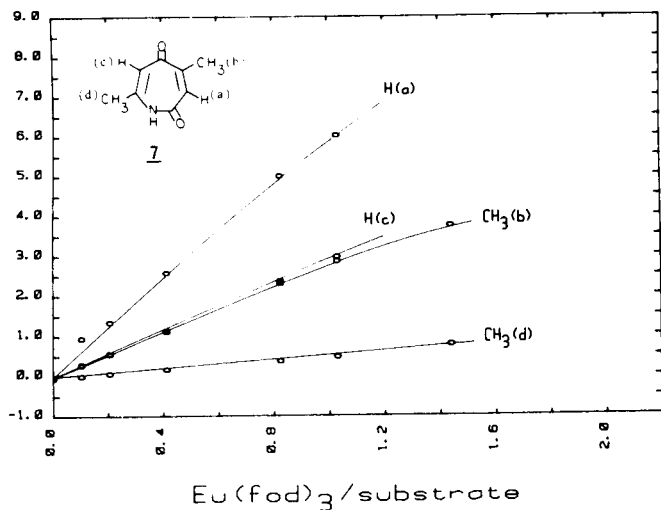|	^{1}H NMR (δ CDCl$_3$)	^{13}C NMR (δ, DMSO-d$_6$)
1	8.70 (bs, 1H), 7.29 (d, 1H, J = 2 Hz), 5.94 (q, 1H, J = 1.1 Hz), 2.24 (s, 3H)	175.8, 162.2, 148.5, 147.5, 131.6, 109.2, 23.3
2	8.72 (bs, 1H), 7.16 (s, 1H), 2.21 (s, 3H), 2.00 (d, 3H, J = 0.6 Hz)	177.5, 161.7, 147.9, 144.9, 130.0, 115.3, 22.0, 15.8
3	9.08 (bs, 1H), 6.84 (d, 1H, J = 2.5 Hz), 2.25 (d, 3H, J = 2.5 Hz)	178.3, 163.9, 148.2, 145.8, 130.0, 118.4, 23.6, 21.6
4	9.03 (bs, 1H), 7.33 (d, 1H, J = 1.8 Hz), 2.55 (s, 3H)	171.4, 161.3, 146.7, 146.3, 130.8, 117.2, 23.9
5	8.97 (bs, 1H), 2.50 (s, 3H), 2.49 (s, 3H)	173.1, 162.9, 144.9, 144.8, 138.5, 116.3, 23.0, 21.3
6	9.05 (bs, 1H), 2.49 (s, 6H)	177.8, 159.8, 146.6, 143.6, 137.7, 117.7, 22.8, 21.5
7	8.63 (bs, 1H), 6.81 (q, 1H), 5.80 (m, 1H), 2.19 (s, 3H), 2.16 (s, 3H)	183.6, 164.7, 150.2, 145.9, 130.8, 111.2, 22.9, 20.6
8	8.48 (bs, 1H), 6.74 (m, 1H), 2.33 (s, 3H), 2.18 (d, 3H, J = 1.5 Hz), 2.00 (s, 3H)	185.6, 164.5, 149.9, 143.1, 129.1, 116.3, 21.6, 21.5, 15.4
9	8.40 (bs, 1H), 2.18 (s, 6H), 2.14 (s, 3H), 1.97 (s, 3H)	190.4, 166.5, 146.2, 140.3, 134.6, 116.7, 20.1, 18.5, 17.8, 15.5

Evaluation of the LIS for **7** (Figure 1) permitted only partial assignment of the observed signals for the substituents. Assignments could be made for the two protons H(a) and H(c) as their initial chemical shifts are separated by 1 ppm, and the downfield shift of H(a) was always more than H(c). The two methyl substituents could not be distinguished by evaluating only Figure 1. Assignments of the LIS for **8** could be readily made for H(a) and CH$_3$(b) due to the proton integration and splitting. While the resonances of the other methyl groups in **8** could not be assigned from Figure 2 alone, comparison of Figures 1 and 2 did allow assignment of the unassigned methyl groups in **7** and **8**. The LIS of CH$_3$(b) in Figure 2 correlated reasonably well with the methyl substituent that was most effected by the Eu(fod)$_3$ in Figure 1. Thus CH$_3$(b) could be tentatively as-

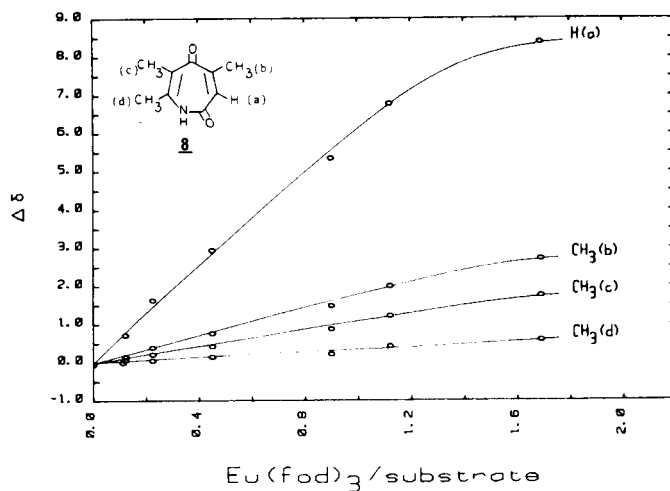Figure 2. Plots of the change in proton chemical shifts observed when Eu(fod)$_3$ was added.

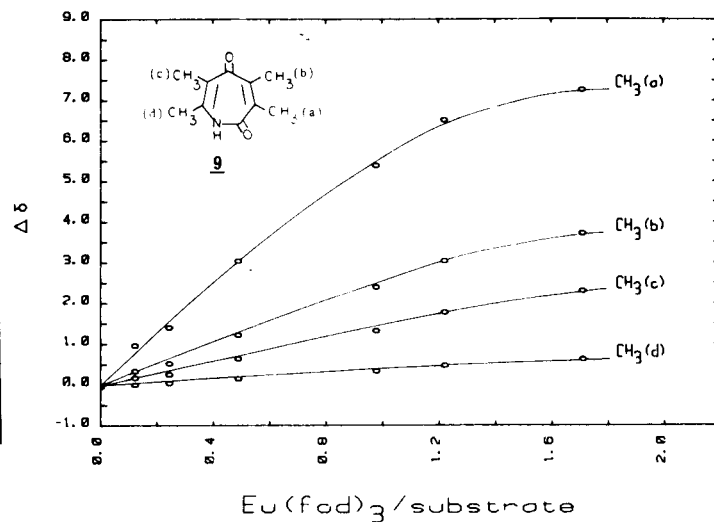Figure 1. Plots of the change in proton chemical shifts observed when Eu(fod)$_3$ was added.

Figure 3. Plots of the change in proton chemical shifts observed when Eu(fod)$_3$ was added.

signed for **7**. This assignment effectively completed the assignments in Figure 1 as only CH$_3$(d) remained unassigned. With the acceptance of the assignments in Figure 1, assignment of CH$_3$(d) in Figure 2 was made by comparing the LIS with Figure 1. Again, a tentative assignment of CH$_3$(d) in Figure 2 completed the assignment as only CH$_3$(c) was left unassigned. Assignments for the LIS of **9** that were consistent with the LIS for **7** and **8** were readily made. The only inconsistency that was seen in the magnitude of LIS observed in **7**, **8**, or **9** was the induced shifts of protons are usually shifted at a faster rate than the chemical shifts of methyl groups [19-21]. The assignments as described above were indeed tenuous at this point, but confidence in the assignments was increased after experiments with the chloroazepinediones were carried out.

The nmr experiments with the chloroazepine-2,5-diones **1-6** using Eu(fod)$_3$ also displayed large differences in the LIS for the substituents at vinyl substituent positions (a) through (d). The data plotted as previously described are shown in Figures 4-9. Evaluation of the structures was accomplished in a manner analogous to the evaluations of **7**, **8**, and **9**. A discussion of how the assignments were made is given in the following text.
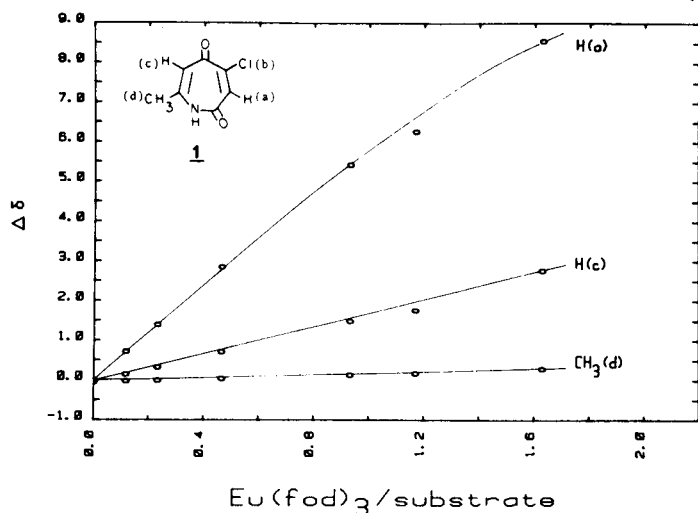

Figure 4.   Plots of the change in proton chemical shifts observed when Eu(fod)$_3$ was added.

The graphed LIS of the disubstituted azepine-2,5-dione **1** (Figure 4) correlated well with the LIS of **7** (Figure 1). In fact, the plots of the LIS of H(a) in Figures 1 and 4 are essentially superimposable. The methyl substituent in **1** showed very little change in chemical shift with added Eu(fod)$_3$. This was consistent with the very small shifts observed for the CH$_3$(d) in Figures 1-3. The chemical shift of the remaining proton resonance H(c) did not change as rapidly as that for H(c) in **7**, however, such differences might be expected when comparing the effect on the $\Delta\delta$ of a methyl group with a chlorine within the molecule.

Comparison of the LIS of the two isomeric trisubstituted monochlorazepinediones **2** and **3** (Figures 5 and 6, respectively) with the LIS of **8** (Figure 2) showed that they also correlated quite well. The chemical shifts of the protons H(a) in Figures 5 and 6 are shifted slightly less than H(a) in Figure 2, but the initial slopes of all three plotted LIS are the same. Assignment of the LIS for CH$_3$(d) in Figure 6 was straightforward as it was a singlet. The remaining signal for CH$_3$(b) was shifted less than CH$_3$(b) in **8**. Likewise, assignment of the non-shifted methyl resonance to CH$_3$(d) in **2** (Figure 5) left only CH$_3$(c), which was also shifted to a less extent than CH$_3$(c) in **8**.
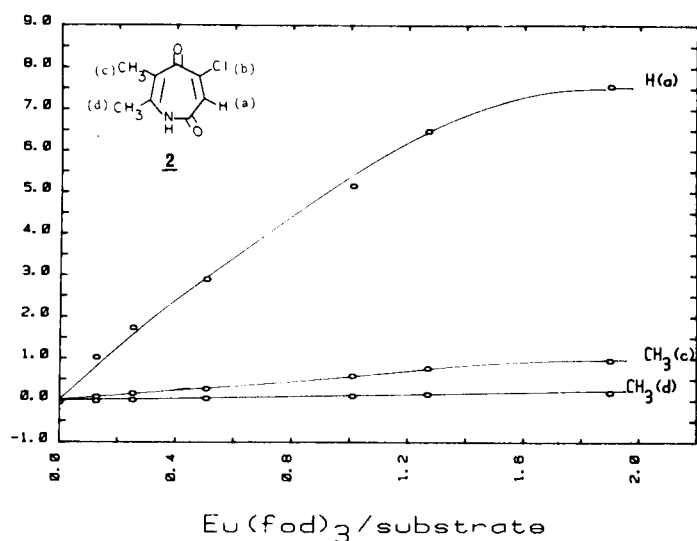

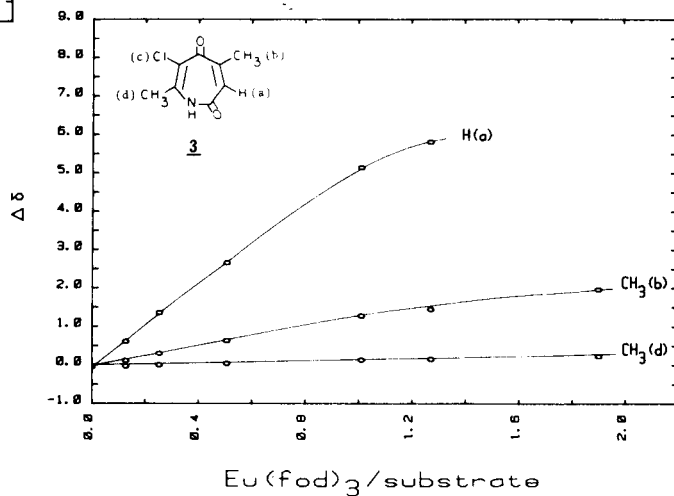Figure 5.   Plots of the change in proton chemical shifts observed when Eu(fod)$_3$ was added.

Figure 6.   Plots of the change in proton chemical shifts observed when Eu(fod)$_3$ was added.

Assignment of the LIS for the trisubstituted dichloroaz-epinedione **4** (Figure 7) was very easy as it had only two proton signals which were distinguishable by integration. The LIS for the proton (a) was shifted nearly the same as H(a) in **8**. The methyl signal was consistent with being at (d) since it was virtually not effected by the added Eu(fod)₃.
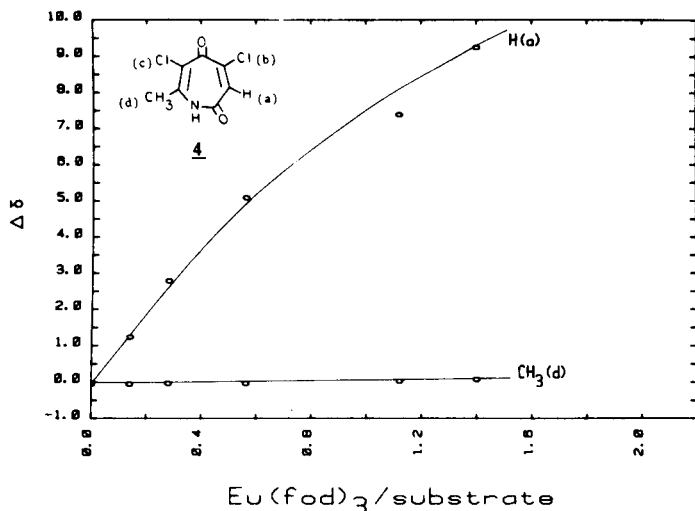

Figure 7.   Plots of the change in proton chemical shifts observed when Eu(fod)₃ was added.

The LIS for the tetra-substituted dichloroazepinediones **5** and **6** (Figures 8 and 9, respectively) were compared with **9** (Figure 3) and the trisubstituted chloroazepinedione **3** (Figure 6). The resonances of the two methyl substituents in **5** were affected very differently by the addition of Eu(fod)₃. The methyl signal that was shifted the most was similar to CH₃(a) in **9**, and the methyl group that was affec-
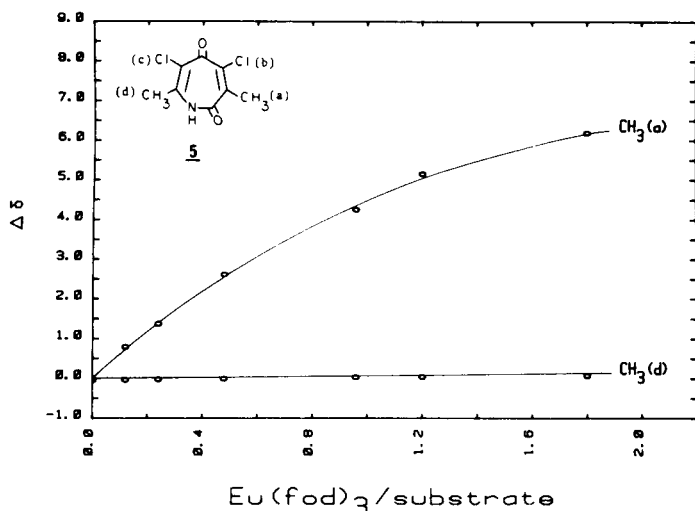

Figure 8.   Plots of the change in proton chemical shifts observed when Eu(fod)₃ was added.

ted very little was similar to CH₃(d). The extents of induc-ed shifts seen in Figure 8 were less than those observed for **9** (Figure 3), but the decrease in the magnitude of the in-duced shifts were consistent with the magnitude of the shifts observed in the other chloroazepinediones. Further-more, a crystal structure determination of **5** has confirmed the structure [22]. The graphed LIS for **6** (Figure 9) does not correlate very well with Figure 3, but it does correlate fairly well with the similar compound **3** (Figure 6). The LIS of the methyl signals for **6** were only slightly decreased from those of **3**. In fact, the initial slopes of the plotted LIS for CH₃(b) are the same.

Comparison of the LIS of the chlorine substituted azep-ine diones and the alkyl substituted azepinediones is com-plicated because the Eu(fod)₃ interaction with the two types of compounds is probably different. The exact na-ture of the interaction of the Eu(fod)₃ with the azepinedi-ones is difficult to analyze since there are interactions pos-sible with both the amide carbonyl [19] and the ketone carbonyl. Fortunately, no interactions have been observed with halogens [23]. Indeed, one possible explanation for the consistent decrease in the magnitude of the induced shifts for the chlorine substituted azepinediones is that there is less binding occurring at the carbonyl in these compounds. This explanation can be supported by the fact that the basicities of the carbonyl decreases as α-chlorine substituents are added (*i.e.*, ¹³C resonances for carbonyls with adjacent halogens are at higher field than those with-out halogens).
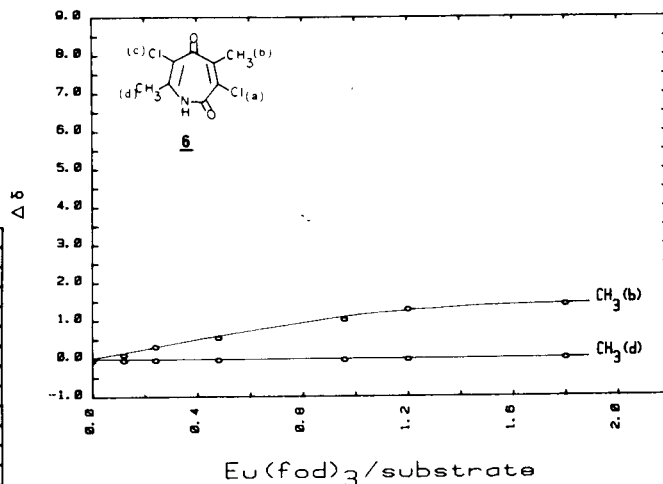

Figure 9.   Plots of the change in proton chemical shifts observed when Eu(fod)₃ was added.

The observed induced shifts of the azepinediones could not be explained by only considering the average distance of the substituent from the europium metal. If one assumes that the predominant interaction is with the amide oxy-gen, the LIS order might be expected to be a > b ~ d > c (see Scheme II), and not the a > b > c > d as observed. This

apparent inconsistency might be explained by considering the dipole-dipole interaction of the azepinedione-europium metal as described by the McConnell/Robertson equation [24]. Their equation (1) defines the change in chemical shift (induced shift) as a function of the distance (r) and the relative average positioning of the substituent with respect to the principle axis of the lanthanide metal (θ), as

$$\Delta\delta = \frac{X \ (3\cos^2\theta - 1)}{r^3} \qquad (1)$$

shown in Scheme II. Plotting the term $3\cos^2\theta - 1$ with respect to the angle demonstrates that null points in the field of influence can be expected at 54.7° and 125.3° [20]. If the Eu atom is 2-3 angstroms from the amide oxygen, an angle θ of approximately 50-55° is reasonable for bisection of the CH$_3$(d). Such positioning may explain the very small induced shifts observed for the methyl substituents at position (d). It could also explain the observed order of the magnitudes of the LIS.

Scheme II
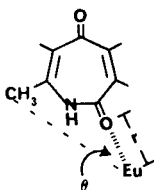
The use of a LSR to aid in the structure determination of azepine-2,5-diones is a rapid, non-destructive method that can be used instead of chemical degradation or transformation. While the method cannot be considered unequivocal, the facts that the structures are consistent with the initial assignments and the LIS can be correlated fairly well, allows a high degree of confidence in the method. Furthermore, none of the other possible regioisomeric products for 1-6 would be expected to give LIS plots similar to those obtained. It is not readily apparent how other substituents might affect the LSR binding to different azepinediones, but this method should be useful in the evaluations of new azepine-2,5-diones.

EXPERIMENTAL

Melting points were determined with a Thomas Hoover Capillary Melting Point apparatus and are uncorrected. The nmr spectra were obtained on either a Varian Model EM-360 or a Bruker model WH-90 spectrometer. All of the Eu(fod)$_3$ experiments were carried out on a Bruker spectrometer. The ir spectra were obtained on a Perkin-Elmer model 273 Infrared Spectrophotometer. Mass spectra were obtained on a Finnigan model 1015 instrument. Elemental analyses were performed by Roberson Laboratories, Florham Park, New Jersey.

LSR Experiments.

Prior to running the Eu(fod)$_3$ experiments, the solubilities of the azepine-2,5-diones had to be determined as some were fairly insoluble in the

desired solvent, chloroform. Once the solubility had been established, a saturated solution of the azepinedione was made in deuteriochloroform. The deuteriochloroform solution was filtered through a Sweeny filter (0.2 microns) and 0.60 ml of the solution was added to each of seven nmr tubes by syringe. This addition was followed by the addition of 0.01 ml of deuteriochloroform which contained 1% TMS to each of the nmr tubes. Finally, varying quantities of a 25 mg/ml solution of Eu(fod)$_3$ in deuteriochloroform was added to six of the sample tubes via a syringe. The proton nmr of each of the samples was taken and the LIS spectra were recorded.

Schmidt Reactions of Quinones.

General synthetic methods are described below for the Schmidt reactions employed to obtain 1-9. As the methods are slightly different from the quinones containing no chlorine substituents, one chlorine substituent, and two chlorine substituents, three procedures are described. Physical and spectral data for the synthesized compounds are given in Tables II and III.

Schmidt Reactions of Non-Halogenated Quinones.

The non-halogenated quinones were reacted as described in the literature [2,3] with the following modifications: (1) after addition of sodium azide at 0° the reaction mixture was stirred at room temperature until no further gas evolution was noticed, and (2) the filtered products were not rinsed with benzene.

Schmidt Reactions of Monochloroquinones.

The monochloro-1,4-benzoquinones were dissolved in concentrated sulfuric acid (1-2 g/10 ml) at 0-5°. One equivalent of sodium azide was added portionwise to the stirred solution. The solution was stirred with cooling for one hour, then allowed to come to room temperature while stirring overnight (16-22 hours). The acid solution was then poured onto ice and the solid precipitate was collected. The crude sample was recrystallized from methanol/water. Analytical samples were prepared either by recrystallization from chloroform/pentanes or sublimation.

Schmidt Reactions of Dichloroquinones.

The dichloro-1,4-benzoquinones were dissolved in concentrated sulfuric acid (1 g/25-50 ml) at room temperature. Three equivalents of sodium azide were added portionwise to the stirred acid solution. The reaction solution was stirred at room temperature for 4 to 5 days, poured onto ice, and the solid precipitate was collected. The solid was recrystallized from either methanol/water or chloroform/pentanes.

Synthesis of Chloroquinones.

The syntheses of the requisite chloroquinones were accomplished by standard methods [26]. The monochlorinated quinones used to prepare 1-3 were synthesized by chlorination of the commercially available methyl-1,4-benzoquinone, 2,3-dimethyl-1,4-benzoquinone, and 2,5-dimethyl-1,4-benzoquinone in acetic acid, followed by dehydrohalogenation using sodium acetate/acetic acid. The dichlorinated quinones that were used to prepare 4-6 were synthesized by reaction of the commercially available m-cresol, 3,5-dimethylphenol, and 2,5-dimethylphenol with chlorine in sulfuric acid/water as described by Muller and Lunde [27].

REFERENCES AND NOTES

[1] Taken in part from Ph.D. Thesis of D. S. Wilbur, University of California, Irvine, 1978.
[2] D. Misiti, H. W. Moore and K. Folkers, *Tetrahedron Letters*, 1071 (1965).

[3] D. Misiti, H. W. Moore and K. Folkers, *Tetrahedron,* **22,** 1201 (1966).

[4] Hydroxynapthoquinones have been shown to undergo ring contraction reactions; H. W. Moore and H. R. Sheldon, *J. Org. Chem.,* **32,** 3603 (1967).

[5] C. G. Hughes, E. G. Lewars and A. H. Rees, *Can. J. Chem.,* **52,** 3327 (1974).

[6] S. Sternhell, *Rev. Pure Appl. Chem.,* **14,** 15 (1964).

[7] R. W. Rickards and R. M. Smith, *Tetrahedron Letters,* **22,** 2361 (1966).

[8] G. R. Bedford, G. Jones and B. R. Webster, *ibid.,* **22,** 2367 (1966).

[9] G. Jones, *J. Chem. Soc. (C),* 1808 (1967).

[10] E. J. Moricone and I. A. Maniscalco, *J. Org. Chem.,* **37,** 208 (1972).

[11] C. A. Flemming, S. C. Gandhi, M. S. Gibson and E. H. Ruediger, *Can. J. Chem.,* **60,** 624 (1982).

[12] Not all of the reactions of chloroquinones yielded azepinediones. Some reaction mixtures turned dark brown instead of the bright red color characteristic of the protonated quinones. Workup yielded only water soluble products which were not characterized.

[13] Elevated temperatures were not attempted due to the violent nature of decompositions of possible side products, azidoquinones.

[14] P. A. S. Smith, "Molecular Rearrangements", Vol 1, P. deMayo, ed, Interscience Publishers, New York, 1963, pp 507-527.

[15] G. E. Maciel, *J. Chem. Phys.,* **42,** 2746 (1965).

[16] The electron rich β-carbon of the vinyl amides and the protons attached to them had distinctive nmr resonances which were upfield from the resonances of the other vinyl carbons and vinyl substituted protons (see Table III). However, this could not be used to assign regiochemistries.

[17] D. S. Dyer, J. A. Cunningham, J. J. Brooks, R. E. Sievers and R. E. Rondeau, "Nuclear Magnetic Resonance Shift Reagents", R. E. Sievers, ed, Academic Press, 1973, pp 21-51.

[18] For a similar evaluation see: J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.,* **93,** 641 (1971).

[19] R. V. Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.,* **11,** 675 (1972).

[20] B. C. Mayo, *Chem. Soc. Rev.,* **2,** 49 (1973).

[21] A. F. Cockerill, G. L. O. Davies, R. C. Harden and D. M. Rackham, *Chem. Rev.,* **73,** 553 (1973).

[22] D. Kunert and R. Doedens, University of California, Irvine, unpublished results.

[23] C. Beaute, Z. W. Wolkowski, J. P. Merda and D. Lelandais, *Tetrahedron Letters,* 2473 (1971).

[24] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.,* **29,** 1361 (1958).

[25] A similar effect is observed for the complexation of Eu(dpm)$_3$ to the amide in piperine; R. B. Lewis and E. Wenkert, "Nuclear Magnetic Resonance Shift Reagents", R. E. Sievers, ed, Academic Press, 1973, pp 99-127.

[26] R. H. Thomson, "The Chemistry of Quinoid Compounds", S. Patai, ed, Part 1, John Wiley and Sons, 1974, pp 111-161.

[27] H. Muller and H. Lunde, *J. Prakt. Chem.,* **4,** 69 (1956).

[28] G. L. Landen, Ph.D. Thesis, University of California, Irvine, 1978.