

and 9)<sup>3a</sup>, 5, ( $n = 6$ ),<sup>3c</sup> and the parent phenols of compounds 1<sup>3a,12</sup> and 4, ( $n = 6$ )<sup>3c</sup> were available from previous investigations.

**6-Bromo-1-hexene and 10-bromo-1-decene** were obtained from 5-hexen-1-ol and 9-decen-1-ol, respectively, and PBr<sub>3</sub>, and purified by elution with light petroleum on silica gel; their structures were confirmed by <sup>1</sup>H NMR spectra.

**Compounds 3 ( $n = 7, 10,$  and  $14$ )** were prepared by adding a concentrated KOH solution (3 mmol) to a boiling solution of catechol (15 mmol) and the proper  $\omega$ -bromo-1-alkene (3.1 mmol) in ethanol. The crude products were eluted with benzene on silica gel. *o*-Hydroxyphenyl 2-propenyl ether ( $3, n = 7$ ) was obtained in 31% yield; *o*-hydroxyphenyl 5-hexenyl ether ( $3, n = 10$ ) in 63% yield; *o*-hydroxyphenyl 9-decenyl ether ( $3, n = 14$ ) in 60% yield.

***o*-Methoxyphenyl decyl ether** was prepared as above from 2-methoxyphenol, 1-bromodecane, and KOH. The compound was purified by microdistillation in vacuo, mp 31–31.5 °C.

The structure of compounds **3** and that of *o*-methoxyphenyl decyl ether was confirmed by <sup>1</sup>H NMR spectra and by elemental analyses (C, H). These were within  $\pm 0.3\%$  of theory in all cases except for **3** ( $n = 10$ ) where C was +0.47%.

**Product Analysis.** The base-solvent system was as previously reported.<sup>13,14</sup> Yields of elimination products were determined

under conditions analogous to those of the kinetic runs.<sup>3d</sup> The calculated amount of KOH stock solution ( $2 \times 10^{-2}$  M) was added to the thermostated solution (50 mL) of the substrate(s). After at least 10 half-lives the mixture was diluted with water, extracted with several portions of pentane, and worked up as usual. After careful evaporation of the solvent, the residue was analyzed by GLC on a 1-m column packed with 2% SE-30 plus 0.5% FFAP on silanized Chromosorb W 60–80 and/or a 1-m column packed with 3% Apiezon on silanized Chromosorb W 60–80. *o*-Methoxyphenyl decyl ether was checked to be formed in high yields ( $95 \pm 5\%$ ) in the conditions of the kinetic runs.

**Kinetic Measurements.** The reaction between *o*-methoxyphenoxide ion and 1-bromodecane was followed as previously described<sup>14</sup> under pseudo-first-order conditions in the presence of a 50-fold excess of 1-bromodecane.

**Registry No.** **1** ( $n = 7$ ), 87013-13-6; **1** ( $n = 8$ ), 87013-14-7; **1** ( $n = 9$ ), 87039-21-2; **1** ( $n = 10$ ), 87013-15-8; **1** ( $n = 14$ ), 87013-16-9; **3** ( $n = 7$ ), 1126-20-1; **3** ( $n = 10$ ), 87013-17-0; **3** ( $n = 4$ ), 87039-22-3; guaiacolate ion, 54976-95-3; 1-bromodecane, 112-29-8; *o*-methoxyphenyl decyl ether, 87013-18-1.

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## The Four-Membered-Ring Chemical Shift Anomaly

Joseph B. Lambert,\*<sup>1a,2</sup> Stephen M. Wharry,<sup>1a</sup> Eric Block,\*<sup>1b,c,2</sup> and Ali A. Bazzi<sup>1b</sup>

Departments of Chemistry, Northwestern University, Evanston, Illinois 60201,  
University of Missouri—St. Louis, St. Louis, Missouri 63121, and State University of New York at Albany,  
Albany, New York 12222

Received March 22, 1983

Anomalously large downfield shifts have been observed for carbon-13 and other nuclei that are  $\alpha$  to sulfonyl or carbonyl groups in four-membered rings. These anomalies are signified by deviations in chemical shift plots for four–seven-membered rings of a functionalized or substituted series vs. the parent cyclic hydrocarbons. Plots are nearly linear for the  $\alpha$  <sup>13</sup>C shifts for all ring sizes of various cyclic hydrocarbons and thioethers. Small deviations are observed for  $\alpha$  <sup>13</sup>C shifts of the four-membered ethers, amines, sulfoxides, and phosphoramidates. Large deviations, signifying an anomaly, are observed for the  $\alpha$  <sup>13</sup>C shifts of the four-membered ketones, lactams, lactones (nuclei  $\alpha$  to carbonyl), and sulfones. The <sup>15</sup>N shifts in the lactams, the endocyclic <sup>17</sup>O shifts in the lactones, and the exocyclic <sup>17</sup>O shifts in the sulfones also appear to be anomalous for the four-membered rings.

The resonances of carbon atoms that are adjacent to a sulfide group normally are shifted downfield 20–25 ppm on oxidation to either the sulfoxide or the sulfone, as a result of the increased electron-withdrawing power of these latter functional groups. Block and co-workers<sup>3</sup> observed that this pattern holds for open-chain systems and for rings of three–eleven members, with the exceptions of four-membered rings. In thietans, oxidation of the sulfide to the sulfone group causes a 40-ppm downfield shift of the  $\alpha$  carbon. The sulfoxide is about 25 ppm downfield from the sulfide. Block found that this anomaly for four-membered rings is quite general: sulfones are shifted unusually

far downfield with respect to sulfides and consequently no longer coincide with the homologous sulfoxide resonance.

In order to define the physical basis for the four-membered-sulfone anomaly, we have now examined a much wider range of four-membered rings. We report that the anomaly is found for functionalities other than sulfones and for nuclei other than <sup>13</sup>C, but for only the four-membered ring.

### Results

Ring size has a significant effect on <sup>13</sup>C shieldings within the homologous series of saturated hydrocarbons (CH<sub>2</sub>)<sub>n</sub> (1).<sup>4</sup> The chemical shift ( $\delta$ ) moves monotonically downfield from the three-membered ring (–2.6 ppm) to the four- (23.3 ppm), five- (26.5 ppm), six- (27.8 ppm), and seven-membered ring (29.4 ppm). The very high-field location for the three-membered ring may be attributed to bond and group anisotropies associated with the geometry of the

(1) (a) Northwestern University. (b) University of Missouri—St. Louis. (c) Present address: State University of New York at Albany.

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ring. Possibly a much diluted effect of this type is responsible for the slight upfield shift in the four-membered ring, in comparison with the common rings (five–seven members). The small relative shifts within the common rings arise from structural and conformational differences and have not been explained in any detail.

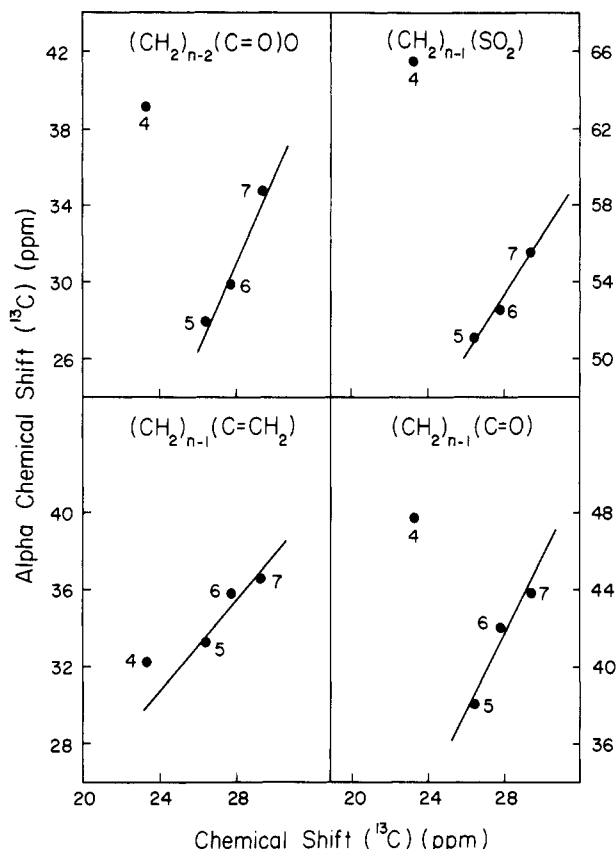
We have used this cyclic hydrocarbon series as the standard of comparison for other homologous series. The four-membered-ring anomaly would show up as a deviation from linearity for that point in a plot of chemical shifts of one series vs. those of the cyclic hydrocarbons. By this procedure, the sulfone anomaly shows up very dramatically, and it gives us a more general handle to search for the effect with other functional groups.

We have gathered data for the following homologous series: hydrocarbons with an exo methylene group,  $(\text{CH}_2)_{n-1}\text{C}=\text{CH}_2$  (2); hydrocarbons with a *gem*-dimethyl group,  $(\text{CH}_2)_{n-1}\text{C}(\text{CH}_3)_2$  (3); hydrocarbons with a 1-amino group,  $(\text{CH}_2)_{n-1}\text{CHNH}_2$  (4); hydrocarbons with a 1-fluoro substituent,  $(\text{CH}_2)_{n-1}\text{CHF}$  (5); ethers,  $(\text{CH}_2)_{n-1}\text{O}$  (6); amines,  $(\text{CH}_2)_{n-1}\text{NH}$  (7); ketones,  $(\text{CH}_2)_{n-1}\text{C}=\text{O}$  (8); lactones,  $(\text{CH}_2)_{n-2}(\text{C}=\text{O})\text{O}$  (9); lactams  $(\text{CH}_2)_{n-2}(\text{C}=\text{O})\text{NH}$  (10); sulfides,  $(\text{CH}_2)_{n-1}\text{S}$  (11); sulfoxides,  $(\text{CH}_2)_{n-1}\text{SO}$  (12); sulfones,  $(\text{CH}_2)_{n-1}\text{SO}_2$  (13); thioketones,  $(\text{CH}_2)_{n-1}\text{C}=\text{S}$  (14); phosphines,  $(\text{CH}_2)_{n-1}\text{PCH}_3$  (15); and phosphoramidates,  $(\text{CH}_2)_{n-1}\text{N}(\text{PO})(\text{OCH}_3)_2$  (16). Data for 1–5 and 11–16 were taken from the literature.<sup>3–18</sup> Data for 6 and 8–10 were recorded in our laboratories. For the amines 7, all data except that for the three-membered ring<sup>19</sup> were recorded in our laboratories. The <sup>17</sup>O data for the sulfoxides and sulfones have been communicated by us previously.<sup>3</sup> The data for all systems have been recorded elsewhere<sup>20</sup> and will be presented here only in part (see the Experimental Section and later figures).

## Discussion

### Carbon-13 Shifts of $\alpha$ Endocyclic Atoms ( $-\text{X}-\text{CH}_2-$ ).

Three-membered rings invariably have resonances that are shifted well upfield from those of six-membered rings. For example, the difference between the resonance positions in three- and six-membered rings ( $\alpha$  carbon in each case) is 30.4 ppm for the hydrocarbons, 19.4 ppm for the dimethyl hydrocarbons, 31.9 ppm for the ethers, 11.0 ppm for the sulfides, 18.8 ppm for the sulfoxides, and 19.4 ppm



**Figure 1.** <sup>13</sup>C chemical shift of cyclic hydrocarbons vs. that of the carbon  $\alpha$  to carbonyl, sulfonyl, or exo methylene in rings, as a function of ring size.

for the sulfones. Because these effects have been thoroughly examined in terms of bond and group anisotropies, we will not include the three-membered rings in our further discussion.

The series of cyclic hydrocarbons 1 serves as a useful reference for examination of the remaining series. Certain factors such as angle strain should remain relatively constant for a given ring size. The <sup>13</sup>C shifts of the hydrocarbons will take these effects into account, so that a plot of the <sup>13</sup>C shifts for one of the other series vs. the shifts for the hydrocarbons will emphasize new properties. Any property that is present throughout a series such as heightened angle strain in the ketones will affect all members of the series monotonically or proportionately and will not give rise to deviations from linearity of the plot. Any effect, however, that is specific for a single ring size will show up as a deviation from linearity defined by the unaffected ring systems. Our plots were constructed for the four–seven-membered rings.

Figure 1 displays several of these plots, all for the carbon atom that is  $\alpha$  to the functionality or substituted atom.<sup>20</sup> The point for the four-membered ring deviates from the line established by the five–seven-membered rings in every case, the four-membered ring being more deshielded than expected. The deviation is quite small for the exo methylene hydrocarbons but is large for the ketones, lactones, and sulfones. This approach gives a more general method for detecting the four-membered-ring anomaly than that used previously in the single case of the sulfones.<sup>3</sup>

A simple but crude method to obtain a quantitative measure of the four-membered ring effect is to subtract the chemical shift for a functionalized or substituted four-membered ring from that of the six-membered ring in the same series (to allow for the effect of the functional group or substituent) and then to subtract this difference

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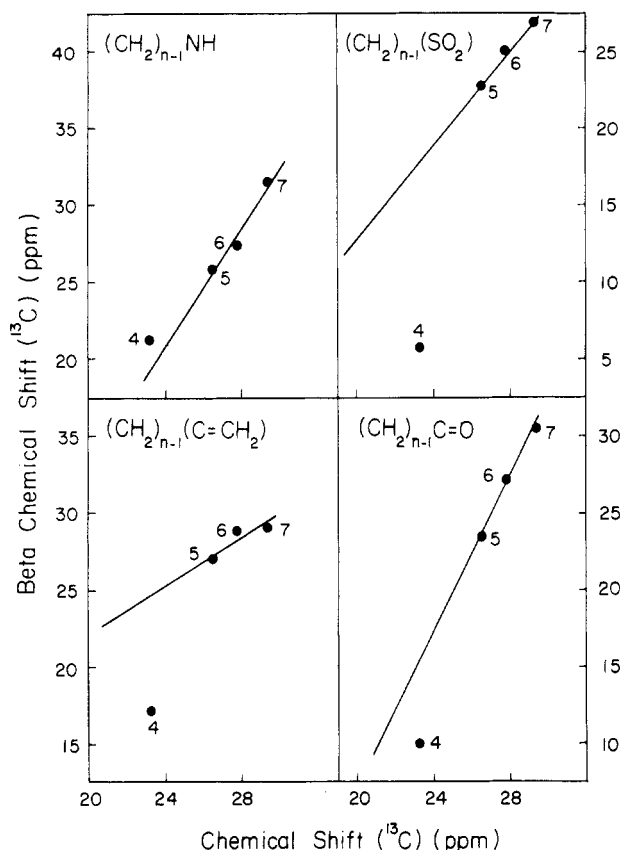
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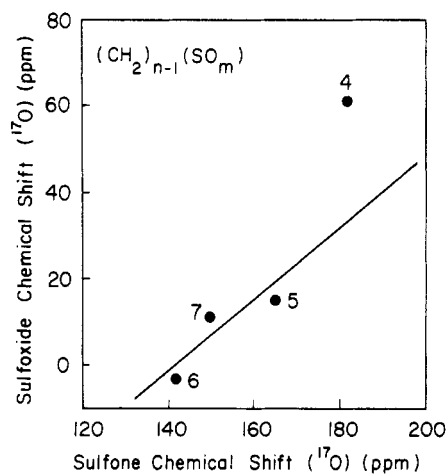
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**Figure 2.**  $^{13}\text{C}$  chemical shift of cyclic hydrocarbons vs. that of the carbon  $\beta$  to amino, sulfonyl, exo methylene, or carbonyl in rings, as a function of ring size.

from the analogous difference in the hydrocarbon series (to allow for normal effects associated with a four-membered ring). A positive number would indicate excess deshielding. This double subtraction yields a very small number (0–2 ppm) for the exo methylene hydrocarbons 2, the dimethyl hydrocarbons 3, and the sulfides 11. Small, negative numbers are obtained for the carbons  $\alpha$  to O or NH in the lactone (9) and lactam (10) series. Intermediate numbers, from 4 to 9 ppm, are obtained for the ethers 6, amines 7, sulfoxides 12, and phosphoramidates 16. Finally, large numbers (10–18 ppm) are obtained for the ketones 8 (10.3 ppm), lactones 9 (carbon  $\alpha$  to the carbonyl, 13.0 ppm), lactams 10 (carbon  $\alpha$  to the carbonyl, 11.2 ppm), and sulfones 13 (17.5 ppm). Thus, the four-membered-ring anomaly is largest by far for the sulfone but still respectable for all the carbonyl systems. These calculations are all confirmed by the deviations seen in the plots analogous to those of Figure 1. No other ring size causes a significant deviation from the plots or yields an appreciable difference by the double subtraction method, with some small exceptions among the five-membered rings. The five-membered sulfoxides, for example, gives the largest such deviations, 6.6 ppm by the double subtraction method.

**Carbon-13 Shifts of  $\beta$  Endocyclic Atoms ( $-\text{X}-\text{CH}_2-\text{CH}_2-$ ).** Figure 2 shows plots for the  $\beta$  carbons that are analogous, except in one case, to those in Figure 1. There are few large deviations. It is possible to make a case for a small four-membered-ring anomaly for the sulfones, in which the  $\beta$  carbon is more shielded than expected (the opposite effect to that for the  $\alpha$  carbon). Any  $\beta$  anomaly, however, is much smaller than the  $\alpha$  anomaly. Thus, with the possible exception of the sulfones, the  $\beta$  chemical shifts of all these rings respond to the same



**Figure 3.**  $^{17}\text{O}$  chemical shift of cyclic sulfones vs. cyclic sulfoxides, as a function of ring size.

factors that are present in the cyclic hydrocarbons.

**Nitrogen-15 and Oxygen-17 Shifts of Endocyclic Atoms.** For nuclei other than  $^{13}\text{C}$ , there is a problem associated with the choice of an appropriate standard series. The  $^{15}\text{N}$  shifts of amines  $7^{21}$  and the  $^{17}\text{O}$  shifts of ethers  $6^{22}$  correlate reasonably well with the  $^{13}\text{C}$  shifts of analogous hydrocarbons in aliphatic cases, so that the  $^{13}\text{C}$  shifts of the cyclic hydrocarbons again might provide an appropriate standard. Most importantly, the four-membered rings show no special effect and have resonances that are upfield from those of the larger rings in all three series.

In contrast, the plots for the  $^{15}\text{N}$  shifts of the lactams and the  $^{17}\text{O}$  shifts (endocyclic oxygen) for the lactones show large downfield shifts for the four-membered rings compared with the others. A double subtraction, like that carried out for the  $^{13}\text{C}$  shifts, can also be done for these nuclei. The  $^{15}\text{N}$  ( $^{17}\text{O}$ ) lactam (lactone) shift is subtracted from the amine (ether) shift for the four- and six-membered rings, and their difference in turn is subtracted. The result for the lactam is 26 ppm, and that for the lactone is 94 ppm. Although these calculations are probably less reliable than those for  $^{13}\text{C}$ , they clearly show that there are very large four-membered-ring anomalies for the nitrogen atom in the lactam for the ring oxygen atom in the lactone. These atoms,  $\alpha$  to carbonyl groups, are structurally analogous to those for which large four-membered-ring anomalies were found for  $^{13}\text{C}$  shifts. We could further predict, for example, that anomalies also would be found for the cyclic series  $(\text{CH}_2)_{n-2}(\text{SO}_2)\text{X}$ , for which X is O (sultones) or NH (sultams).

**Chemical Shifts of Exocyclic Atoms.** When the ring atom that is functionalized is  $\text{sp}^2$  hybridized, a useful reference system might be the exo methylene series 2. Plots of the  $^{17}\text{O}$  shift of the carbonyl group in the ketone, lactone, and lactam series vs. the  $^{13}\text{C}$  shift of the exocyclic carbon in 2 are monotonic but not linear. Deviations of both the four- and the five-membered rings from the line determined by the larger rings make any interpretation difficult.

When the ring atom that is functionalized or substituted is  $\text{sp}^3$  hybridized, there is no convenient reference system. We have explored both the  $^1\text{H}$  shift of the hydrocarbons 1 and the  $^{19}\text{F}$  shift of the fluoroalkanes 5. There are no common patterns. Comparison of the  $^{17}\text{O}$  shifts of the

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Table I. Chemical Shifts (ppm) for Heterocycles (CH<sub>2</sub>)<sub>n-1</sub>X and (CH<sub>2</sub>)<sub>n-2</sub>(C=O)Y

X	Y	n	C1 <sup>a</sup>	C2 <sup>a</sup>	C3 <sup>a</sup>	C4 <sup>a</sup>	C5 <sup>a</sup>	C6 <sup>a</sup>	C7 <sup>a</sup>	N1 <sup>b</sup>	O1 <sup>c,d</sup>	O2 <sup>c,e</sup>	
O		3		40.5	40.5							-50	
		4		72.5	23.1	72.5						-13	
		5		69.1	26.2	26.2	69.1					16	
		6		68.8	27.4	24.3	27.4	68.8				7	
		7		70.2	31.6	27.5	27.5	31.6	70.2			6	
NH		4		47.2	21.2	47.2				25.3			
		5		47.4	25.8	25.8	47.4			40.7			
		6		47.5	27.3	25.3	27.3	47.5		40.9			
		7		49.5	31.6	27.3	27.3	31.6	49.5	39.4			
C=O		4	208.2	47.8	9.9	47.8					546		
		5	218.6	38.1	23.4	23.4	38.1				547		
		6	211.0	42.0	27.2	25.2	27.2	42.0			554		
		7	219.3	43.8	30.6	24.5	24.5	30.6	43.8		562		
	O		4		169.4	39.2	59.1					347	241
			5		178.2	28.0	22.7	69.0				343	181
			6		171.3	29.9	19.1	22.4	69.4			369	169
		7		175.7	34.8	23.7	30.1	29.2	69.1		379	173	
NH		4		169.6	38.3	35.2				128.7	295		
		5		179.4	30.4	20.9	42.5			118.8	292		
		6		172.5	31.6	21.1	22.5	41.9		118.3	317		
		7		179.4	36.8	23.4	30.7	29.9	42.5	121.7	326		

<sup>a</sup> Referenced to Me<sub>4</sub>Si. <sup>b</sup> Referenced to NH<sub>3</sub>. <sup>c</sup> Referenced to H<sub>2</sub>O. <sup>d</sup> Carbonyl oxygen. <sup>e</sup> Ester or ether oxygen.

sulfoxides with those of the sulfones does yield a plot (Figure 3) with a deviant point from the four-membered ring. From this plot alone, however, one cannot specify whether it is the sulfoxide or the sulfone that is anomalous.

**Conclusions.** Anomalously low-field shifts have been found for <sup>13</sup>C, <sup>15</sup>N, and <sup>17</sup>O shifts of the atoms next to sulfonyl and carbonyl groups in four-membered rings. Somewhat smaller effects have been found for the <sup>13</sup>C shifts of carbons next to ether, amino, sulfinyl, and phosphoramido groups. Normal shifts are observed for <sup>13</sup>C shifts in various hydrocarbons and thioethers. Rings of five or more members do not exhibit the effect. The ring atoms that are β to these functionalities show little or no anomaly.

A simple polar effect, which would have to be enhanced for some reason in the four-membered rings, does not explain these results. There is no apparent relationship between the magnitude of the four-membered-ring anomaly and the group electronegativity of the functionality.

A more likely explanation would come from structural, conformational, or orbital properties that are unique to four-membered rings. The anomaly is observed only when the functionality is sp<sup>2</sup> (carbonyl) or sp<sup>3</sup>d<sup>2</sup> (sulfonyl). Examination of a large range of four-membered sulfones showed that the anomaly is independent of exocyclic substituents, replacement of endocyclic atoms by heteroatoms, and incorporation into polycyclic structures.<sup>3</sup> The higher angle strain of the cyclobutanone and thietane 1,1-dioxide rings may contribute in some way to the anomaly.

Preliminary ab initio calculations on the <sup>13</sup>C shift of the carbon α to the carbonyl group in the ketone series closely reproduce the observed data for all rings of three, four, and

five members.<sup>23</sup> This result suggests that the four-membered-ring anomaly is an inherent property of the carbon orbitals that contribute to the paramagnetic shielding, σ<sup>p</sup>. The calculated four-membered-ring anomaly did not appear to be sensitive to the puckering dihedral angle up to an angle of 20°.

### Experimental Section

NMR spectra were recorded on Varian CFT-20 (<sup>13</sup>C) and JEOL FX-90Q (<sup>13</sup>C, <sup>15</sup>N, and <sup>17</sup>O) spectrometers. Chemical shifts were referenced to Me<sub>4</sub>S for <sup>13</sup>C, 2 M aqueous HNO<sub>3</sub> (labeled 30 atom %) for <sup>15</sup>N (converted to NH<sub>3</sub> at 0 ppm by subtraction of 375.5 ppm), and H<sub>2</sub>O for <sup>17</sup>O (for D<sub>2</sub>O solutions, 3 ppm was subtracted from the observed values; for acetone solutions, 573 ppm was added to the observed values). Positive shifts are downfield in all cases. Compounds that were not commercially available were prepared locally. These included thiane 1-oxide,<sup>24</sup> thiane 1,1-dioxide,<sup>24</sup> and β-propiolactam.<sup>25</sup> The sulfoxides and sulfones for the most part were supplied from earlier work.<sup>26</sup> Chemical shift data not previously reported are given in Table I.

**Registry No.** (CH<sub>2</sub>)<sub>2</sub>O, 75-21-8; (CH<sub>2</sub>)<sub>3</sub>O, 503-30-0; (CH<sub>2</sub>)<sub>4</sub>O, 109-99-9; (CH<sub>2</sub>)<sub>5</sub>O, 142-68-7; (CH<sub>2</sub>)<sub>6</sub>O, 592-90-5; (CH<sub>2</sub>)<sub>3</sub>NH, 503-29-7; (CH<sub>2</sub>)<sub>4</sub>NH, 123-75-1; (CH<sub>2</sub>)<sub>5</sub>NH, 110-89-4; (CH<sub>2</sub>)<sub>6</sub>NH, 111-49-9; (CH<sub>2</sub>)<sub>3</sub>C=O, 1191-95-3; (CH<sub>2</sub>)<sub>4</sub>C=O, 120-92-3; (CH<sub>2</sub>)<sub>5</sub>C=O, 108-94-1; (CH<sub>2</sub>)<sub>6</sub>C=O, 502-42-1; (CH<sub>2</sub>)<sub>2</sub>(C=O)O, 87-57-8; (CH<sub>2</sub>)<sub>3</sub>(C=O)O, 22929-52-8; (CH<sub>2</sub>)<sub>4</sub>(C=O)O, 542-28-9; (CH<sub>2</sub>)<sub>5</sub>(C=O)O, 562-44-3; (CH<sub>2</sub>)<sub>2</sub>(C=O)NH, 930-21-2; (CH<sub>2</sub>)<sub>3</sub>(C=O)NH, 616-45-5; (CH<sub>2</sub>)<sub>4</sub>(C=O)NH, 675-20-7; (CH<sub>2</sub>)<sub>5</sub>(C=O)NH, 105-60-2.

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