fraction of bicyclo endoperoxides (R_f 0.25–0.37), and 328 mg of more polar components.[9] Two subfractions of the R_f 0.25–0.37 fraction were obtained as pure compounds and were shown by further analysis to be isomers of structure **6**, with R_f's of 0.37 (**6a**) and 0.34 (**6b**). Each showed a single peak on analytical high-pressure liquid chromatography (LC) μ-Porasil, 75:25 (v/v) hexane–ethyl acetate) with capacity factors of 1.1 and 1.4 for **6a** and **6b**, respectively.

^1H and ^{13}C NMR spectroscopic analyses[10,11] confirm the structure assignments shown in Scheme I. Thus, proton decoupling experiments established that the hydroperoxy group in each isomer is attached to C-9. The δ 35–50 region of the ^{13}C spectra shows a unique set of three peaks for each isomer (48.7, 48.1, and 39.3 for **6a**; 46.0, 45.4, and 44.1 for **6b**). These peaks are due to carbons 12, 14, and 16 and reflect differences in ring stereochemistry. Although each isomer is spectroscopically unique, it is difficult to assign the specific stereochemistry of either on the basis of NMR spectral analysis, because no model compounds for comparison exist. Stereochemical assignments, however, could be made with the corresponding triols for which there are several appropriate models available.

Reduction of **6a** and **6b** with stannous chloride[12] gave triols which were shown to have structures **7a** and **7b**, respectively. Mass spectral analysis[13] of their trimethylsilyl derivatives revealed the expected fragmentation patterns[3b,14] and gave the correct exact masses for selected large fragments of the assigned structures. ^1H and ^{13}C NMR spectral analysis of **7a** and **7b** and their acetate derivatives allowed the assignment of ring stereochemistry. In the ^{13}C spectra the exocyclic methylene carbons (C-17) differ significantly in chemical shift (22.1 for **7a** vs. 19.3 for **7b**); the C-11 carbons show similar differences (128.7 for **7a** vs. 128.0 for **7b**). By analogy with the results of Mizsak and Slomp[16] in a study of isomeric prostaglandins, we conclude that in each case the higher field absorbance indicates a cis relationship and the lower field absorbance a trans relationship between that carbon and the ring hydroxyls. De Clerq and Samson[17] have also established an easy method of ring configuration assignment based on high-field ^1H NMR studies of acetate derivatives. For each of the four possible ring isomers, there is a unique combination of $J_{12,16}$ and the chemical shifts of H-14β and H-13 (H-15). We found ^1H NMR data for the triacetate of **7a** to be 4.89 ppm (H-13 and H-15), 2.70 ppm (H-14β), $J_{12,16}$ = 6.8 Hz and for the triacetate of **7b** to be 5.02 ppm (H-13), 2.62 ppm (H-14β), $J_{12,16}$ = 6.6 Hz. These data show that **7a** has both alkyl substituents on the ring trans to the hydroxyls and **7b** has the alkyl substituents and hydroxyls cis. On the basis of these assignments the structures of the bicyclo endoperoxides must therefore be both substituents exo for **6a** and both substituents endo for **6b**.

The bicyclo endoperoxide fraction (R_f 0.25–0.37) contains additional components that appear to be other isomers of **6**, but the ring stereochemistries of **6a** and **6b** account for a large percentage of the total fraction. Our data indicate that **6a** and **6b** actually are each single diastereoisomers whose C-9 epimers are chromatographically separated from them. They appear on high-pressure LC to comprise about half of the total bicyclo endoperoxide fraction; however, the combination of **6a** and **6b** and their C-9 epimers constitute >75% of the total.[18]

The selectivities shown in this reaction are quite remarkable: the dioxolane ring formation (**2** → **3**) gives exclusively cis substitution; the oxygenation of intermediate **5** occurs predominantly at C-9; perhaps most noteworthy, the ring closure (**3** → **5**) primarily forms bicyclo endoperoxides with cis substituents. This last feature departs radically from enzyme-mediated endoperoxide formation in that the natural prostaglandin stereochemistry is disfavored.

Acknowledgment. We thank Drs. A. J. De Stefano and T. W. Keough for mass spectral analyses and Dr. F. S. Ezra, Dr. J. P. Yesinowski, and Ms. C. S. Yeakle for the 300-MHz ^1H NMR data.

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(9) In a number of runs we have isolated ~20% of a monocyclic peroxide fraction, 15–20% of a bicyclo endoperoxide fraction and 40–50% of a more polar residue. However, TLC suggests that the two peroxide fractions constitute the major part of the reaction mixture and shows little of the more polar materials. These peroxides are not very stable to the chromatographic conditions and, we believe, are converted to more polar materials during chromatography.

(10) All NMR spectra were taken in dilute solutions of deuteriochloroform and are referenced to tetramethylsilane internal standard. Proton assignments were substantiated by homonuclear decoupling experiments.

(11) Selected NMR absorption bands. **6a**: ^1H NMR (300 MHz) δ 7.94 (s br, 1, OOH), 5.52 (dd, 1, J = 15.5, 7.2 Hz, H-10), 5.44 (dd, 1, J = 15.5, 9.8 Hz, H-11), 4.53 (s br, 1, H-15), 4.42 (s br, 1, H-13), 4.26 (m, 1, H-9), 2.92 (m, 1, H-12), 2.16 (m, 2, contains H-16), 0.95 (t, 3, J = 7.2 Hz, H-18); ^{13}C (22.5 MHz) δ 174.3 (C-1), 132.5, 131.1 (C-10, C-11), 86.3 (C-9), 81.7, 80.5 (C-13, C-15), 51.4 (CO_2CH_3), 48.7, 48.1, 39.3 (C-12, C-14, C-16), 21.9 (C-17), 13.2 (C-18). **6b**: ^1H NMR (300 MHz) δ 7.89 (s br, 1, OOH), 6.02 (dd, 1, J = 15.5, 9.9 Hz, H-11), 5.47 (dd, 1, J = 15.5, 7.5 Hz, H-10), 4.64 (s br, 1, H-15), 4.47 (s br, 1, H-13), 4.33 (m, 1, H-9), 2.66 (m, 1, H-12) 1.90 (m, 1, H-16), 0.88 (t, 3, J = 7.3 Hz, H-18); ^{13}C (22.5 MHz) δ 174.3 (C-1), 132.8, 132.2 (C-10, C-11), 86.6 (C-9), 83.0, 80.1 (C-13, C-15), 51.4 (CO_2CH_3), 46.0, 45.4, 44.1 (C-12, C-14, C-16), 18.8 (C-17), 13.0 (C-18).

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(13) Mass spectra were obtained on an AEI/Kratos MS-30 dual beam, double focusing mass spectrometer. Principal fragments were (mass, % of base peak) **7a**: 543, 0.3; 468, 10; 401, 7; 378, 7.8; 352, 10; 323, 3; 311, 40; 285, 24; 259, 6; 217, 13; 195, 45; 73, 100. **7b**: 558, 0.2; 543, 1; 468, 48; 401, 28; 378, 12; 352, 31; 323, 22; 311, 48; 285, 31; 259, 15; 217, 16; 195, 32; 73, 100. Parent ions were too weak for their exact masses to be determined. However, the exact masses of fragments derived from the well-established loss of one and two trimethylsilanol units were obtained. For the fragments $C_{25}H_{48}O_4Si_2$ ($M - (CH_3)_3SiOH$) and $C_{22}H_{38}O_3Si$ ($M - 2(CH_3)_3SiOH$): calcd, 468.3091, 378.2590; found, **7a**, 468.3186, 378.2643; **7b**, 468.3140, 378.2630.

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(15) Selected NMR absorption bands. **7a**: ^1H NMR (300 MHz) δ 5.59 (dd, 1, J = 15.4, 6.3 Hz, H-10), 5.42 (dd, 1, J = 15.4, 9.0 Hz, H-11), 4.15 (m, 3, H-9, -13, -15), 2.79 (m, 1, H-12), 2.41 (m, 1, H-14β), 2.03 (m, 1, H-16), 1.66 (m, 1, H-14α); ^{13}C (22.5 MHz) 174.3 (C-1), 135.8 (C-10), 128.7 (C-11), 76.5, 76.4, 72.7 (C-9, C-13, C-15), 51.4 (CO_2CH_3), 53.6, 52.5, 42.8 (C-12, C-14, C-16), 22.1 (C-17), 12.8 (C-18). **7b**: ^1H NMR (300 MHz) δ 5.85 (dd, 1, J = 15.5, 10.4 Hz, H-11), 5.59 (dd, 1, J = 15.5, 6.2 Hz, H-10), 4.19 (m, 3, H-9, -13, -15), 2.76 (ddd, 1, J = 10.4, 8.8, 6.3 Hz, H-12), 2.17 (ddd, 1, J = 14.5, 6.7, 5.6 Hz, H-14β), 1.85 (ddd, 1, J = 14.5, 4.6, 2.0 Hz, H-14α), 1.82 (m, 1, $J_{12,16}$ = 8.8 Hz, H-16); ^{13}C (22.5 MHz) δ 174.3 (C-1), 137.7 (C-10), 128.0 (C-11), 76.3, 73.8, 72.5 (C-9, C-13, C-15), 51.5 (CO_2CH_3), 50.1, 49.0, 43.0 (C-12, C-14, C-16), 19.3 (C-17), 12.9 (C-18).

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(18) A high-pressure LC of the R_f 0.25–0.37 fraction shows four peaks containing endoperoxides; the **6a** and **6b** peaks (capacity factors, 1.1 and 1.4) are 17% and 38% of the total area, respectively, with the third peak (capacity factor, 1.7) and fourth peak (capacity factor, 2.4) accounting for 29% and 16%. A ^{13}C NMR spectrum of the 2.4 capacity factor component was essentially identical with that of **6b**, suggesting it is the C-9 epimer; a ^{13}C NMR spectrum of the 1.7 capacity factor component shows multiple peaks in the δ 35–50 region, with the major ones being identical with those of **6a**. Reduction of this 1.7 capacity factor material gave a mixture of triols; the ^1H NMR spectrum of the acetate derivative of one of these indicated it has the same ring sterochemistry as **7a** and thus must be its C-9 epimer. Further evidence for the great preponderance of two ring configurations lies in the ^{13}C NMR spectrum of the crude reaction mixture. The δ 35–50 region shows as the only significant peaks those of **6a** and **6b** plus one each for the two monocyclic peroxides **4**.

Influence of ^{14}N on ^{13}C NMR Spectra of Solids

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Resonances from carbons bonded to nitrogen are often broadened and split into asymmetric doublets in ^{13}C NMR spectra of polycrystalline organic molecules obtained with proton decoupling and magic-angle sample spinning.[1-6] The influence of

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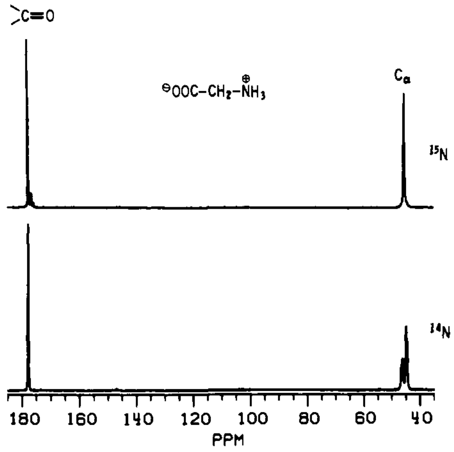

Figure 1. ^{13}C NMR spectra of polycrystalline glycine. The ^{14}N natural abundance sample was from Sigma Biochemicals and the ^{15}N-labeled sample from Kor Isotopes. The spectra were obtained on a home-built double resonance spectrometer with a ^{13}C resonance frequency of 37.84 MHz by using cross polarization with 1-ms mixes, 200-ms acquisition time with a proton decoupling field of 4.0 mT, and a recycle delay of 4.0 s. About 300 mg of material was packed in Andrew type rotors and rotated at 4.0 kHz at the magic angle. The data points from the Delrin rotor material resonance near 90 ppm are zeroed.

nitrogen on the appearance of ^{13}C NMR spectra of solids is so strong that it dictates experimental design for the study of many molecules, especially those important to biochemistry such as nucleotides or amino acids and their polymers. In addition to predicting the resonance line shapes of carbons bonded to nitrogen, the results presented here show that ^{13}C NMR spectra can be used to measure ^{14}N quadrupole coupling constants or obtain structural information.

Spectral perturbations caused by dipolar coupling to a nucleus with a quadrupole moment have been described experimentally and theoretically by others for stationary powders[7] and single crystals.[8,9] Magic-angle sample spinning has the dual role of averaging chemical shielding powder patterns to single lines with isotropic chemical shifts and averaging out dipolar interactions. However, magic-angle sample spinning is unable to suppress the ^{13}C–^{14}N dipolar interaction, because the ^{14}N quadrupole moment tilts the axis of quantization of the ^{14}N spins away from the direction of the applied magnetic field, modifying the angular dependence necessary for rotational averaging of the dipolar interaction.

The influence of the quadrupole moment of nitrogen on the α-carbon resonance of glycine is shown in Figure 1. ^{15}N-Labeled glycine has a ^{13}C spectrum with sharp single lines for both carbons, while the natural isotope [^{14}N]glycine has an asymmetrically split α-carbon resonance. Even though the gyromagnetic ratio, γ, of ^{15}N is greater than that of ^{14}N, ^{15}N has no quadrupole moment and the ^{13}C–^{15}N dipolar couplings are averaged out by the magic-angle sample spinning while the ^{13}C–^{14}N dipolar couplings are not. The deleterious effect of ^{14}N on ^{13}C spectral resolution is apparent when the 7-Hz line width of the carbonyl resonance is compared to the 90-Hz breadth of the C_α resonance for ^{14}N glycine in Figure 1.

The total effective Hamiltonian in the laboratory frame that describes the ^{13}C spins in the presence of ^{14}N spins is

$$H^{C}_{total} = H^{C}_{Z} + H^{C-N}_{D} \qquad (1)$$

H^{C}_{Z} is the ^{13}C Zeeman interaction. H^{C-N}_{D} is the heteronuclear dipolar coupling which is dependent on $\gamma_C\gamma_N\hbar/r_{CN}^3$, where r_{CN} is the ^{13}C–^{14}N bond length, and the Euler angles α^D and β^D, which orient the internuclear vector in the laboratory axis system (the Z axis is along the applied magnetic field, Z_{lab}, and the X axis is coplanar with the applied magnetic field and the Z axis of the ^{14}N electric field gradient, Z_{efg}).[9] Basis functions for calculating the dipolar matrix H^{C-N}_{D} were taken as product functions of the ^{13}C Zeeman states with ^{14}N wave functions obtained by diagonalizing the total ^{14}N spin Hamiltonian

$$H^{N}_{total} = H^{N}_{Z} + H^{N}_{Q} \qquad (2)$$

where H^{N}_{Z} is the ^{14}N Zeeman interaction and H^{N}_{Q} is the quadrupole coupling.[5] The quadrupole coupling is dependent on the Euler angles α^Q and β^Q which orient the applied magnetic field in the principal axis system of the electric field gradient with principal value $e^2Qq/[2I(2I-1)h]$ and asymmetry parameter η.

These Hamiltonians were written in terms of irreducible spherical tensor operators,[10] the spatial components of which were then transformed into the principal axis system of the various interactions. To account for magic-angle spinning the spatial components were further transformed to the Euler angles $(0, \theta_M, \phi)$, where θ_M is the magic angle (54.7°) and ϕ is the azimuthal angle describing rotation about the rotor axis. The shifts in the ^{13}C energy levels were then calculated with zero-order average Hamiltonian theory (first-order perturbation theory), assuming the dipolar coupling was a small perturbation. The admixture of Zeeman states induced by the quadrupole coupling leads to expectation values of the ^{14}N raising and lowering operators which are stationary in a coordinate system rotating at the ^{13}C Larmor frequency; therefore these terms contribute to diagonal elements of the dipolar matrix. The distribution in angles β^D and γ^D in a polycrystalline sample results in a powder average of dipolar-induced shifts for each ^{13}C resonance. ^{14}N quadrupole coupling constants are typically 1–3 MHz,[11] which is several orders of magnitude larger than achievable rates of sample rotation. This invalidates using zero-order average Hamiltonian theory to average H^{D}_{CN} over the rotation period.[12] Because first-order and higher order terms of the average Hamiltonian become intractably difficult to evaluate, the average over rotation was obtained by diagonalizing the ^{14}N matrix and calculating the induced dipolar shifts for sufficient points to allow numerical integration of the dipolar matrix.

The dipolar shifts of the α-carbon resonance of glycine were calculated by using a ^{13}C–^{14}N bond length, r_{CN}, of 1.49 Å[13] and a ^{14}N quadrupole coupling constant, e^2Qq/h, of 1.18 MHz with asymmetry parameter, η, of 0.54.[14-16] The angle between the internuclear vector and the Z axis of the electric field gradient is 5°.[16]

The calculated α-carbon spectrum in Figure 2c is the sum of three first-order quadrupole powder patterns[12] which have been reflected into the ^{13}C spectrum via the dipolar coupling. The separation into two upfield and one downfield powder patterns arises from the contribution to the dipolar coupling from the expectation values of the ^{14}N raising and lowering operators, the spatial dependence of which is not averaged to zero as is the

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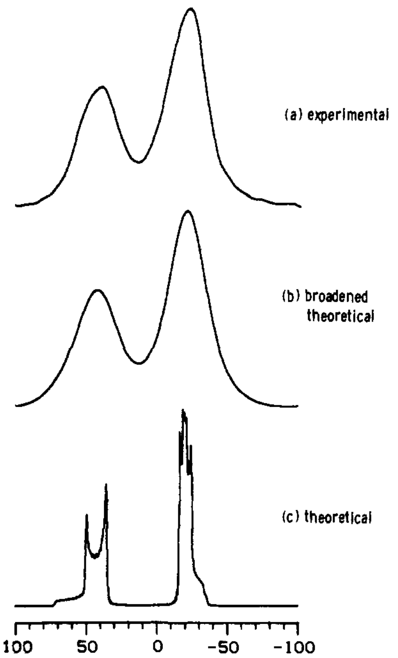

Figure 2. α-Carbon resonance of glycine. (a) Expansion of experimental spectrum where the zero frequency is the chemical shift of ^{15}N labeled glycine; (b) theoretical spectrum c with approximately 20 Hz of line broadening added; (c) theoretical spectrum calculated for a C–N bond length of 1.49 Å in a magnetic field of 3.5338 T with e^2Qq/h = 1.18 MHz and η = 0.54. The dipolar shifts were calculated to ±0.1 Hz for 1000 data points.

expectation value of the Z spin component. The upfield two powder patterns are nearly superimposed and correspond to the shifts caused by the highest and lowest energy states of ^{14}N (n = 1 and n = 3). The shift due to the n = 2 spin state of ^{14}N is twice as large and occurs in the opposite direction; thus the downfield pattern is twice as broad with the shift for any crystal orientation twice the magnitude of the upfield patterns. There is a 2:1 ratio of areas between the two regions.

When the theoretical α-carbon spectrum is broadened by convolution with a function corresponding to about 20 Hz of line broadening at half-height, the spectrum in Figure 2b results, which closely matches the appearance of the experimental spectrum in Figure 2a. In particular, the peak to peak separation is 61 Hz in both the theoretical and experimental spectra. The observed splitting would increase with an increase in the ^{14}N quadrupole coupling constant, a decrease in the ^{13}C–^{14}N bond length, or a decrease in the strength of the applied magnetic field.

Several types of molecular information can be derived from ^{13}C NMR spectra where the resonance line shapes are determined by ^{14}N properties. For molecules where the C–N bond length is known, the magnitude of the split of the peaks can be used to determine the quadrupole coupling constant. Conversely, for those molecules where a quadrupole coupling constant has been measured independently, structural parameters can be obtained. An accurate measurement of the C–N bond length is possible. The ^{13}C spectrum depends on the relative orientation of the quadrupolar and dipolar principal axis systems which is fixed in the molecular frame; therefore geometrical information is potentially available. This may prove useful in determining peptide group conformations of polycrystalline proteins, since splits of both carbonyl and α-carbon resonances are induced by the ^{14}N of the peptide bonds.[5,6]

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Unusual Photoisomerization of an "Encased" α-Diketone

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Unstrained aliphatic and alicyclic α-diketones possessing γ-hydrogens characteristically undergo photoinduced 1,5-hydrogen transfer to yield exclusively 2-hydroxycyclobutanones.[1-3] The normal absence of competing δ-hydrogen abstraction suggests an overwhelming kinetic preference for passage through a strain-free pseudo-six-membered ring which incorporates an sp^2-hybridized carbon. In this communication, we wish to describe the unprecedented photochemical behavior of **4**, an α-diketone which cannot undergo 1,5-hydrogen transfer. Our expectation was that **4**, for reasons of exceptionally favorable spatial proximity, would undergo twofold δ-hydrogen abstraction and deliver **5**. The subsequent cleavage of this *gem*-diol with lead tetraacetate was to serve as the basis of an expedient route to a suitably functionalized trisecododecahedrane (**7**). Actually, there can be found numerous examples of monocarbonyl compounds which yield cyclopentanols by 1,6-hydrogen transfer upon irradiation.[4] Such departures from normal type II behavior are particularly common when γ C–H bonds are lacking and the δ C–H bonds are inductively activated.[5-7] Although the latter of these conditions is not met in **4**, steric congestion was expected to facilitate δ-hydrogen abstraction.[8]

The topologically attractive diketone was conveniently prepared in five steps from the previously described dilactone **1**.[9] When heated with trimethyloxonium fluoroborate in 1,1-dichloroethane, **1** experienced cleavage of both lactone rings to give a mixture of diene diesters, the catalytic hydrogenation of which over Pd–C produced **2** (70% overall).[10] Reduction of **2** with sodium in liquid ammonia resulted in fission of the central bond and generation of a dianion whose methylation can only proceed from the exo surface. This transformation afforded the axially symmetric **3**

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(10) This route is more efficient than that previously described by us.

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