Nuclear magnetic resonance study of cyclopentenone and some of its derivatives

Charles Edward Lyons
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NUCLEAR MAGNETIC RESONANCE STUDY OF CYCLOPENTENONE
AND SOME OF ITS DERIVATIVES

by

Charles Edward Lyons

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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Dean of Graduate College

Iowa State University
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1961
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INTRODUCTION

During the past several years progress has been made in exploring the chemistry of cyclopentenone and some of its derivatives. This work has led to the preparation of several new compounds and simpler synthetic routes to others.

The advent of nuclear magnetic resonance spectrometry and the recent commercial availability of n.m.r. spectrometers presented the opportunity to examine these interesting compounds with a powerful new research tool.

Thus this study was undertaken with the object of obtaining the NMR spectra of many of the more recently synthesized cyclopentenone derivatives. No spectra of these compounds have previously been reported in the literature.

The object of this study was not only to add to the growing body of NMR spectra of organic compounds, but also to confirm previous structure assignments and to observe interesting aspects of NMR spectroscopy as evidenced in the cyclopentenones.
HISTORICAL

Theory of Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) was first observed in bulk matter in 1945.\(^1\), \(^2\) The first spectra with separate lines for chemically different nuclei in the same molecule were obtained for alcohols by Arnold and co-workers\(^3\) in 1951. In the succeeding decade NMR techniques have rapidly advanced and wide applications to organic chemistry have been made.

Many treatments of NMR theory exist in the literature,\(^4\), \(^5\) consequently only a brief review of the theory will be undertaken here.

The nuclei of certain isotopes behave as if they were charged spinning bodies. This circulation of charge produces a magnetic moment along the axis of rotation. Certain of these isotopes are of particular interest in organic chemistry, e.g. \(^1\)H, \(^13\)C, \(^15\)N, \(^19\)F and \(^31\)P. They are considered to have nuclear spin \(I\) of \(\frac{1}{2}\). This means that the magnitude of their magnetic moments in any given direction has only two equal, but

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\(^4\)For leading references to the early literature see J. E. Wertz, Chem. Revs., 55, 829 (1955).

opposite, observable values that correspond to spin quantum numbers equal to $+\frac{1}{2}$ and $-\frac{1}{2}$.

If an external magnetic field is applied to a group of these nuclei, these nuclear magnets will experience torques and will tend to line up with the field ($I = -\frac{1}{2}$) or against the field ($I = +\frac{1}{2}$). The more favorable energy state is the one corresponding to alignment with the field. The difference in energy between the states, $\Delta E$, is proportional to the strength of the applied field $H$ at the nucleus. At ordinary temperatures within the practically attainable range of values for $H$, the equilibrium concentrations of nuclei in the two possible states are always very nearly equal. This is because the energy differences between the states are quite small and because alignment of the nuclei with the field is opposed by thermal agitation in accord with the Boltzmann distribution law. It has been calculated\(^6\) that at $300^\circ$K in a field of 9,400 gauss that the ratio is $1.0000066/1$ in favor of the spin state $I = -\frac{1}{2}$.

When a nucleus with a magnetic moment is acted upon by a magnetic field its magnetic vector behaves as if it were undergoing precession around the field axis at an angular velocity that is proportional to the magnetic field at the nucleus and is exactly equal to the frequency of electromagnetic radiation which is necessary to induce a transition from one nuclear spin state to an adjacent level.

To summarize, under appropriate conditions these nuclei can absorb

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energy from a magnetic field, in a direction at right angles to the main field, oscillating with a frequency in the radio-frequency region to cause transitions between adjacent energy levels. Such absorption gives rise to what is termed the nuclear magnetic resonance spectrum.

A nucleus in an upper spin state returns to a lower state by means of radiationless transitions of energy to a neighboring nucleus or to the entire molecular system. These energy dissipation processes are termed relaxation processes.

The local magnetic field near a particular nucleus is to a small degree dependent on its molecular environment. This is because the extranuclear electrons magnetically screen the nucleus so that the magnetic field felt by the nucleus is not quite the same as the applied field. The observed resonance frequency of a given nucleus is thus a very sensitive function of this molecular environment.

Experimental Method

An NMR spectrometer consists essentially of four parts: (1) a magnet capable of producing a very strong, highly homogeneous field, (2) a means of continuously varying the magnetic field over a very small range, (3) a radio-frequency oscillator, and (4) a radio-frequency receiver.

A large magnetic field is directed along the z-axis, and the alternating magnetic field produced by the oscillator is directed along the x-axis. The receiver coil is oriented so as to respond to an alternating magnetic field along the y-axis. Thus the oscillator must
induce a component of y-magnetization in the sample if a signal is to be picked up by the receiver.

Experimentally one changes the precession frequency of the nuclei by varying the applied magnetic field while the oscillator frequency is kept constant. At some value of the field the nuclear precession frequency becomes equal to the frequency of the rotating field vector produced by the oscillator and the energy may then be transferred from the oscillator to the nuclei, causing some of them to go to the higher energy state with $I = \frac{1}{2}$. At the same time the rotating field vector acts to tip the vectors of the individual nuclear magnets, with which it is 90° out of phase, away from the field axis and thus causes the axis of the cone of vectors to rotate around the field axis at the precession frequency. This has the result of producing a rotating component of magnetization in the x and y directions which precesses around the field axis with the same angular velocity as the individual nuclei. This alternating field in the y-direction induces a current in the receiver coil and generates an NMR signal. As the magnetic field is further increased the nuclei drop out of phase with the rotating field vector. As the y-magnetization decreases the signal dies away in the receiver.

Conventions and Terminology

**Chemical shift**

Differences in absorption line positions for nuclei of the same kind, but located in different molecular environments, are called chemical shifts. Chemical shifts have their origin in diamagnetic and
paramagnetic shielding effects produced by circulation of both bonding and non-bonding electrons in the neighborhood of the nuclei. These effects are proportional to the applied field.

The magnitude of a given chemical shift is usually taken with reference to a standard. Tetramethylsilane (TMS) is widely used as an "internal standard." A very small amount of TMS is mixed with the sample to provide an internal proton reference line.

**Spin-spin coupling**

Spin-spin coupling usually manifests itself as fine structure in main absorption peaks. It is explained by the fact that the field experienced by the protons of one group is influenced by the spins of protons in the neighboring group. In a saturated system proton spin coupling is usually negligible over more than three bonds. Coupling is independent of the applied field because it arises from fixed increments in the total magnetic field produced at a given nucleus by the magnetic moments of neighboring nuclei and is transmitted by the bonding electrons.

Spin-spin coupling is expressed in cycles per second (cps) and denoted by the coupling constant $J$. Usually subscripts are appended to $J$ to denote the protons involved in the particular coupling.

Coupling constants for proton line values are to some extent characteristic of the structure and stereochemistry of the system involved. The correlation of $J$ with structure is a subject that is presently undergoing further development.
Designation of absorption line positions

It is desirable to express line positions in a form which is independent of field strength and frequency. For this purpose Tiers has introduced the quantity $\tau$ which is defined as $\tau = \Delta \text{TMS} \times 10^6/\text{osc. freq. (cps)}$. It is positive for all but very acidic protons if the standard line position is that of TMS. The larger the value of $\tau$, the greater is the magnetic shielding of the nucleus to which it refers.

Nuclei groupings

Some groups of two or more protons produce characteristic absorption patterns. It is therefore often convenient to consider a group of nuclei as a whole. For this purpose the conventions introduced by Bernstein, et al. have been widely adopted. Groups of equivalent nuclei for which the chemical shifts and coupling constants are of the same order are symbolized by $A_n, B_m \ldots$ where the subscripts refer to the number of nuclei in the group. If the groups of nuclei $A, B, \text{etc.}$ are coupled to other nuclei, the chemical shifts of which are very different from $A, B, \text{etc.}$, the latter are symbolized by $X_n, Y_m, \text{etc.}$

---

Quantum Mechanical Procedure for the Analysis of NMR Spectra

McConnell, et al.⁹ have outlined the quantum mechanical procedure for the analysis of spin-spin multiplets of NMR spectra. The following summation of the derivation of this procedure is adapted from Conroy.¹⁰

The electron coupled spin-spin interaction is postulated¹¹ to be of the form \( E = J_{ij} \langle I_i \cdot I_j \rangle \) where \( E \) is the energy of interaction, \( J_{ij} \) is a proportionality constant, the coupling constant describing the magnitude of the interaction, and \( I_i \) and \( I_j \) are the spin angular momentum vectors of nuclei \( i \) and \( j \). The equation shows that the energy will depend on the dot product of the two vectors, and hence on the relative spatial orientation of the two nuclear magnets. \( J \) will be positive when the state with spins parallel has the high energy.

In the presence of an external field \( H_i \) at the nucleus \( i \), a field which by convention is directed along the \( z \)-axis, the energy of the system will also depend on the interaction of the nuclear magnet with \( H_i \) as follows: \( E' = \gamma_i H_i I_i(z) \) where \( 2m \gamma_i = \gamma_i \), the gyromagnetic ratio of nucleus \( i \) and \( I_i(z) \) is the \( z \) component of the vector \( I_i \). Only the \( z \) component is taken because only this component will interact with

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the steady field $H_1$ along $z$. The sign convention is such that nuclei with positive spins have high energies. If there are a number of nuclei one introduces a summation. Considering both interactions one obtains the total energy $\mathcal{H}$ to be $\sum_i \gamma_i H_i I_i(z) + \sum_{i<j} I_{ij} [I_i I_j]$ which, by postulate, is the correct "high resolution" Hamiltonian for nuclear spin interactions.

The energy will be quantized, that is, there will be various stationary states of the system to which will correspond discrete values of $E$, $I_i$ and $I_j$. In order to find the discrete values of energy and hence the characteristic nuclear magnetic resonance frequencies $\nu = \frac{\Delta E}{\hbar}$, the Schrodinger equation must be used. Its form is $\mathcal{H} \psi = E \psi$ where $\mathcal{H}$ can take the desired discrete values, $\psi$ is a variable of the system (called the wave function) which in this problem describes the condition of the various nuclear spins; and $\mathcal{H}$ is the Hamiltonian which operates on $\psi$ in order to quantize the energy function. The Hamiltonian thus contains within it the information needed to relate a set of spins to energy.

Values of $E$ are obtained by solving the wave function by the Variation Method. The secular equation obtained by this method factors into equations of lower degree in $E$ if one makes use of certain "mixing rules." Energies and wave functions are then calculated by diagonalizing the submatrices of the total Hamiltonian. In general, the $n$ proton problem will involve $2^n$ spin functions and a matrix with $2^n$ columns or

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rows. The possible transitions are limited by a selection rule and by symmetry considerations.

Interpretation of NMR Spectra

In undertaking the interpretation of an NMR spectrum one is guided by three main considerations: (1) absorption line positions, (2) spin-spin multiplicities and (3) line intensities.

If the spectrum contains only a few, well-separated absorption lines the assignment of accurate values of \( r \) and \( J \) will usually be a simple matter. In more complex cases, especially in absorption line clusters where the spin-spin splitting is large compared to the chemical shift, \( r \)-values and \( J \)'s may only be available from a mathematical analysis of the spectral lines involved.

Of particular assistance in the interpretation of certain complex groupings such as ABX and \( A_2B_2 \) is the series of papers by Pople and co-workers starting in 1957.\(^{13}\) Most of this material was included in a later book by the same authors.\(^{14}\)

The analysis of complex NMR patterns is also the subject of an informative review by Corio.\(^{15}\)

The interpretation of several complex spectra of cyclopentenones will be undertaken in the Discussion section of this thesis.

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\(^{13}\) Bernstein, Pople and Schneider, op. cit.

\(^{14}\) Pople, Schneider and Bernstein, op. cit.

Previous NMR Studies of Cyclopentenones

A survey of the literature did not reveal any reported NMR spectra of cyclopentenones.

The spectrum of the related compound, cyclopentanone, has been reported.¹⁶ Its spectrum is of interest because it consists of one intense peak, the difference in chemical shift between the two methylene groups of the $A_2B_2$ pattern being abnormally small in this case.

DISCUSSION

Introduction

The NMR spectrum of each cyclopentenone will be considered individually and interpreted. Trends among groups of related derivatives and other data obtainable from the spectra will then be noted and discussed. The interpretations outlined herein are based upon analysis of absorption line positions. It is possible, by use of computing equipment, to calculate energies and coupling parameters for NMR spectra. By this means one may, by trial and error fitting, obtain virtually exact correspondence between calculated and experimental values.

Reproductions of the NMR spectra will be found in the Spectra section of this thesis.

For the purposes of this discussion the carbon atoms of the cyclopentenone ring will be numbered as shown in Figure 1.

![Figure 1. Designation of the carbons of the cyclopentenone ring](image)

**Cyclopentenone**

In discussing the spectrum of cyclopentenone the absorption lines of the spectrum will be considered in order of increasing applied magnetic
field, i.e. from left to right as they appear on the recorder chart.

Of the six protons of cyclopenteneone, the two vinyl protons would be expected to produce separate absorption patterns in the region $\gamma = 2-4$. The four methylene protons constitute an $A_2B_2$ grouping and would be expected to produce an absorption pattern in the region $\gamma = 6-8$.

Examination of the spectrum shows the first cluster encountered to be a sextet centered at 457.8 cps or a $\gamma$-value of 2.37. This sextet, or more precisely two triplets, is in the region where vinyl protons characteristically absorb. One assigns this cluster to the more deshielded vinyl proton—the $\beta$-vinyl one. The absorption cluster appears as two triplets due to spin-spin coupling of the $\beta$-vinyl proton with the $\beta$-methylene protons and with the $\alpha$-vinyl proton. The triplet pattern arises originally from the interaction of the $\beta$-vinyl proton with the three spin arrangements of protons contained in the methylene group. The triplet thus produced is further split into two triplets by coupling of the $\beta$-vinyl and $\alpha$-vinyl protons. Calibration of the exact position of the six lines of the sextet and the knowledge that two olefinic protons should be more strongly coupled than an olefinic proton and a methylene proton leads one to assign spin coupling constants as follows: $J_{32} = 5.7$ cps and $J_{34} = 2.6$ cps.

The next cluster of absorption lines appears about 100 cps upfield from the $\beta$-vinyl proton. It is also a sextet consisting of two triplets and is centered at a $\gamma$-value of 3.89. This cluster is assigned to the $\alpha$-vinyl proton. Again the three spin arrangements of the $\beta$-methylene protons couple with the $\alpha$-vinyl proton so as to produce a triplet
absorption pattern. This triplet is, in turn, split by coupling of the
\(\alpha\)-vinyl proton with the \(\beta\)-vinyl proton. The spin coupling constants
are calculated to be \(J_{24} = 2.2\ \text{cps}\) and \(J_{23} = 5.8\ \text{cps}\). As would be
expected the \(\alpha\)-vinyl and \(\beta\)-vinyl protons split each other equally in
the two absorption clusters, i.e. \(J_{32} = J_{23}\).

Farther upfield are two neighboring absorption clusters that com­
prise the \(A_2B_2\) pattern produced by the four methylene protons.

The number and position of the absorption lines of an \(A_2B_2\) pattern
is determined in a complicated way by the relative chemical shift and
spin coupling constants. For this reason the interpretation of this type
of absorption pattern is often difficult. Of great assistance, however,
is the fact that absorption line assignments have been worked out for
several general classes of \(A_2B_2\) patterns\(^{17,18}\) and thus it is possible
by analogy and deduction to undertake the interpretation of most \(A_2B_2\)
systems. To aid in the interpretation of cyclopentenone, terminology and
some tables of data will be taken from the above-mentioned sources.

In an \(A_2B_2\) system there are four different spin coupling constants
as shown in Figure 2. It is convenient to define new quantities as
follows: \(K = J_A + J_B; M = J_A - J_B; L = J - J'\) and \(N = J + J'\). In the
quantum mechanical solution of the \(A_2B_2\) pattern a complete set of basic

\(^{17}\) J. A. Pople, W. G. Schneider and H. J. Bernstein, Canad. J. Chem.,
25, 1060 (1957).

\(^{18}\) J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution
1959, p. 138.
functions is set up and all stationary state wave functions are expressed as linear combinations of them. The complete matrix of the spin Hamiltonian has been evaluated and values of the diagonal and off-diagonal elements given in terms of $v_A$, $v_B$, $K$, $L$, $M$ and $N$. $v_A > v_B$ where $v_A$ and $v_B$ are the frequencies the lines would have were there no spin coupling. Transitions will only occur between states of the same symmetry whose total spin components differ by $+1$ or $-1$. This leads to a total of 24 possible transitions, or absorption lines, divided into two groups that are mirror images of each other.

Turning to the spectrum of cyclopentenone one notes that the two $A_2B_2$ clusters do not appear as mirror images. This is because the downfield cluster (the $\beta$-methylene grouping) is split by coupling with the two vinyl protons. Since the downfield cluster is highly split, interpretation may be best attempted by considering only the upfield, or B

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19Ibid., p. 140.
cluster. Expansion of this cluster shows it to consist of eight major lines or peaks. The positions of these peaks are calibrated to be 139.4, 138.4, 136.6, 134.1, 133.0, 131.3, 129.6 and 128.7 cps. The peaks are schematically shown in Figure 3. The band center of the pattern is calculated to be 146.5 cps.

![Figure 3](image)

Figure 3. Schematic representation of the upfield half of the $A_2B_2$ pattern of cyclopentenone.

The general case of the B spectrum where $J \gg J' > 0$ and $J_B \gg J_A > 0$ is adapted from the case of the A spectrum\textsuperscript{20} and is shown as Figure 4. The energies of the twelve theoretical $A$ transitions have been calculated by Pople et al.\textsuperscript{21} and some are given in Table 1. From Table 1 it can be seen that it is advantageous if lines 1 and 3 can be obtained by inspection of the spectrum. If this can be accomplished then $\nu_6 \delta$ (which is $\nu_A - \nu_B$) and $N$ (which is $J + J'$) may be determined

\textsuperscript{20}Ibid., p. 147.

\textsuperscript{21}Ibid., p. 144.
Figure 4. Schematic representation of the general case of the $A_2B_2$ pattern

Table 1. Energies of the $A$ transitions for four nuclei, $A_2B_2$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy relative to $\frac{1}{4}(\nu_A + \nu_B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $1s_1^1 \rightarrow a_2$</td>
<td>$\nu N + \frac{1}{4}(\nu_0 S + N^2)^{\frac{1}{4}}$</td>
</tr>
<tr>
<td>3. $s_{-2} \rightarrow 1s_{-1}$</td>
<td>$-\frac{1}{4}N + \nu_0$</td>
</tr>
<tr>
<td>9. $2a_0^1 \rightarrow 2a_1^1$</td>
<td>$\frac{1}{4}(\nu_0 S - M^2 + L^2)^{\frac{1}{4}} + \frac{1}{4}(M^2 + L^2)^{\frac{1}{4}}$</td>
</tr>
<tr>
<td>10. $2a_{-1}^1 \rightarrow 1a_0^1$</td>
<td>$\frac{1}{4}(\nu_0 S - M^2 + L^2)^{\frac{1}{4}}$</td>
</tr>
<tr>
<td>11. $1a_0^1 \rightarrow 2a_1^1$</td>
<td>$\frac{1}{4}(\nu_0 S + M^2 + L^2)^{\frac{1}{4}} - \nu_0$</td>
</tr>
<tr>
<td>12. $2a_{-1}^1 \rightarrow 2a_0^1$</td>
<td>$\frac{1}{4}(\nu_0 S - M^2 + L^2)^{\frac{1}{4}}$</td>
</tr>
</tbody>
</table>
simply by solving two simultaneous equations.

Inspection of the upfield or B cluster of cyclopentenone's $A_2B_2$ pattern shows the first two (139.4 and 138.4 cps) peaks to be the most intense of the eight. If this spectrum were to follow that of the general case as shown in Figure 4 these two peaks are quite likely to be absorption lines 4 and 3, respectively. The last two (129.6 and 128.7 cps) peaks are still quite intense relative to the others. It is thus unlikely that they are lines 5 and 10. One tentatively assigns these peaks as transitions 2 and 1, respectively. A value of 138.4 cps has thus been assigned to transition 3 and 128.7 cps to transition 1. Referring to Table 1 and solving the two simultaneous equations:

\[
\begin{align*}
17.3 &= \frac{\Delta h}{2} + \frac{1}{2} \left[ (\nu_0 \Delta)^2 + h_0^2 \right]^{\frac{1}{2}} \\
8.1 &= -\frac{\Delta h}{2} + ...
\end{align*}
\]

one obtains a value of 24.0 cps for $\nu_0 \Delta$ and 9.7 cps for $h$. 

One now makes the assumption that $K$ (which is $J_A + J_B$) is relatively large. (It is estimated that $K$ is approximately 38 cps from the value of $J_{55}$ of 4-bromo-cyclopentenone and $J_{44}$ of 5-ethoxy-cyclopentenone.) If $K$ is relatively large certain transitions will not occur and transitions 1, 2, 3, 4, 6, and 7 should have the same energy as they would have in the case where $J = J'$. Also, lines 5 and 8 are effectively forbidden. One may thus refer to a table of energies of transitions for the case $J = J'$.

---

and obtain calculated values of transitions 1, 2, 3, 4, 6 and 7. If \( J \)
were to equal \( J' \) in cyclopentenone these two quantities would be \( 9.7/2 \)
or 4.8 cps. The ratio \( J / v_0 \) is \( 4.8 / 24.0 = 0.2 \). This ratio is used
to ascertain the energies of transition as tabulated in Pople et al.\(^2\). The
calculated transitions and the actual spectrum lines are tabulated in
Table 2. It is seen that there is excellent agreement of the calculated
transitions with the actual lines of the spectrum.

The remaining two lines of the spectrum are assigned as follows:
136.6 cps to transitions 11 and 12, and 131.8 cps to transitions 9 and
10. The basis for these assignments is found by examination of Table 1.
It is first assumed that \( M^2 \) is negligible. (Values obtained in other
cyclopentenones indicate that \( M \) is probably less than one in the case of
cyclopentenone.) If \( M \) is negligible then lines 9 and 10 should have the
same value. Similarly, lines 11 and 12 should have the same value and
should differ from 9 and 10 by \( L \) (which is \( J - J' \)). It was calculated
above that \( J + J' \) is 9.7 cps. Values of \( J \) and \( J' \) are thus chosen such
that one obtains the best fit between the calculated transitions 9, 10,
11 and 12 and the actual spectrum lines remaining to be assigned. It is
found that assuming a value of 4.7 cps for \( L \) leads to a value of 131.8
cps for lines 11 and 12 and 136.6 cps for lines 9 and 10. These calcu-
lated transitions correspond exactly with the two remaining lines of the
actual spectrum.

\(^2\) J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution
1959, p. 144.
Table 2. Calculated and actual transitions of the upfield cluster of the $A_2B_2$ spectrum of cyclopentenone

<table>
<thead>
<tr>
<th>Transition</th>
<th>Calculated energy</th>
<th>Actual spectrum lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>139.1</td>
<td>139.4</td>
</tr>
<tr>
<td>3</td>
<td>138.4</td>
<td>138.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>136.6</td>
</tr>
<tr>
<td>6</td>
<td>133.9</td>
<td>134.1</td>
</tr>
<tr>
<td>7</td>
<td>133.2</td>
<td>133.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>131.8</td>
</tr>
<tr>
<td>2</td>
<td>129.8</td>
<td>129.6</td>
</tr>
<tr>
<td>1</td>
<td>128.8</td>
<td>128.7</td>
</tr>
</tbody>
</table>

One may sum up the following values for the chemical shift and various parameters of cyclopentenone: $\nu_0 \delta = 24.0$ cps, $\nu_A = 146.5 + 12.0 = 158.5$ cps, $\nu_B = 146.5 - 12.0 = 134.5$ cps., $M = 9.7$ cps, $L = 14.7$ cps, $M = 130.1$ cps, $J = 7.2$ cps and $J' = 2.5$ cps.

The value of $K$ cannot be determined directly but it must be large enough to prevent any significant mixing of the $3s_0$ basic functions with other functions. Otherwise the calculated and experimental values discussed herein would not be in such good agreement.

4-Bromo-cyclopentenone

It would be anticipated that 4-bromo-cyclopentenone would contain two vinyl absorption clusters and an ABX pattern. Indeed, these patterns appear clearly in the NMR spectrum. The lines of the spectrum will be considered in order of increasing applied magnetic field.
The first cluster encountered is a quartet centered at $\tau = 2.59$. This cluster is assigned to the most deshielded proton, i.e. the $\beta$-vinyl one. The splitting of 5.5 cps and 2.6 cps is caused by coupling with the $\alpha$-vinyl proton and the methinyl proton, respectively.

The next cluster upfield is a quartet centered at $\tau = 3.79$ and assigned to the $\alpha$-vinyl proton. The splitting of 5.7 cps and 1.2 cps arises from coupling with the $\beta$-vinyl and methinyl protons, respectively.

The next cluster appears as a highly split multiplet centered at $\tau = 4.87$. This is assigned to the methinyl or X proton which, along with the two methylene protons, comprises an ABX system.

The ABX system has been discussed by Pople and co-workers.\textsuperscript{24, 25} The theory and terminology used herein are drawn from these sources.

The X spectrum theoretically consists of six lines, two of which are of low intensity and often not observed. The theoretical X spectrum is shown schematically in Figure 5.

---

\[ |J_{AX} + J_{BX}| \]

\[ 2|D_+ - D_-| \]

Figure 5. Theoretical X pattern of the ABX grouping

\textsuperscript{24} Ibid., p. 132.

Expansion of the \( I \) multiplet of 4-bromo-cyclopentenone shows the multiplet to consist of twelve lines. The spectrum is schematically shown in Figure 6. The lines are seen to be derived from four original lines. The four spectrum lines that are double the intensity of the others arise from the overlapping of some lines. Each of the four theoretical lines has been split twice: once, 2.7 cps, by the \( \beta \)-vinyl proton, and once, 1.3 cps, by the \( \alpha \)-vinyl proton. \(|J_{AX} + J_{BX}|\) is calculated to be 8.3 cps and \(2|D_+ - D_-|\) to be 3.0 cps.

\[\text{Figure 6. I pattern of the ABX grouping of 4-bromo-cyclopentenone}\]

Farther upfield is a cluster of eight lines, the inner four of which are more intense than the outer lines. This octet is assigned to the methylene or AB protons. This pattern is typical of the AB portion of an ABX grouping and is in reality two overlapping quartets. The AB spectrum of 4-bromo-cyclopentenone with theoretical \( J \) distances and various parameters indicated is shown schematically in Figure 7.
Figure 7. The AB pattern of the ABX grouping of 4-bromo-cyclopentenone

The two overlapping quartets are lines 1, 3, 5, 7 and 2, 4, 6, 8. The interval $|J_{AB}|$ occurs four times. The difference between quartet centers is $\frac{1}{2}|J_{AX} + J_{BX}|$. A cross check is possible between the AB and X patterns with regards to the values obtained for $|J_{AX} + J_{BX}|$, $D_+$, and $D_-$. From the AB pattern $|J_{AB}|$ is found to be 19.3 cps and $|J_{AX} + J_{BX}|$ to be 8.2 cps. $D_+$ is 14.4 cps and $D_-$ is 12.8 cps. Comparing these values with those obtained from the X multiplet one finds good agreement for the values of $|J_{AX} + J_{BX}|$ and $2|D_+ - D_-|$.

The quantities $(\sqrt{J_A - \sqrt{J_B}})$ and $(J_{AX} - J_{BX})$ may be obtained by use of the following definitions:

$$D_+ \cos 2\phi_+ = \frac{1}{2}(J_A - J_B) + \frac{i}{2}(J_{AX} - J_{BX})$$
$$D_+ \sin 2\phi_+ = \frac{1}{2}J_{AB}$$
$$D_- \cos 2\phi_- = \frac{1}{2}(J_A - J_B) - \frac{i}{2}(J_{AX} - J_{BX})$$
$$D_- \sin 2\phi_- = \frac{1}{2}J_{AB}$$

\[26\]

By substituting values obtained for $D_+$, $D_-$, and $\frac{3}{2} J_{AB}$ into the above equations one obtains $(\gamma_A - \gamma_B) = 19.1$ cps and $J_{AX} - J_{BX} = 4.6$ cps. Since it previously had been calculated that $J_{AX} + J_{BX} = 8.2$ cps, one may now solve and obtain $J_{AX}$ to be $6.4$ cps and $J_{BX}$ to be $1.8$ cps. The signs of $J_{AX}$ and $J_{BX}$ are taken to be positive although it is not possible to determine them absolutely.

The band center is considered to be midway between the two quartet centers and is $167.4$ cps. If it is assumed that trans protons are more strongly coupled than cis protons, the $\gamma$-value of the methylene proton that is cis to the bromine atom is $7.05$ and the proton trans to the bromine is $7.37$.

The AB octet could have been interpreted by selecting a different set of quartets, i.e. $1, 3, 6, 8$ and $2, 4, 5, 7$ as numbered in Figure 7. This possibility was considered and new parameters calculated on this basis. Relative intensities were then calculated for each of the two possible interpretations. The intensities calculated on the basis of quartet $1, 3, 5, 7$, etc. were found to more nearly fit the actual spectrum. The intensities predicted on this basis were $.25, .33, 1.74, 1.67, 1.74, 1.67, .25$ and $.33$ for transitions $1$ through $8$. Although the predicted intensities are greater than the actual values for the four inner peaks, the relative intensity for the four weaker outer peaks is accurately predicted. The set $1, 3, 6, 8$, etc. led to generally similar values for the inner four peaks but did not reflect so accurately the

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27 Ibid., p. 192.
four outer peaks especially in the case of lines 7 and 8.

The coupling constants for the quartets 1, 3, 6, 8, etc. were calculated to be $J_{AX} = 7.6$ cps and $J_{BX} = -4.4$ cps. It is difficult to ascertain with certainty the signs of the coupling constants in a spectrum. The magnitude of this negative coupling constant, however, appears to be high in comparison with other negative coupling constants.

On the basis of present evidence the original selection of the quartets seems to best fit the actual spectrum.

4-Acetoxy-cyclopentenone

The spectrum of this compound would be expected to be quite similar to that of the bromo analog except for the addition of an intense absorption line for the methyl group. This is indeed what the actual spectrum shows.

The first cluster of the spectrum is a quartet centered at $\tau = 2.49$ and is assigned to the $\beta$-vinyl proton. $J_{32}$ is calculated to be 5.5 cps and $J_{34}$ is 2.4 cps.

The $\alpha$-vinyl absorption cluster is centered at $\tau = 3.75$ and is also a quartet. $J_{23}$ is 5.7 cps and $J_{24}$ is 1.3 cps.

The methiryl or I multiplet is centered at $\tau = 4.22$ and consists of eleven lines. These are schematically shown in Figure 8. The four main lines of the X spectrum have each been split twice and some overlapping occurs. $J_{43}$ is calculated to be 2.5 cps and $J_{42}$ to be 1.3 cps. From the X spectrum one also obtains $J_{AX} + J_{BX} = 8.6$ cps and $2|D_+ - D_-| = 3.7$ cps.
The methylene or AB pattern of the ABX grouping appears as the expected octet with the exception that the two low intensity upfield peaks are obscured by the intense methyl absorption peak. From the AB spectrum one obtains the following values: $J_{AB} = 18.6$ cps, $D_+ = 18.6$ cps, $D_- = 16.9$ cps, $(\nu_A - \nu_B) = 30.4$ cps, $J_{AX} = 6.4$ cps and $J_{BX} = 2.4$ cps.

As in the case of the bromo analog, one again notes good agreement among those values that permit cross-checking of the AB pattern with the X pattern.

The midpoint of the two AB quartet centers is 147.9 cps. Thus the two methylene protons are centered at 132.7 and 163.1 cps. Assuming trans protons to be more strongly coupled than cis protons, the $\gamma$-value of the proton cis to the acetoxy group is 7.28 and the proton trans is 7.79.

5-Oxalyl-cyclopentenone

The NMR spectrum of this compound is of special interest because it contains several different types of protons including a very acidic one. The oxalyl keto group involving the carbon adjacent to the ring
would be expected to be enolic and thus give rise to a proton hydrogen bonded with the keto group of the cyclopentenone ring. The NMR spectrum confirms this. The singlet at the far left of the spectrum (760.3 cps) may be assigned to this acidic proton. The \( \gamma \)-value is -2.7.

The next upfield cluster is assigned to the \( \beta \)-vinyl proton. The cluster consists of two triplets and is centered at \( \gamma = 2.44 \). The triplets arise from coupling with the methylene group and with the \( \alpha \)-vinyl proton. The coupling constants are \( J_{32} = 5.6 \) cps and \( J_{34} = 2.3 \) cps.

Farther upfield is the cluster assigned to the \( \alpha \)-vinyl proton. Expansion shows it to also consist of two triplets. The cluster is centered at \( \gamma = 3.64 \) and the coupling constants are \( J_{23} = 6.0 \) and \( J_{24} = 2.0 \) cps.

The next upfield cluster is a quartet centered at \( \gamma = 5.68 \). This quartet and the triplet centered at \( \gamma = 8.62 \) are easily recognizable as belonging to the oxalyl ethyl grouping.

Between the above mentioned quartet and triplet is a triplet at \( \gamma = 6.50 \). This is assigned to the ring methylene group. The splitting is caused by coupling with the vinyl protons. \( J_{43} = J_{42} = 2.1 \) cps.

5-Ethoxy-cyclopentenone

The NMR spectrum of 5-ethoxy-cyclopentenone in CCl\(_4\) shows the absorption peaks of the methinyl hydrogen and the side chain methylene group to intermingle in a complex pattern. When the spectrum is run using D\(_2\)O as a solvent the two groups produce clearly separated and more
characteristic patterns. The spectrum will therefore be discussed as it appears when run in D$_2$O. Tau values are solvent dependent and thus values obtained in D$_2$O may be expected to differ, in varying degrees, from values that would have been obtained using a less polar solvent. The spectrum peaks were originally calibrated against the HOD peak present in the D$_2$O, and the HOD peak, in turn, calibrated against a capillary of benzene ($\gamma = 2.74$) placed inside the sample tube.

The $\beta$-vinyl proton appears as two triplets centered at $\gamma = 1.27$. $J_{32}$ is 6.4 cps and $J_{34}$ is 2.9 cps.

The $\alpha$-vinyl proton is centered at $\gamma = 2.95$ and also appears as two triplets. The coupling constants are $J_{23} = 6.3$ cps and $J_{24} = 2.1$ cps.

The residual HOD in the D$_2$O causes the sharp peak at $\gamma = 4.50$.

The four sharp peaks centered at $\gamma = 4.98$ are due to the methinyl proton. This proton is, of course, the X proton of an ABX system.

The quartet centered at $\gamma = 5.47$ and the triplet at $\gamma = 7.96$ are recognized as belonging to the side-chain ethoxy grouping.

The ring methylene group would be expected to be the AB part of an ABX grouping, further split by coupling with the vinyl protons. Instead of the expected octet pattern, however, four equally spaced and highly split multiplets centered at $\gamma = 6.33$ are obtained. These appear to be best interpreted as a conventional AB system, in which case $J_{AB}$ is found to be 19.5 cps.

The values obtained in D$_2$O are shifted considerably downfield from the values obtained using CCl$_4$ as solvent. In CCl$_4$ the $\beta$-vinyl proton absorbs at $\gamma = 2.49$ and the $\alpha$-vinyl proton at 3.95.
Cyclopentane-1,2-dione

This compound exists predominantly in the enolic form, i.e. as 2-hydroxy-cyclopent-2-enone.\textsuperscript{23} Examination of the NMR spectrum shows a broad, low peak at the downfield end. This peak, centered at $\gamma = 3.19$, is assigned to the hydroxy proton.

The cluster immediately upfield is a triplet centered at $\gamma = 3.54$ and is assigned to the vinyl proton. The splitting, $J_{34} = 2.5$ cps, is caused by coupling with the 3-methylene group.

The intense upfield peak centered at $\gamma = 7.56$ is due to absorption by the methylene protons. Even upon expansion the expected $A_2B_2$ pattern cannot be separated enough to permit interpretation. It is apparent that the chemical shift between the two methylene groups is very small thus permitting the two mirror image clusters to coalesce.

3,4-Diethoxy-cyclopent-2-enone

This compound contains an $\alpha$-vinyl proton, an ABX grouping and two ethoxy groups.

The olefinic proton appears as a singlet with a $\gamma$-value of 4.81. The peak is unsplit since there are no protons on adjacent carbons for the proton to couple with.

The next absorption is a cluster of four sharp peaks centered at $\gamma = 5.63$. This is assigned to the methylnyl or X proton of the ABX pattern.

\textsuperscript{23}G. Hesse and E. Bücking, \textit{Ann.}, \textbf{563}, 31 (1949).
The next upfield peaks may be assigned to the two methylene groups of the two ethoxy groupings. The downfield quartet is centered at 5.94 and is the expected quartet pattern of intensity 1331. The other methylene pattern is immediately upfield and centered at γ = 6.39. This is seen to be a conventional 1331 pattern in which each peak of the quartet has been split 3.1 cps. This methylene group is assigned to the ethoxy grouping on carbon 4.

The next upfield cluster is the octet pattern of the two ring methylene protons. These protons constitute the AB portion of the ABX grouping. From calculations similar to those outlined for 4-bromo-cyclopentenone the following values are obtained: J_{AB} = 17.6 cps, J_{AX} = 6.5 cps and J_{BX} = 2.3 cps. The chemical shifts of the two protons are at γ = 7.45 and 7.79.

Farther upfield are the two triplet groupings of the two methyl groups. The triplet centered at γ = 8.55 is assigned to the ethoxy group on carbon 3 and that centered at γ = 8.81 is assigned to the similar group on carbon 4.

Cyclic ethylene ketal of cyclopentenone

The effect of replacing cyclopentenone's carbonyl group with a cyclic ketal would be expected to lead to more shielding of the protons of the ring and, consequently, to higher γ-values. The spectrum confirms this expectation.

The first downfield cluster appears as a pair of triplets centered at γ = 4.04. This absorption is assigned to the α-vinyl proton on the
grounds that the inductive effect of the ketal grouping should make the α-vinyl proton the most deshielded one of the molecule. \( J_{23} \) is calculated to be 5.4 cps and \( J_{24} \) is 2.0 cps.

The next upfield cluster is also a pair of triplets and is assigned to the β-vinyl proton. This cluster is centered at \( \gamma = 4.42 \) and the coupling constants are \( J_{32} = 5.6 \) cps and \( J_{34} = 2.0 \) cps.

The intense singlet at \( \gamma = 6.17 \) is caused by the methylene groups of the ketal ring.

The two methylene groups form an \( A_2B_2 \) pattern whose band center is 128.8 cps. To interpret this \( A_2B_2 \) pattern one proceeds in much the same manner as in the case of cyclopentenone. Since the downfield half of the cluster is split by the vinyl protons one must restrict interpretation to only the upfield half of the pattern. This half consists of ten major peaks: 123.6, 122.2, 121.4, 118.4, 117.0, 116.1, 114.9, 113.3, 111.4 and 109.8 cps.

These peaks are schematically shown in Figure 9.

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**Figure 9.** Schematic representation of the upfield half of the \( A_2B_2 \) pattern of the cyclic ethylene ketal of cyclopentenone
From observation of the spectrum and experience gained from interpreting cyclopentenone one tentatively assigns the second peak (122.2 cps) to transition 3 and the last peak (109.8 cps) to transition 1. Equating these with the transition energies of Table 1 one obtains $N$ (which is $J + J'$) = 12.4 cps and $\nu_0 S = 22.4$ ops. As in the case of cyclopentenone $K$ is assumed to be relatively large and thus one is able to calculate transitions 4, 3, 6, 7, 2 and 1 to have the values they would have if $J = J'$. The ratio $J / \nu_0 S = 6.2 / 22.4 = 0.28$. If one considers this ratio to be 0.3 one may readily refer to previously calculated data to obtain values for the transitions listed above. The calculated transitions and the actual spectrum lines are listed in Table 3.

Transitions 9, 10, 11 and 12 are obtained by examination of Table 1 and by deduction. If one assumes $M$ to be negligible then lines 9 and 10 and the pair 11 and 12 will be equally split. Examination of the four remaining unassigned lines of the actual spectrum shows that there is 3.0 cps difference between lines 121.4 and 118.4 and a difference of 2.8 cps between lines 113.3 and 116.1. One thus assigns the four remaining lines of the spectrum as follows: transition 12, 121.4 cps; transition 11, 118.4 cps; transition 10, 116.1 cps and transition 9, 113.3 cps.

The two methylene protons are centered at 117.6 cps and 140.0 cps, or at $\tau$-values of 8.04 and 7.67.

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Table 3. Calculated and actual transitions of the upfield cluster of the $A_2B_2$ spectrum of the cyclic ethylene ketal of cyclopentenone

<table>
<thead>
<tr>
<th>Transition</th>
<th>Calculated energy (cps)</th>
<th>Actual spectrum lines (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>123.6</td>
<td>123.6</td>
</tr>
<tr>
<td>3</td>
<td>122.5</td>
<td>122.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>121.4</td>
</tr>
<tr>
<td></td>
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<td>7</td>
<td>114.7</td>
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<td>111.4</td>
</tr>
<tr>
<td>1</td>
<td>109.0</td>
<td>109.8</td>
</tr>
</tbody>
</table>

Cyclopentene-3,5-dione

This compound contains two equivalent vinyl protons and two equivalent methylene protons. Since the two types of protons are separated from each other by carbonyl groups no splitting due to spin coupling would be expected. It would also be anticipated that the absorption lines would be shifted downfield due to the deshielding effect of the two carbonyl groups.

Indeed, such is the case. The NMR spectrum consists of two sharp singlets. The absorption at $\gamma = 2.69$ is assigned to the vinyl protons and the peak at $\gamma = 7.10$ to the methylene protons.

Gutowsky et al.\textsuperscript{30} have recorded the spectrum of this compound

monodeuterated on the methylene carbon. The presence of deuterium caused a slight upfield shift (0.8 cps) for the proton on the methylene carbon. \(J_{HD}\) was found to be 3.3 cps.

4,4-Dibromo-cyclopentene-3,5-dione

The two vinyl protons of this compound are equivalent and appear as a singlet, \(\gamma = 2.77\).

1,8-Diketo-4,7-methano-3a,4,7,7a-tetrahydroindene

The NMR absorption of this compound, which is the Diels-Alder adduct of cyclopentadiene, occurs in three main groupings. Farthest downfield is the absorption grouping caused by the \(\beta\)-vinyl proton of the cyclopentenone ring. The next upfield grouping is more complex and contains the patterns arising from the \(\alpha\)-vinyl proton of the cyclopentenone ring and the two olefinic protons of the six-carbon ring. The large grouping farthest upfield is a very complex pattern and is produced by the intermingling of the patterns of the four tertiary protons.

Simplest of all the groupings is that due to the \(\beta\)-vinyl proton of the cyclopentenone ring and centered at \(\gamma = 2.58\). It is, as expected, a quartet. The coupling constants are \(J_{32} = 5.6\) cps and \(J_{34} = 2.5\) cps. Expansion of the cluster further reveals that each peak of the quartet is split by approximately 0.6 cps. This additional fine splitting would seem to be due to coupling either with the proton on carbon 5 of the cyclopentenone ring or with the proton on the nearest bridgehead in the six-carbon ring. As we shall observe later it appears more likely that this coupling is with the bridgehead proton.
The $\alpha$-vinyl proton of the cyclopentenone ring would be expected to produce a quartet with $J_{23} = 5.6$ cps. Examination of the four major down-field peaks of the second absorption grouping show them to fit this specification well. Assignment of these four peaks to the $\alpha$-vinyl proton gives a $\gamma$-value of 3.63 and coupling constants of $J_{23} = 5.7$ cps and $J_{24} = 1.4$ cps.

There remain in this grouping two intense lines plus several others of varying and lesser intensity on either side of them. These lines must be assigned to the six-carbon ring olefinic protons. If some of the weakest of the lines are neglected there remain a total of six lines, the middle two being more intense than the outer ones. Construction of a molecular model shows that one of the olefinic protons is so oriented as to be in a position to experience some diamagnetic shielding from the cyclopentenone carbonyl group. If the two olefinic protons are assumed to be non-equivalent it would be expected that they would each be split by each other and by the two bridgehead protons. From the spacing and intensity of the lines, the possibility arises that this absorption is two overlapping quartets of splittings 3.4, 3.4, and 1.7 cps. Although the exact derivation of the pattern is not known with certainty it seems quite certain that the lines under consideration may be assigned to the olefinic protons mentioned. The olefinic protons of the analogous system, 7-isopropylidene-bicyclohept-2-ene\textsuperscript{31} show a quite similar but

more split pattern.

The complex upfield absorption grouping contains the absorption lines of the four tertiary protons of the molecule. Although there is much splitting and some intermingling of lines, some assignments and generalizations may be made. Expansion shows four clearly separated and intense peaks on the upfield side of the grouping. These are centered at $\tau = 7.04$. The splitting is calculated to be 5.6 and 4.8 ops. Of the four tertiary protons in the molecule there is only one that should be coupled with only two other protons and produce a quartet pattern, and that is the proton on carbon 5 of the cyclopentenone ring. One therefore assigns this quartet to that proton. If this assignment is correct then it would seem apparent that this proton is not weakly coupled with the $\beta$-vinyl proton of the cyclopentenone ring since one observes no evidence of fine splitting in this quartet.

The remaining absorption peaks of this grouping are considerably split and are intermingled to some extent. Although there are no clear separations it seems possible to pick out at least the outlines of the three remaining tertiary protons. To facilitate discussion one first divides these remaining lines into thirds.

In the upfield one-third we observe several relatively intense peaks which appear to belong to the same pattern. These peaks are assigned to the proton on carbon 4 of the cyclopentenone ring. One is led to this assignment because these peaks can be made to fit the estimated splitting pattern for this proton. From splitting patterns of protons coupled with it we estimate that the proton of carbon 4 should have splitting
constants of about 5.6, 4.8, 2.6 and 1.4 cps. Indeed, it is possible to pick out such a pattern from the lines in the upfield one-third of the portion of the spectrum under consideration.

The remaining peaks of the grouping must be assigned to the two bridgehead protons. A clear interpretation does not seem to present itself, however, it is possible to distinguish the general areas of absorption of each proton. If one examines the middle one-third of the lines under consideration it is seen that they all contain fine splitting of the order 0.2-0.6 cps. The lines of the downfield one-third are of similar intensity and spacing but do not contain fine splitting. It is therefore postulated that the fine splitting occurs in the case of the bridgehead proton that is weakly coupled with the \( \beta \)-vinyl proton of the cyclopentenone ring. Hence the series of lines containing such splitting is assigned to the bridgehead proton on the opposite side of the molecule from the cyclopentenone carbonyl group. The remaining downfield lines of this grouping are then assigned to the other bridgehead proton.

2-Methyl-cyclopent-2-enone

One should expect this spectrum to be quite similar to that of cyclopentenone, except for the addition of a methyl absorption cluster and the absence of the \( \alpha \)-vinyl cluster. Such, indeed, is the case. More interesting, however, is the fact that long-range coupling occurs between the protons of the methyl and methylene groups.

The downfield cluster of the spectrum is assigned to the vinyl proton and is a highly split multiplet centered at \( \gamma = 2.79 \). This
multiplet is split by coupling with the protons of both the methyl and 3-methylene groups.

The two methylene groups comprise an $A_2B_2$ grouping. Of the two mirror image clusters the downfield one is split by the vinyl and methyl protons. Interpretation must be based upon consideration only of the upfield or B cluster. The band center of the $A_2B_2$ system is 143.7 cps. The upfield cluster is schematically shown in Figure 10. The cluster consists of six lines: 140.5, 138.6, 136.2, 133.5, 131.7 and 130.0 cps. There is obviously more overlapping of lines than in the case of cyclopentenone. As a start, the assumption is made that the first peak (140.5 cps) corresponds to transitions 4 and 3 and that the last peak (130.0 cps) corresponds to transition 1. One then proceeds in much the same manner as in the case of cyclopentenone and related $A_2B_2$ systems. One assumes $K$ to be relatively large and hence lines 1, 2, 3, 4, 6 and 7 are the same as they would be in the case where $J = J'$. The ratio $J / \nu_0S$ is calculated to be $5.3 / 13.3 = 0.4$. Referring to a table of
transition energies one obtains calculated values for the transitions as shown in Table 4.

Table 4. Calculated and actual transitions of the upfield cluster of the $A_2B_2$ spectrum of 2-methyl-cyclopent-2-enone

<table>
<thead>
<tr>
<th>Transition</th>
<th>Calculated energy (cps)</th>
<th>Actual spectrum lines (cps)</th>
</tr>
</thead>
<tbody>
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<td>141.4</td>
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<td>3</td>
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<td>133.8</td>
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<td>2</td>
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<td>131.7</td>
</tr>
<tr>
<td>1</td>
<td>129.9</td>
<td>130.0</td>
</tr>
</tbody>
</table>

Lines 9, 10, 11 and 12 are calculated on the basis that $M$ is negligible and that $(J - J')$ is 4.7 cps, the same value as in cyclopentenone. Proceeding on this basis one obtains a value of 134.2 cps for transitions 9 and 10 and 139.0 cps for 11 and 12. The 139.0 is in reasonably good agreement with the actual peak at 138.6 cps. The 134.2 peak would be expected to reinforce the peak at 133.5 and indeed this peak is about twice the intensity of its neighbors. The $\alpha$-methylene group is centered at $\tau = 7.72$ and the $\beta$-methylene group at 7.49.

The methyl absorption cluster appears outwardly to be a quartet centered at $\tau = 8.29$. However this pattern is unreasonable to account for coupling with the methylene group and with the vinyl proton. It
would seem that there are in actuality two triplets partially superimposed as shown in Figure 11. $J_{\text{H},4}$ is 1.9 cps and $J_{\text{H},3}$ is also 1.9 cps.

Figure 11. Schematic representation of the methyl absorption cluster of 2-methyl-cyclopent-2-enone

2-Methyl-4-diazo-cyclopent-2-enone

The first cluster encountered in the spectrum of this compound is a highly split multiplet centered at $\tau = 3.29$. This is assigned to the vinyl proton.

The methylene group appears as a quintet centered at $\tau = 6.43$. The quintet arises from the overlapping of two quartets as shown schematically in Figure 12. The quartet originally arises from

Figure 12. Schematic representation of the methylene absorption cluster of 2-methyl-4-diazo-cyclopent-2-enone
long-range splitting of the methylene protons by the protons of the methyl group. This quartet is, in turn, split by coupling with the vinyl proton. $J_{43}$ is calculated to be 2.2 cps and $J_{4,Me}$ to be 2.2 cps.

The methyl group appears as a quartet centered at $\tau = 3.20$. The quartet is actually two partially overlapping triplets. Coupling of the methyl group with the methylene protons gives rise to a triplet pattern for the methyl protons. This triplet is, in turn, split by coupling with the vinyl proton. $J_{Me,4} = J_{Me,3} = 1.9$ cps.

1-Methyl-cyclopentene-4,5-dione

In the spectrum of this compound one again observes long-range coupling between the methyl and methylene groups.

The vinyl proton gives rise to a highly split multiplet centered at $\tau = 2.28$.

The methylene protons appear as a quintet centered at $\tau = 6.97$. As in the 4-diazo analog, it is a case of two overlapping quartets. $J_{43}$ and $J_{4,Me}$ are 2.6 cps.

The methyl group appears as a sextet centered at $\tau = 8.03$. This pattern arises from the splitting of a triplet. $J_{Me,4}$ is 2.5 cps and $J_{Me,3}$ is 1.3 cps.

Generalisations Concerning Chemical Shifts and Coupling Constants of Protons on the Cyclopentenone Ring

The chemical shifts and coupling constants of the ring protons of cyclopentenones are, of course, dependent upon the position or positions substituted and the nature of the substituent. Although the number of
compounds examined was not large enough to constitute a definitive study; it is, none the less, possible to note general trends and to make reasonable correlations of the data obtained.

**α-vinyl protons**

The protons on the α-vinyl carbon of the cyclopentenones studied, arranged in order of increasing tau-value, are summarized in Table 5.

The tau-values fall within the range 3.63-3.95 for cyclopentenone and its derivatives monosubstituted on carbon 4 or carbon 5, or on both as in dicyclopentadienone. In the case of the 3,4-diethoxy derivative the resonance effect of the β-ethoxy group is electron donating, thereby shielding the α-vinyl proton and shifting its absorption to higher field.

**Table 5. Chemical shifts and coupling constants of the α-vinyl proton of some cyclopentenones in CCl₄**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tau value</th>
<th>J₂₃ (cps)</th>
<th>J₂₄ (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicyclopentadienone</td>
<td>3.63</td>
<td>5.7</td>
<td>1.3</td>
</tr>
<tr>
<td>5-Oxalyl-cyclopentenone</td>
<td>3.64</td>
<td>6.0</td>
<td>2.0</td>
</tr>
<tr>
<td>4-Acetoxy-cyclopentenone</td>
<td>3.75</td>
<td>5.7</td>
<td>1.3</td>
</tr>
<tr>
<td>4-Bromo-cyclopentenone</td>
<td>3.79</td>
<td>5.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>3.89</td>
<td>5.8</td>
<td>2.2</td>
</tr>
<tr>
<td>5-Ethoxy-cyclopentenone</td>
<td>3.95</td>
<td>5.9</td>
<td>2.1</td>
</tr>
<tr>
<td>3,4-Diethoxy-cyclopentenone</td>
<td>4.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*In CDCl₃.*
It is of interest to note the shift in value of \( J_{24} \) from 2.0-2.2 cps when carbon 4 is unsubstituted to 1.2-1.3 cps when carbon 4 is monosubstituted. \( J_{34} \), however, retains the same value of approximately 2.5 cps. Preliminary calculations of the NMR spectrum of the recently prepared\(^{32}\) compound, 4-dimethylamino-cyclopentenone, indicate that this compound also shows diminished coupling between the 2 and 4 positions. When the carbonyl group is replaced by an ethylene ketal ring \( J_{24} \) apparently does not undergo an analogous shift in value. The cyclic ethylene ketal of cyclopentenone has a \( J_{24} \) of 2.0 cps and the 4-dimethylamino derivative has a value of 2.1 cps.

No coupling was found between the protons of carbon 2 and carbon 5 of the cyclopentenones examined.

\( \beta \)-Vinyl Protons

The chemical shifts and coupling constants of the \( \beta \)-vinyl protons of the cyclopentenones examined are summarized in Table 6.

Cyclopentenone and its derivatives monosubstituted in the 4 or 5 position have \( \tau \)-values in the range 2.37-2.49. Substitution of a methyl or hydroxyl group for the \( \alpha \)-vinyl proton shifts the absorption to higher field except in the case of 1-methyl-cyclopentene-4,5-dione where the additional carbonyl group, as expected, deshields the \( \beta \)-vinyl proton.

The coupling constant \( J_{34} \) is in the range 2.2-2.8 cps regardless of

Table 6. Chemical shifts and coupling constants of the $\beta$-vinyl proton of some cyclopentenones in $\text{CCl}_4$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tau value</th>
<th>$J_{34}$ (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methyl-cyclopentene-4,5-dione</td>
<td>2.28$^{a}$</td>
<td>2.6</td>
</tr>
<tr>
<td>Cyclopentone</td>
<td>2.37</td>
<td>2.6</td>
</tr>
<tr>
<td>4-Bromo-cyclopentone</td>
<td>2.39</td>
<td>2.6</td>
</tr>
<tr>
<td>5-Oxalyl-cyclopentone</td>
<td>2.44</td>
<td>2.3</td>
</tr>
<tr>
<td>4-Acetoxy-cyclopentone</td>
<td>2.49</td>
<td>2.4</td>
</tr>
<tr>
<td>5-Ethoxy-cyclopentone</td>
<td>2.49</td>
<td>2.8</td>
</tr>
<tr>
<td>Dicyclopentadienone</td>
<td>2.58$^{a}$</td>
<td>2.5</td>
</tr>
<tr>
<td>2-Methyl-cyclopent-2-enone</td>
<td>2.79</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-4-diazo-cyclopent-2-enone</td>
<td>3.29</td>
<td>2.2</td>
</tr>
<tr>
<td>2-Hydroxy-cyclopent-2-enone</td>
<td>3.54</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^{a}$In $\text{CDCl}_3$.

No coupling was observed between the protons on carbon 3 and carbon 5 of the cyclopentenones examined.

Protons on carbon 4

The chemical shifts of protons on carbon 4 are listed in Table 7. The chemical shift of protons on carbon 4 varies considerably with the nature of the substitution. The lowest tau-values are obtained when the
Table 7. Chemical shifts of protons on carbon 4 of some cyclopentanones in CCl₄

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tau value</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Acetoxy-cyclopentenone</td>
<td>4.22</td>
</tr>
<tr>
<td>4-Bromo-cyclopentenone</td>
<td>4.87</td>
</tr>
<tr>
<td>3,4-Diethoxy-cyclopentanone</td>
<td>5.63</td>
</tr>
<tr>
<td>5-Ethoxy-cyclopentenone</td>
<td>6.33ᵇ</td>
</tr>
<tr>
<td>2-Methyl-4-diazo-cyclopentenone</td>
<td>6.43ᵇ</td>
</tr>
<tr>
<td>5-Oxalyl-cyclopentenone</td>
<td>6.50</td>
</tr>
<tr>
<td>Dicyclopentadienone</td>
<td>6.70ᵇ</td>
</tr>
<tr>
<td>1-Methyl-cyclopentene-4,5-dione</td>
<td>6.97ᵇ</td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>7.36</td>
</tr>
<tr>
<td>2-Methyl-cyclopentenone</td>
<td>7.49</td>
</tr>
<tr>
<td>2-Hydroxy-cyclopent-2-ene</td>
<td>7.56</td>
</tr>
</tbody>
</table>

ᵃIn D₂O.
ᵇIn CDCl₃.

4-position is monosubstituted as in the case of 4-bromo or 4-acetoxy-cyclopentanone. Substitution in the 5-position shifts absorption of protons on carbon 4 to higher field.

When the protons on carbon 4 are part of an A₂B₂ system, the absorption varies within the range τ = 7.36-7.56. The substitution of a methyl group for the α-vinyl proton somewhat compresses the A₂B₂
spectrum of cyclopentenones and thus the absorption of the protons on carbon 4 is shifted upfield from 7.36 to 7.49. The case of cyclopentane-1,2-dione is unusual in that the A2B2 pattern virtually coalesces at $\gamma = 7.56$.

Protons on carbon 5

The protons on carbon 5 of the compounds examined are, with one exception, part of either an ABX or A2B2 system. The chemical shifts and coupling constants for these protons are listed in Table 8.

Table 8. Chemical shifts and coupling constants of the protons on carbon 5 of some cyclopentenones in CCl₄

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tau value</th>
<th>J₅₅</th>
<th>J₆₅</th>
<th>J₇₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Bromo-cyclopentenone</td>
<td>7.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Acetoxy-cyclopentenone</td>
<td>7.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,4-Diethoxy-cyclopentenone</td>
<td>7.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-Ethoxy-cyclopentenone</td>
<td>4.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dicyclopentadienone</td>
<td>7.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Hydroxy-cyclopent-2-ene</td>
<td>7.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl-cyclopent-2-ene</td>
<td>7.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>7.76</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a In D₂O.*

*b In CDCl₃.*
In general, the protons on carbon 5 absorb at lower field when they are part of an ABX system. The coupling constants between the protons of the three ABX systems examined show quite similar values regardless of the nature of the substituent.

When the protons on carbon 5 are part of an A2B2 grouping the absorption falls in the range \( \tau = 7.56-7.76 \). It can be seen that in this type of A2B2 grouping the protons alpha to the carbonyl group absorb at somewhat higher field than do the protons beta to the carbonyl. Substitution of a methyl group for the \( \alpha \) -vinyl proton has only a small effect on the A2B2 spectrum of cyclopentenone.

**Correlation of Coupling Constants with Structure of Cyclopentenones**

Karplus and co-workers\(^{33, 34}\) have published calculations, using a valence bond treatment, which show the coupling constant between geminal protons and also between protons on adjacent carbons to be a sensitive function of the bond angles involved.

These calculations indicate that as \( J \) varies from 25 to 0, the geminal H-C-H angle varies from about 102° to 0°. The geminal carbons of cyclopentenones containing an ABX system thus afford an opportunity to obtain values for H-C-H angles in these systems. Table 9 tabulates data for three such cyclopentenones in which the methylene group under consideration is alpha to the carbonyl group.


Table 9. Predicted geminal angle H-C-H in three cyclopentenones

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_{AB}$ (cps)</th>
<th>H-C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Bromo-cyclopentenone</td>
<td>19.3</td>
<td>106°</td>
</tr>
<tr>
<td>4-Acetoxy-cyclopentenone</td>
<td>18.6</td>
<td>106°</td>
</tr>
<tr>
<td>3,4-Diethoxy-cyclopentenone</td>
<td>17.6</td>
<td>107°</td>
</tr>
</tbody>
</table>

The spin coupling constant between adjacent protons of a saturated system is predicted to vary from about 8 at 0° to 0 or less at 90° and 9 at 180°. Conroy\textsuperscript{35} has published a graph based on a molecular orbital treatment and supported by some experimental data, that shows a somewhat modified correlation. He differs from Karplus' values in the region 90-180°, the J's being somewhat greater for a given angle in this region. The J at 180° is shown as approximately 11. Shown in Table 10 are $J_{AX}$, $J_{BX}$ and predicted\textsuperscript{36} dihedral angles for three cyclopentenones.

It can be seen that if the geminal angle of 106° is correct, and models indicate that this is approximately the case, then the predicted dihedral angles do not agree with the actual angles. For example, in the case of 4-bromo-cyclopentenone 145° - 59° is 86° instead of 106°.

Karplus has also calculated that the theoretical spin coupling

\textsuperscript{35} Conroy, op. cit., pp. 308-311.

\textsuperscript{36} Karplus, op. cit., p. 11.
Table 10. Predicted dihedral angle H-C-C-H in three cyclopentenones

<table>
<thead>
<tr>
<th>Compound</th>
<th>( J_{AX} ) (cps)</th>
<th>Dihedral angle</th>
<th>( J_{BX} ) (cps)</th>
<th>Dihedral angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Bromo-cyclopentenone</td>
<td>6.4</td>
<td>145°</td>
<td>1.8</td>
<td>59°</td>
</tr>
<tr>
<td>4-Acetoxy-cyclopentenone</td>
<td>6.4</td>
<td>145°</td>
<td>2.4</td>
<td>56°</td>
</tr>
<tr>
<td>3,4-Diethoxy-cyclopentenone</td>
<td>6.5</td>
<td>146°</td>
<td>2.3</td>
<td>56°</td>
</tr>
</tbody>
</table>

Constant for protons of ethylene is 6.1 cps when the dihedral angle is 0° and 11.9 when it is 180°. Most of the cyclopentenones examined have coupling between the ring vinyl protons in the range 5.6–6.0 cps.

Trends among the Cyclopentendiones

The chemical shifts of the vinyl protons of the two cyclopentendiones examined are listed in Table 11. These tau-values fall between the average values for the vinyl protons of the cyclopentenones. They are, however, closer to the \( \beta \)-vinyl values.

Table 11. Chemical shifts of the vinyl protons of two cyclopentendiones

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tau value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopenten-3,5-dione</td>
<td>2.69</td>
</tr>
<tr>
<td>4,4-Dibromo-cyclopenten-3,5-dione</td>
<td>2.77</td>
</tr>
</tbody>
</table>
Trends within the 2-Methyl-cyclopent-2-enone Series

An interesting feature of the three methylcyclopentenones examined is that all of them show long-range coupling between the protons of the methyl group and the protons of the carbon 4 methylene group. The chemical shifts and coupling constants of these compounds are summarized in Table 12.

Table 12. Chemical shifts and coupling constants for some methylcyclopentenones in CCl₄

<table>
<thead>
<tr>
<th>Compound</th>
<th>-CH₃</th>
<th>C₃-H</th>
<th>C₄-H</th>
<th>Jₜ₄,4 (cps)</th>
<th>Jₜ₃,4 (cps)</th>
<th>Jₜ₃ (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methyl-cyclopent-2-enone</td>
<td>8.29</td>
<td>2.79</td>
<td>7.49</td>
<td>1.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-4-diazo-cyclopent-2-enone</td>
<td>8.20</td>
<td>3.29</td>
<td>6.43</td>
<td>1.9</td>
<td>1.9</td>
<td>2.2</td>
</tr>
<tr>
<td>1-Methyl-cyclopentene-4,5-dione*</td>
<td>8.03</td>
<td>2.28</td>
<td>6.97</td>
<td>2.5</td>
<td>1.3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*In CDCI₃.

The tau-values of the methyl and β-vinyl protons show the expected trends. The absorption of the enone is shifted downfield by the deshielding effect of the extra carbonyl group.

The protons on carbon 4 do not show such a clear trend. The absorption at 7.49 in the case of methyl cyclopentenone is in the region where other cyclopentenone A₂B₂ systems absorb. The tau-value of 6.97 for the
Endione is farther upfield than might be expected and perhaps reflects shielding due to electrons drawn toward carbon 4 from the double bond.

The long-range coupling between the methyl group protons and the methylene group is 1.9 cps for the enone and diazoenone, but is 2.5 cps in the case of the endione. In the case of the endione, $J_{\text{Me},3}$ has a lower value than in the other two compounds. This lowering of $J_{\text{Me},3}$ may reflect the withdrawal of electrons from the double bond by the extra carbonyl group.

$J_{43}$ is approximately the same value as in other cyclopentenones.

The long-range coupling between the methyl protons and the methylene protons occurs over four single bonds and one double bond. The magnitude of the coupling constants obtained agree substantially with the calculations of Karplus. He points out that in unsaturated systems the $\pi$-electron contribution to the long-range coupling constants is much larger than the contribution of the sigma bonds. $J_{\text{HH}}(\pi)$ of the protons in the system H-C-C=CH is calculated to be 2.0 cps.

To clarify the methyl-methylene splitting an attempt was made to exchange the methylene protons in D$_2$O. The diazo-enone immediately decomposed in basic D$_2$O. Treatment of the endione in D$_2$O led to what appears to be addition of D$_2$O to the molecule and subsequent rearrangement as shown in Figure 13. When this reaction was followed by NMR the vinyl absorption virtually disappeared and new absorption, very similar to an ABX pattern, arose upfield. When the reaction was followed by UV

---

*37H. Karplus, J. Am. Chem. Soc., 82, 4432 (1960).*
Figure 13. Postulated reaction of 1-methyl-cyclopentene-4,5-dione in D$_2$O

spectroscopy the absorption peak shifted from 245 m$\mu$ to 265 m$\mu$.

Equilibration of Cyclopentenones in D$_2$O

Several equilibration experiments involving cyclopentenones were run in D$_2$O and the progress of the equilibration followed by NMR. The replacement of a proton by deuterium is evidenced by the disappearance of the original proton absorption and by diminished splitting in the absorption lines of protons that were coupled with it.

Equilibration of cyclopentenone

Equilibration of cyclopentenone was followed in D$_2$O made 0.25 N. basic with Na$_2$CO$_3$ and also in D$_2$O made 0.9 N. acidic with HCl. In each case the upfield cluster of the A$_2$B$_2$ pattern steadily diminished in intensity until it had virtually disappeared. In the basic medium this took about 15 hours and in the acidic medium about 24 hours. In each case the downfield half of the A$_2$B$_2$ pattern retained approximately its original intensity but exhibited less splitting. The vinyl protons
retained their original intensity and splitting.

The disappearance of the upfield half of the $A_2B_2$ pattern coincident with no change in the vinyl peaks would indicate that deuterium is exchanging directly with the protons of the $\alpha$-methylene group. It would appear to rule out exchange with another proton of the molecule and subsequent tautomerization of the double bond.

**Equilibration of 5-ethoxy-cyclopentenone**

Equilibration of this compound in 0.05 N. basic D$_2$O was inconclusive due to polymerization. After two hours there was no evidence of exchange taking place, but polymerization had proceeded to such an extent that later spectra were not well resolved. The solution became yellow and a white precipitate formed.

The spectrum of 5-ethoxy-cyclopentenone in 0.9 N. acidic D$_2$O remained unchanged during 60 hours. The solution remained clear and colorless.

**Equilibration of 3,4-diethoxy-cyclopentenone**

The equilibration of this compound was carried out in D$_2$O made basic to 0.25 N. by the addition of Na$_2$CO$_3$. NMR spectra were taken at intervals. A study of the spectra, however, does not lead to a clear conclusion as to whether exchange is taking place in preference to elimination of ethanol from the molecule.

Spectra taken during the first several hours showed little change except for a slight lessening of intensity of the AB octet. The HOD peak maintained its original intensity. Direct observation of the methinyl
proton of the ABX system was not possible since its absorption was largely obscured by the HOD peak.

After nine hours a weak new quartet could be observed intermingled with, and slightly upfield of, the corresponding peaks of the methylene quartet of the ethoxy group on carbon 4. The newly emerging quartet continued to slowly increase in intensity. The HOD peak also became more intense and the AB octet continued to slowly diminish.

After 45 hours the AB octet was still clearly discernable but it had diminished to about one-half its original intensity. The HOD peak had continued to increase in intensity as had the emerging methylene quartet which had by now attained about \( \frac{1}{4} \) the intensity of the original upfield methylene quartet. There were also indications of a new triplet intermingled with, and slightly upfield of, the original upfield methyl group triplet. All the other peaks had retained approximately their original intensity and splitting. The solution became yellow, but no precipitation occurred.

It would appear that both exchange and elimination are taking place at relatively slow rates. In any event, the exchange of the proton on the carbon alpha to the carbonyl group is taking place at a much slower rate than in the case of cyclopentenone.

To test the conclusion that ethanol is slowly being eliminated from the molecule, a solution of 3,4-diethoxy-cyclopentenone in basic D\textsubscript{2}O was prepared as above except that 10 \( \mu \text{L} \) of ethanol were added. The NMR spectrum of this prepared solution was similar with respect to line positions to that obtained above after 45 hours of equilibration. The
added ethanol had produced a new quartet in the same position, and of similar intensity, as that of the newly formed quartet mentioned above. A new methyl triplet was produced slightly upfield from the original upfield methyl quartet.

**Equilibration of 4-acetoxy-cyclopentenone in basic D₂O**

The equilibration of this compound was followed in D₂O made basic to 0.75 N. by the addition of Na₂CO₃.

An NMR spectrum taken in the interval ½-minute to 2 minutes after base addition showed the appearance of a new strong singlet about 15 cps upfield from the acetoxy methyl peak. This new peak was approximately one-half the intensity of the original methyl peak. The new peak rapidly increased in intensity and became equal to the original methyl peak after twelve minutes. By this time the solution had become bright yellow and cloudy.

After twenty-four hours the new methyl peak was more intense than the old methyl peak by a factor of about three to one. The rate of growth of the peak had slowed considerably in the past twelve hours. The β-vinyl and methinyl clusters had remained much the same or slightly diminished in intensity. The HOAc peak had increased only slightly. The α-vinyl cluster showed the presence of some new peaks on the upfield side. The AB octet had diminished somewhat in intensity and some new peaks and broad low intensity absorption had arisen in this region.

To ascertain if the new peak was due to the formation of acetic acid a blank run of 8 µL of acetic acid in 400 µL of the base solution
used in the equilibration was prepared. The NMR spectrum of this prepared solution showed a methyl group singlet that coincided exactly with that of the new peak described above.

The immediate appearance of the acetic acid peak in the spectrum indicates that elimination occurs very rapidly in the case of 4-acetoxy-cyclopentenone. That elimination takes place is supported by the fact that when a sodium carbonate solution is slowly added to an aqueous solution of the acetoxy-enone a bridged carbonyl peak appears at 5.63 microns in the IR spectrum. This indicates elimination and Diels-Alder dimerization is probably taking place.

Cyclopentenone Photodimer

The photodimerization of cyclopentenone is outlined in Figure 14. The product of the irradiation should be one or more of four possible isomers: head-to-head cis or trans; and head-to-tail cis or trans.

The NMR spectrum of the photodimer shows all the absorption lines of the twelve protons to be grouped in the approximate range \( \gamma = 7.0-8.0 \). The complexity of so many intermingled absorption patterns prevents a comprehensive interpretation of this spectrum.

\[ \text{Cyclopentenone Photodimer} \]

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The NMR spectrum of the photodimer shows all the absorption lines of the twelve protons to be grouped in the approximate range \( \gamma = 7.0-8.0 \). The complexity of so many intermingled absorption patterns prevents a comprehensive interpretation of this spectrum.

\[ \text{Cyclopentenone Photodimer} \]

The photodimerization of cyclopentenone is outlined in Figure 14. The product of the irradiation should be one or more of four possible isomers: head-to-head cis or trans; and head-to-tail cis or trans.

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The NMR spectrum of the photodimer shows all the absorption lines of the twelve protons to be grouped in the approximate range \( \gamma = 7.0-8.0 \). The complexity of so many intermingled absorption patterns prevents a comprehensive interpretation of this spectrum.
In an attempt to clarify the structure of the photodimer, it was treated with trifluoroperacetic acid and the dilactone derivative obtained. The expected structure of the dilactone is the one in which the oxygens are inserted into the cyclopentane rings in a position adjacent to the cyclobutane ring as shown in Figure 15.

![Dilactone derivative of the photodimer of cyclopentenone](image)

Figure 15. Dilactone derivative of the photodimer of cyclopentenone

The NMR spectrum of the dilactone is more informative. The absorption lines are spread over a longer range of the spectrum and thus it is possible to surmise the protons responsible for the various absorption clusters.

In examining the spectrum of the dilactone the first group encountered is a sharp quartet centered at \( \tau = 5.23 \). The fact that only four lines are present and also that the cluster is shifted noticeably downfield from the other absorption leads one to assign this quartet to the two tertiary protons adjacent to the ester groupings. The splittings
of the quartet are 4.1 and 8.3 cps.

The next cluster upfield is an octet, the four inner lines of which are more intense than the outer lines. Most of the splittings of the octet match well with the splittings of the downfield quartet. This, as well as the fact that the intensities are similar, leads one to assign this octet to the two tertiary protons of the cyclobutane ring that are not adjacent to the ester oxygens.

Immediately upfield from the octet is a series of lines which are presumed to arise from the methylene protons. The series of lines is seen to divide itself into halves, the upfield half consisting of more highly split and less intense peaks. Some of the fine structure of these peaks matches with the fine structure of the octet which had been assigned to the tertiary protons adjacent to the \( \beta \)-methylene protons. These less intense peaks are therefore assigned to the \( \beta \)-methylene protons and the downfield half, containing the more intense peaks are assigned to the methylene group adjacent to the carbonyl grouping.

The protons of the cyclobutane ring of the dilactone derivative would be expected to constitute an \( A_2X_2 \) grouping. The protons adjacent to the ester group oxygens should give rise to the less split downfield portion of the absorption pattern, while the protons adjacent to the \( \beta \)-methylene group would be expected to show absorption at higher field and also to exhibit more splitting.

Examination of the dilactone spectrum is thus undertaken on the assumption that the four sharp downfield peaks arise from the \( A \) protons of an \( A_2X_2 \) system. If this be the case then one should be able to
match this A pattern against the predicted A patterns of the four possible isomers and thus obtain a tentative identification of the correct isomer.

The energies and intensities for the A transitions of the \( A_2X_2 \) patterns of the four possible isomers were calculated and the conclusions are summarized below.

In the case of the head-to-tail cis isomer one would have identical protons opposite one another in the cyclobutane ring. Assuming no coupling occurs across the ring, each A proton would be split only by two identical protons and thus a triplet pattern would be expected.

In the case of the head-to-head cis and head-to-head trans isomers \( J_{AA} = J_{BB} > 0, J_{AB} = 0 \) and \( J_{AB} > 0 \). Calculations made on this basis indicate that six A transitions should arise, two of which are approximately twice as intense as the other four.

In the head-to-tail trans isomer, \( J_{AA} = J_{BB} = 0, J_{AB} = J_{AB}^\prime \) and both are greater than zero. Calculations made on this basis indicate that four A lines of equal intensity should be present.

From this interpretation of the NMR spectrum of the dilactone derivative it would appear that the solid cyclopentenone photodimer may tentatively be assigned as the head-to-tail trans isomer.

There is a very recent report of the irradiation of cyclopentenone

with light above 300 \text{m} \mu \text{ to obtain a photodimer.}^{39} \text{ The abstract of the paper, however, does not mention the stereochemistry of the dimer.}

\footnotesize

SPECTRA

The NMR spectra were taken with a Varian Model HR-60 high-resolution n.m.r. spectrometer.

Chemical shifts were measured with respect to tetramethylsilane as an internal reference using side-bands applied by a calibrated audio oscillator. The spectra were recorded on a Mosely Recorder, Model 2S.

In most instances the tube containing the sample solution was evacuated and sealed so as to minimize line broadening due to O₂ present.

The accuracy of a given absorption line is estimated to be ±0.4 cps.
Figure 16. NMR spectrum of cyclopentenone
25μL / 500μL CC14
Figure 17. Expansion of cyclopentenone spectrum
Figure 18. NMR spectrum of 4-bromo-cyclopentenone
0
Figure 19. Expansion of 4-bromo-cyclopentenone spectrum
Figure 20. NMR spectrum of 4-acetoxy-cyclopentenone
Figure 21. Expansion of 4-acetoxy-cyclopentenone spectrum
Figure 22. NMR spectrum of 5-oxalyl-cyclopentenone
$\text{HOCCOEt}$

100 mg / 500 mL $\text{CCl}_4$

5.68  6.50  8.62
Figure 23. Expansion of 5-oxalyl-cyclopentene spectrum.
Figure 24. NMR spectrum of 5-ethoxy-cyclopentenone
Figure 25. Expansion of 5-ethoxy-cyclopentenone spectrum
Figure 26. NMR spectrum of cyclopentane-1,2-dione
Figure 27. Expansion of cyclopentane-1,2-dione spectrum
Figure 28. NMR spectrum of 3,4-disthoxycyclopentenone
Figure 29. Expansion of 3,4-diethoxy-cyclopentenone spectrum
Figure 30. NMR spectrum of ethylene ketal of cyclopentenone
Figure 31. Expansion of cyclopentanone ketal spectrum
Figure 32. NMR spectrum of cyclopentene-3,5-dione
$\text{50MG/400\mu L CDCl}_3$
Figure 33. NMR spectrum of dicyclopentadienone
U I 4C0m

C. 3M / 400μL CDCl₃
Figure 34. Expansion of dicyclopentadienone spectrum
Figure 35. NMR spectrum of 2-methyl-cyclopent-2-enone
Figure 36. Expansion of 2-methyl-cyclopent-2-enone spectrum