

1961

Nuclear magnetic resonance study of cyclopentenone and some of its derivatives

Charles Edward Lyons
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Organic Chemistry Commons](#)

Recommended Citation

Lyons, Charles Edward, "Nuclear magnetic resonance study of cyclopentenone and some of its derivatives " (1961). *Retrospective Theses and Dissertations*. 1975.
<https://lib.dr.iastate.edu/rtd/1975>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

This dissertation has been 62-1359
microfilmed exactly as received

LYONS, Charles Edward, 1929-
NUCLEAR MAGNETIC RESONANCE STUDY OF
CYCLOPENTENONE AND SOME OF ITS DERIVA-
TIVES.

Iowa State University of Science and Technology
Ph.D., 1961
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

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
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1961

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	2
DISCUSSION	12
SPECTRA	61
EXPERIMENTAL	91
SUMMARY	96
ACKNOWLEDGEMENTS	97
APPENDIX	98

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-workers³ 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. ^1H , ^{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

¹E. M. Purcell, H. C. Torrey and R. V. Pound, Phys. Rev., 69, 37 (1946).

²F. Bloch, W. W. Hansen and M. Packard, Phys. Rev., 69, 127 (1946).

³J. T. Arnold, S. S. Dharmatti and M. E. Packard, J. Chem. Phys., 19, 507 (1951).

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

⁵A recent comprehensive treatment of NMR theory may be found in J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959.

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, ΔE , 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 calculated⁶ that at 300°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

⁶J. D. Roberts, Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959, p. 9.

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 Tiers⁷ has introduced the quantity τ 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 τ , 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.*⁸ have been widely adopted. Groups of equivalent nuclei for which the chemical shifts and coupling constants are of the same order are symbolized by $A_n, B_m \dots$ where the subscripts refer to the number of nuclei in the group. If the groups of nuclei A, B, etc. are coupled to other nuclei, the chemical shifts of which are very different from A, B, etc., the latter are symbolized by X_n, Y_m , etc.

⁷G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

⁸H. J. Bernstein, J. A. Pople and W. G. Schneider, *Canad. J. Chem.*, **35**, 65 (1957).

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 $E = J_{ij} [I_i \cdot I_j]$ 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_1 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_1 as follows: $E' = \gamma_i H_1 I_{i(z)}$ where $2\pi\gamma_i = \delta_i$, 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

⁹H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys., 23, 1152 (1955).

¹⁰H. Conroy. Nuclear Magnetic Resonance, in R. A. Raphael, E. C. Taylor and H. Wynberg, eds. Advances in Organic Chemistry, Vol. 2, New York, N.Y., Interscience Publishers, Inc., 1960, p. 296.

¹¹H. S. Gutowsky, D. W. McCall and C. P. Slichter, J. Chem. Phys., 21, 279 (1953).

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 $\sum_i \gamma_i \cdot H_1 I_{1i}(z) + \sum_{i < j} I_{1i} [I_{1i} \cdot I_{1j}]$ 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_{1i} and I_{1j} . In order to find the discrete values of energy and hence the characteristic nuclear magnetic resonance frequencies $\nu = \frac{\Delta E}{h}$, the Schrodinger equation must be used. Its form is $\mathcal{H}\psi = E\psi$ where E can take the desired discrete values, ψ 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 ψ 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.¹² 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

¹²C. A. Coulson, Valence, Oxford, England, University Press, 1953, pp. 54-67.

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 τ 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, τ -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 A₂B₂ 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.

¹³Bernstein, Pople and Schneider, op. cit.

¹⁴Pople, Schneider and Bernstein, op. cit.

¹⁵P. L. Corio, Chem. Revs., 60, 363 (1960).

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.

¹⁶H. Primas, K. Frei, Hs. H. Günthard, Helv. Chim. Acta, 41, 35 (1958).

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.

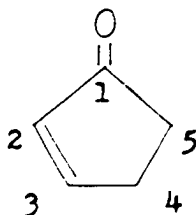


Figure 1. Designation of the carbons of the cyclopentenone ring

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

Examination of the spectrum shows the first cluster encountered to be a sextet centered at 457.8 cps or a τ -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 β -vinyl one. The absorption cluster appears as two triplets due to spin-spin coupling of the β -vinyl proton with the β -methylene protons and with the α -vinyl proton. The triplet pattern arises originally from the interaction of the β -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 β -vinyl and α -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 β -vinyl proton. It is also a sextet consisting of two triplets and is centered at a τ -value of 3.89. This cluster is assigned to the α -vinyl proton. Again the three spin arrangements of the β -methylene protons couple with the α -vinyl proton so as to produce a triplet

absorption pattern. This triplet is, in turn, split by coupling of the α -vinyl proton with the β -vinyl proton. The spin coupling constants are calculated to be $J_{24} = 2.2$ cps and $J_{23} = 5.8$ cps. As would be expected the α -vinyl and β -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 comprise 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

¹⁷J. A. Pople, W. G. Schneider and H. J. Bernstein, Canad. J. Chem., **35**, 1060 (1957).

¹⁸J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959, p. 138.

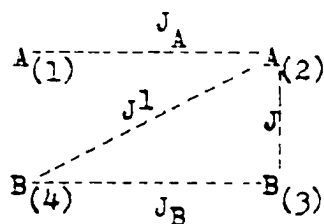


Figure 2. Spin-coupling constants for four nuclei, A_2B_2

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 evaluated¹⁹ and values of the diagonal and off-diagonal elements given in terms of ν_A , ν_B , K, L, M and N. $\nu_A > \nu_B$ where ν_A and ν_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 + 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 β -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

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, 131.8, 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.

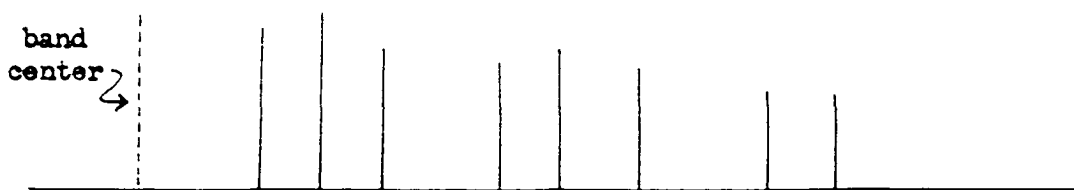


Figure 3. Schematic representation of the upfield half of the A_2B_2 pattern of cyclopentenone

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 spectrum²⁰ and is shown as Figure 4. The energies of the twelve theoretical A transitions have been calculated by Pople *et al.*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 $\nu_0\delta$ (which is $\nu_A - \nu_B$) and N (which is $J + J'$) may be determined

²⁰*Ibid.*, p. 147.

²¹*Ibid.*, p. 144.

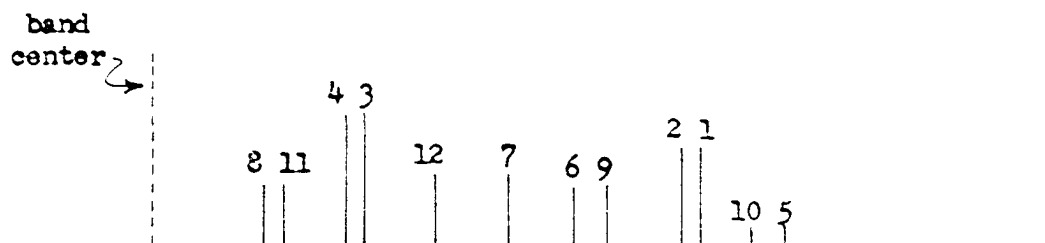


Figure 4. Schematic representation of the general case of the A_2B_2 pattern

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

Transition	Energy relative to $\frac{1}{2}(\nu_A + \nu_B)$
1. $1s_1' \rightarrow s_2$	$\frac{1}{2}N + \frac{1}{2}[(\nu_0 S)^2 + N^2]^{\frac{1}{2}}$
3. $s_{-2} \rightarrow 1s_{-1}'$	$-\frac{1}{2}N + \quad "$
9. $2a_0' \rightarrow 2a_1'$	$\frac{1}{2}[(\nu_0 S + M)^2 + L^2]^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$
10. $2a_{-1}' \rightarrow 1a_0'$	$\frac{1}{2}[(\nu_0 S - M)^2 + L^2]^{\frac{1}{2}} + \quad "$
11. $1a_0' \rightarrow 2a_1'$	$\frac{1}{2}[(\nu_0 S + M)^2 + L^2]^{\frac{1}{2}} - \quad "$
12. $2a_{-1}' \rightarrow 2a_0'$	$\frac{1}{2}[(\nu_0 S - M)^2 + L^2]^{\frac{1}{2}} - \quad "$

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:

$$17.3 = \frac{1}{2}N + \frac{1}{2}[(\nu_0\delta)^2 + N^2]^{\frac{1}{2}}$$

$$8.1 = -\frac{1}{2}N + \quad "$$

one obtains a value of 24.0 cps for $\nu_0\delta$ and 9.7 cps for N.

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 $J = J'$.²² Also, lines 5 and 8 are effectively forbidden. One may thus refer to a table of energies of transitions for the case $J = J'$

²²J. A. Pople, W. G. Schneider and H. J. Bernstein, Canad. J. Chem., 35, 1064 (1957).

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 $J / \nu_0 \delta$ is $4.8 / 24.0 = 0.2$. This ratio is used to ascertain the energies of transition as tabulated in Pople *et al.*²³ 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 calculated transitions correspond exactly with the two remaining lines of the actual spectrum.

²³J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959, p. 144.

Table 2. Calculated and actual transitions of the upfield cluster of the A_2B_2 spectrum of cyclopentenone

Transition	Calculated energy	Actual spectrum lines
4	139.1	139.4
3	138.4	138.4
		136.6
6	133.9	134.1
7	133.2	133.0
		131.8
2	129.8	129.6
1	128.8	128.7

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, $L = \pm 4.7$ cps, $N = \pm 0-1$ 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 $\tau = 2.39$. This cluster is assigned to the most deshielded proton, i.e. the β -vinyl one. The splitting of 5.5 cps and 2.6 cps is caused by coupling with the α -vinyl proton and the methinyl proton, respectively.

The next cluster upfield is a quartet centered at $\tau = 3.79$ and assigned to the α -vinyl proton. The splitting of 5.7 cps and 1.2 cps arises from coupling with the β -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.^{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.

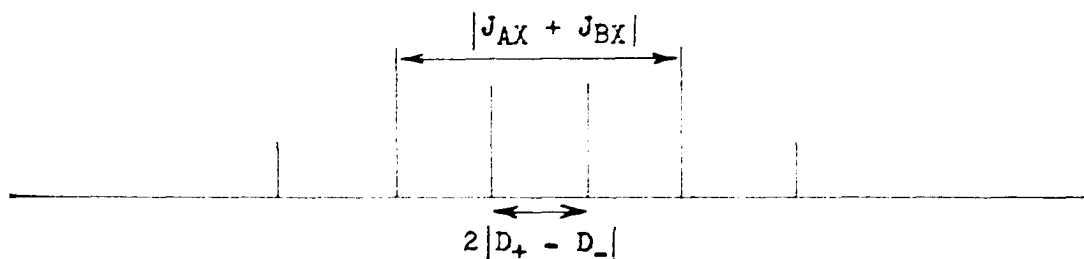


Figure 5. Theoretical X pattern of the ABX grouping

²⁴Ibid., p. 132.

²⁵H. J. Bernstein, J. A. Pople and W. G. Schneider, Canad. J. Chem., **35**, 65 (1957).

Expansion of the X 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 β -vinyl proton, and once, 1.3 cps, by the α -vinyl proton. $|J_{AX} + J_{BX}|$ is calculated to be 8.3 cps and $2|D_+ - D_-|$ to be 3.0 cps.

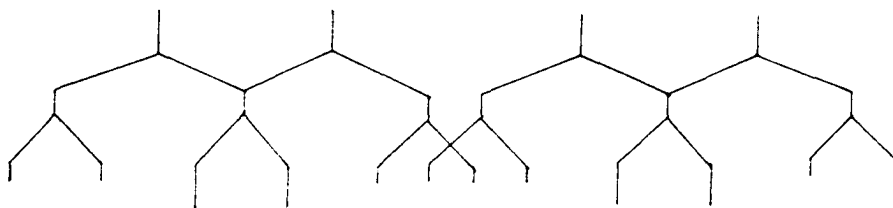


Figure 6. X pattern of the ABX grouping of 4-bromo-cyclopentenone

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.

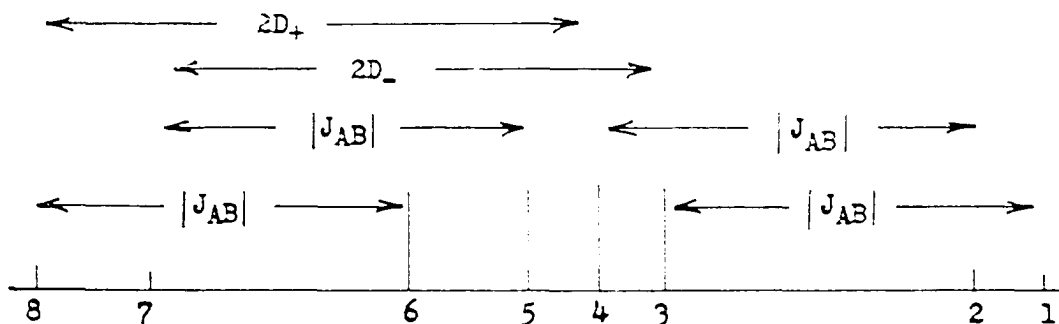


Figure 7. The AB pattern of the ABX grouping of 4-bromo-cyclopentenone

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 $(\nu_A - \nu_B)$ and $(J_{AX} - J_{BX})$ may be obtained by use of the following definitions:²⁶

$$D_+ \cos 2\phi_+ = \frac{1}{2}(\nu_A - \nu_B) + \frac{1}{4}(J_{AX} - J_{BX})$$

$$D_+ \sin 2\phi_+ = \frac{1}{2}J_{AB}$$

$$D_- \cos 2\phi_- = \frac{1}{2}(\nu_A - \nu_B) - \frac{1}{4}(J_{AX} - J_{BX})$$

$$D_- \sin 2\phi_- = \frac{1}{2}J_{AB}$$

²⁶J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959, p. 133.

By substituting values obtained for D_+ , D_- , and $\frac{1}{2}J_{AB}$ into the above equations one obtains $(\nu_A - \nu_B) = 19.1$ 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,²⁷ the γ -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

²⁷Ibid., 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 β -vinyl proton. J_{32} is calculated to be 5.5 cps and J_{34} is 2.4 cps.

The α -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 methinyl or X 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.

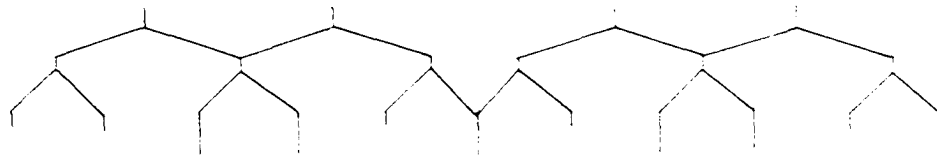


Figure 8. The X pattern of the ABX grouping of 4-acetoxycyclopentenone

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 τ -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 cyclopentanone 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 τ -value is -2.7.

The next upfield cluster is assigned to the β -vinyl proton. The cluster consists of two triplets and is centered at $\tau = 2.44$. The triplets arise from coupling with the methylene group and with the α -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 α -vinyl proton. Expansion shows it to also consist of two triplets. The cluster is centered at $\tau = 3.64$ and the coupling constants are $J_{23} = 6.0$ and $J_{24} = 2.0$ cps.

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

Between the above mentioned quartet and triplet is a triplet at $\tau = 6.50$. 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-cyclopentanone

The NMR spectrum of 5-ethoxy-cyclopentanone 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_2O 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_2O . Tau values are solvent dependent and thus values obtained in D_2O 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_2O , and the HOD peak, in turn, calibrated against a capillary of benzene ($\tau = 2.74$) placed inside the sample tube.

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

The α -vinyl proton is centered at $\tau = 2.95$ 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_2O causes the sharp peak at $\tau = 4.50$.

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

The quartet centered at $\tau = 5.47$ and the triplet at $\tau = 7.98$ 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 $\tau = 6.33$ 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_2O are shifted considerably downfield from the values obtained using CCl_4 as solvent. In CCl_4 the β -vinyl proton absorbs at $\tau = 2.49$ and the α -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.²⁸ Examination of the NMR spectrum shows a broad, low peak at the downfield end. This peak, centered at $\tau = 3.19$, is assigned to the hydroxyl proton.

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

The intense upfield peak centered at $\tau = 7.56$ 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 α -vinyl proton, an ABX grouping and two ethoxy groups.

The olefinic proton appears as a singlet with a τ -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 $\tau = 5.63$. This is assigned to the methinyl or X proton of the ABX pattern.

²⁸G. Hesse and E. Bücking, Ann., 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 $\tau = 6.39$. 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-bromocyclopentenone 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 $\tau = 7.45$ and 7.79.

Farther upfield are the two triplet groupings of the two methyl groups. The triplet centered at $\tau = 8.55$ is assigned to the ethoxy group on carbon 3 and that centered at $\tau = 8.81$ 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 τ -values. The spectrum confirms this expectation.

The first downfield cluster appears as a pair of triplets centered at $\tau = 4.04$. 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 $\tau = 4.42$ and the coupling constants are $J_{32} = 5.6$ cps and $J_{34} = 2.0$ cps.

The intense singlet at $\tau = 6.17$ 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.

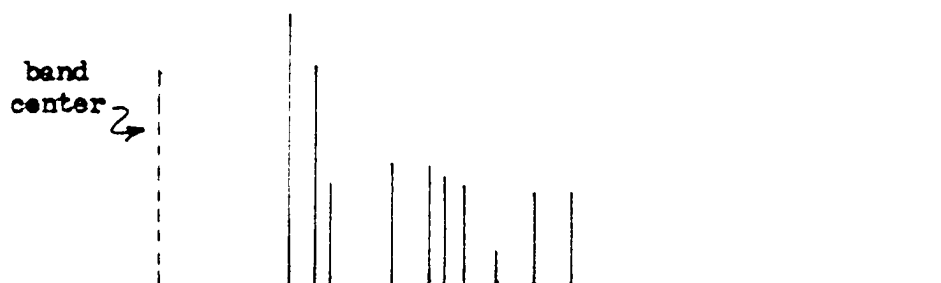


Figure 9. Schematic representation of the upfield half of the A_2B_2 pattern of the cyclic ethylene ketal of cyclopentenone

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 $\nu_0 S = 22.4$ cps. 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 data²⁹ 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 τ -values of 8.04 and 7.67.

²⁹J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959, p. 144.

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

Transition	Calculated energy (cps)	Actual spectrum lines (cps)
4	123.6	123.6
3	122.5	122.2
		121.4
		118.4
6	116.3	117.0
		116.1
7	114.7	114.9
		113.3
2	111.2	111.4
1	109.0	109.8

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 $\tau = 2.69$ is assigned to the vinyl protons and the peak at $\tau = 7.10$ to the methylene protons.

Gutowsky *et al.*³⁰ have recorded the spectrum of this compound

³⁰H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1282 (1959).

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, $\tau = 2.77$.

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

The NMR absorption of this compound, which is the Diels-Alder adduct of cyclopentadienone, occurs in three main groupings. Farthest downfield is the absorption grouping caused by the β -vinyl proton of the cyclopentenone ring. The next upfield grouping is more complex and contains the patterns arising from the α -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 β -vinyl proton of the cyclopentenone ring and centered at $\tau = 2.58$. 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 α -vinyl proton of the cyclopentanone ring would be expected to produce a quartet with $J_{23} = 5.6$ cps. Examination of the four major downfield peaks of the second absorption grouping show them to fit this specification well. Assignment of these four peaks to the α -vinyl proton gives a τ -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 cyclopentanone 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-ene³¹ show a quite similar but

³¹C. H. DePuy, Ames, Iowa, NMR spectrum of 7-isopropylidene-bicyclohept-2-ene, Private communication, 1961.

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 cps. 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 β -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 β -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 α -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 $\tau = 2.79$. This

multiplet is split by coupling with the protons of both the methyl and β -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

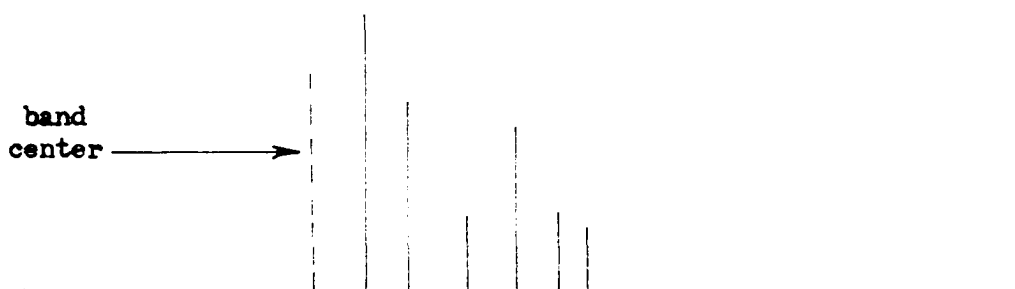


Figure 10. Schematic representation of the upfield half of the A_2B_2 pattern of 2-methyl-cyclopent-2-enone

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 $J / \nu_0 S$ 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

Transition	Calculated energy (cps)	Actual spectrum lines (cps)
4	141.4	140.5
3	140.5	138.6
6	136.6	136.2
7	133.8	133.5
2	132.1	131.7
1	129.9	130.0

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 α -methylene group is centered at $\tau = 7.72$ and the β -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. $J_{Me,4}$ is 1.9 cps and $J_{Me,3}$ is also 1.9 cps.

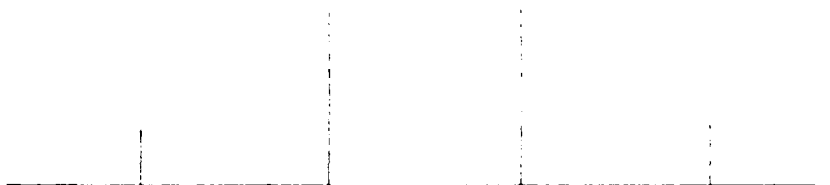


Figure 11. Schematic representation of the methyl absorption cluster of 2-methyl-cyclopent-2-enone

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

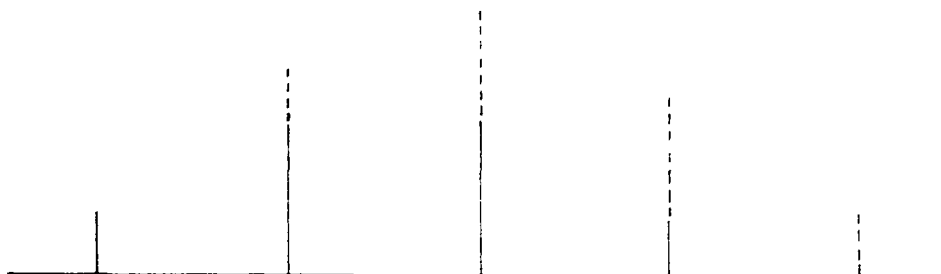


Figure 12. Schematic representation of the methylene absorption cluster of 2-methyl-4-diazo-cyclopent-2-enone

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 $\tau = 8.20$. 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.

Generalizations 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, dependant 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 CCl_4 .

Compound	Tau value	J_{23} (cps)	J_{24} (cps)
Dicyclopentadienone	3.63 ^a	5.7	1.3
5-Oxalyl-cyclopentenone	3.64	6.0	2.0
4-Acetoxy-cyclopentenone	3.75	5.7	1.3
4-Bromo-cyclopentenone	3.79	5.7	1.2
Cyclopentenone	3.89	5.8	2.2
5-Ethoxy-cyclopentenone	3.95	5.9	2.1
3,4-Diethoxy-cyclopentenone	4.81	-	-

^aIn CDCl_3 .

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 prepared³² 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.

β -vinyl protons

The chemical shifts and coupling constants of the β -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 α -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 β -vinyl proton.

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

³²J. F. Fitzpatrick, Ames, Iowa, NMR spectrum of 4-dimethylamino-cyclopentenone, Private communication, 1961.

Table 6. Chemical shifts and coupling constants of the β -vinyl proton of some cyclopentenones in CCl_4

Compound	Tau value	J_{34} (cps)
1-Methyl-cyclopentene-4,5-dione	2.28 ^a	2.6
Cyclopentenone	2.37	2.6
4-Bromo-cyclopentenone	2.39	2.6
5-Oxalyl-cyclopentenone	2.44	2.3
4-Acetoxy-cyclopentenone	2.49	2.4
5-Ethoxy-cyclopentenone	2.49	2.8
Dicyclopentadienone	2.58 ^a	2.5
2-Methyl-cyclopent-2-enone	2.79	
2-Methyl-4-diazo-cyclopent-2-enone	3.29	2.2
2-Hydroxy-cyclopent-2-enone	3.54	2.5

^aIn CDCl_3 .

substitution.

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 cyclopentenones in CCl_4

Compound	Tau value
4-Acetoxy-cyclopentenone	4.22
4-Bromo-cyclopentenone	4.87
3,4-Diethoxy-cyclopentenone	5.63
5-Ethoxy-cyclopentenone	6.33 ^a
2-Methyl-4-diazo-cyclopentenone	6.43
5-Oxalyl-cyclopentenone	6.50
Dicyclopentadienone	6.70 ^b
1-Methyl-cyclopentene-4,5-dione	6.97 ^b
Cyclopentenone	7.36
2-Methyl-cyclopentenone	7.49
2-Hydroxy-cyclopent-2-enone	7.56

^aIn D_2O .

^bIn CDCl_3 .

4-position is monosubstituted as in the case of 4-bromo or 4-acetoxy-cyclopentenone. 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 A_2B_2 system the absorption varies within the range $\tau = 7.36-7.56$. The substitution of a methyl group for the α -vinyl proton somewhat compresses the A_2B_2

spectrum of cyclopentenone 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 A_2B_2 pattern virtually coalesces at $\tau = 7.56$.

Protons on carbon 5

The protons on carbon 5 of the compounds examined are, with one exception, part of either an ABX or A_2B_2 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 CCl_4

Compound	Tau value	J_{55} (cps)	J_{AX} (cps)	J_{BX} (cps)
4-Bromo-cyclopentenone	7.05 7.37	19.3	6.4	1.8
4-Acetoxy-cyclopentenone	7.28 7.79	18.6	6.4	2.4
3,4-Diethoxy-cyclopentenone	7.45 7.79	19.5	6.5	2.3
5-Ethoxy-cyclopentenone	4.98 ^a			
Dicyclopentadienone	7.04 ^b			
2-Hydroxy-cyclopent-2-enone	7.56			
2-Methyl-cyclopent-2-enone	7.72		7.7	3.0
Cyclopentenone	7.76		7.2	2.5

^aIn D_2O .

^bIn $CDCl_3$.

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 α -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.

³³H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

³⁴M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

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

Compound	J_{AB} (cps)	H-C-H
4-Bromo-cyclopentenone	19.3	106°
4-Acetoxy-cyclopentenone	18.6	106°
3,4-Diethoxy-cyclopentenone	17.6	107°

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°. Conroy³⁵ 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 predicted³⁶ 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

³⁵Conroy, op. cit., pp. 308-311.

³⁶Karplus, op. cit., p. 11.

Table 10. Predicted dihedral angle H-C-C-H in three cyclopentenones

Compound	J_{AX} (cps)	Dihedral angle	J_{BX} (cps)	Dihedral angle
4-Bromo-cyclopentenone	6.4	145°	1.8	59°
4-Acetoxy-cyclopentenone	6.4	145°	2.4	56°
3,4-Diethoxy-cyclopentenone	6.5	146°	2.3	56°

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 β -vinyl values.

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

Compound	Tau value
Cyclopenten-3,5-dione	2.69
4,4-Dibromo-cyclopenten-3,5-dione	2.77

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 CCl_4

Compound	Tau-values			$J_{\text{Me},4}$ (cps)	$J_{\text{Me},3}$ (cps)	J_{43} (cps)
	-CH ₃	C ₃ -H	C ₄ -H			
2-Methyl-cyclopent-2-enone	8.29	2.79	7.49	1.9	1.9	
2-Methyl-4-diazo-cyclopent-2-enone	8.20	3.29	6.43	1.9	1.9	2.2
1-Methyl-cyclopentene-4,5-dione ^a	8.03	2.28	6.97	2.5	1.3	2.6

^aIn CDCl_3 .

The tau-values of the methyl and β -vinyl protons show the expected trends. The absorption of the endione 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 A_2B_2 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, $J_{Me,3}$ has a lower value than in the other two compounds. This lowering of $J_{Me,3}$ 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.³⁷ He points out that in unsaturated systems the π -electron contribution to the long-range coupling constants is much larger than the contribution of the sigma bonds. $J_{HH}(\pi)$ of the protons in the system $H-C=C-C-H$ is calculated to be 2.0 cps.

To clarify the methyl-methylene splitting an attempt was made to exchange the methylene protons in D_2O . The diazo-enone immediately decomposed in basic D_2O . Treatment of the endione in D_2O led to what appears to be addition of D_2O 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

³⁷M. Karplus, J. Am. Chem. Soc., 82, 4432 (1960).

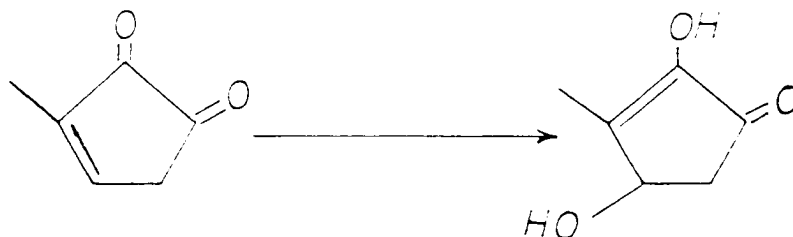


Figure 13. Postulated reaction of 1-methyl-cyclopentene-4,5-dione in D_2O

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

Equilibration of Cyclopentenones in D_2O

Several equilibration experiments involving cyclopentenones were run in D_2O 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_2O made 0.25 N. basic with Na_2CO_3 and also in D_2O made 0.9 N. acidic with HCl. In each case the upfield cluster of the A_2B_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_2B_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 α -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_2O 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_2O 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_2O made basic to 0.25 N. by the addition of Na_2CO_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 D₂O was prepared as above except that 10 μ 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 $\frac{1}{2}$ -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 HOD 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 μ L of acetic acid in 400 μ L of the base solution

In an attempt to clarify the structure of the photodimer, it was treated with trifluoroacetic 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.

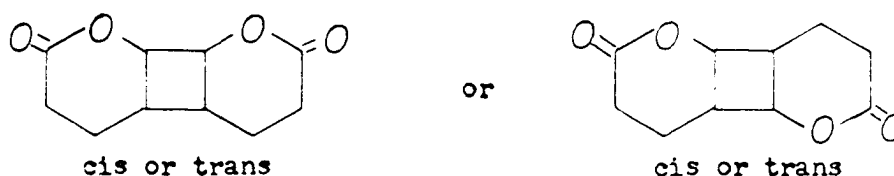


Figure 15. Dilactone derivative of the photodimer of cyclopentenone

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 β -methylene protons. These less intense peaks are therefore assigned to the β -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 β -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 calculated³⁸ 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 $J_{AA} \approx J_{BB} > 0$, $J'_{AB} = 0$ 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, $J_{AA} = J_{BB} = 0$, $J_{AB} = J'_{AB}$ 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

³⁸J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York, N.Y., McGraw-Hill Book Co., Inc., 1959, pp. 140-141.

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

³⁹P. E. Eaton, The Photodimer of Cyclopentenone, 140th National Meeting of the American Chemical Society, Chicago, 1961. Abstract of Papers Presented to the Division of Organic Chemistry, p. 57.

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.

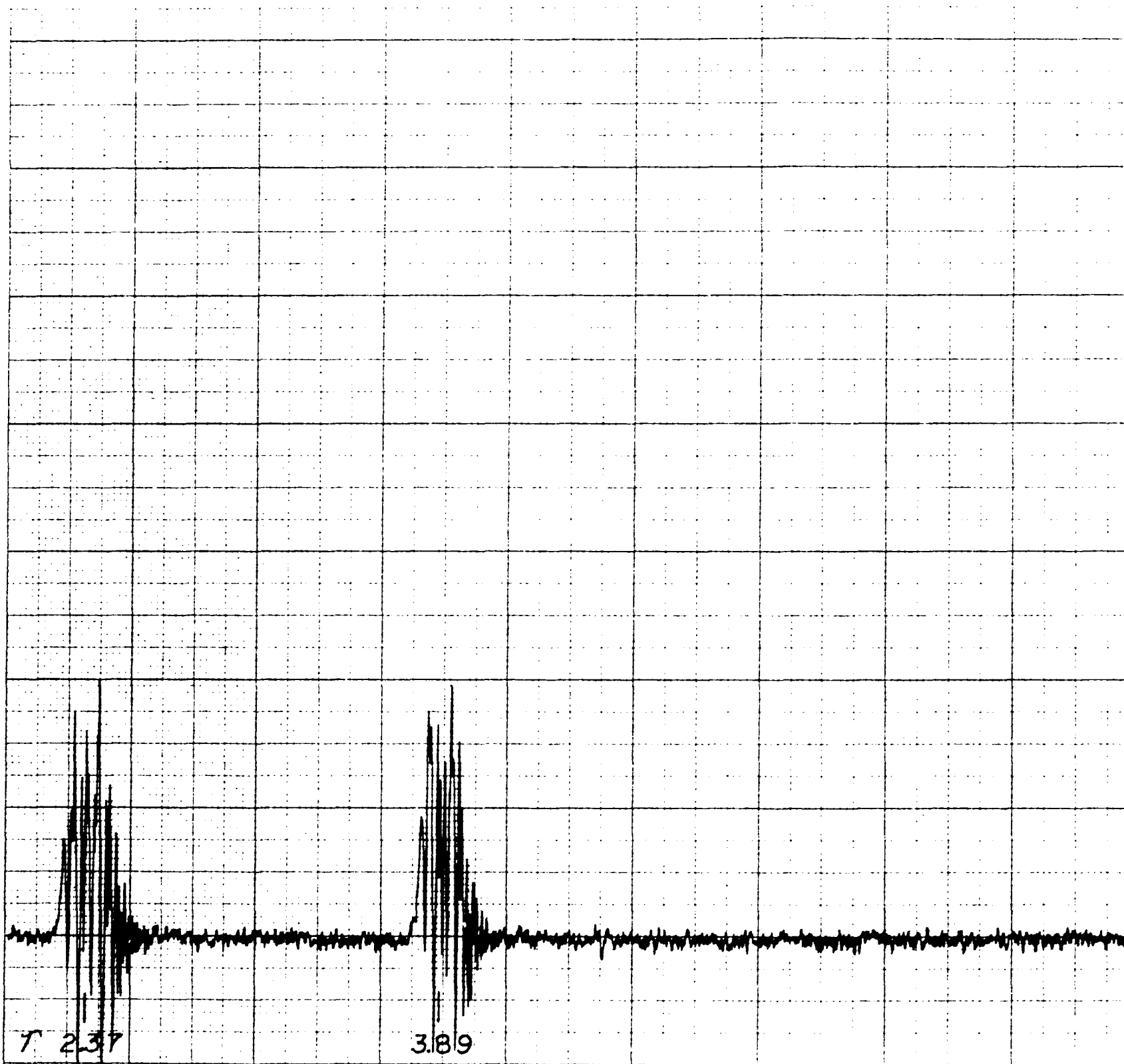
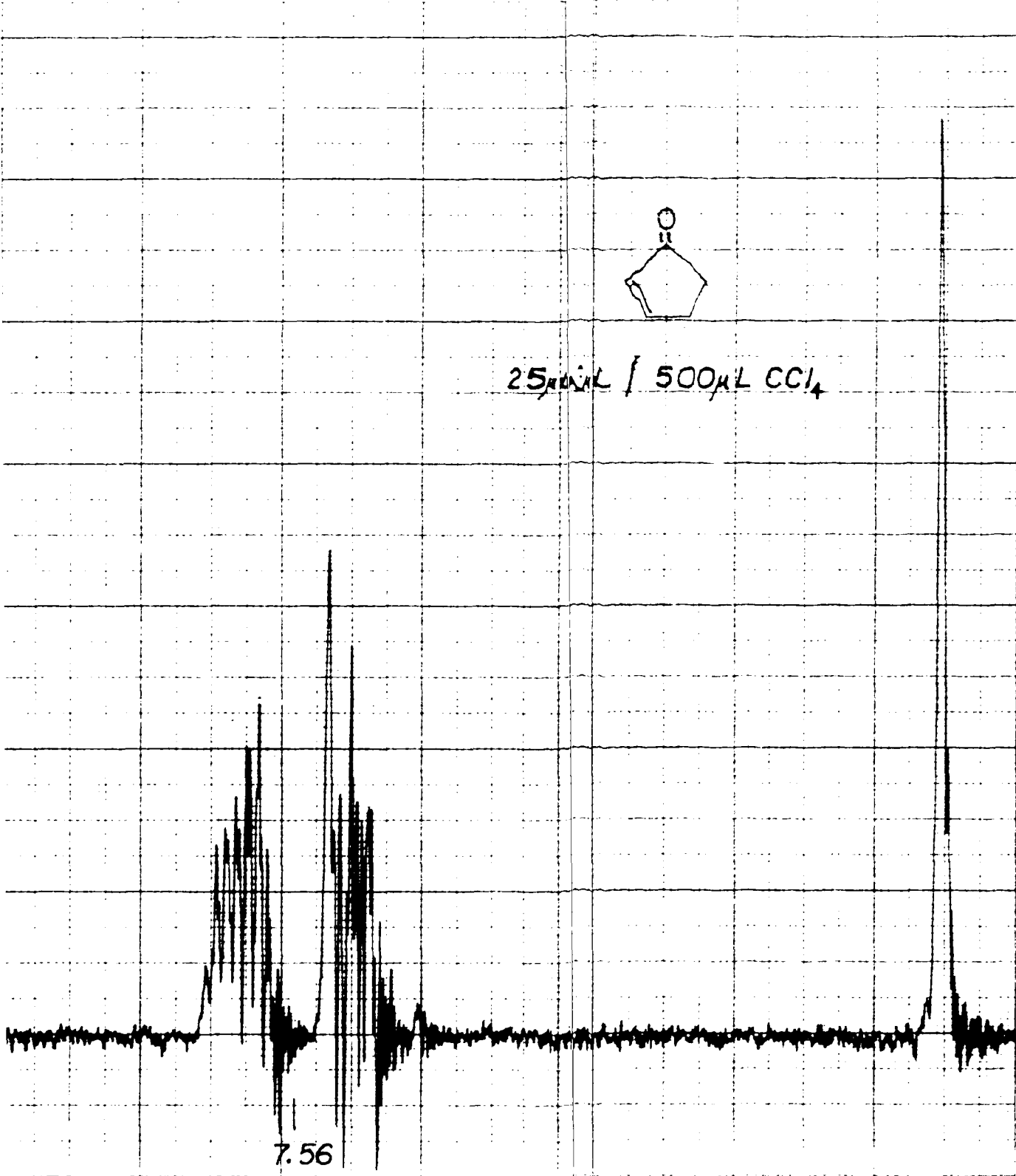


Figure 16. NMR spectrum of cyclopentenone



25 μ L / 500 μ L CCl_4

7.56



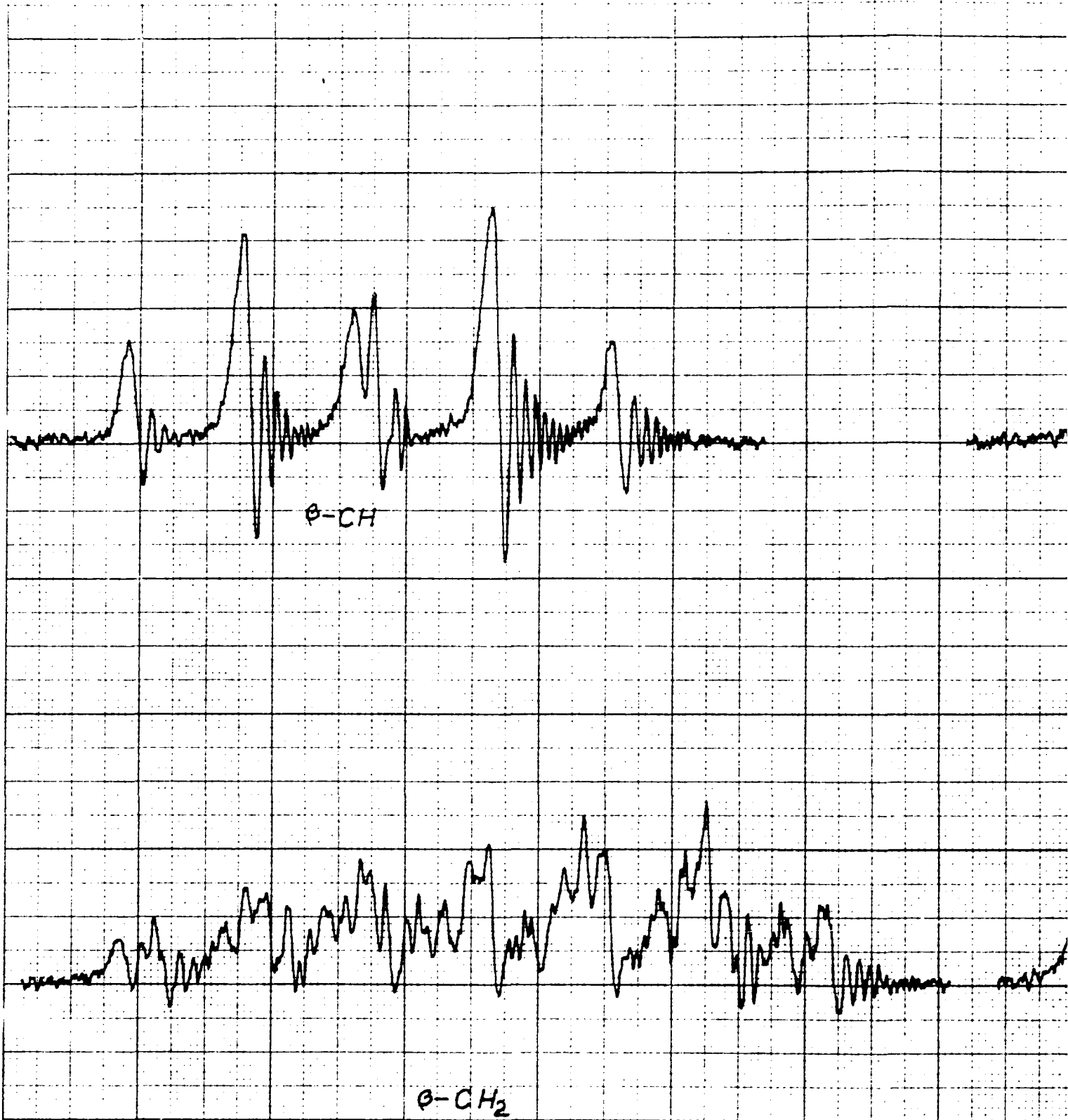
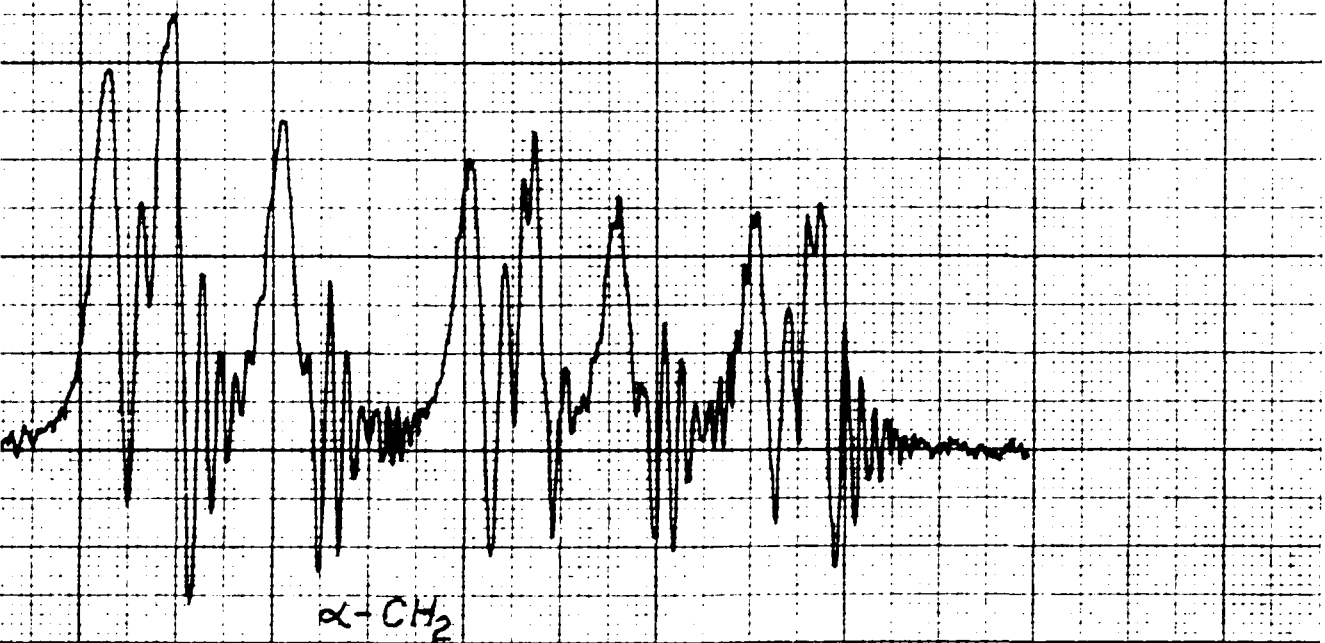
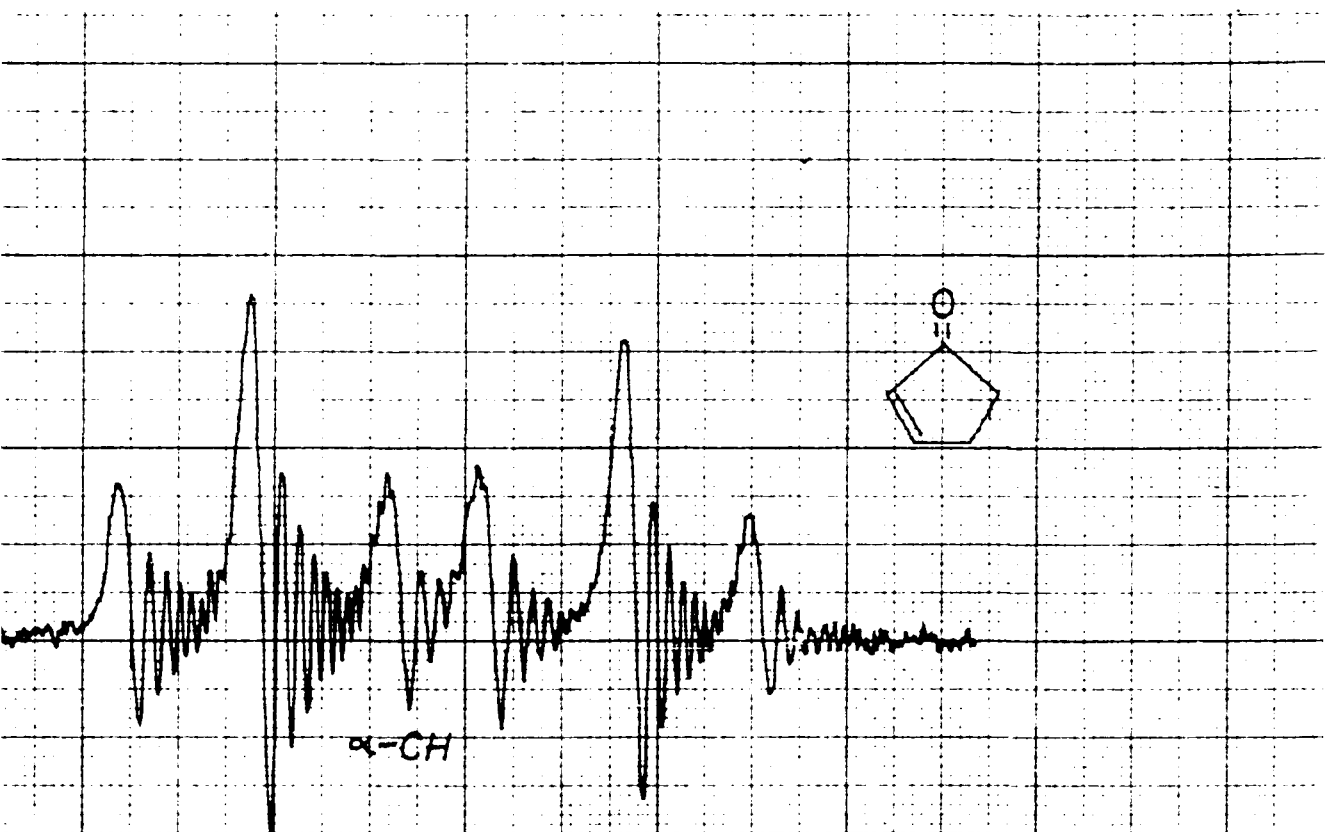


Figure 17. Expansion of cyclopentenone spectrum



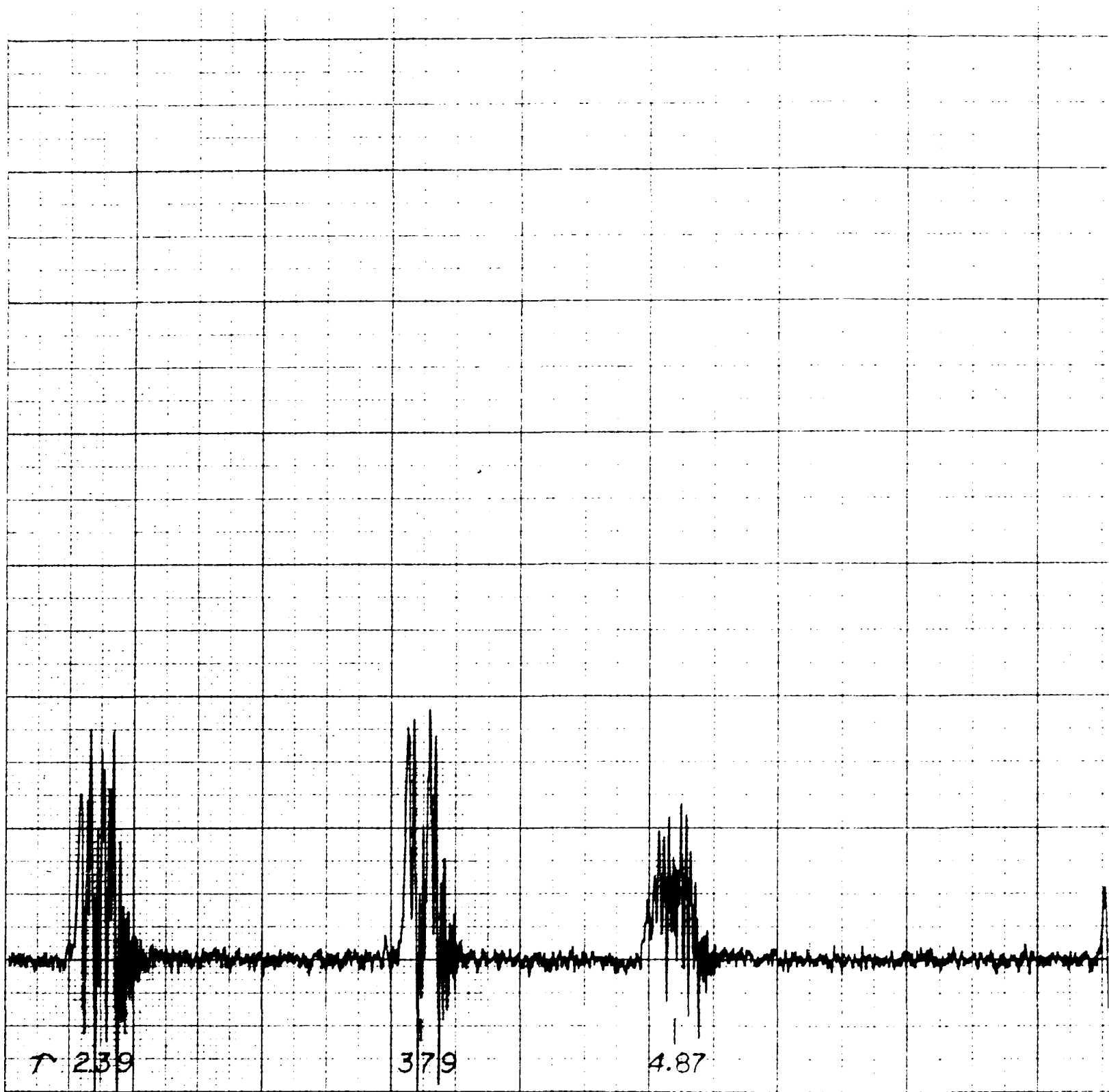
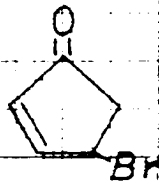


Figure 18. NMR spectrum of 4-bromo-cyclopentenone



30 μ L / 500 μ L CCl₄

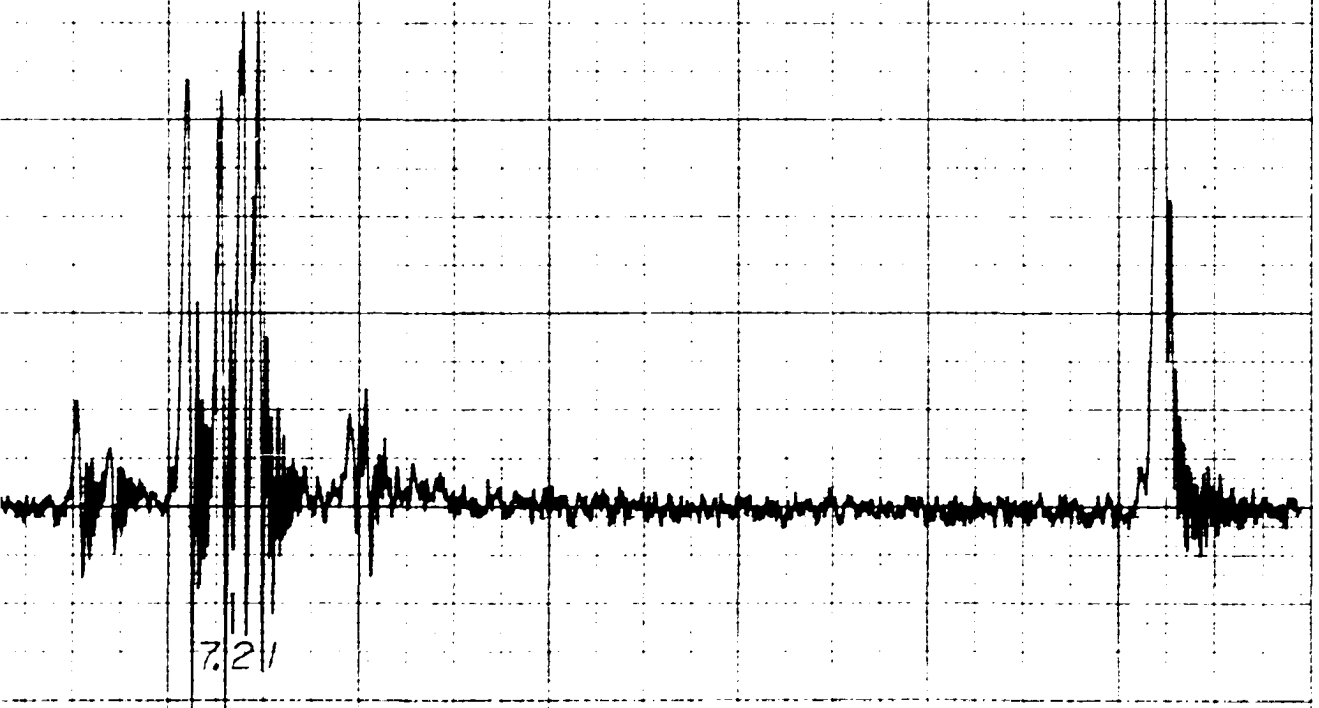
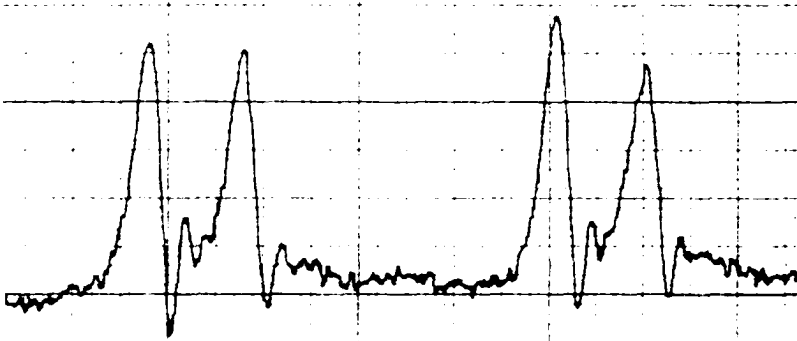
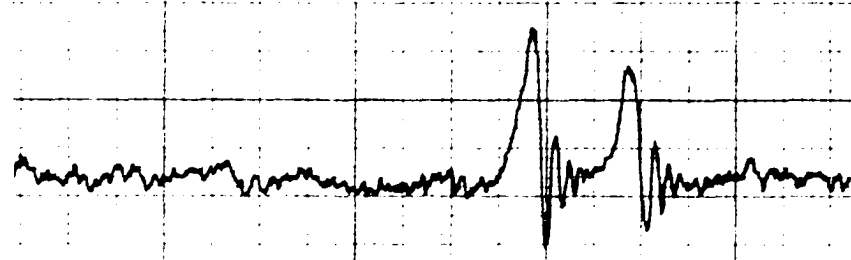
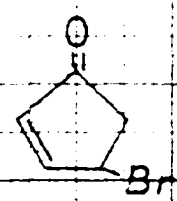
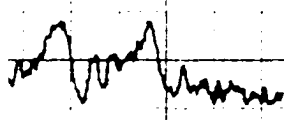




Figure 19. Expansion of 4-bromo-cyclopentenone spectrum



α -CH



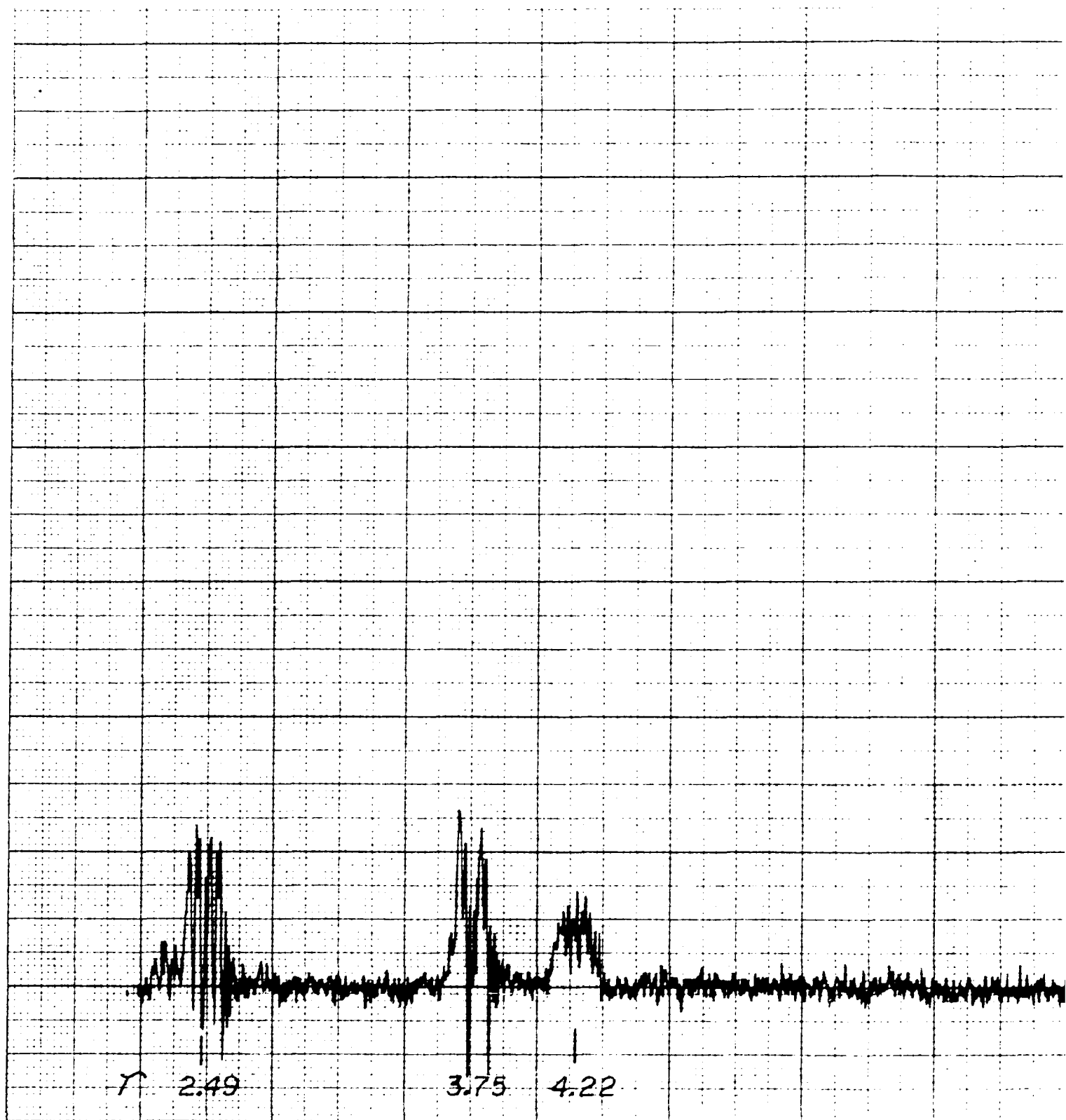
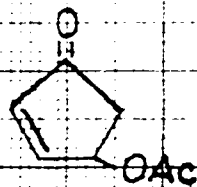
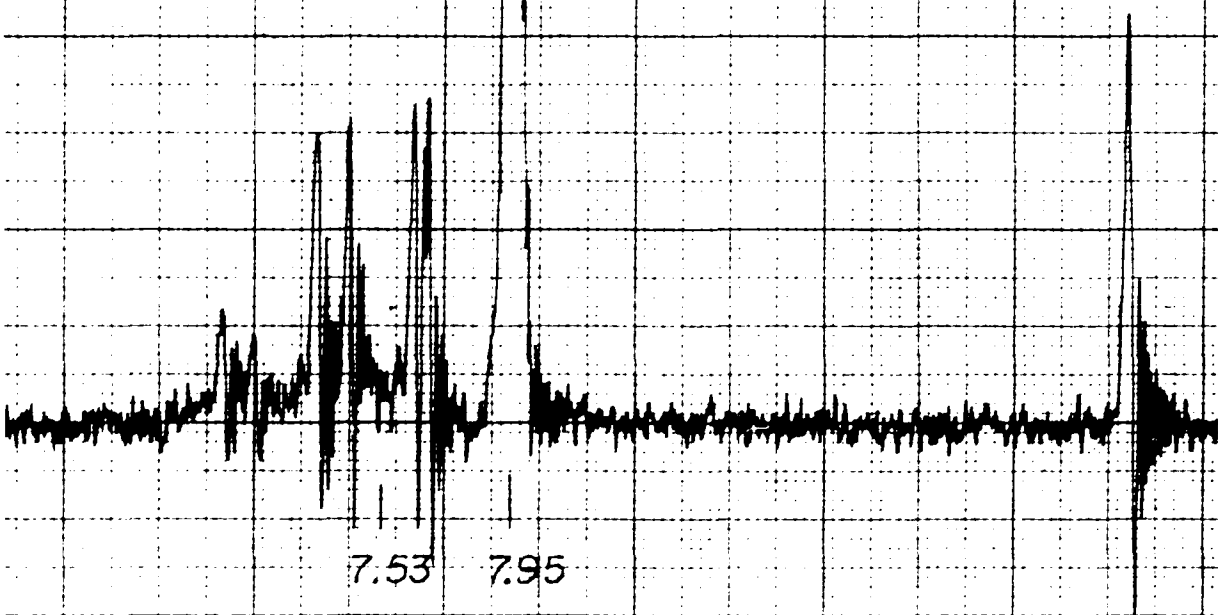


Figure 20. NMR spectrum of 4-acetoxy-cyclopentenone



30 μ L / 400 μ L CCl_4



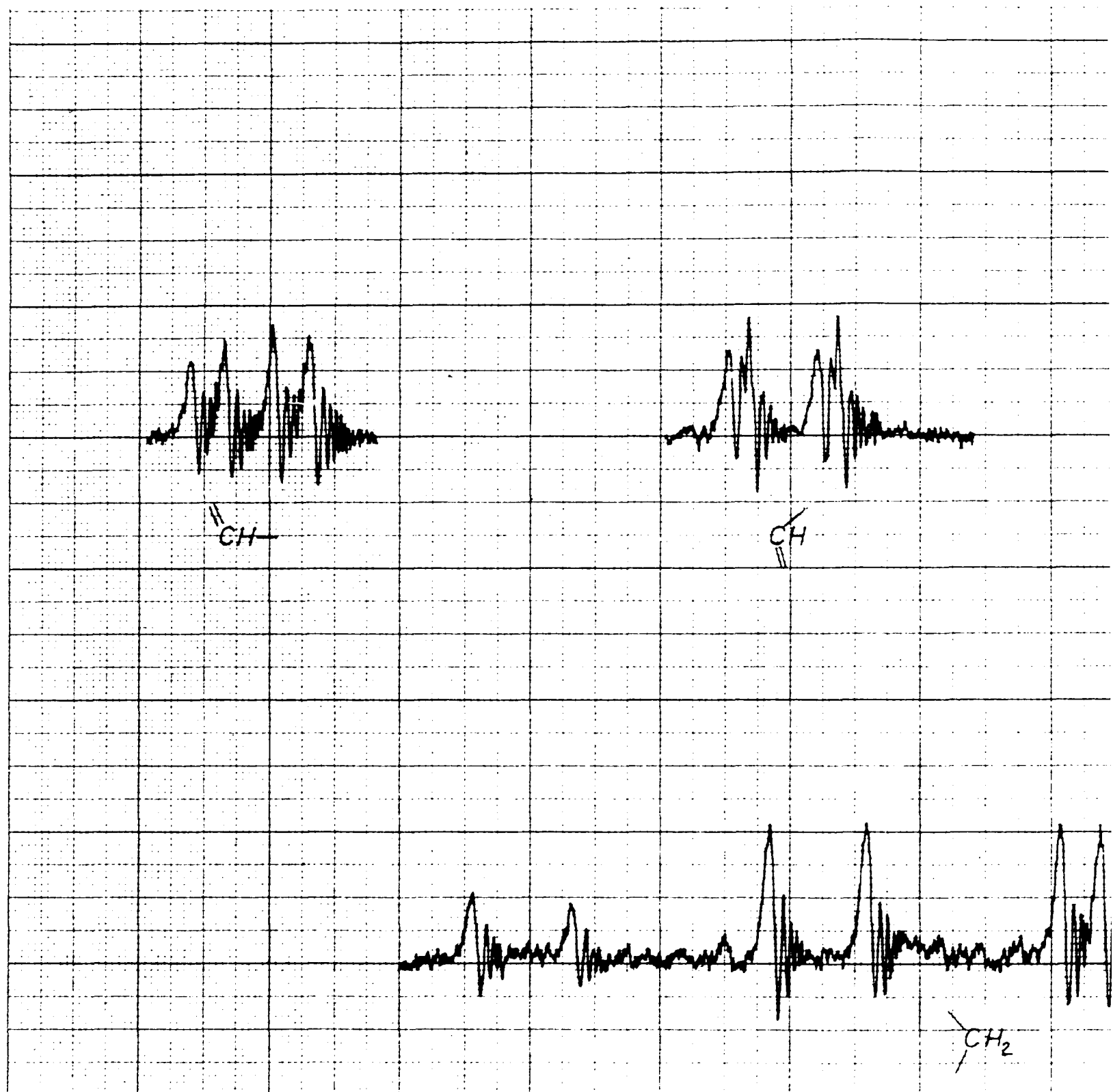


Figure 21. Expansion of 4-acetoxy-cyclopentenone spectrum

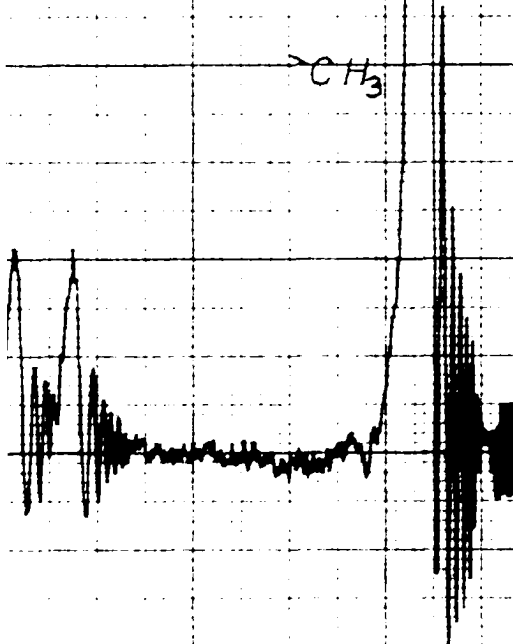
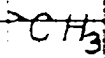
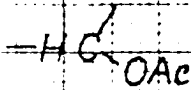
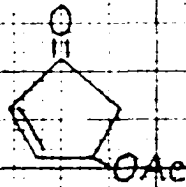
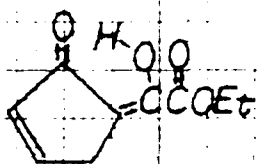




Figure 22. NMR spectrum of 5-oxalyl-cyclopentenone



100 MG / 500 μ L CCl₄

5.68

6.50

8.62

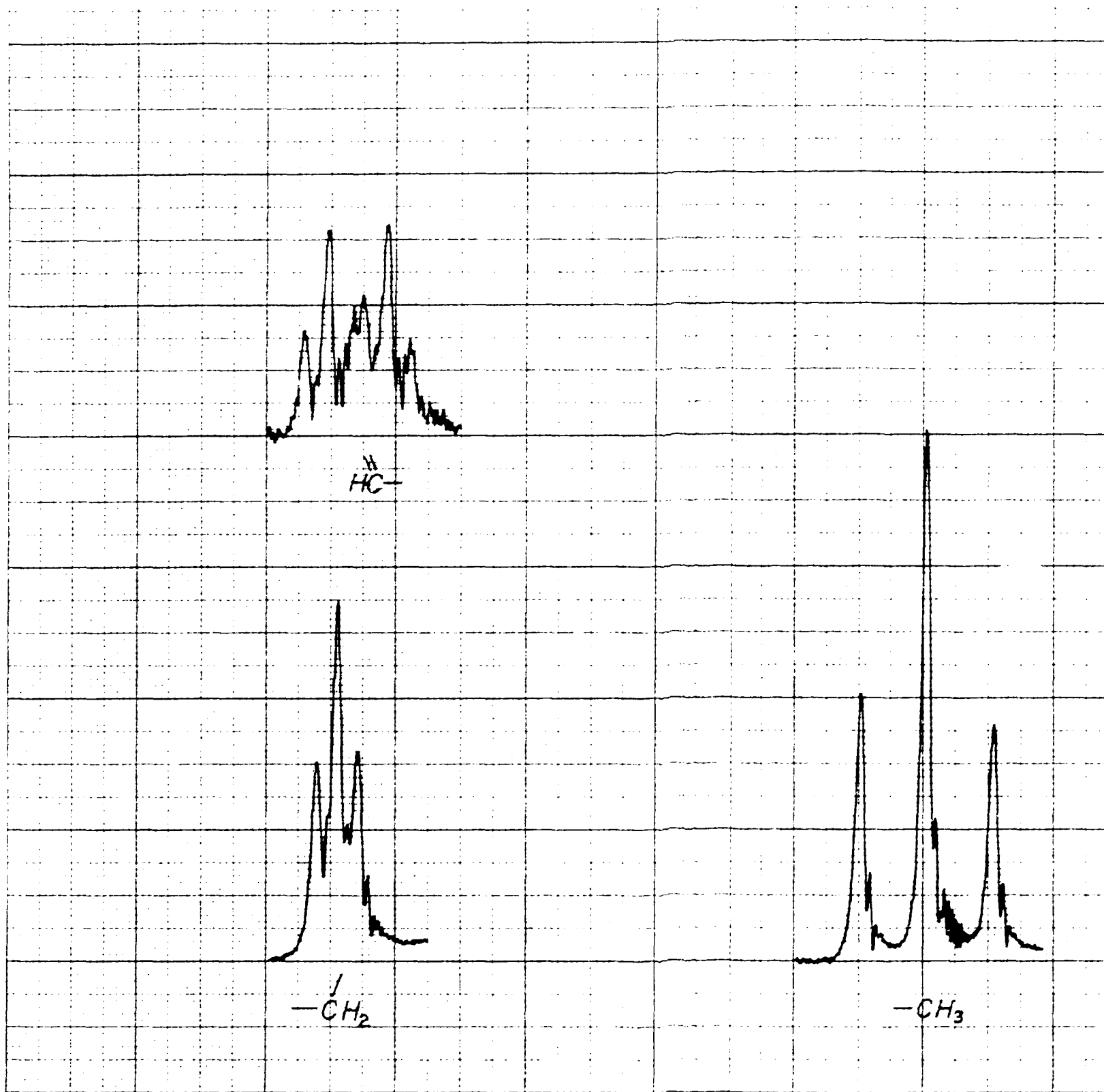
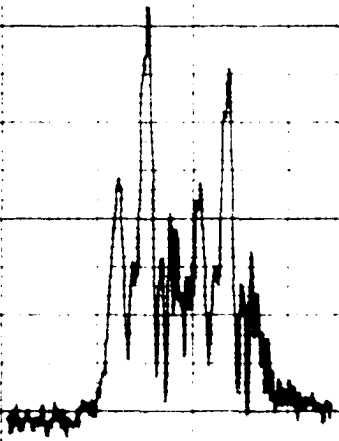
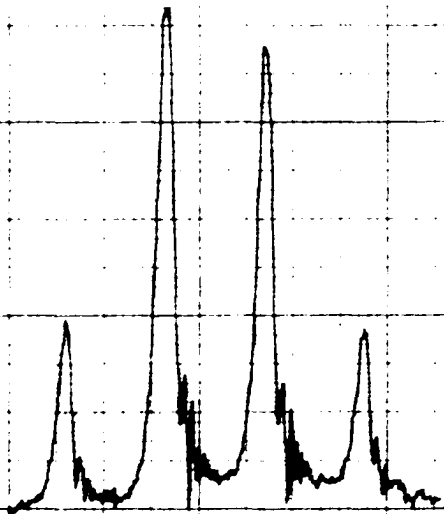
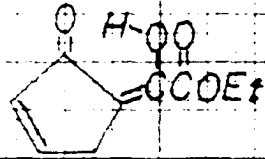


Figure 23. Expansion of 5-oxalyl-cyclopentene spectrum



H-C



-CH₂-

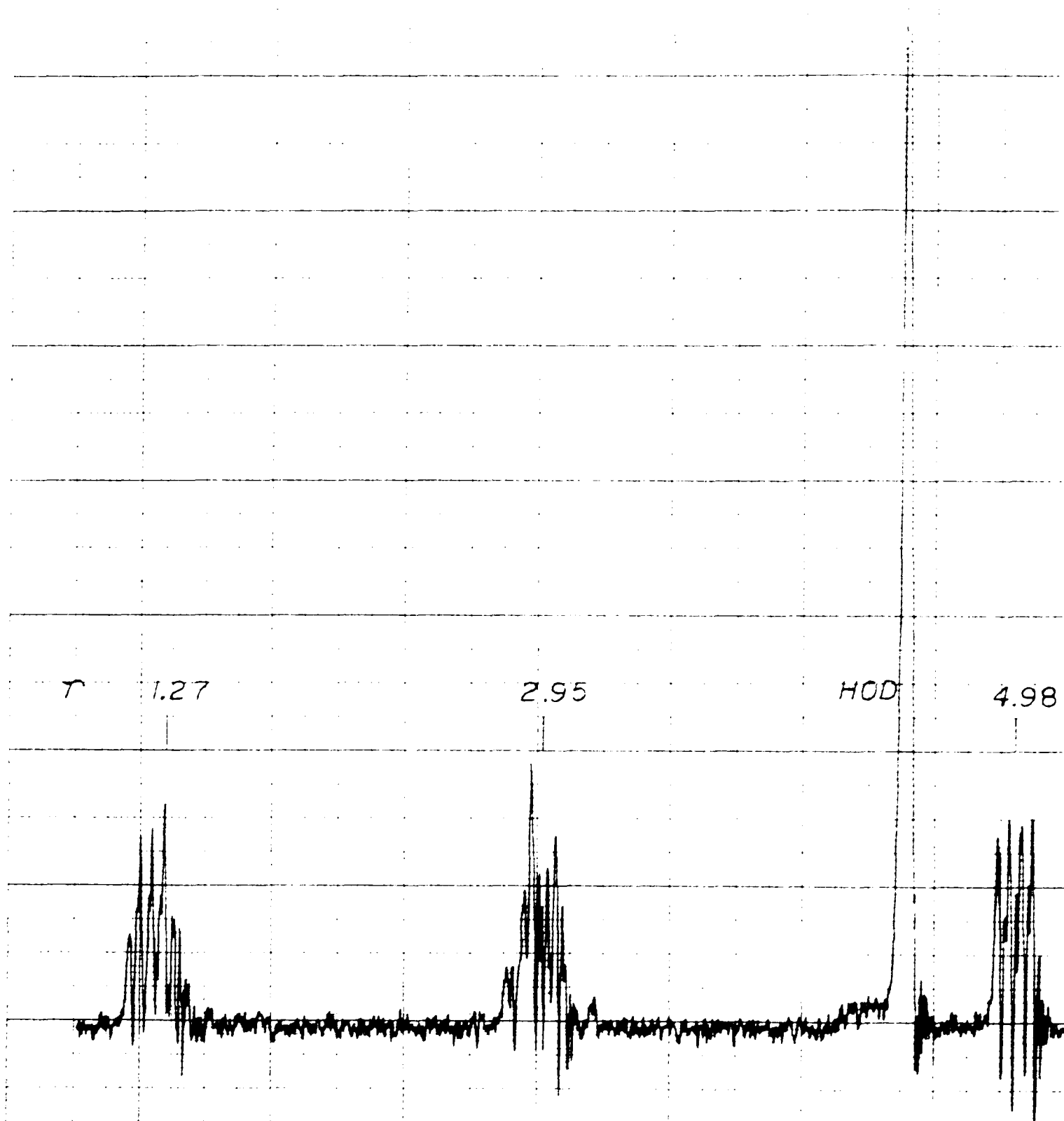
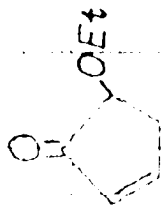
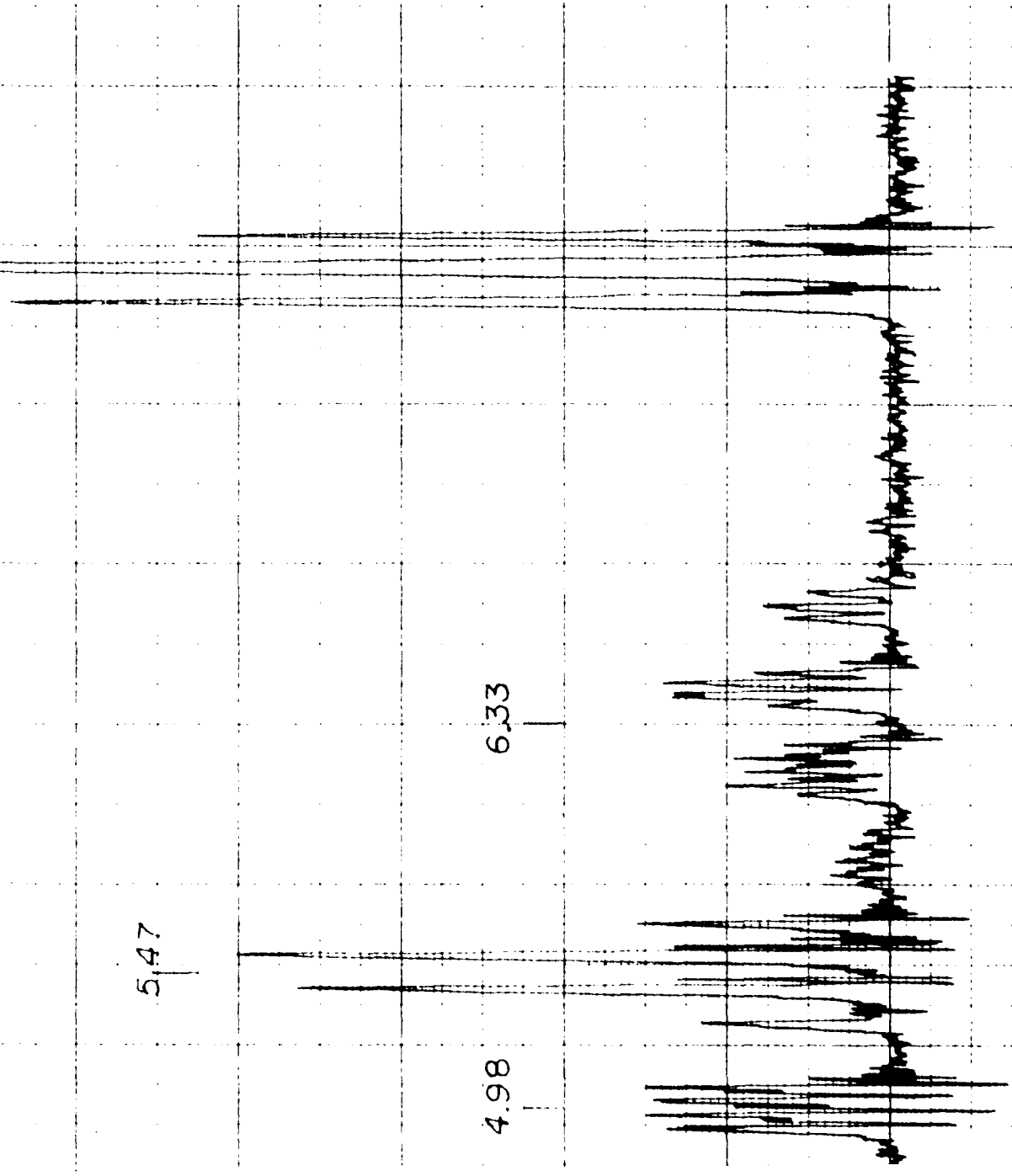


Figure 24. NMR spectrum of 5-ethoxy-cyclopentenone



30 μ L / 400 μ L D₂O



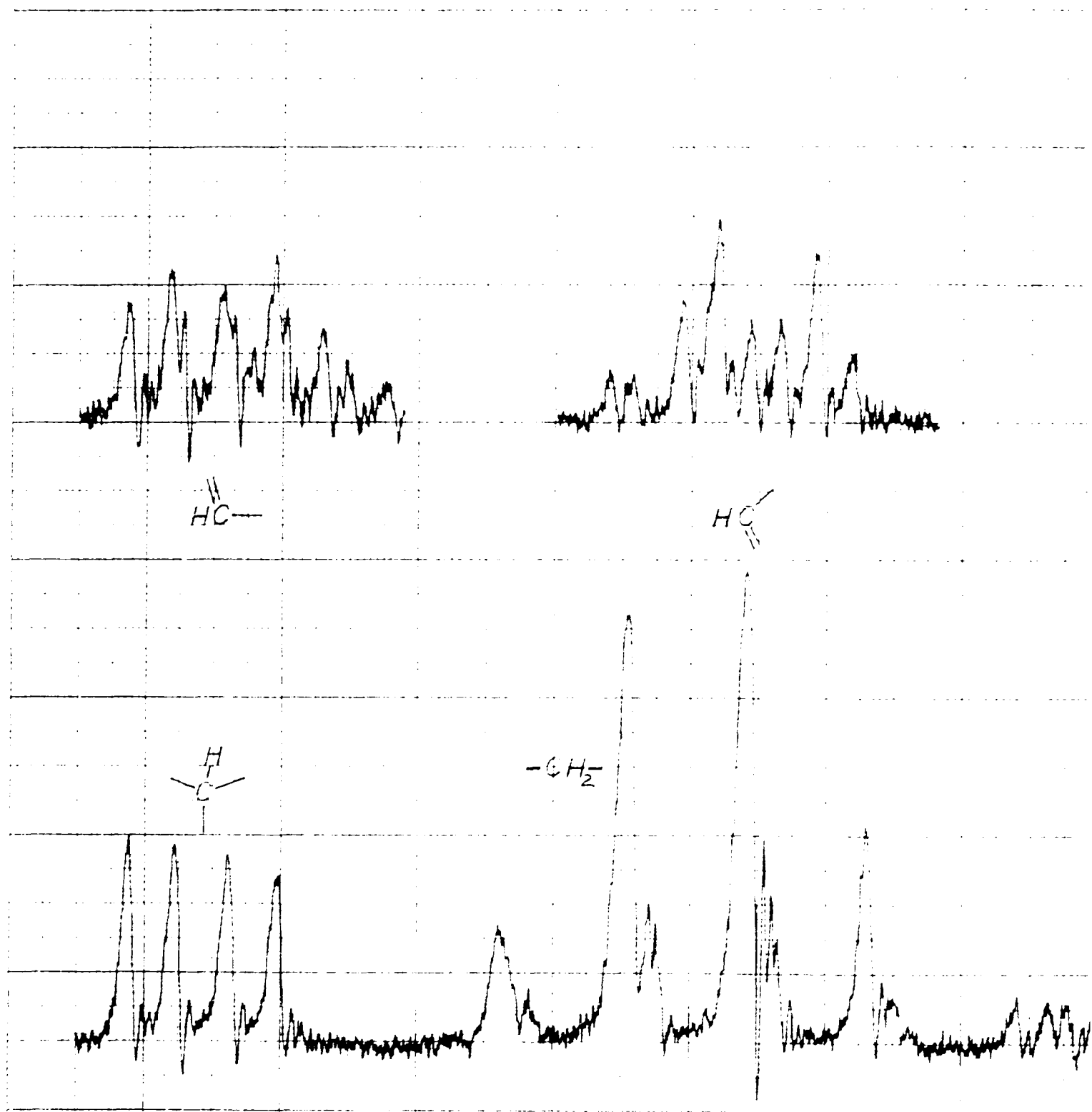
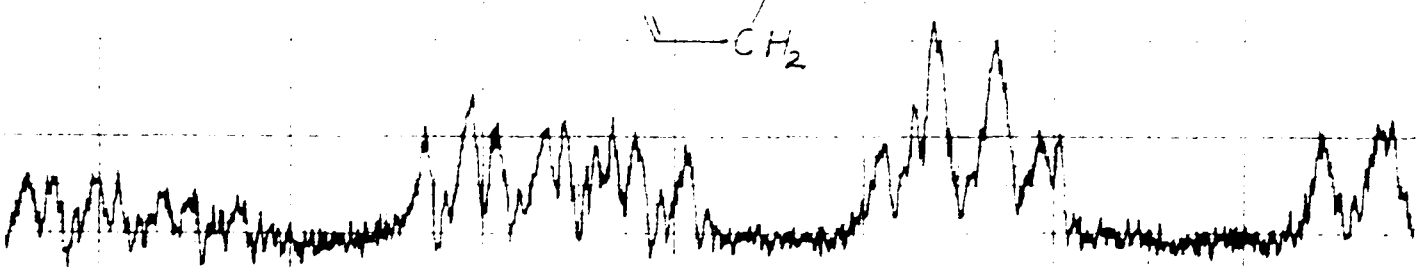
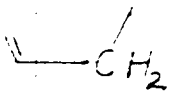
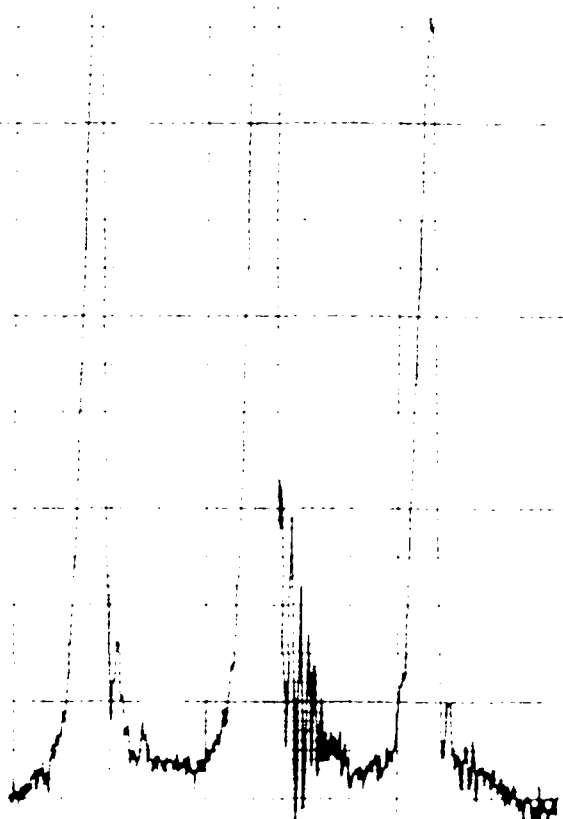
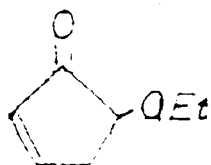


Figure 25. Expansion of 5-ethoxy-cyclopentanone spectrum



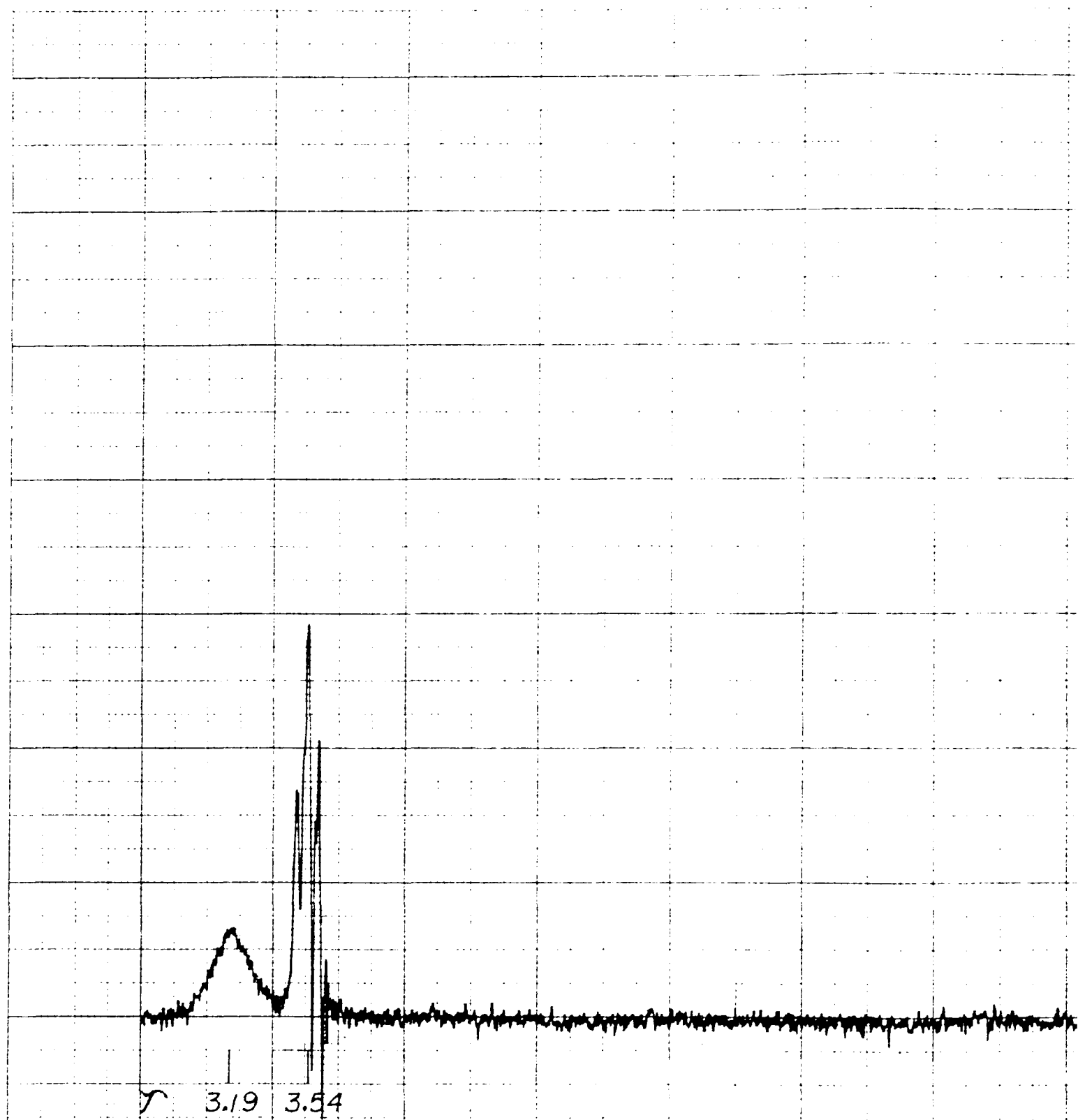
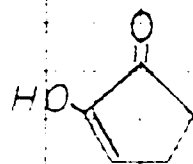
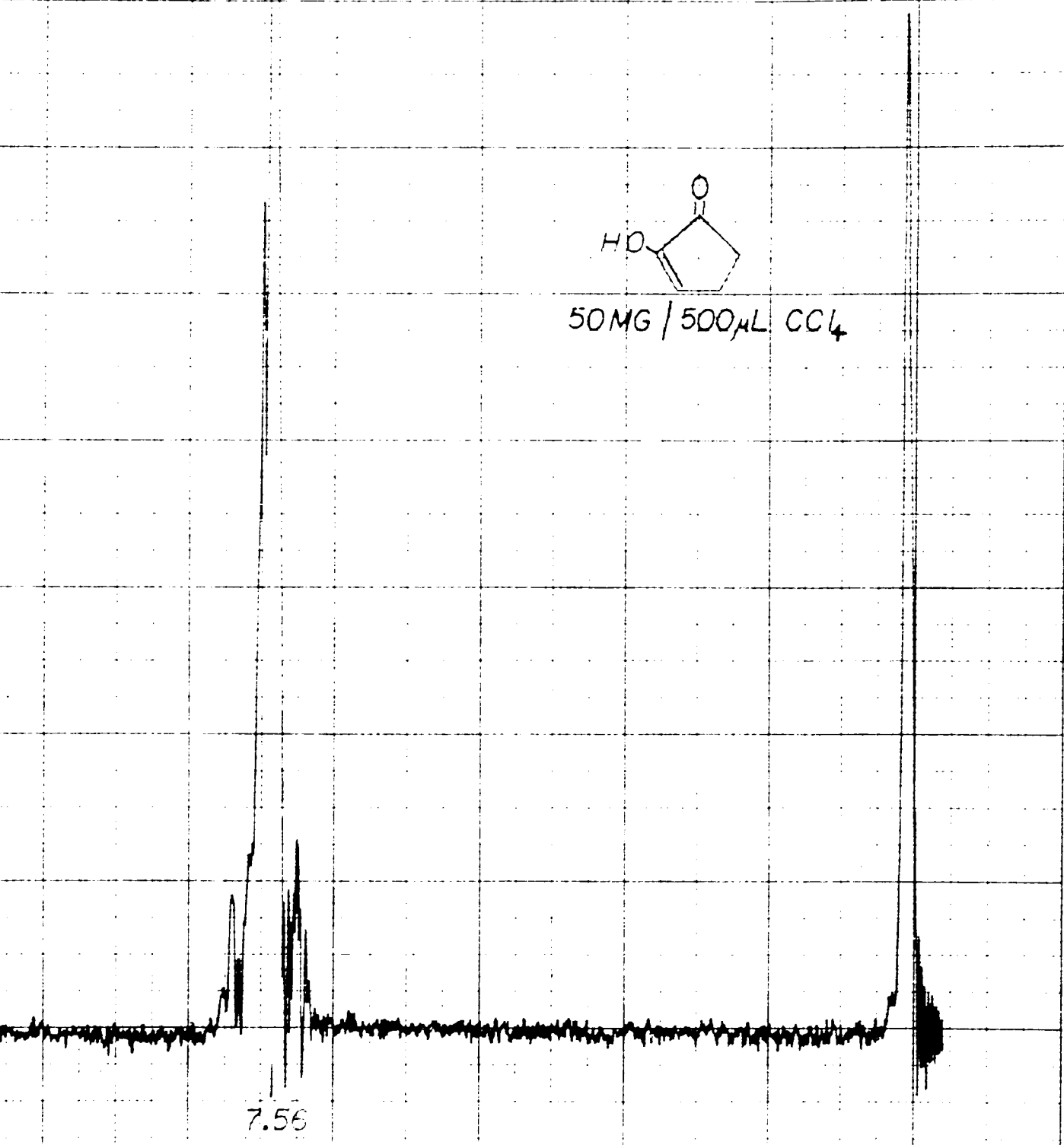


Figure 26. NMR spectrum of cyclopentane-1,2-dione



50MG / 500 μ L CCl₄



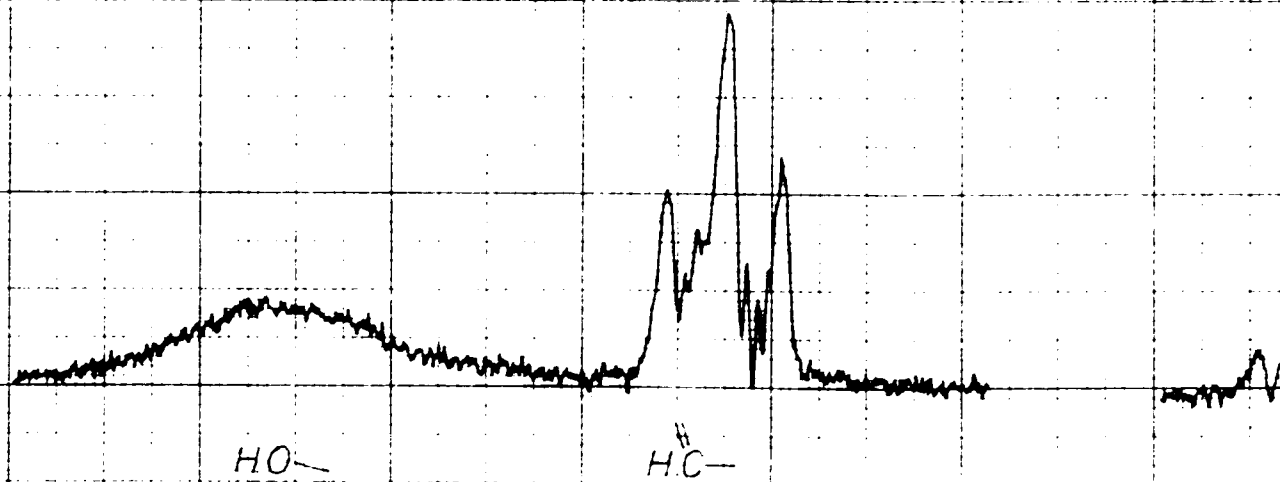
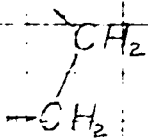
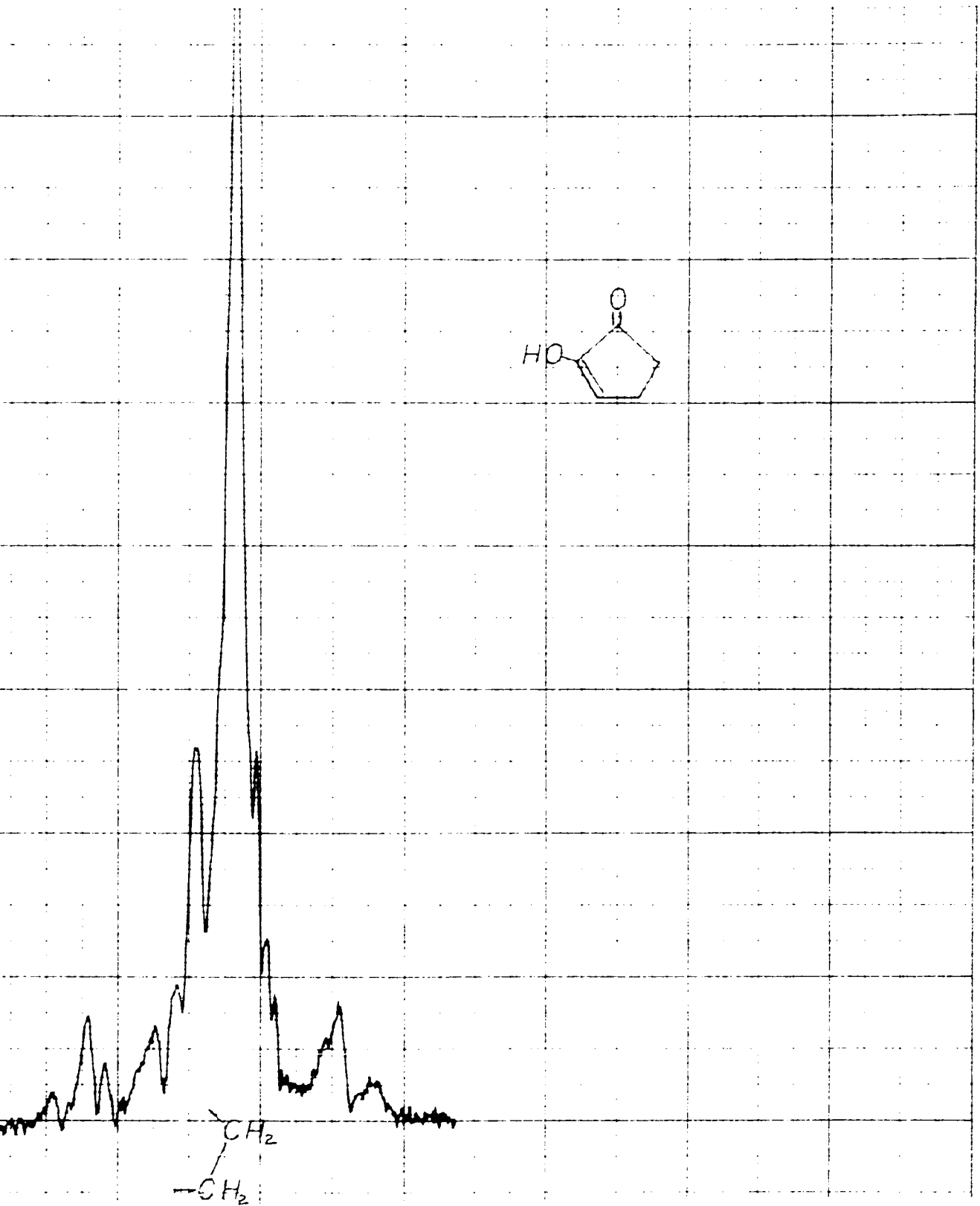
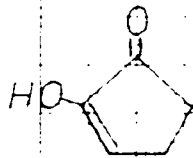


Figure 27. Expansion of cyclopentane-1,2-dione spectrum



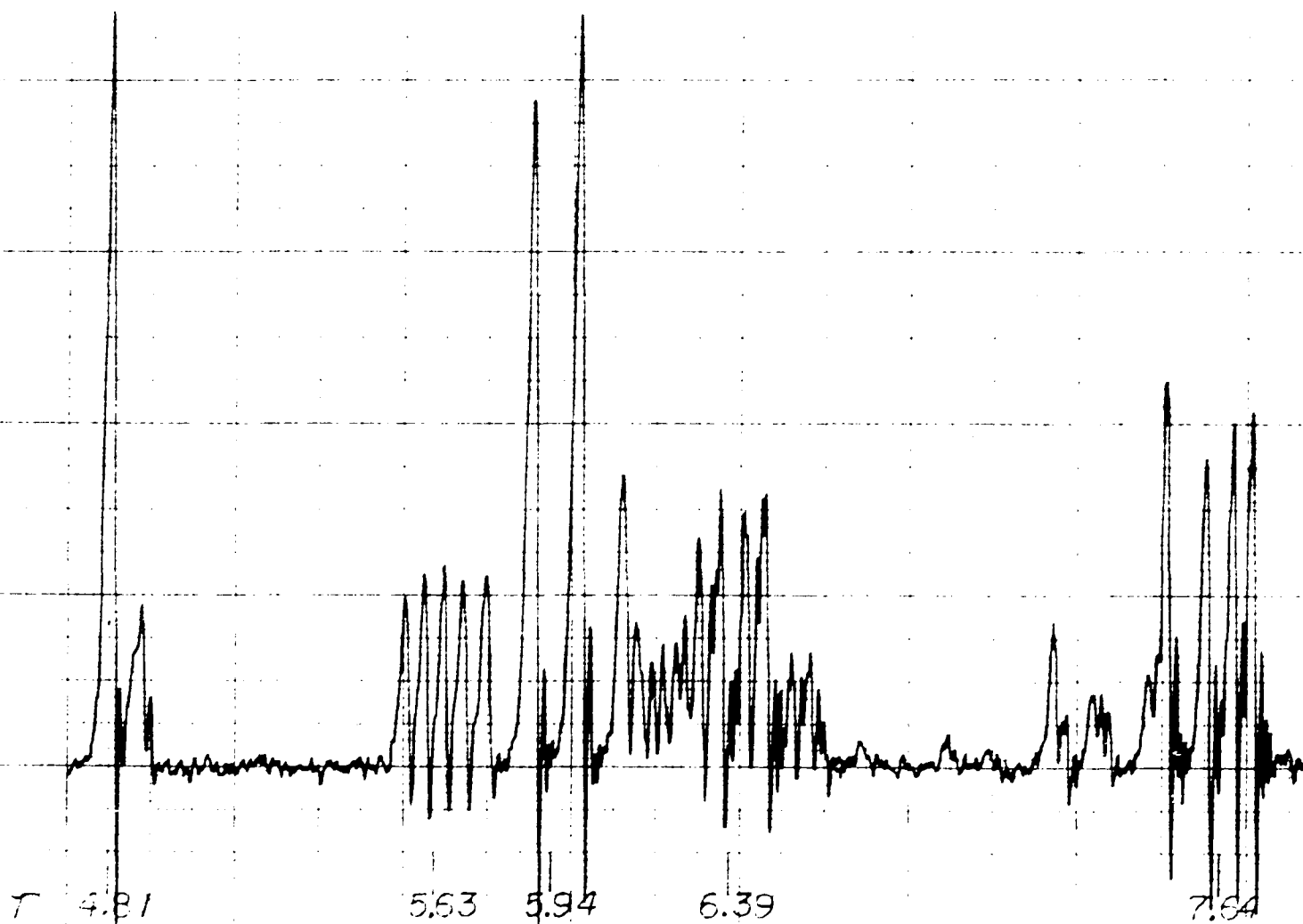
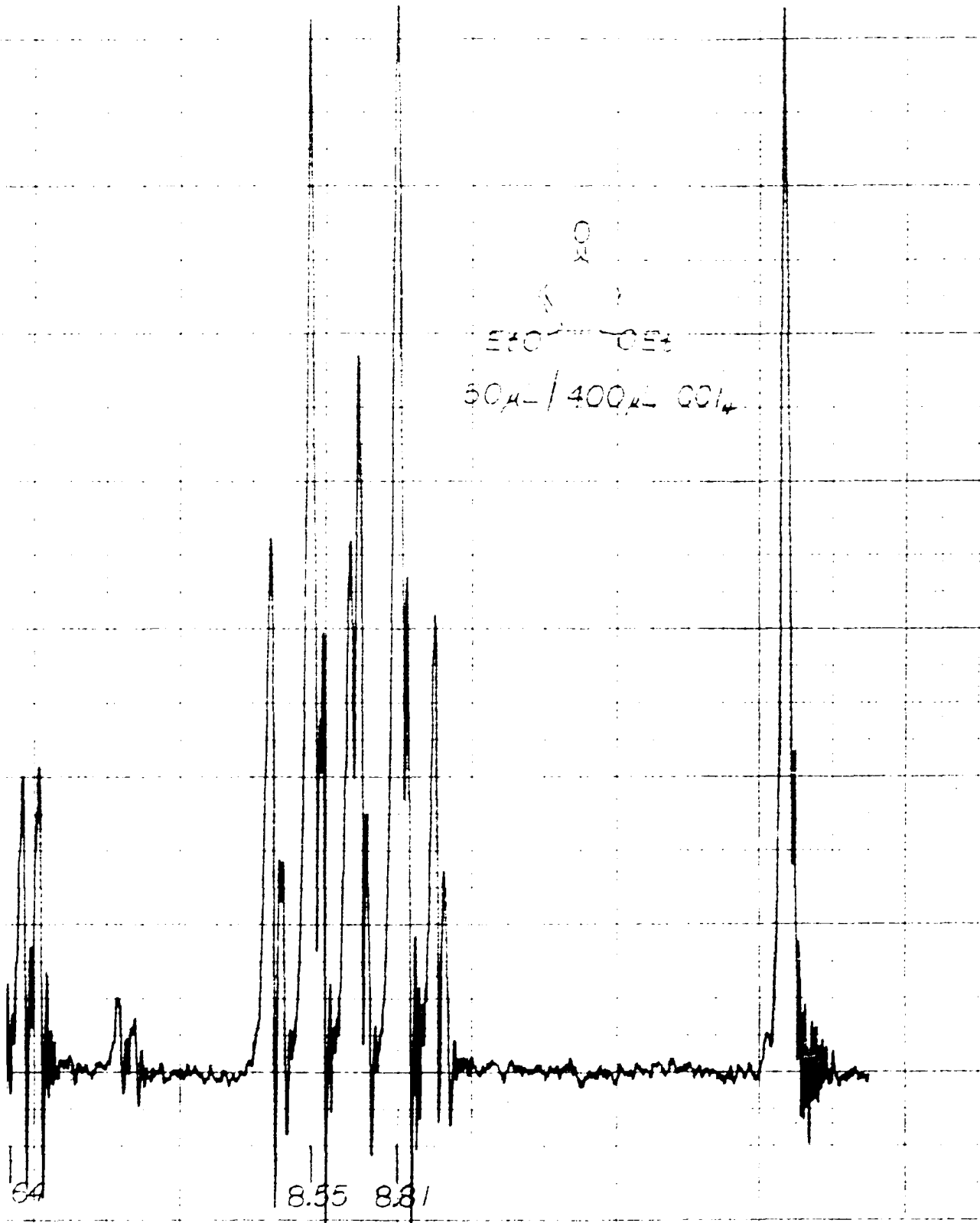


Figure 28. NMR spectrum of 3,4-diethoxy-cyclopentenone

OR
O
EHO — OEH
50 μ L / 400 μ L CCl_4



64

8.55 8.81

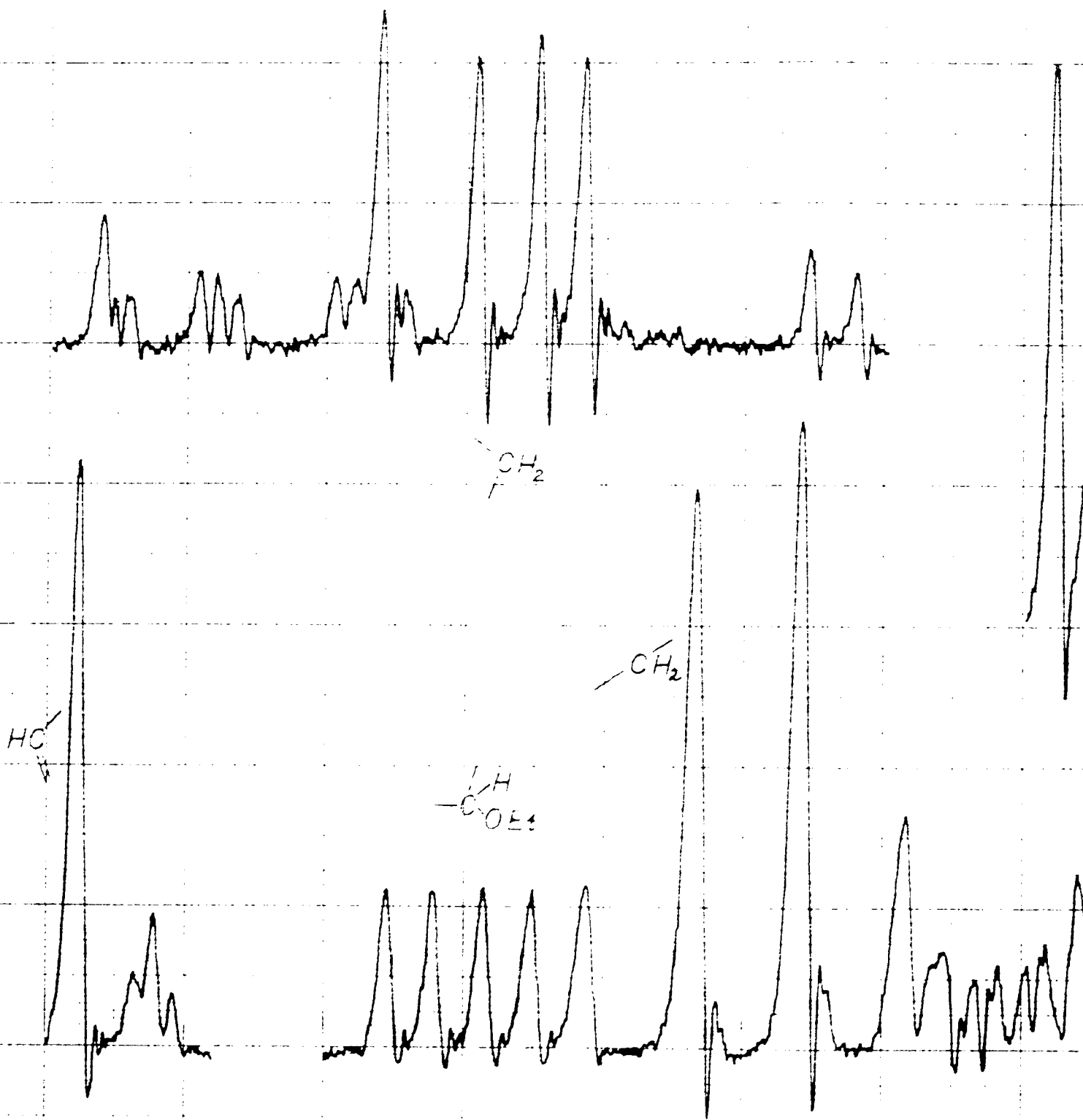
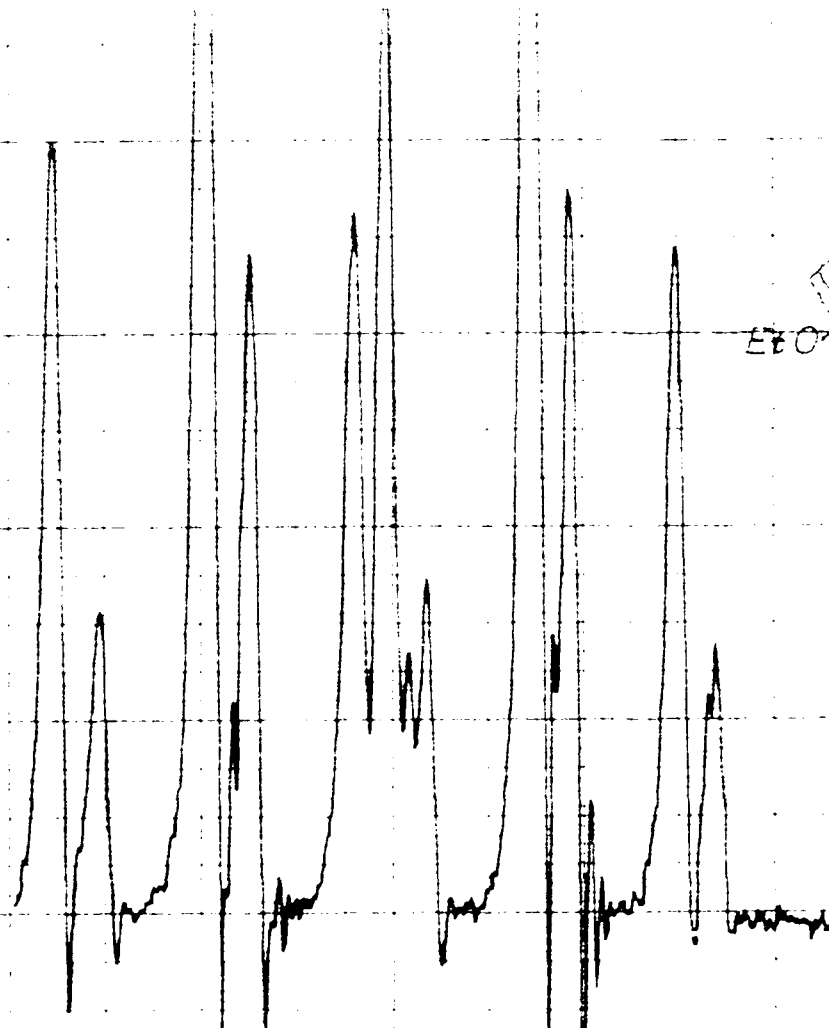
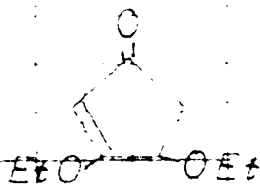


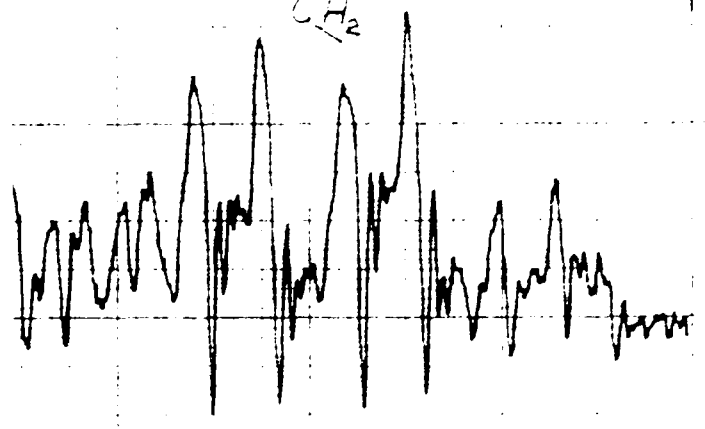
Figure 29. Expansion of 3,4-diethoxy-cyclopentenone spectrum



-CH₃

-CH₃

-CH₂



-CH₂

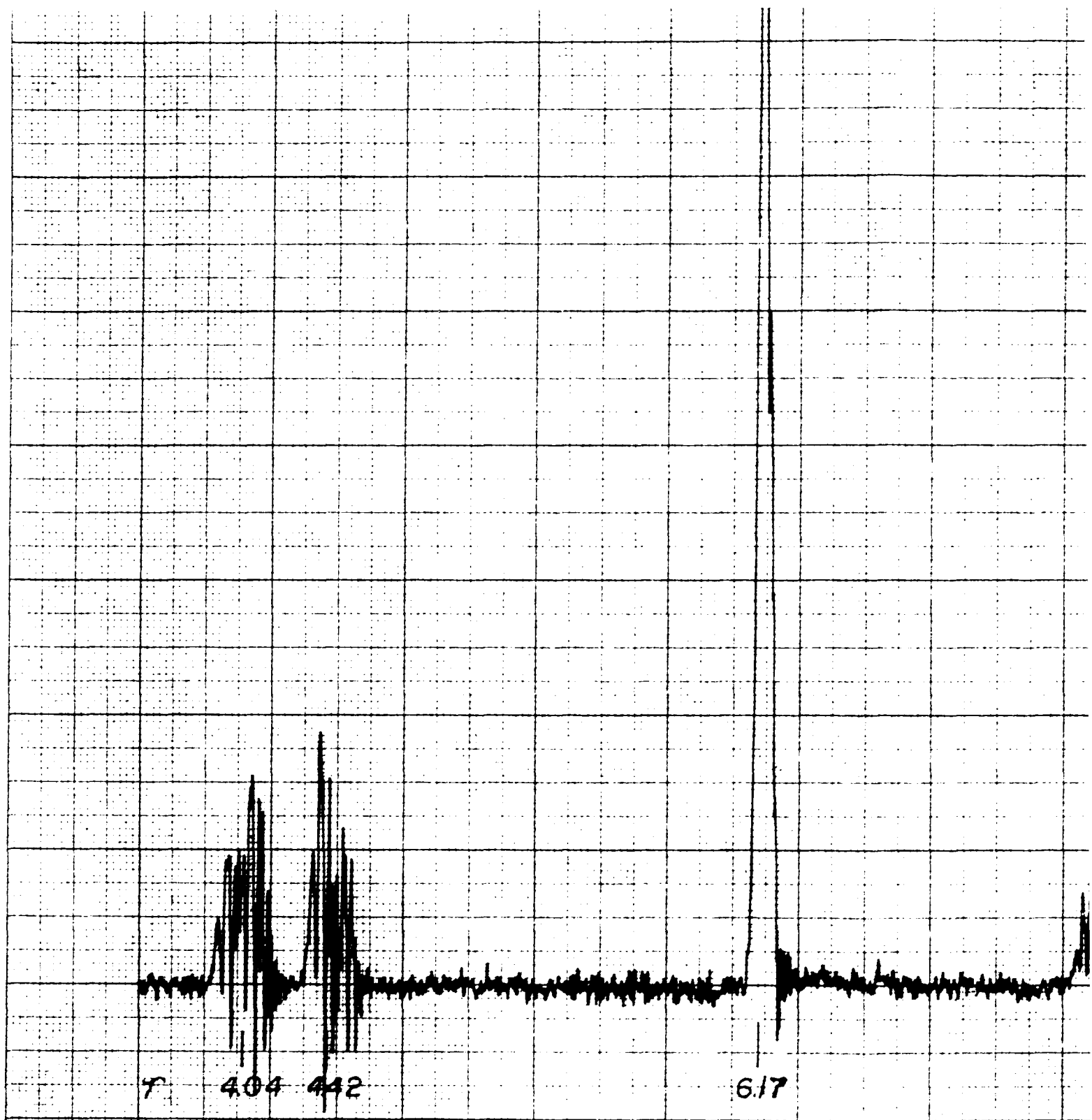
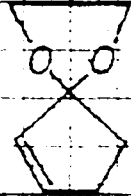
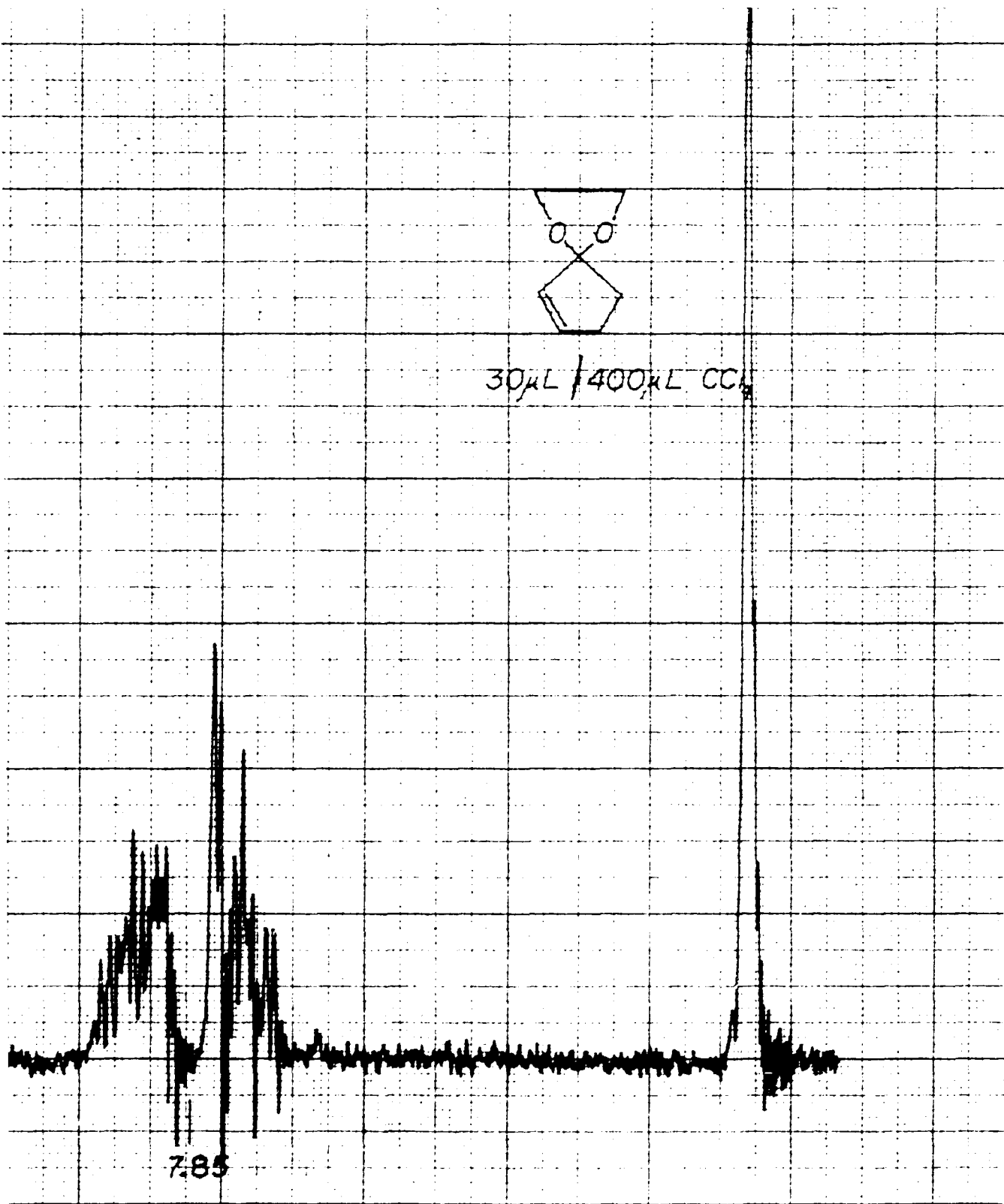


Figure 30. NMR spectrum of ethylene ketal of cyclopentanone



30 μ L / 400 μ L CCl₄

7.85



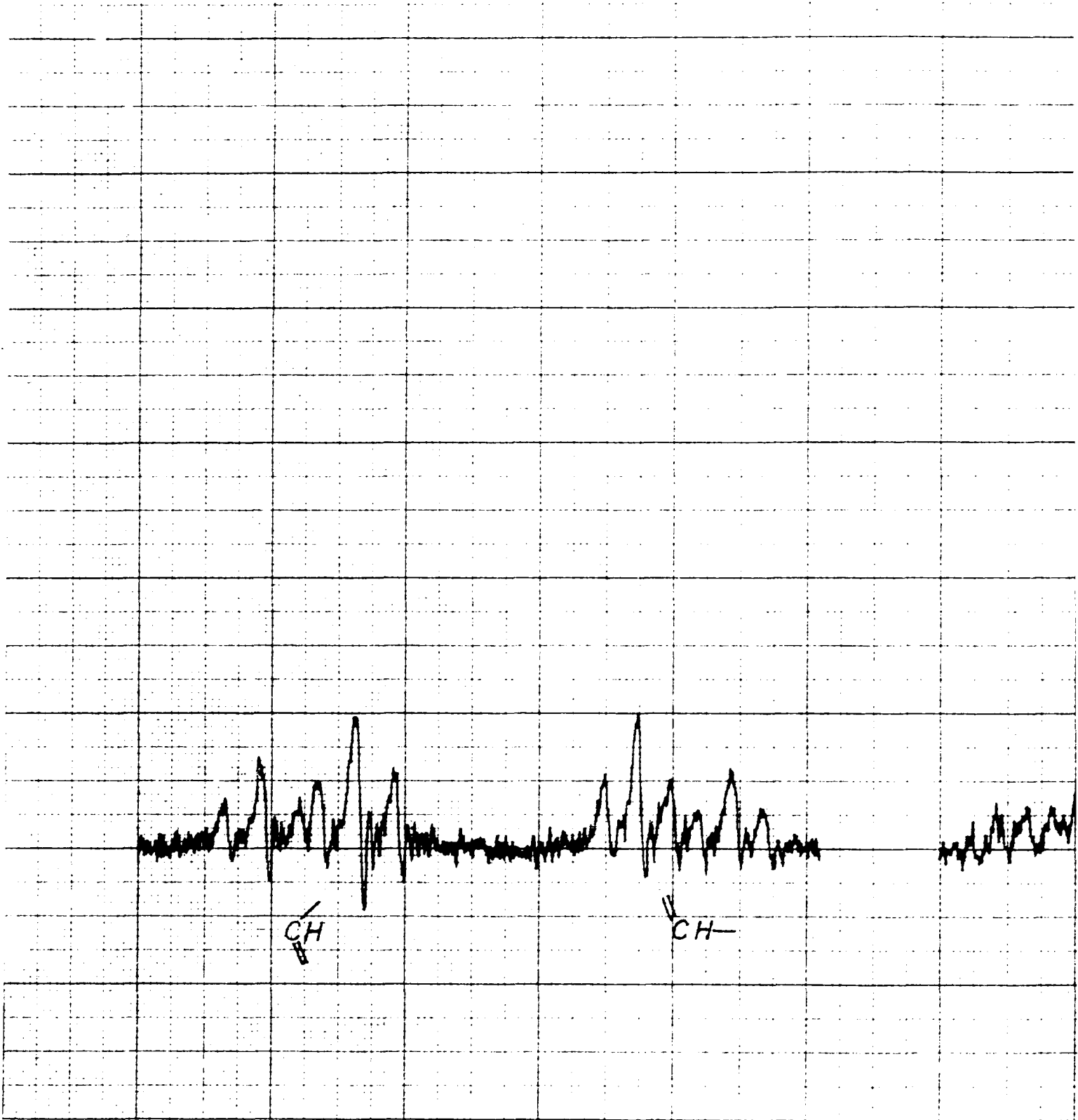
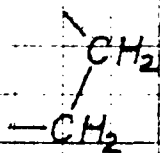
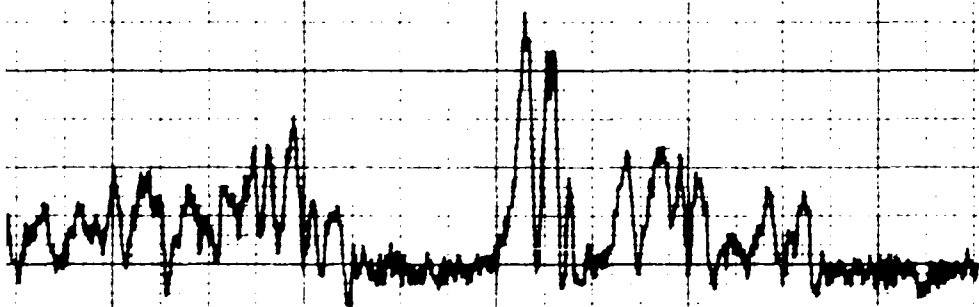


Figure 31. Expansion of cyclopentenone ketal spectrum



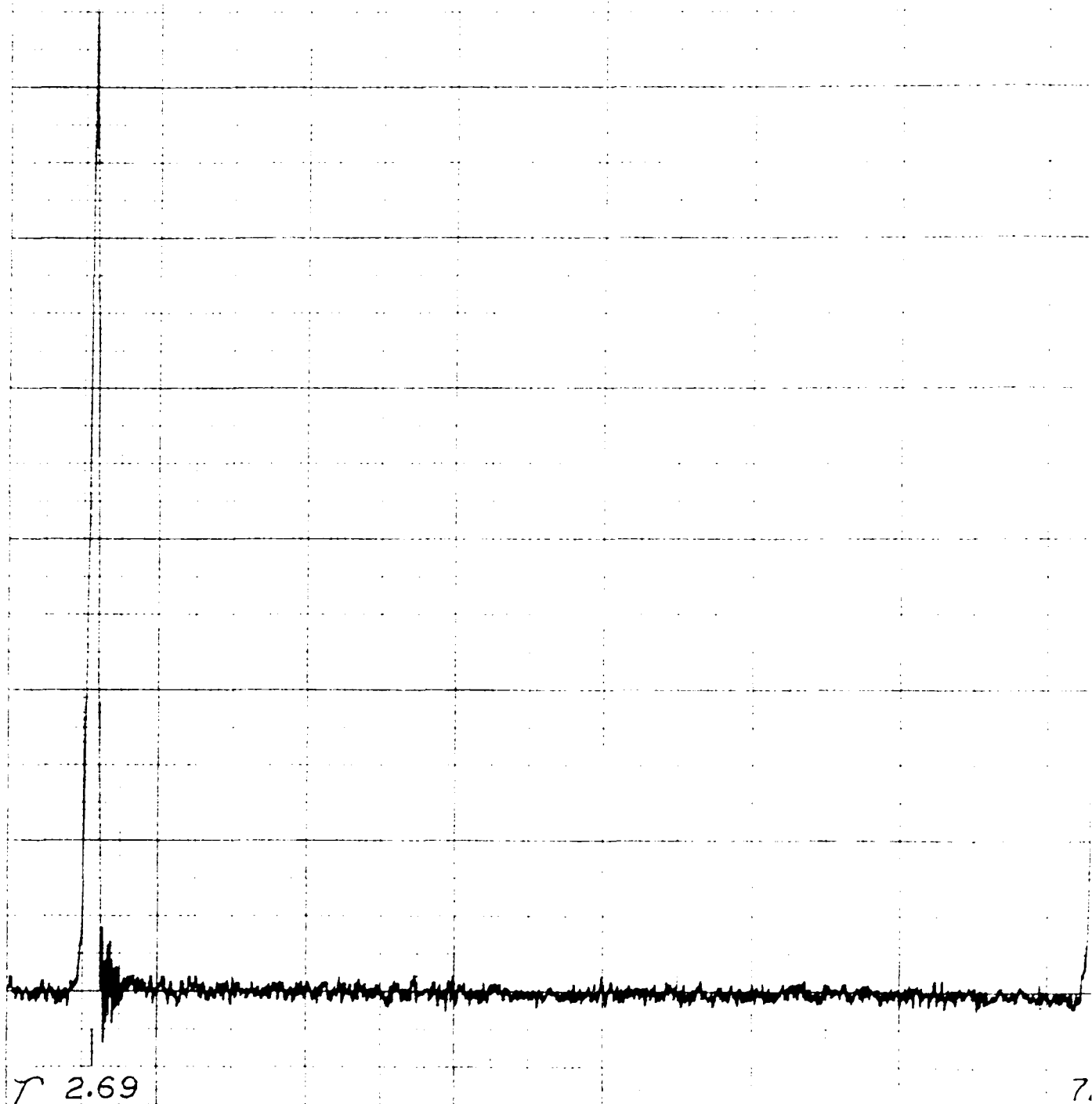
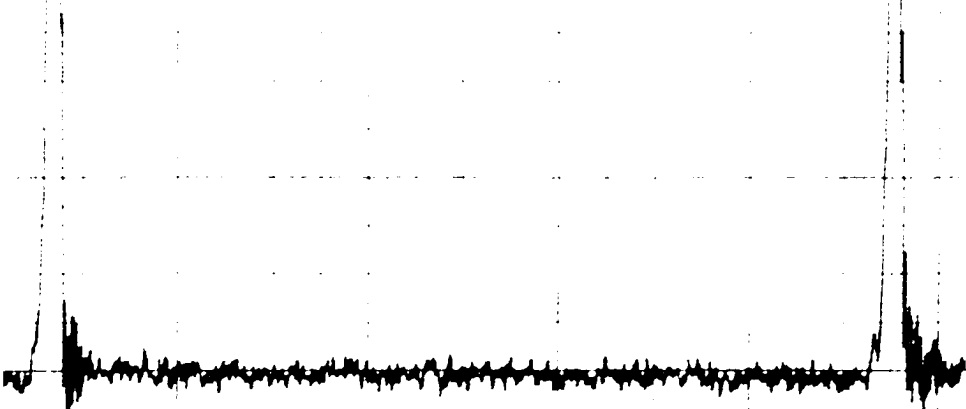


Figure 32. NMR spectrum of cyclopentene-3,5-dione



50 MG / 400 μ L $CDCl_3$



7.10

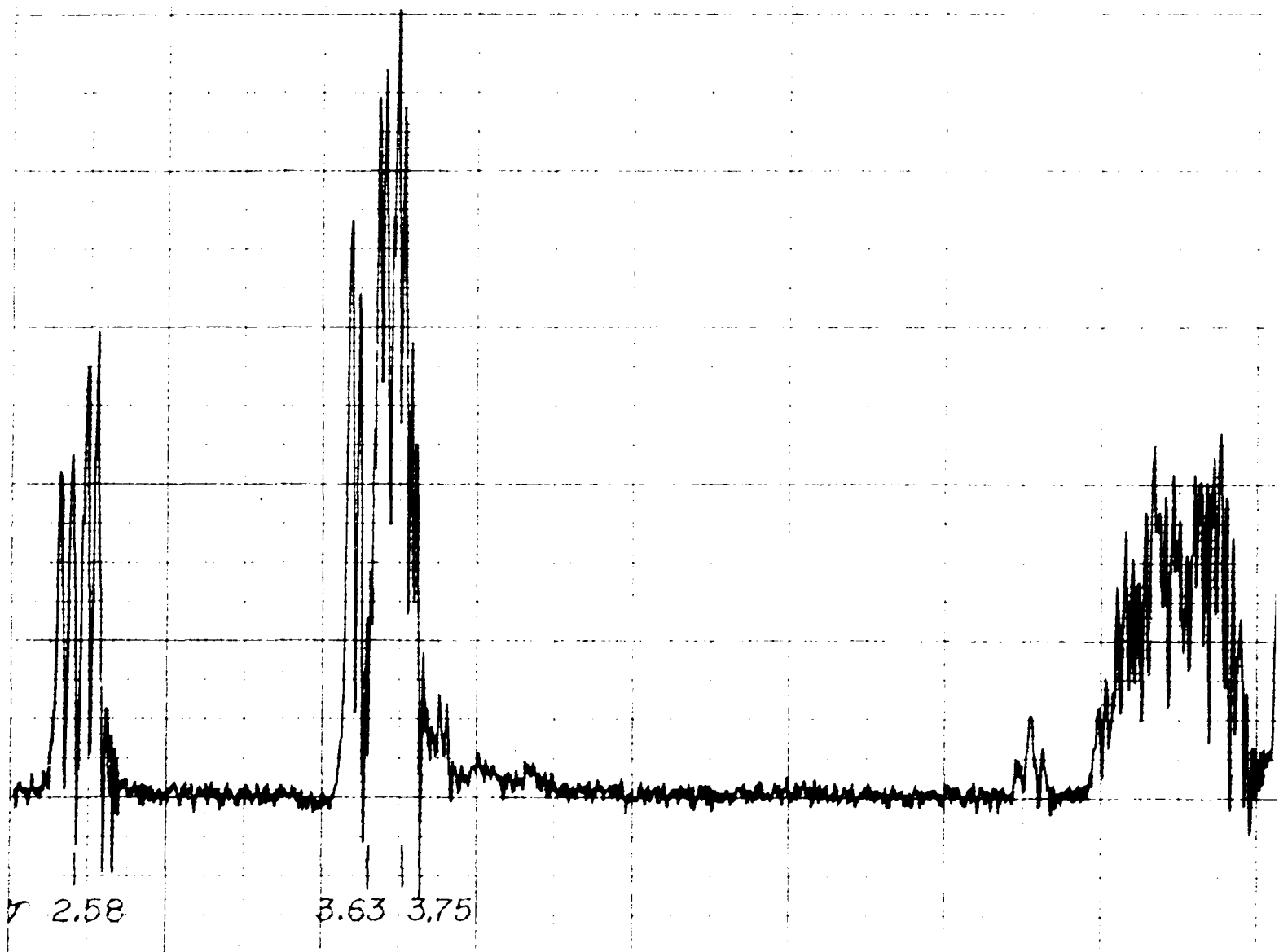
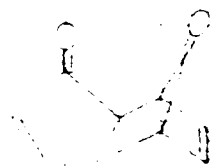
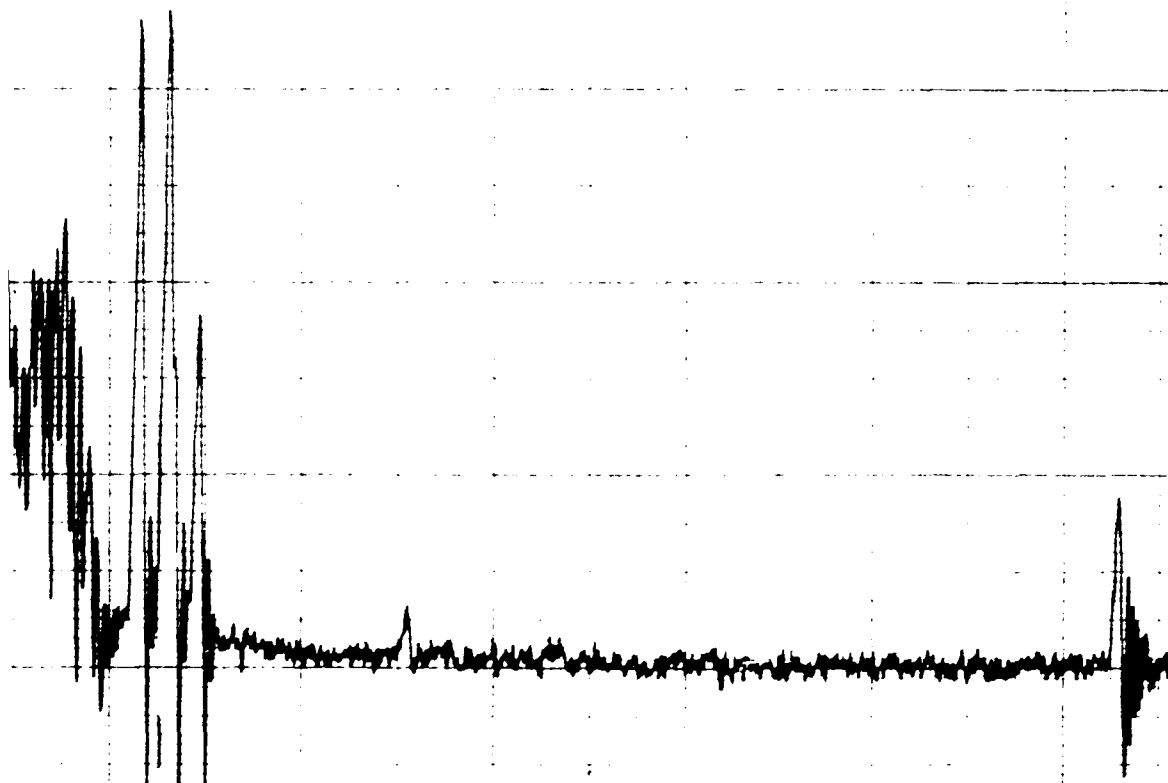


Figure 33. NMR spectrum of dicyclopentadienone



0.15M / 400 μ L CDCl₃



7.04

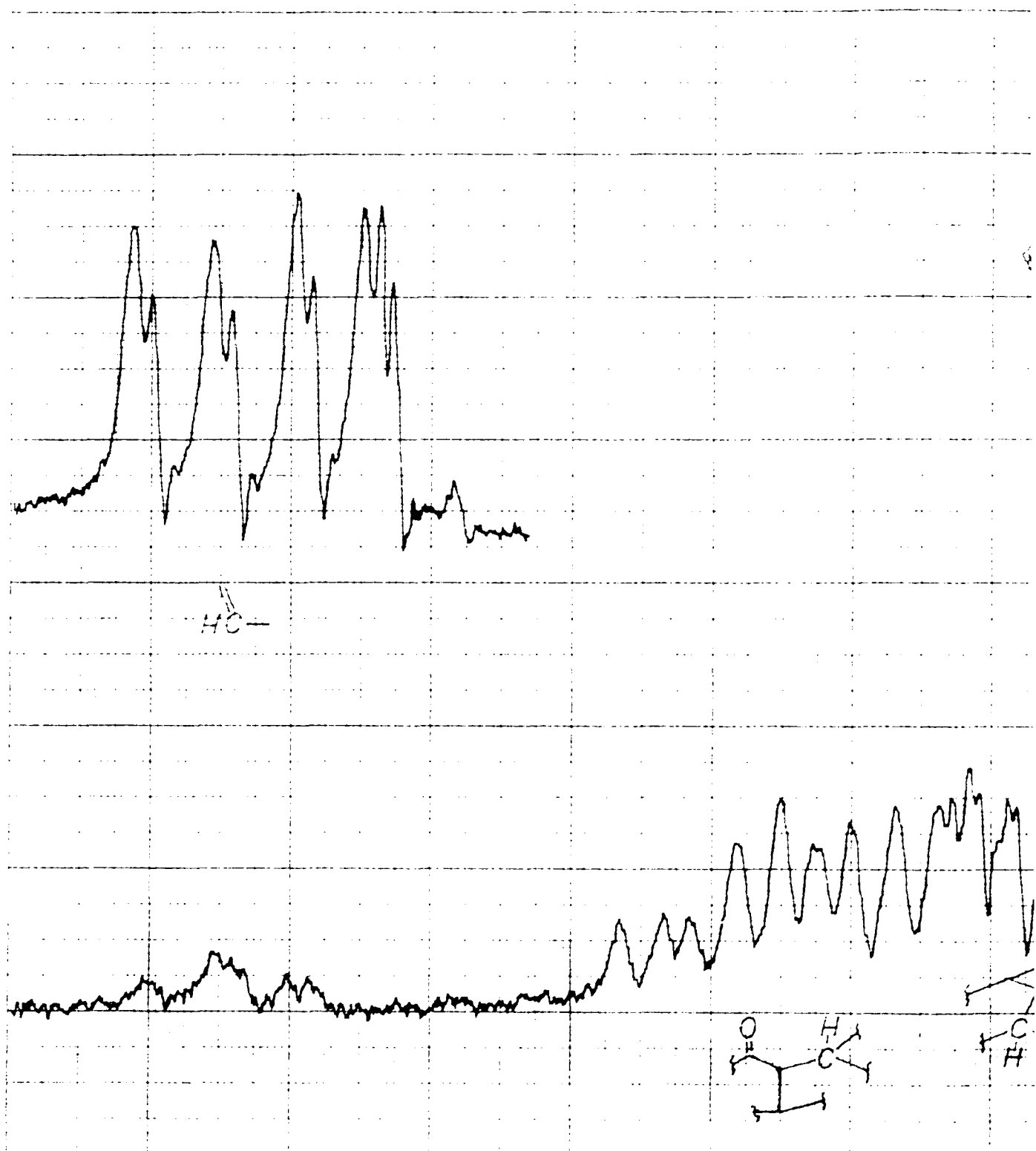
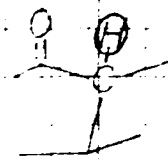
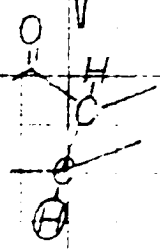
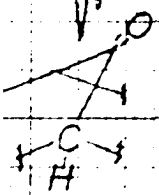
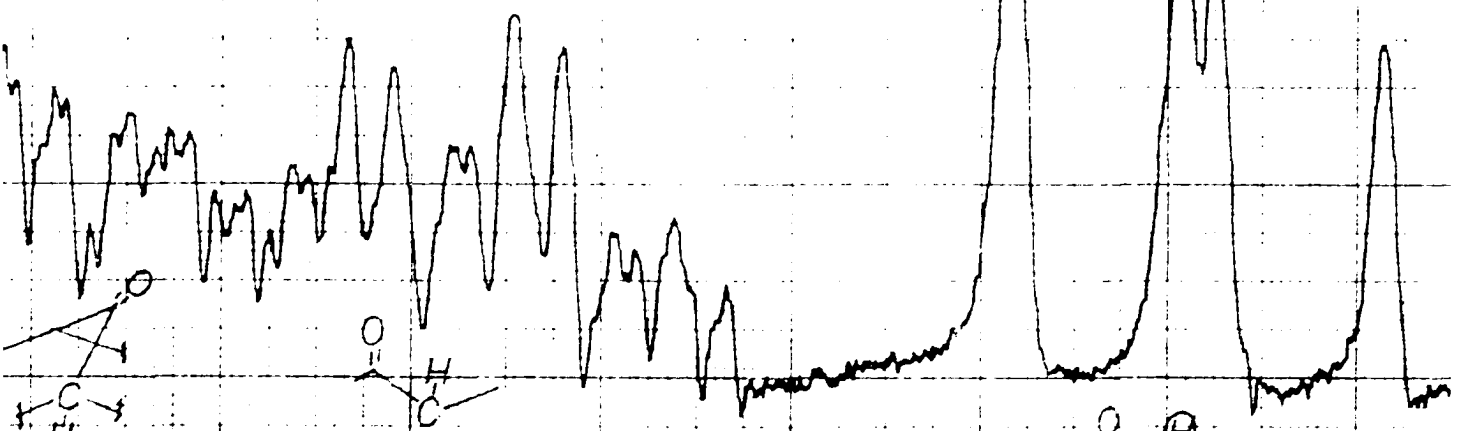
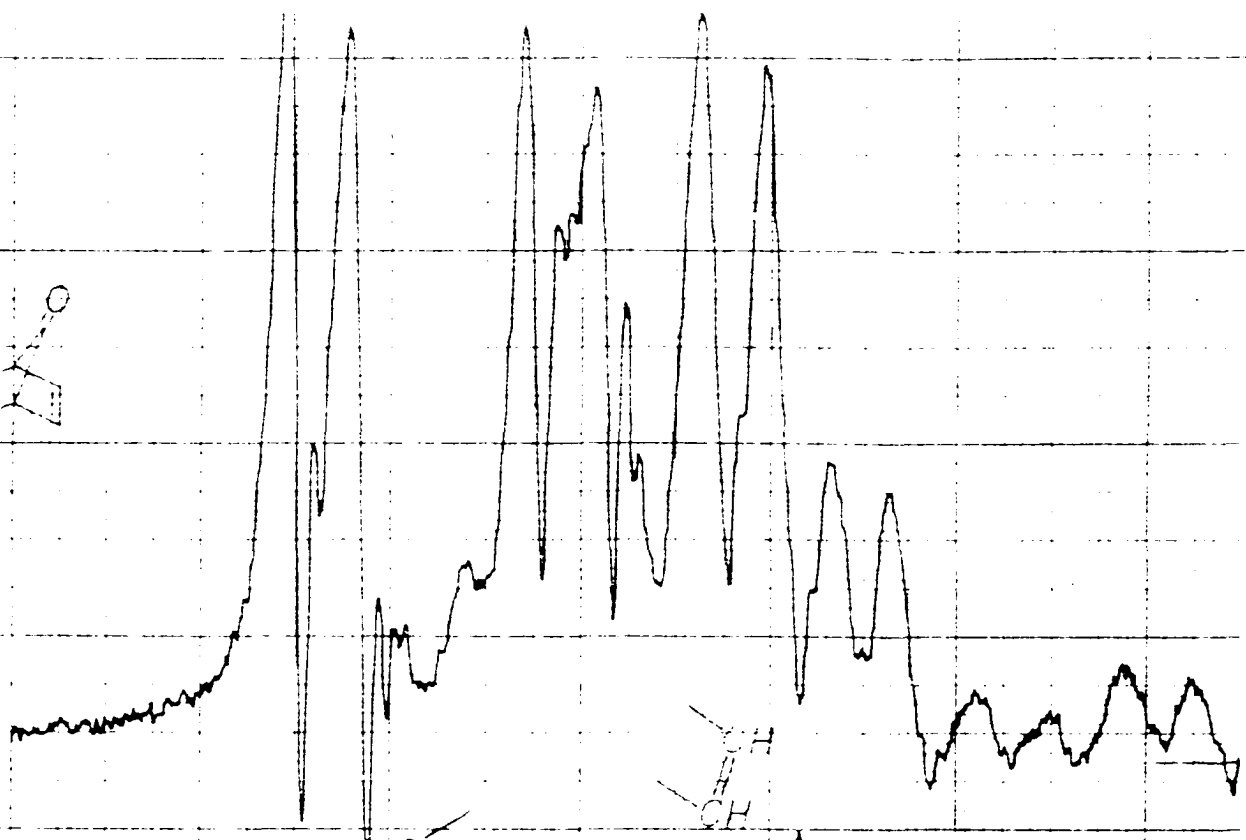


Figure 34. Expansion of dicyclopentadienone spectrum



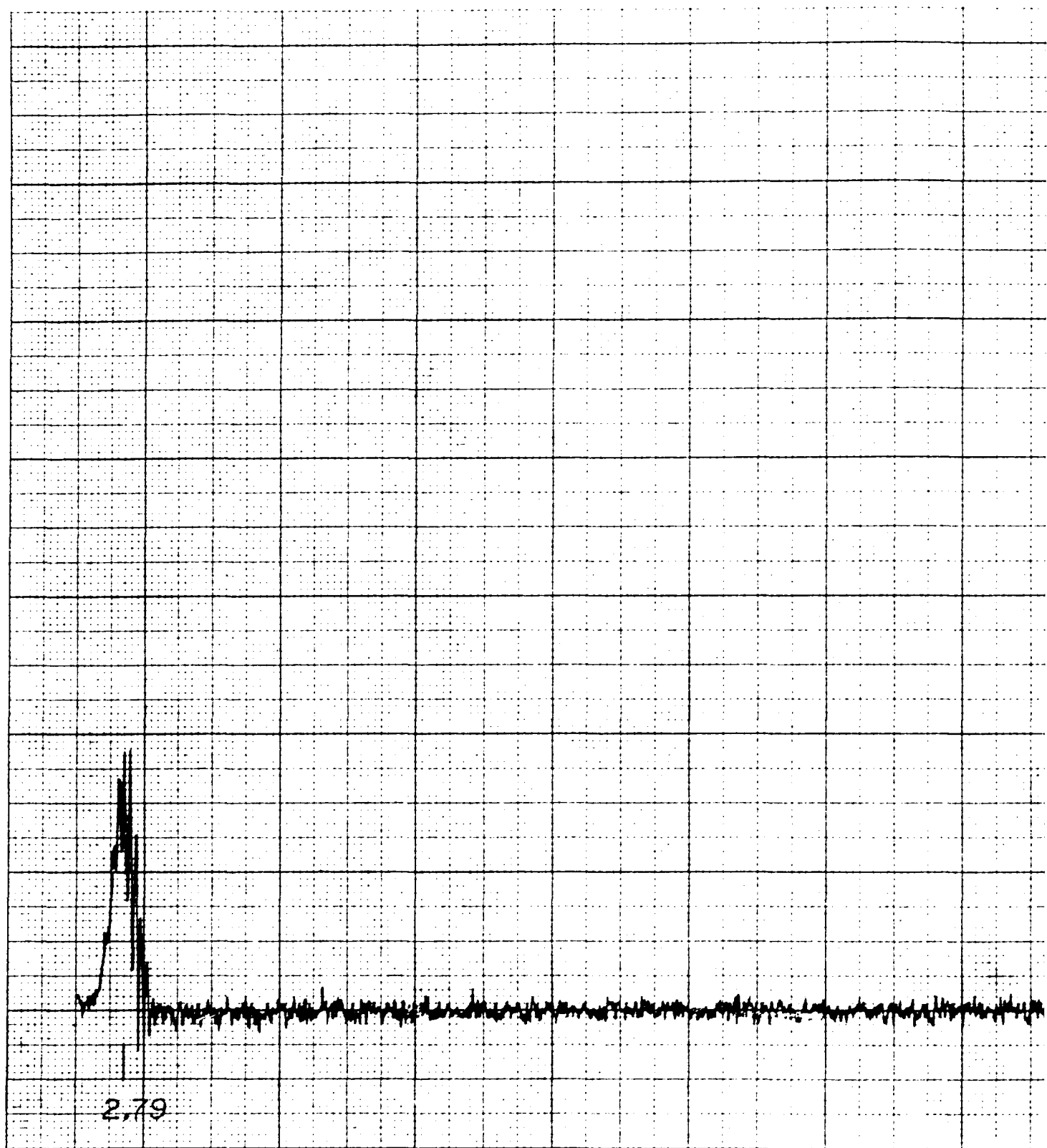
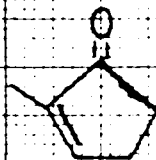
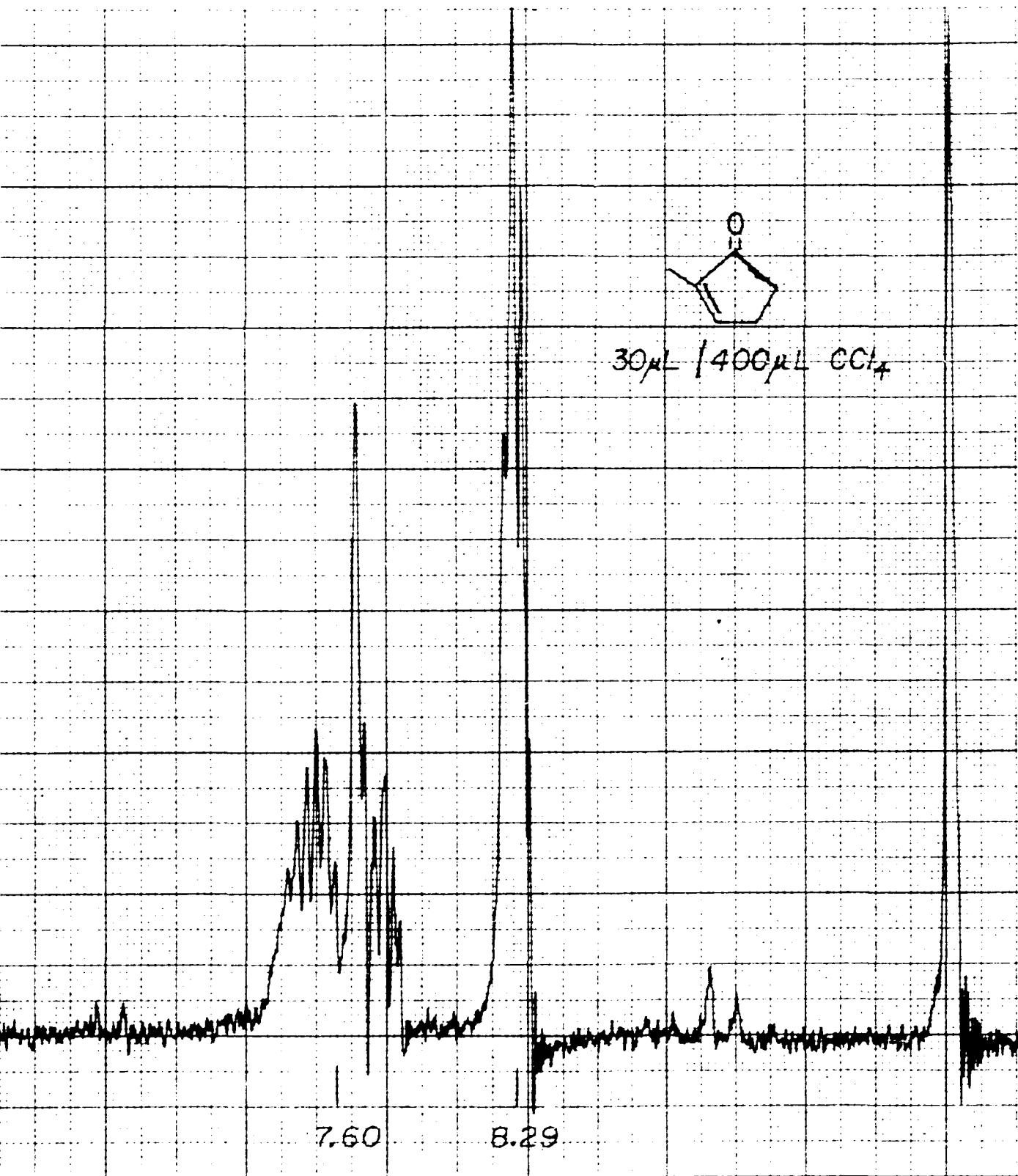


Figure 35. NMR spectrum of 2-methyl-cyclopent-2-enone



30 μ L / 400 μ L CCl_4



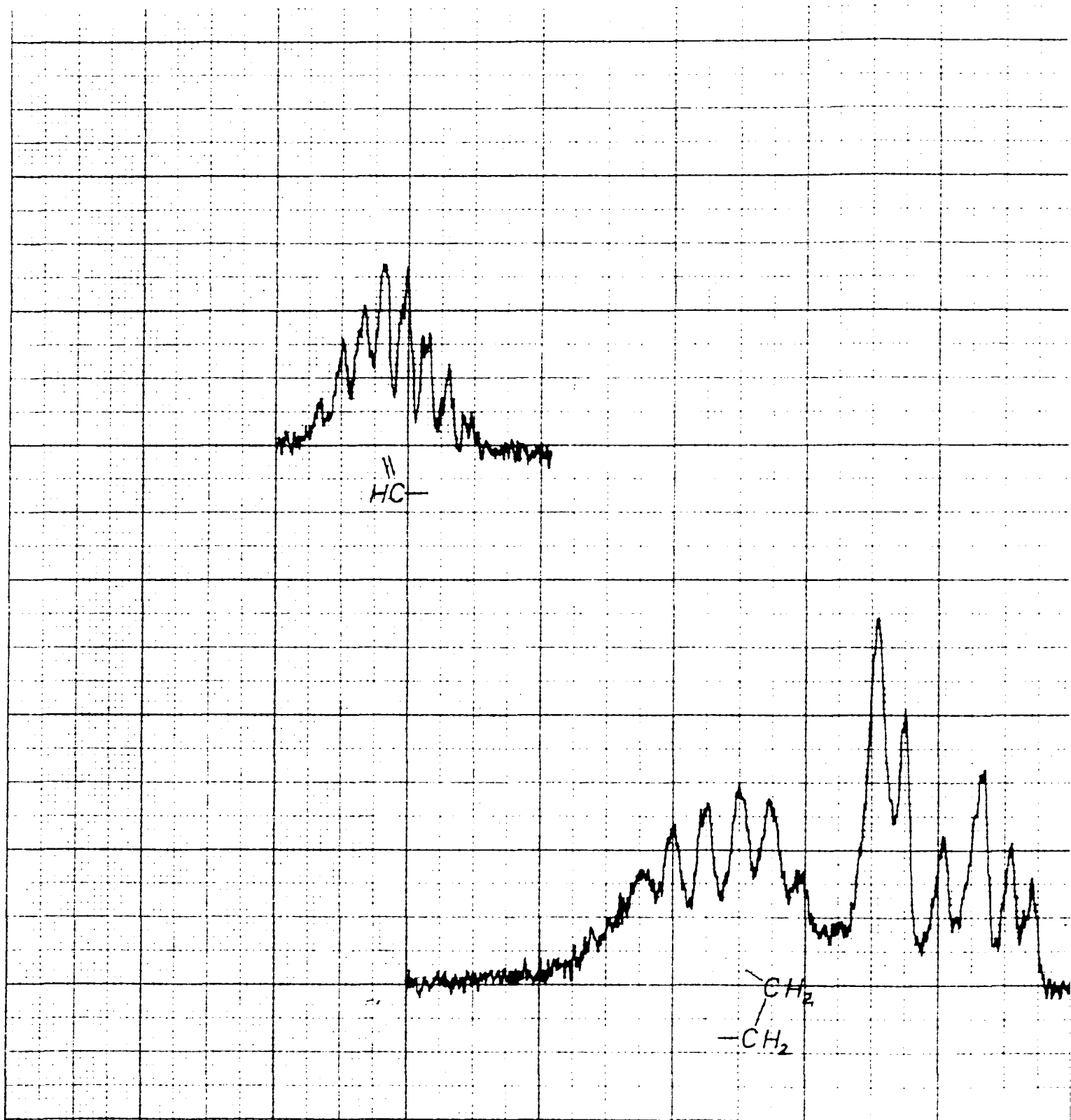
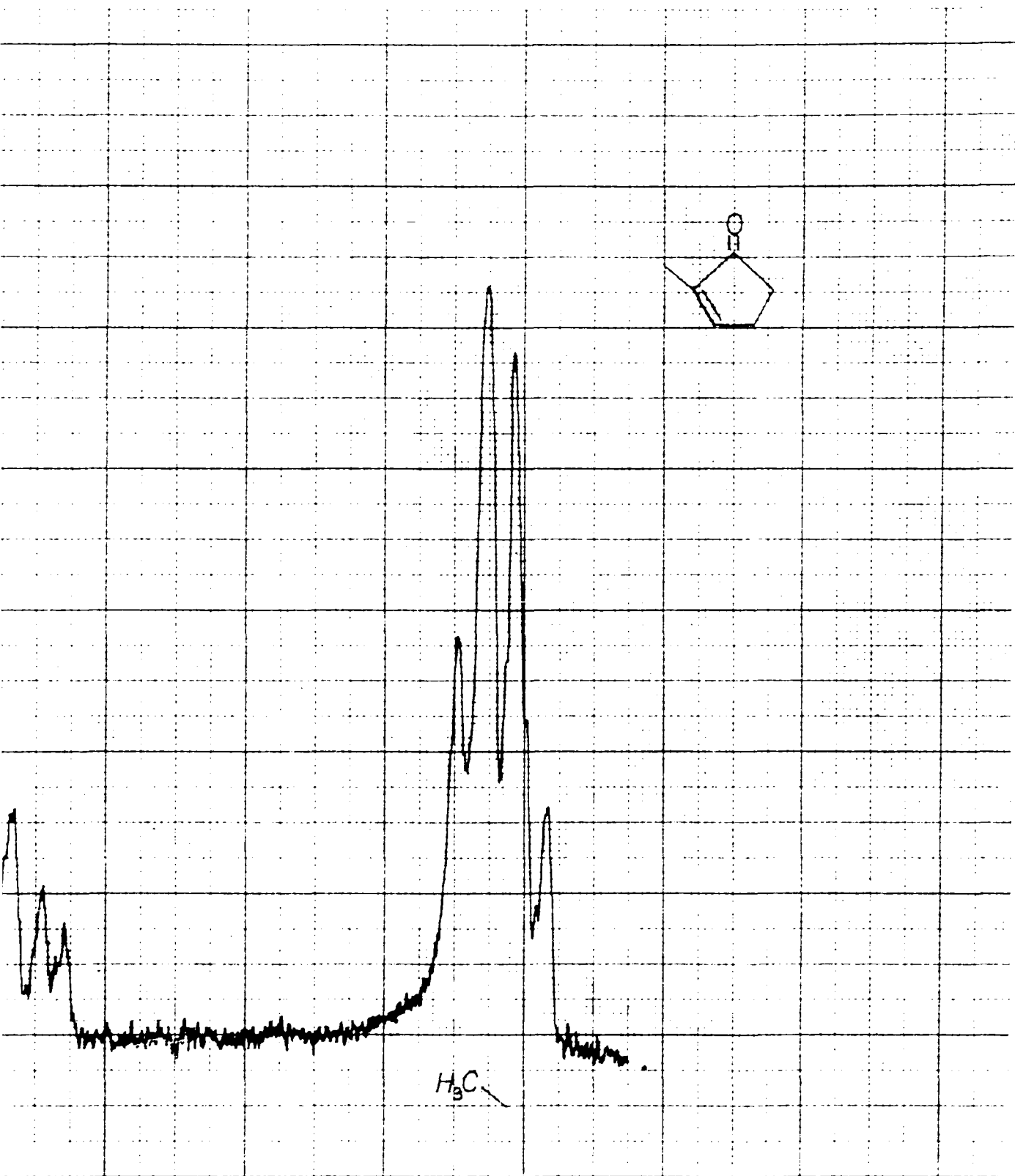


Figure 36. Expansion of 2-methyl-cyclopent-2-enone spectrum



H_3C