1968

Palladium and platinum complexes of substituted 4-vinylcyclohexene

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Recommended Citation

PALLADIUM AND PLATINUM COMPLEXES OF

SUBSTITUTED 4-VINYLCYCLOHEXENE

A Thesis

Presented to

the Faculty of the Graduate School

University of the Pacific

In Partial Fulfillment

of the Requirement for the Degree

Master of Science

by

Donald Y. Chinn

May 1968

This thesis, written and submitted by

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Dated *May 22, 1968*

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CHAPTER I

INTRODUCTION

In recent years numerous complexes have been reported
in which olefins were chelated to transition metals. Ever
since the generally regarded first olefin complex, Zeise's
salt (32) $KPt(C_2H_4)Cl_3$, the interest in this field of
organometallic chemistry has expanded to several families of
olefinic ligands and metals like palladium(II), platinum(II)
copper(I), silver(I), and more recently vanadium and
titanium.

One particular group of olefinic compounds that has
provided another dimension in coordination chemistry were
the cyclic alkadienes. However, only limited informations
were available. In 1951, a class of "sandwich" bonded
complexes were reported beginning with ferrocene $(C_5H_5)_2Fe$
where the metal was bonded to two cyclopentadienyl anions.
Fischer and Werner in 1959 reported a select family of these
"sandwich" complexes. Hallam and Pauson in 1958 reported
1,3-cyclohexadiene-iron tricarbonyl $C_6H_8Fe(CO)_3$. Only a
few complexes of cycloheptadiene had been reported. The
most widely studied cyclic diolefin complexes were those
prepared from 1,5-cyclooctadiene and the transition metals in
their low oxidation state. Chatt and Venanzi (4) reported on
rhodium(I) complex of 1,5-cyclooctadiene. More recently,

Huttel, Reinhemier, and Dielt (18) reported on the gold(I)

chloride complex of the same diolefin. Several workers have

reported on the palladium and platinum complexes of

1,5-cyclooctadiene.

Of special interest was the cyclic olefin 4-vinyl-

cyclohexene which was complexed with palladium(II) and

platinum(II) chlorides and bromides as reported by Kuljian

and Frye (24). 4-Vinylcyclohexene provided two possible

olefin system for complexation— as a diolefin or and olefinic

system where there was a preference in pi bonding of one

olefin site over the other. (See figure A)
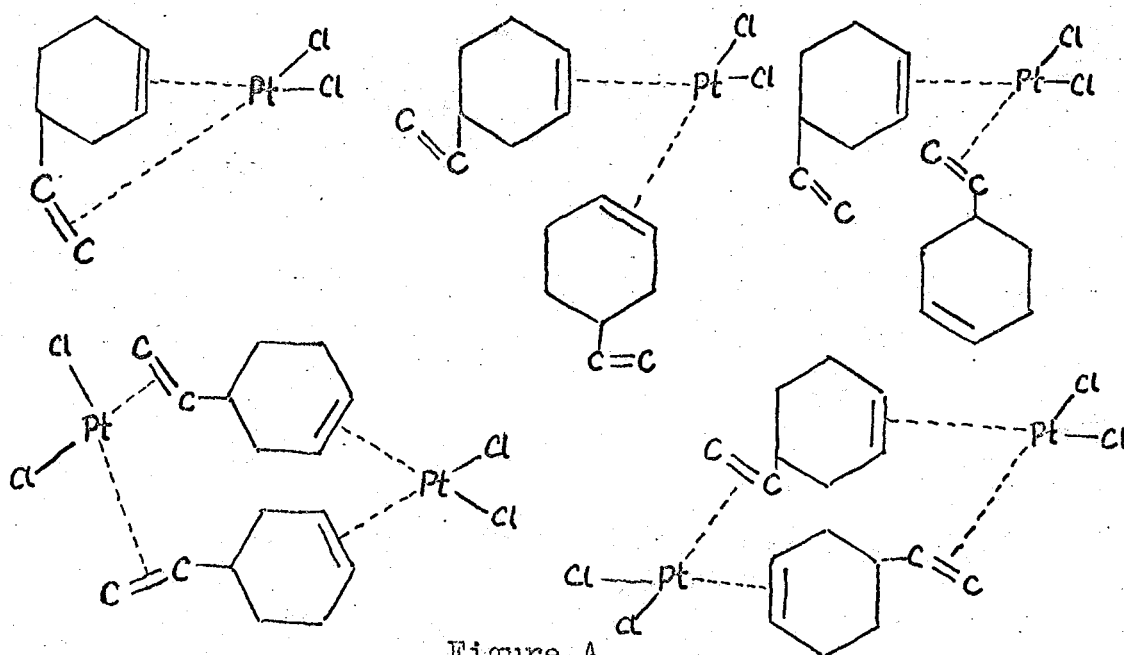
Figure A

It was observed by Frye, Kuljian, and Viebrock (14) that

upon complexation of 4-vinylcyclohexene with palladium(II)

chloride and bromide, rearrangement occurred whereby the

the complex of 1,5-cyclooctadiene was formed.

The effect of rearrangement during complexing have been observed by several workers involving several ligands. Frye, Kuljian, and Viebrock (13) reported the ligand rearrangement of 1,3-cyclooctadiene to 1,5-cyclooctadiene via complex with palladium and platinum. This particular rearrangement was also reported by Reinhart and Lasky (29) via the rhodium(I) complex. More recently, isomerization of 1,5-cyclodecadiene by palladium(II) and platinum(II) complexes to 1,2-divinylcyclohexane was reported by Trebellas, Olechowski, and Jonassen (31). They also reported later the isomerization of 1,5-cyclodecadiene to 1,6-cyclodecadiene by rhodium(I) complex.

The nature of the bonding of olefins to metal atoms seemed to involved the interaction between pi electrons in the unsaturated molecule and the hybrid orbitals of the metal rather than a localized sigma bonds between the metal atom and a particular carbon atom. The metal was complexed to a hydrocarbon which possessed a surplus of electrons. The direct overlap of a sigma orbital of the metal and the p-orbital of the carbon atom formed a sigma type bond. The ligand carbon atom donated a surplus bonding pi-p electrons to a vacant sigma orbital of the metal while at the same time the excess negative charge was released back to the olefin from a pi-d orbital of the metal to an empty antibonding pi-p

orbital of the carbon atom. Dewar (9) illustrated this point by molecular orbital diagram. (See figure B)
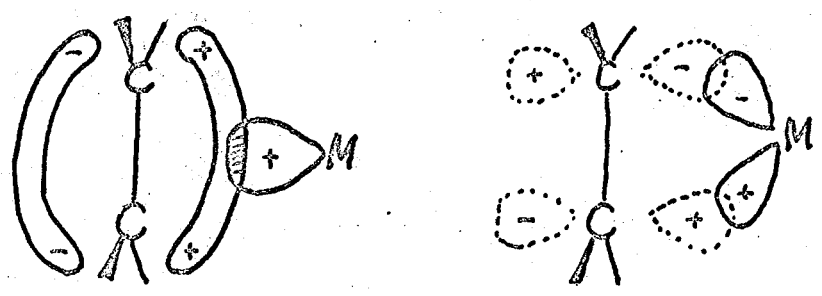
Figure B

The metal to olefin bond consisted of two parts: (a) overlap of the pi electron density of the olefin with sigma type acceptor orbital on the metal atom and (b) a "back-bonding" resulting from flow of electron density from filled metal d_{xy} or other $d_\pi - p_\pi$ hybrid orbitals into antibonding orbital on the carbon atom. A schematic diagram of platinum olefin complexes can be shown as:
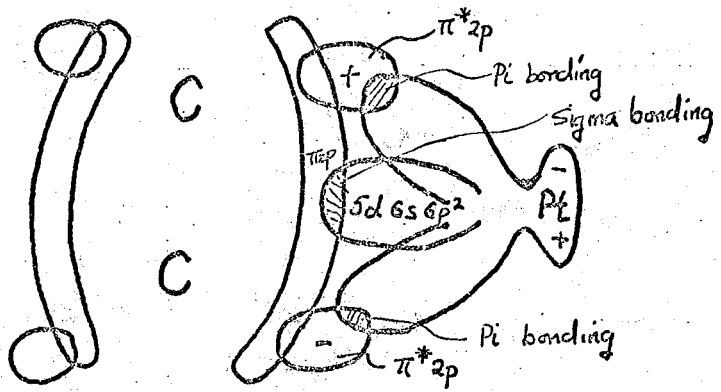
Figure C

It was the intention of this research to increase our understanding of these stable diolefin complexes. In particular, the occurrence of rearrangement upon complexation of

certain ligands to most likely a more stable configuration posed an interesting project. The syntheses of diolefin complexes provided an establishment of good technique and verification of reported data.

CHAPTER II

FORMULATION OF PROGRAM OF STUDY

The program of study was concentrated on the complexation of cyclic diolefins with primarily palladium(II) and platinum(II) chloride. The ground work has been initiated by several people, but experimentation in this research was a continuation of the study made by Frye and Kuljian (13, 14, 24). In the complex formation with 4-vinylcyclohexene via palladium(II) chloride and bromide, it was observed by Frye, Kuljian, and Viebrock (14) that a ligand rearrangement occurred in which 4-vinylcyclohexene was readily converted to 1,5-cyclooctadiene. The corresponding platinum(II) reaction yielded the expected pi complex in which the 4-vinylcyclohexene did not rearrangement. (See figure D and E)

Figure D

$$+ PdCl_2 \longrightarrow$$

Figure E

$$+ PtCl_2 \longrightarrow$$
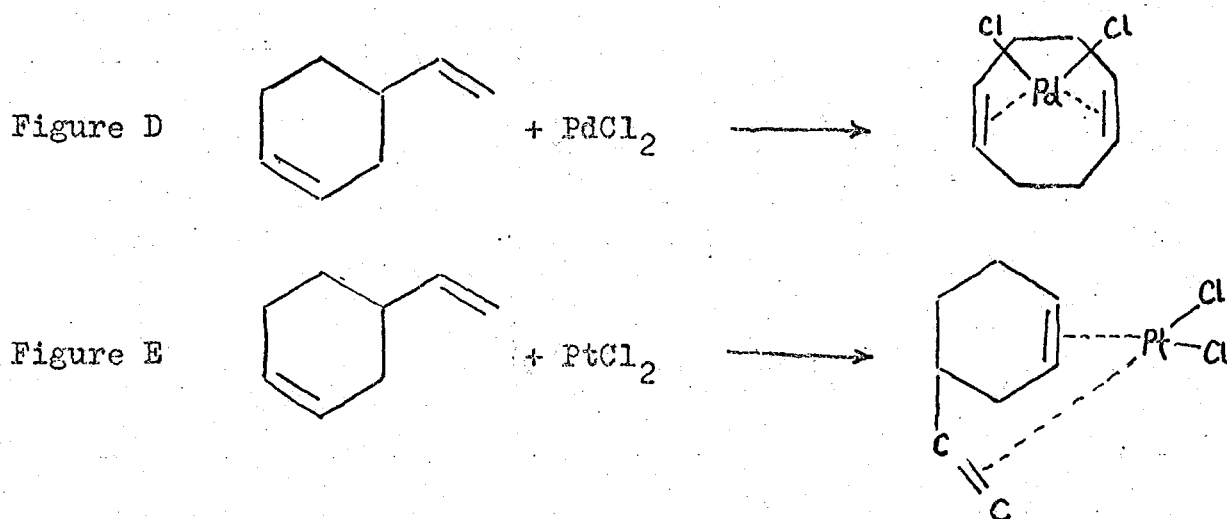
It was under this premise that the first part of the research

began;   to study the rearrangement reaction of 4-vinylcyclo-
hexene to 1,5-cyclooctadiene via palladium(II) complexation.
The work of Frye and co workers was repeated to insure a more
complete laboratory background as well as verification of
previously reported literature data.

Inspired by the approach of McCauley (26) on the
ligand isomerization of 1,3-cyclooctadiene to 1,5- cycloocta-
diene via palladium and platinum, whereby he substituted
alkyl groups on the cyclooctadiene ring and studied the induc-
tive and steric effect on complexation, the research here
followed a similar route in approaching the problem for
4-vinylcyclohexene. The syntheses of the substituted 4-vinyl-
cyclohexene were accomplished by means of allylic bromination
with N-Bromosuccinimide followed by a Grignard reaction.
With the knowledge that rearrangement occurred upon complexa-
tion of 4-vinylcyclohexene it was of interest to observe the
inductive and steric effect here also. The possibility of
tracing the mechanism by which rearrangement occurred was
considered in this approach.

Inductively, substituted alkyl groups on any of the
three possible allylic position on 4-vinylcyclohexene would
reinforce the electron cloud of the double bond thereby
strengthed the pi cloud by donating its electron more readily
to the metal atom amd make for a stronger metal-carbon bond or
a faster rate of complexation. Electron donating groups on

any of the vinyl carbon atom would provide donation directly
into the pi system.

Sterically, the substituents on the allylic carbon
atom would have little effect unless the group was of suffi-
cient length. Conversely, the groups on the vinyl position
would provide some steric hinderance upon complexation.

The study of inductive and steric effect of substit-
uents on the vinyl position was accomplished by investigating
d-Limonene (p-mentha-1,8-diene). (See figure F) Platinum(II)
chloride complex of d-Limonene has been reported by Kharasch
and Ashford (21) as an exceptionally stable complex. The work
was repeated here as well as the preparation of the palladium
complex of d-Limonene.
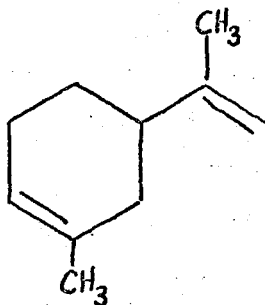
Figure F

The final part of this research program was to study
l-vinylcyclohexene. Having the double bond system in con-
jugation, it was interesting to observe whether l-vinylcyclo-
hexene undergo rearrangement upon complexation with palladium
or form the normal pi complex. l-Vinylcyclohexene was
synthesized by the procedure of Bergmann and Becker (3) where
l-ethynylcyclohexanol was dehydrated with phosphorus oxychlor-

ide followed by the selective hydrogenation with Lindlar

catalyst of 1-ethynylcyclohexene to 1-vinylcyclohexene.
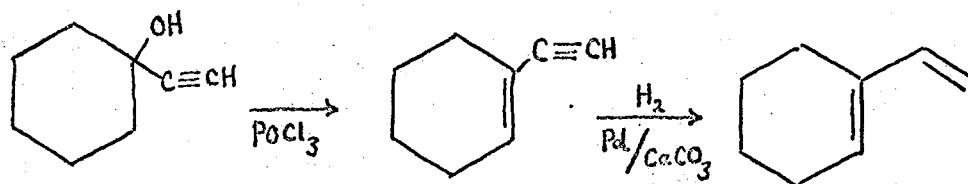
Figure G

The palladium and platinum complexes of the various

diolefins mentioned previously were investigated by infrared

and ultrviolet spectra as well as carbon and hydrogen analsis

as to their structure. Nuclear magnetic resonance data was

available for selected organic compounds prepared to help

determine the structure of the complexes prepared.

CHAPTER III

REAGENTS REQUIRED

4-Vinylcyclohexene and 1,5-Cyclooctadiene: Laboratory
size samples of these olefins were obtained through the cour-
tesy of Columbian Carbon Company. Each olefin was fractional
distilled in order to increase their purity and remove the
small amount of stablizer. Vapor phase chromatographic
analysis showed the 4-vinylcyclohexene to be 99% pure.
Infrared spectra and nuclear magnetic resonance spectra
are available for 4-vinylcyclohexene in chapter X.

1-Ethynylcyclohexanol. This reagent was obtained from
Matheson-Coleman- Bell as reagent grade. This was redistilled
and retaining the 97°C (14 mm) fraction.

N-Bromosuccinimide. Arapahoe reagent grade. No further
purification was needed.

_Bromobenzene; n-Butylbromide; Ethylbromide; Methyl
Iodide._ These reagents required for the Grignard reaction
were obtained from readily available stock supplies. They
were distilled and the middle fractions collected for use
with no further analyses.

Limonene (p-Mentha-1,8-diene). This was obtained from
Eastman Organic Chemicals and was distilled.

Benzonitrile. Eastman Organic Chemical reagent grade was redistilled, retaining the 190-192°C fraction.

Lithium Aluminum Hydride; Calcium Hydride. These were obtained from readily available stock supplies and no further purification was used.

Common Solvents. Dry carbon tetrachloride was prepared by distillation, discarding the first 25% fraction and storing over phosphorus pentoxide. Dry ether was prepared by the usual treatment over sodium metal and distilling directly into the reaction vessel. Dry pyridine was prepared by first refluxing over potassium hydroxide and barium oxide and then distilling. Solvents such as benzene, petroleum ether, ethanol, etc. were reagent grade and were subject to no further treatment except drying as called for. For preparation of any spectra, only spectra grade solvents were used.

Palladium(II) and Platinum(II) salts. These salts were obtained from K and K Laboratories and were used with no further purification.

CHAPTER IV

EXPERIMENTAL

I. PREPARATION OF THE LIGANDS

4-Bromo-4-Vinylcyclohexene. This new compound was prepared according to previous procedure of Cope and co-workers (6) in their preparation of 3-bromo-1,5-cycloocta-diene by means of allylic bromination of the diene system.

58.5 ml. (0.45 mole) of previously distilled 4-vinyl-cyclohexene was added to a mixture of 53.0 grams (0.30 mole) N- Bromosuccinimide and 2 grams of benzoyl peroxide in 250 ml. dry carbon tetrachloride. This mixture was refluxed for three hours after which a noticeable solid floated on the surface of the solution. This solid was identified as the byproduct of the reaction, succinimide (mp. 124°C). The reaction mix-ture was cooled and then filtered through a buchner funnel separating the solid succinimide from the mother liquid. The filtrate was wash twice with dilute solution of sodium carbon-ate and then with water. Thecarbon tetrachloride was removed and the product dried over anhydrous calcium chloride. The product was fractionally distilled under vacuum with a vigreaux column. The product was collected at 76.5°C (6 mm). The yield was 26.04 grams (46.4%). Refractive index: 1.5350 at 22°C. Calculated: Br - 42.72%; Actual: Br - 41.20%. Infrared spectra available. See figure 6-1.

Vapor phase chromatography indicated one major isomer. Nuclear magnetic resonance data was taken for this isomer. (See figure 6-27) Discussion of data and description of the proof of structure is given in chapter V. Tentatively, the product was considered to be 4-bromo-4-vinylcyclohexene. No literature value was found for this compound and therefore assumed to be a new organic compound.

Hydrogenolysis of 4-Bromo-4-Vinylcyclohexene by Lithium Aluminum Hydride.

In order to study whether isomerization occurred during the free radical bromination of 4-vinylcyclohexene, the bromo group was removed to recover possibly the original starting material, 4-vinylcyclohexene.

Using the procedure of hydrogenolysis of alkyl halides by lithium aluminum hydride of Johnson, Blizzard, and Carhart (10), tetrahydrofuran, dried over calcium hydride, was added slowly to a cold flask containing 2.46 grams (0.065 mole) of lithium aluminum hydride. The mixture was stirred and reflux gently for $\frac{1}{2}$ hour. The flask was cooled again and then 15.18 grams (0.081 mole) 4-bromo-4-vinylcyclohexene was added to the mixture while maintaining a moderate reflux. The mixture was refluxed for another hour, then cooled to $10^{\circ}C$. A mixture of approximately 30 ml. of tetrahydrofuran/water 20/10 by volume was added cautiously with stirring keeping the temperature below $20^{\circ}C$. Then the

mixture was transferred to a beaker containing 20ml. H_2SO_4 in ice and water. The product layer was separated, wash twice with water and dried over anhydrous potassium carbonate and then distilled. Yield was 12.0 grams (80%). Observed boiling point was 118°C. Refractive index: 1.4680 at 26°C. Infrared spectra data available. See figure 6-2. Actual boiling point was 128°C and refractive index was 1.464 at 20°C for 4-vinylcyclohexene. The observed values of the recovered product seemed to correspond to the actual values of 4-vinylcyclohexene. The infrared spectra data showed the major bands to be similar to the actual spectra.

1-Vinylcyclohexene. This compound was prepared as directed by Bergmann and Becker (3).

55 ml. of phosphorus oxychloride in 55 ml. dry pyridine was added slowly to a solution of 100 grams (0.80 mole) 1-ethynylcyclohexanol in 50 ml. dry pyridine in a flask fitted with a stirrer and a reflux condenser. The addition rate was such that the mixture just boiled. After gently heating over a steam bath for one hour (internal temperature - 85°C), the reaction mixture was cooled and pour on ice and the product isolated with hexane. The mixture was dried over anhydrous calcium chloride and fractionally distilled to give 1-ethynylcyclohexene. Yield: 32.92 grams (40%). Boiling point: 56-59°C at 40 mm Hg. Literature value for boiling point was 53-56°C at 40 mm.

32.92 grams of 1-ethynylcyclohexene was selectively hydrogenated with one gram Lindlar catalyst in a Parr Hydrogenation apparatus. The Lindlar catalyst was prepared by conditioning palladium/calcium carbonate with lead acetate. The reaction mixture was placed in a 500 ml reaction bottle and filled to about the half mark using hexane as the solvent. The mixture was hydrogenated with one milliliter of quinoline to poison the catalyst. The hydrogen uptake at room temperature was tenth a mole of hydrogen corresponding to approximately 8 p.s.i. drop. After two hours, the reaction mixture was filtered from the catalyst. The hexane was removed and the product was fractionally distilled collecting the $147^{\circ}C$ fraction. Yield: 17.12 grams (51%). Refractive index: 1.5030 at $25^{\circ}C$. Infrared spectra available. See figure 6-5. The observed data for this reaction seemed to correlate with the values of Bergmann and Becker. The infrared spectra showed distinctly the characteristic carbon-carbon double bond stretching of a conjugated system at 1600 cm^{-1} and 1650 cm^{-1}.
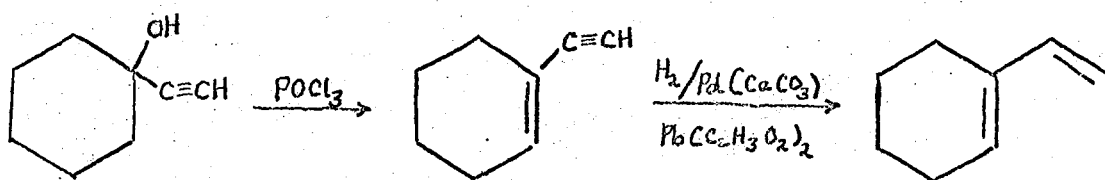

Figure H

4-Phenyl-4-Vinylcyclohexene. The procedure for preparing a typical Grignard reagent (23) is well known. In preparing this new compound, 6.0 grams (0.25 mole) of magnesium turnings were reacted with an ether solution of freshly distilled bromobenzene (31.4 ml. or 0.30 mole). A couple drops of bromine was added to catalyze the reaction. The mixture was refluxed for one half hour over a steam bath. The reaction flask was cooled over an ice bath and the 4-bromo-4-vinylcyclohexene was added slowly. After the 0.30 mole amount was added, the reaction was refluxed for an hour. During one and half hour the ether was removed by distillation to allow the reaction temperature to rise. The flask was cooled again and the ether return to the mixture. The latter was decomposed by slowly adding 10 ml. ice water and 40 ml. ice cold 10% HCl. The ether layer and aqueous layer was separated. The ether solution was dried over anhydrous calcium chloride. The ether was removed and the residue fractionally distilled. The fraction boiling at 121°C at 10 mm Hg was collected. The yield was 22.3 grams or about 30%. Refractive index: 1.5570 at 17.5°C. Calculated: C 91.31%; H 8.68%. Actual: C 91.51%; H 8.63%. Infrared spectra available. See figure 6-6.

This compound has not been reported in literature and therefore a new compound. Discussion of structure will be given in chapter V.

<u>4-Butyl-4-Vinylcyclohexene</u>. The procedure for preparing this new compound was the same as for 4-phenyl-4-vinylcyclohexene. 6.0 grams of magnesium turnings were reacted with an ether solution of n-butylbromide (31.7 ml. or 0.30 mole). After refluxing, 0.30 mole of 4-bromo-4-vinylcyclohexene was added. The usual work-up followed. The solution was fractionally distilled with a vigreaux column. The fraction coming over at 78-80°C at 5 mm Hg was collected. Yield was 25%. The refractive index: 1.4724 at 29°C. Infrared spectra data available. See figure 6-7.

There was no literature value for this compound and therefore considered a new compound. Discussion of this compound will be in chapter V.

<u>4-Ethyl-4-Vinylcyclohexene</u>. This new compound was prepared, as before, using 22.8 ml. (0.30 mole) ethylbromide and 6.0 grams magnesium turnings in an ether medium. After refluxing for half an hour, 0.30 mole 4-bromo-4-vinyl -cyclohexene was added and solution was refluxed for another hour. The usual workup followed and the solution was fractionally distilled with a vigreaux column under reduced pressure. The fraction, 40°C at 6 mm Hg was collected and stored over Drierite. The yield was 16.2 grams or 29%. Refractive index: 1.4704 at 29°C. Infrared spectra available. See figure 6-8. Calculated: C 88.25%; H 11.75%. Actual: C 88.54% H 11.74%.

<u>4-Methyl-4-Vinylcyclohexene</u>. This new compound was prepared as before by Grignard reaction. 6.0 grams of magnesium turnings was reacted with an ether solution of 18.7 ml. (0.30 mole) methyl iodide. The solution was catalyzed with a crystal of iodine. After refluxing for half hour, 0.30 mole of 4-bromo-4-vinylcyclohexene was added and the refluxing continued for another hour. The reaction mixture was cooled and the usual workup followed. The product was separated from the aqueous layer and then fractionally distilled with a vigreaux column under reduced pressure. The fraction boiling at 65-67°C at 12 mm Hg was collected and stored over anhydrous calcium chloride. The yield was 16.3 grams or 45%. Refractive index: 1.4680 at 25°C. Vapor phase chromatography showed this fraction to be 98% pure. Calculated: C 88.52% H 11.47%. Actual: C 88.41%; H 11.01%. Infrared spectra data available. See figure 6-9.

No literature value was found for this compound and will be assumed to be a new compound. Nuclear magnetic resonance data is available for structural verification. See figure 6-27. Discussion and interpretation of data will be in chapter V.

II. PREPARATION OF THE COMPLEXES

4-Vinylcyclohexene Palladium Chloride. Using the
method of Frye, Kuljian, and Viebrock (14), equimolar
portions of 4-vinylcyclohexene and bis(benzonitrilo)palladium
chloride were dissolved with stirring in benzene solution. A
dark brown precipitate formed almost immediately and upon
sitting overnight at room temperature the brown precipitate
was converted to bright yellow crystals. The yellow crystals
were filtered and wash with petroleum ether. The crystals
were recrystallized from boiling glacial acetic acid. Another
method which worked equally well was found by dissolving
0.294 grams (0.001 mole) Na_2PdCl_4 in about 15 ml. absolute
ethanol. Due to some incomplete dissolution of a small
amount of insoluble starting material and some reduction of
the palladium salt, the solution was filtered and the residue
rinsed with 5 ml. absolute ethanol. To this filtrate one half
milliliter of 4-vinylcyclohexene was added. A brown precipi-
tate formed upon addition and after sitting overnight the
bright yellow crystals was formed. The crystals were washed
with petroleum ether and recrystallized from hot glacial acetic
acid. The crystals were dried and stored over Drierite.
These crystals melted sharply with decomposition at $205^{\circ}C$.
The yield was 45%. Calculated: C - 33.65% ; H - 4.23%.
Actual: C - 33.74% ; H - 4.35%. These values corresponded
to literature value of Frye and coworkers.

Infrared spectra data are available. (See figure 6-11)

4-Vinylcyclohexene Platinum Chloride. Using the method of Kuljian and Frye (24), 0.383 grams (0.001 mole) Na_2PtCl_4 was dissolved in 20 ml. absolute methanol and the solution was warmed to $50^{\circ}C$. The solution was filtered from the insoluble salts that formed. To the filtrate was added two milliliters of 4-vinylcyclohexene. There was no immediate reaction, but after two days at room temperature, straw yellow crystals formed. These were washed with petroleum ether and recrystallized from boiling glacial acetic acid. The crystals were dried and stored over Drierite. The yield was about 50%. Melting point was $215^{\circ}C$. No carbon-hydrogen analyses were taken. Infrared spectra are available. (See figure 6-12) The values obtained correspond to the values of Kuljian and Frye.

1,5-Cyclooctadiene Palladium Chloride. The procedure used to prepare this complex was the classical Kharasch method (22) where 0.300 grams (0.100 mole) of bis(benzonitrilo)palladium(II) chloride was added to 25 ml. benzene. To this solution, one milliliter of 1,5-cyclooctadiene was added. Immediately, fine yellow crystals began to precipitate. The crystals were filtered and wash with petroleum ether and dried. Recrystallization was accomplished with hot glacial acetic acid of chloroform. Another method which

worked equally well was used by McCauley (26) where he used
0.295 grams (0.001 mole) Na_2PdCl_4 in about 20 ml. absolute
ethanol. To this solution was added one milliliter of
1,5-cyclooctadiene. Fine yellow needles formed almost im-
mediately. The reaction was left overnight to insure com-
plete reaction. The crystals were filtered and wash with
petroleum ether. The yield was 35%. Melting point: 205°C
with decomposition. No carbon-hydrogen analyses were taken.
Infrared spectra (See figure 6-13) verified previous data
for this complex.

1,5-Cyclooctadiene Platinum Chloride. This compound
was prepared according to the procedure of McCauley (26)
by reacting 0.383 grams (0.001 mole) Na_2PtCl_4 in 25 ml.
absolute methanol. To this solution was added one milliliter
of 1,5-cyclooctadiene. After several days, yellow needles
were formed. The crystals were filtered and wash with pet-
roleum ether and recrystallization with hot glacial acetic
acid. The yield was around 25%. The melting point was 250°C
with decomposition. No elemental analyses were taken.
Infrared spectra (See figure 6-14) showed the values
corresponded to previous literature values.

d-Limonene Palladium Chloride. This new compound was
prepared by initially dissolving 0.294 grams (0.001 mole)
Na_2PdCl_4 in 15 ml. absolute ethanol. The solution was fil-

tered to remove undissolved salts. To the filtrate was added 0.5 ml. d-Limonene. After several days, a fine plate-like precipiate formed. The precipiate was filtered and wash with more absolute ethanol. They were dried and stored over Drierite. The yield was very small and insufficient amount for analyses. Melting point: 147°C with decomposition. Infrared spectra are available. (See figure 6-15)

d-Limonene Platinum Chloride. This complex has been prepared by Kharasch and Ashford (21). 0.5 grams platinic chloride suspended in 10 ml. of glacial acetic acid and 0.5 ml. of the d-Limonene was added. The mixture was warmed in a steam bath for about 10 minutes. During this time the platinic chloride goes into solution and the reaction was completed. Crystals began to appear after several hours. A better method of preparing this was by dissolving 0.383 grams (0.001 mole) Na_2PtCl_4 in absolute ethanol. The solution was filtered from the insoluble salts. To the filtrate was added 0.5 ml. d-Limonene. After several days, bright yellow crystals formed. The crystals were filtered and wash with absolute ethanol. The yield was 35%. Melting point: 152°C. Elemental analyses: Calculated: C - 29.86%; H - 3.97%. Actual: C -- 29.50%; H - 4.08%. Infrared spectra available. (See figure 6-16). The observed values corresponded to the literature values. The second method of preparation seemed

to give a better yield as well as an easier procedure to work with.

1-Vinylcyclohexene Palladium Chloride. This new compound was prepared analogous to the method used in preparing 4-vinylcyclohexene palladium chloride. 0.294 grams (0.001 mole) Na_2PdCl_4 was dissolved in 20 ml. absolute ethanol. After filtering this solution, 0.5 ml. 1-vinylcyclohexene was added to the filtrate. A light brown precipitate formed after sitting several hours. The precipitate turned to gray color after several days. The precipitate was filtered and wash with petroleum ether. The yield was 25%. The observed melting point was very high with decomposition and the infrared spectra (See figure 6-18) showed little resolution indicating the possible product to be the oxide of palladium.

1-Vinylcyclohexene Platinum Chloride. This new complex was prepared by dissolving 0.383 grams (0.001 mole) Na_2PtCl_4 in 20 ml. n-propanol. The solution was warmed and then filtered. To the filtrate 0.5 ml. 1-vinylcyclohexene was added. After several hours, a fine white precipitate appeared. The solution was left for several days to insure complete reaction. The precipitate was filtered and wash with petroleum ether and dried in a desiccator. This compound also appeared to be the oxide of platinum, This was evident by the high melting point and infrared spectra. (See figure 6-19)

However, elemental analyses showed: Calculated: C - 25.68%
H - 3.24%. Actual: C - 25.66%; H - 3.48%.

4-Phenyl-4-Vinylcyclohexene Palladium Chloride. This
new complex was prepared by initially dissolving 0.294 grams
(0.001 mole) Na_2PdCl_4 in 20 ml. absolute ethanol. This
solution was filtered from the insoluble salts and some
reduction product of the palladium salt. To the filtrate was
added 0.5 ml. of the prepared ligand 4-phenyl-4-vinylcyclo-
hexene. After several minutes the solution faded to a yellow
color from the original orange color and a precipitate was
formed. The reaction was left for several days to insure
complete reaction. The orange color product was washed with
absolute ethanol. Recrystallization was accomplished by
chloroform or hot glacial acetic acid. The crystals were
dried and stored in a desiccator. Calculated: C - 46.52%;
H - 4.42%. Actual: C - 46.56%; H - 4.39%. Melting
point: 123°C. Infrared spectra data available. See
figure 6-20.

4-Phenyl-4-Vinylcyclohexene Platinum Chloride. This
new compound was prepared by initially dissolving 0.383 grams
(0.001 mole) Na_2PtCl_4 in 20 ml. absolute ethanol. To this
solution one milliliter of 4-phenyl-4-vinylcyclohexene was
added. After several hours, a light color precipitate was
formed. The precipitate was filtered and wash with absolute

ethanol. The product was recrystallized from hot glacial acetic acid. The precipitate was washed and dried in a desiccator. Calculated: C - 37.35%; H - 3.55%. Actual: C - 33.68%; H -3.21%. Melting point: 135°C. Infrared spectra available. See figure 6-21.

4-Butyl-4-Vinylcyclohexene Palladium Chloride. The method used to prepared this new compound was the same for the preparation of 4-phenyl-4-vinylcyclohexene palladium chloride. One milliliter of the 4-butyl-4-vinylcyclohexene was added to the alcoholic solution of palladium chloride. Immediate change in color of the solution from the original orange color to a light yellow color was observed and a precipitate formed. The reaction mixture was left overnight to insure complete reaction. The orange color precipitate was filtered and wash with absolute ethanol. Yield was 35%. Melting point: 174°C with decomposition. Infrared spectra available. See figure 6-22.

4-Butyl-4-vinylcyclohexene Platinum Chloride. To prepare this compound, 0.383 grams (0.001 mole) Na_2PtCl_4 was dissolved in 20 ml. absolute ethanol. One milliliter of the 4-butyl-4vinylcyclohexene was added to this solution. After sitting overnight, a plate-like precipitate deposited on the surface of the container. The precipitate was filtered and wash with absolute ethanol. The yellow crystals were

recrystallized with chloroform. The yield was 25%. The
melting point was 200°C with decomposition. Infrared spectra
available. See figure 6-23.

4-Ethyl-4-Vinylcyclohexene Palladium Chloride. This

new compound was prepared similar to above procedures.
0.294 grams (0.001 mole) Na_2PdCl_4 was dissolved in absolute
ethanol. The mixture was filtered and wash with more ethanol.
To the filtrate, 0.5 ml. 4-ethyl-4-vinylcyclohexene was
added. After 24 hours, a fine yellow solid precipitated
out of solution. The precipitate was filtered and wash with
absolute ethanol and dried. The yield was 27%. The melting
point was 150°C with decomposition. Calculated: C 39.60%;
H 5.28%. Actual: C 45.37%; H 5.99%. Infrared spectra
available. See figure 6-24.

4-Ethyl-4-Vinylcyclohexene Platinum Chloride.

0.383 grams (0.001 mole) Na_2PtCl_4 was dissolved in 20 ml.
absolute ethanol. The solution was filtered from the insol-
uble salts and to the filtrate, 0.5 ml. 4-ethyl-4-vinylcyclo-
hexene was added. After several days, no appreciable
precipitate was formed. The small amount of solid that did
form was found to be the oxide of platinum. The experiment
was repeated several times with different solvents as well
as changing the temperature condition. However, the same
unsuccessful result was observed.

4-Methyl-4-Vinylcyclohexene Palladium Chloride.

The procedure for preparing this new compound was the same as previous palladium complexes. 0.294 grams (0.001 mole) Na_2PdCl_4 was dissolved in 20 ml. absolute ethanol. The solution was filtered and to the filtrate was added 0.5 ml. 4-methyl-4-vinylcyclohexene. A dark gray precipitate formed after several hours. The precipitate was collected and wash with more absolute ethanol. The yield was small. Melting point was about $200^\circ C$ with decomposition. Infrared spectra available. See figure 6-25.

4-Methyl-4-Vinylcyclohexene Platinum Chloride.

The preparation of this new compound was with little success. 0.383 grams (0.001 mole) Na_2PtCl_4 was dissolved in 20 ml. absolute ethanol. The mixture was filtered and wash with more ethanol. To the filtrate, 0.5 ml. 4-methyl-4-vinyl-cyclohexen was added. After several days, a gray precipitate was deposited on the surface of the container. The precipitate was collected and wash with ethanol and then petroleum ether. The precipitate was dried and stored in a desiccator. The yield was very small. The melting point was very high and the infrared spectra showed little resolution. The product seemed to be the oxide of the metal, platinum.

The palladium(II) and platinum(II) complexes of substituted 4-vinylcyclohexene were regarded as new compounds.

No literature values were found for these complexes. Also no literature values were found for d-Limonene palladium complex or for both palladium(II) and platinum(II) complexes of 1-vinylcyclohexene. They were tentatively regarded as new compounds.

TABLE I

TABLE OF MELTING POINTS AND YIELDS OF COMPOUND PREPARED

Compound	Melting point	Yield (%)
4-Vinylcyclohexene PdCl$_2$	205°C dec.	45
4-Vinylcyclohexene PtCl$_2$	215°C	50
1,5-Cyclooctadiene PdCl$_2$	205°C dec.	50
1,5-Cyclooctadiene PtCl$_2$	250°C dec.	35
d-Limonene PdCl$_2$	147°C dec.	20
d-Limonene PtCl$_2$	152°C	35
1-Vinylcyclohexene PdCl$_2$	above 275°C dec.	25
1-Vinylcyclohexene PtCl$_2$	ca. 250°C dec	25
4-Methyl-4-Vinylcyclohexene PdCl$_2$	ca. 200°C dec.	15
4-Methyl-4-Vinylcyclohexene PtCl$_2$	ca. 225°C dec.	15
4-Ethyl-4-Vinylcyclohexene PdCl$_2$	150°C	27
4-Ethyl-4-Vinylcyclohexene PtCl$_2$	ca. 200°C dec.	15
4-Butyl-4-Vinylcyclohexene PdCl$_2$	174°C	35
4-Butyl-4-Vinylcyclohexene PtCl$_2$	200°C dec.	25
4-Phenyl-4-Vinylcyclohexene PdCl$_2$	123°C	60
4-Phenyl-4-Vinylcyclohexene PtCl$_2$	135°C	50

INSTRUMENTATION

All infrared spectra data was obtained using a Perkin-Elmer model 137 infrared spectrophotometer. Solid samples were made into pellets with spectral grade potassium bromide. Approximately 2 milligrams sample was grounded with 300 milligrams of KBr and pelletized under 24000 psi pressure. Liquid samples were spread into thin film between solid KBr cells.

Ultraviolet spectra information for checking samples and discussion purposes were made available from a Perkin-Elmer Model 202 spectrophotometer using a one centimeter quartz cell. Most samples were run using chloroform and hexane as solvents.

Vapor phase chromatography was made on a Varian Aerograph Model P-90-A gas chromatograph. Injection of 10 microliter samples were used for checking the purity of reagents and products formed.

Nuclear magnetic resonance analyses were made on a Nuclear Magnetic Resonance Specialties spectrometer. The work was performed at the Analytical Division, Shell Development Company, Emeryville, California. Carbon tetrachloride and deuterated chloroform were used as solvents. Tetramethylsilane was the standard reference used in all analyses. The spectrums were run on 60 Mc proton analyses with sweep width at 500cps and sweep offset at 0.

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA

CHEMICAL SHIFTS OF SOME PREPARED ORGANIC COMPOUNDS

Compound	Shifts from Tetramethylsilane Reference (p.p.m.)		
	methylene	vinyl	methyl
4-Vinylcyclohexene	1.95	4.95 5.60	
4-Br-4-vinylcyclohexene	2.1	5.00 5.78	
4-Methyl-4-vinylcyclohexene	1.8	5.00 5.50	0.95

See Figure 6-26, 6-27, 6-28
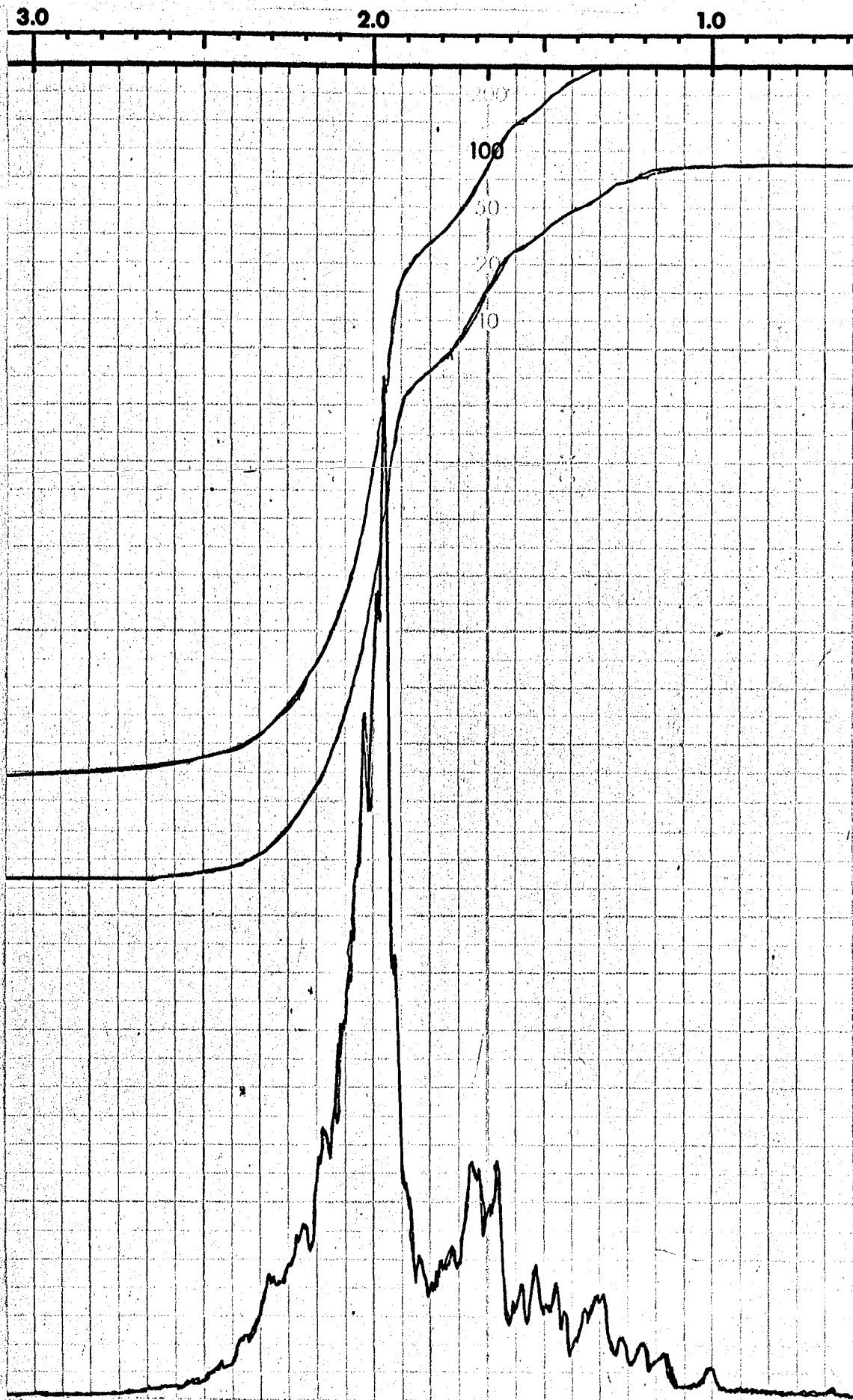
Fig. 6-26   Nuclear Magnetic Resonance spectra of
liquid 4-vinylcyclohexene
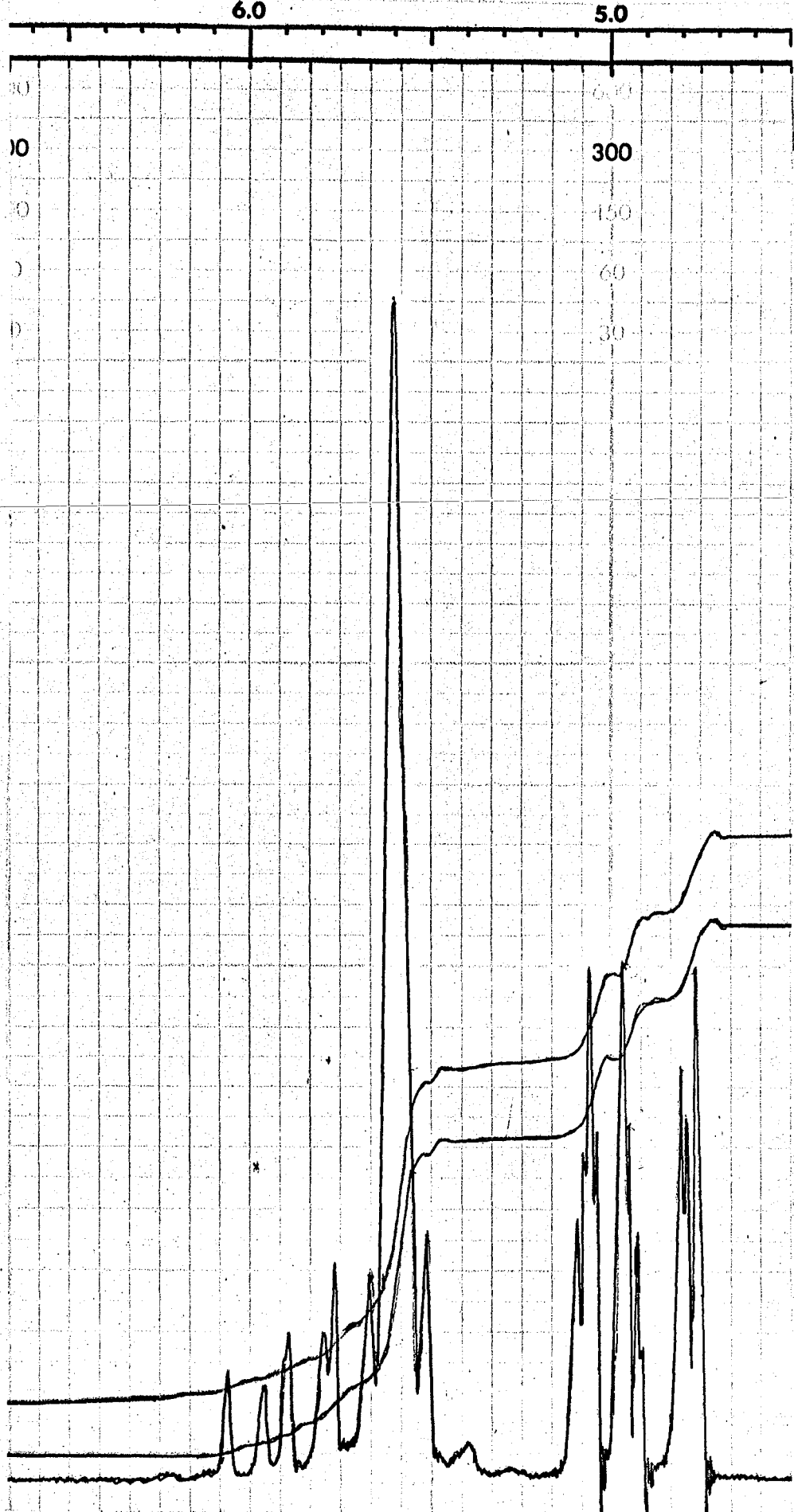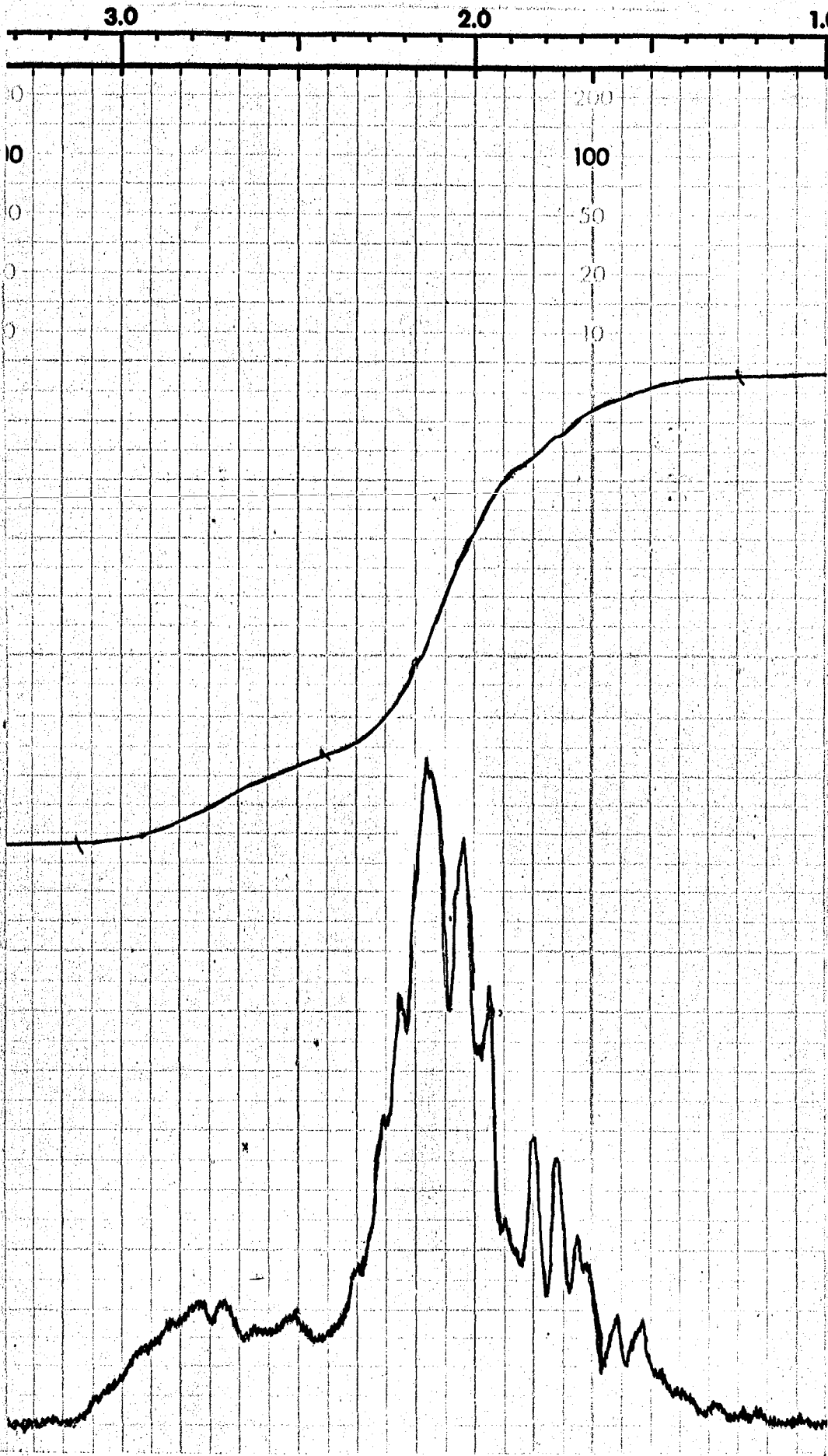
Fig. 6-26   Nuclear Magnetic Resonance spectra of
liquid 4-vinylcyclohexene

Fig. 6-27   Nuclear Magnetic Resonance spectra of
            liquid 4-bromo-4-vinylcyclohexene
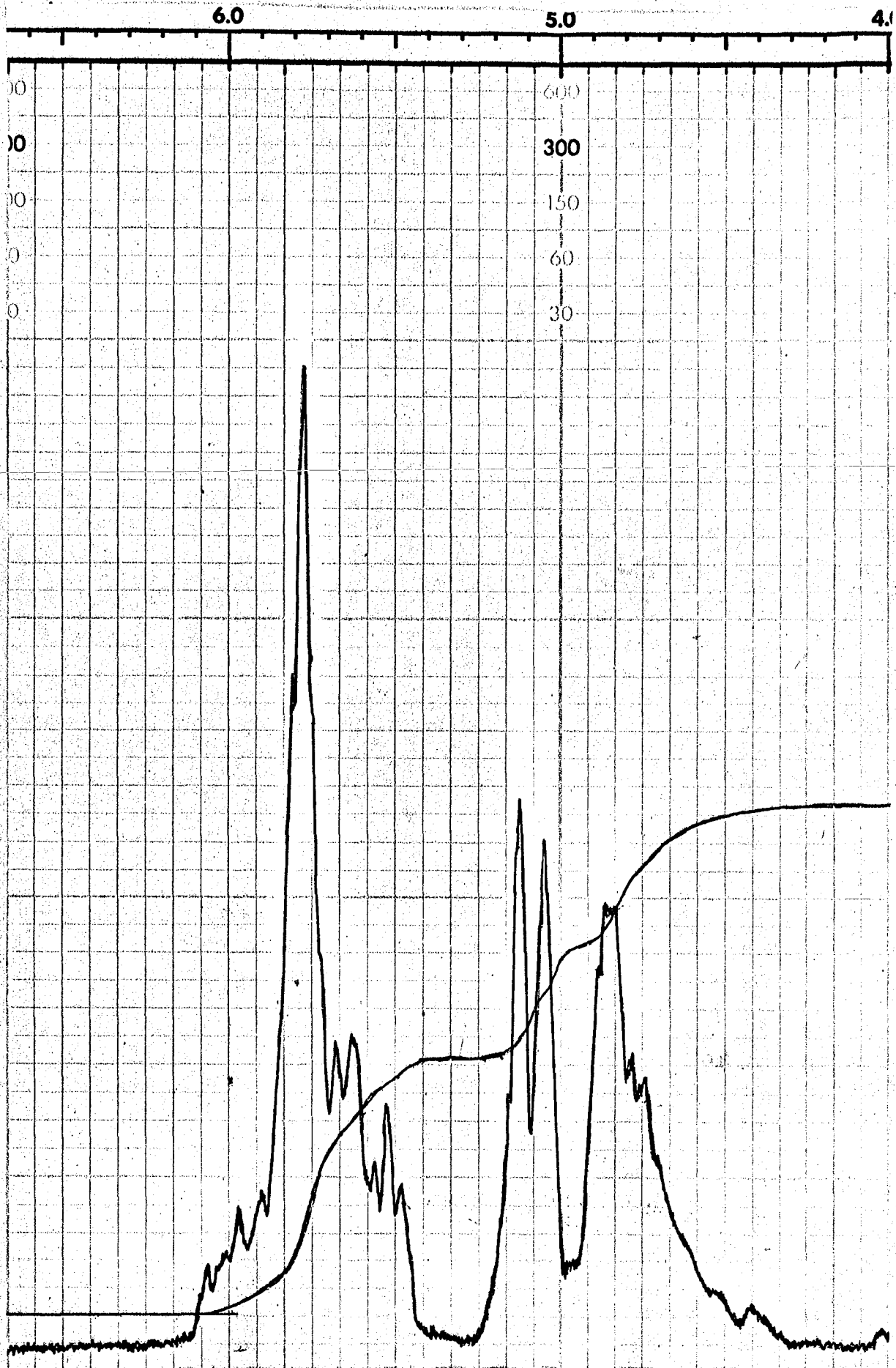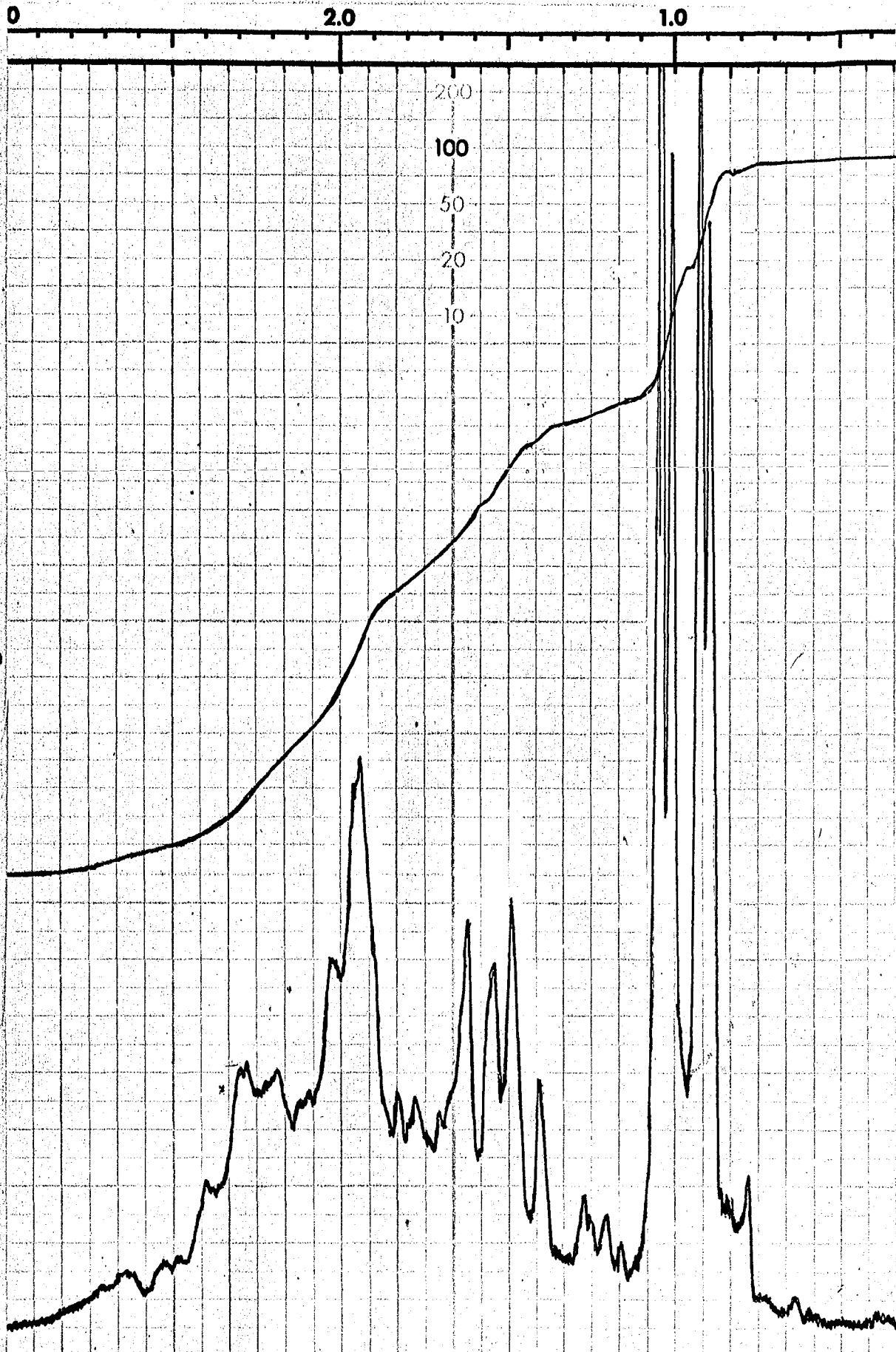
33

Fig. 6-27   Nuclear Magnetic Resonance spectra of
liquid 4-bromo-4-vinylcyclohexene

34

Fig. 6-28   Nuclear Magnetic Resonance spectra of
             liquid 4-methyl-4-vinylcyclohexene

35
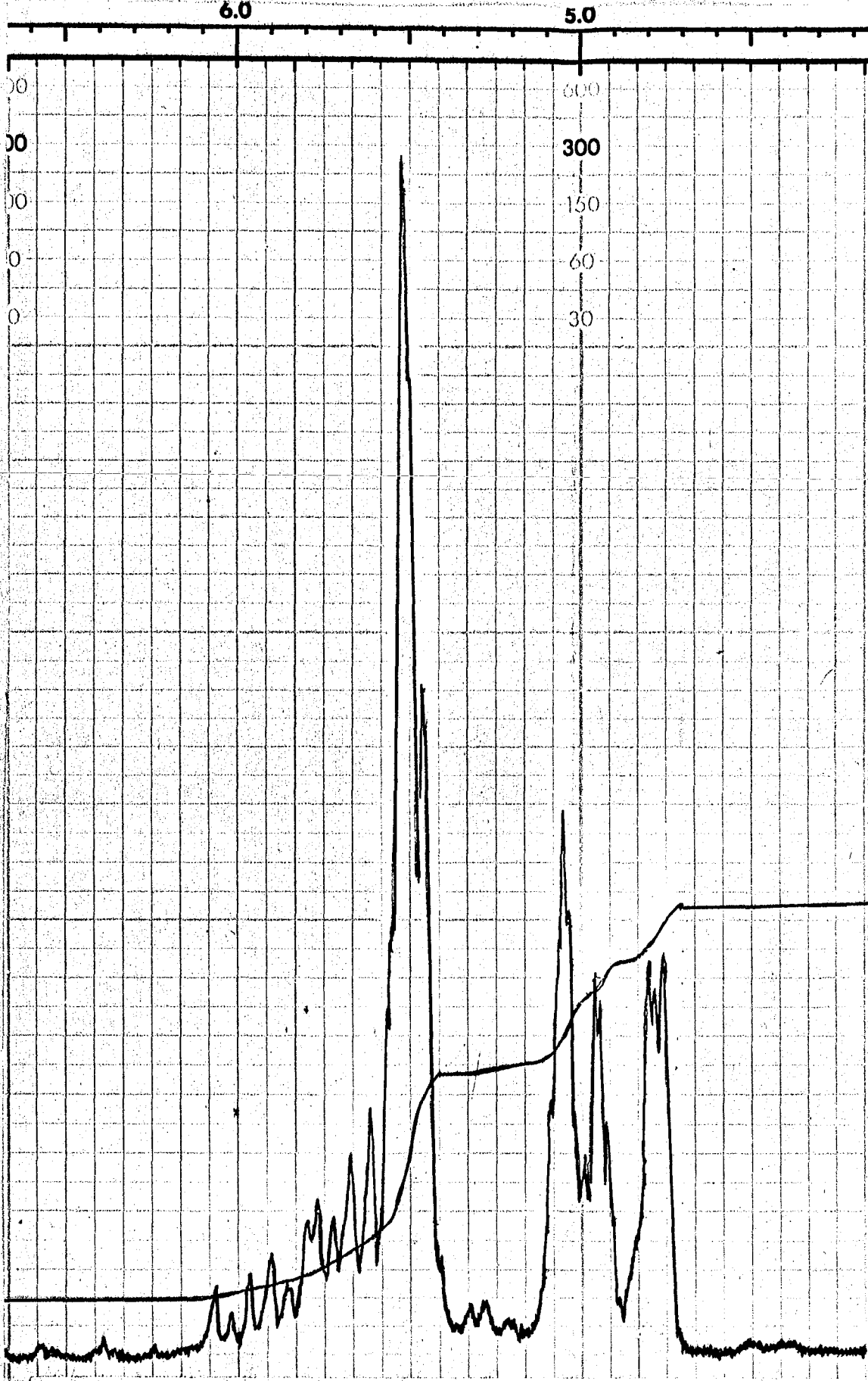
Fig. 6-28   Nuclear Magnetic Resonance spectra of
liquid 4-methyl-4-vinylcyclohexene
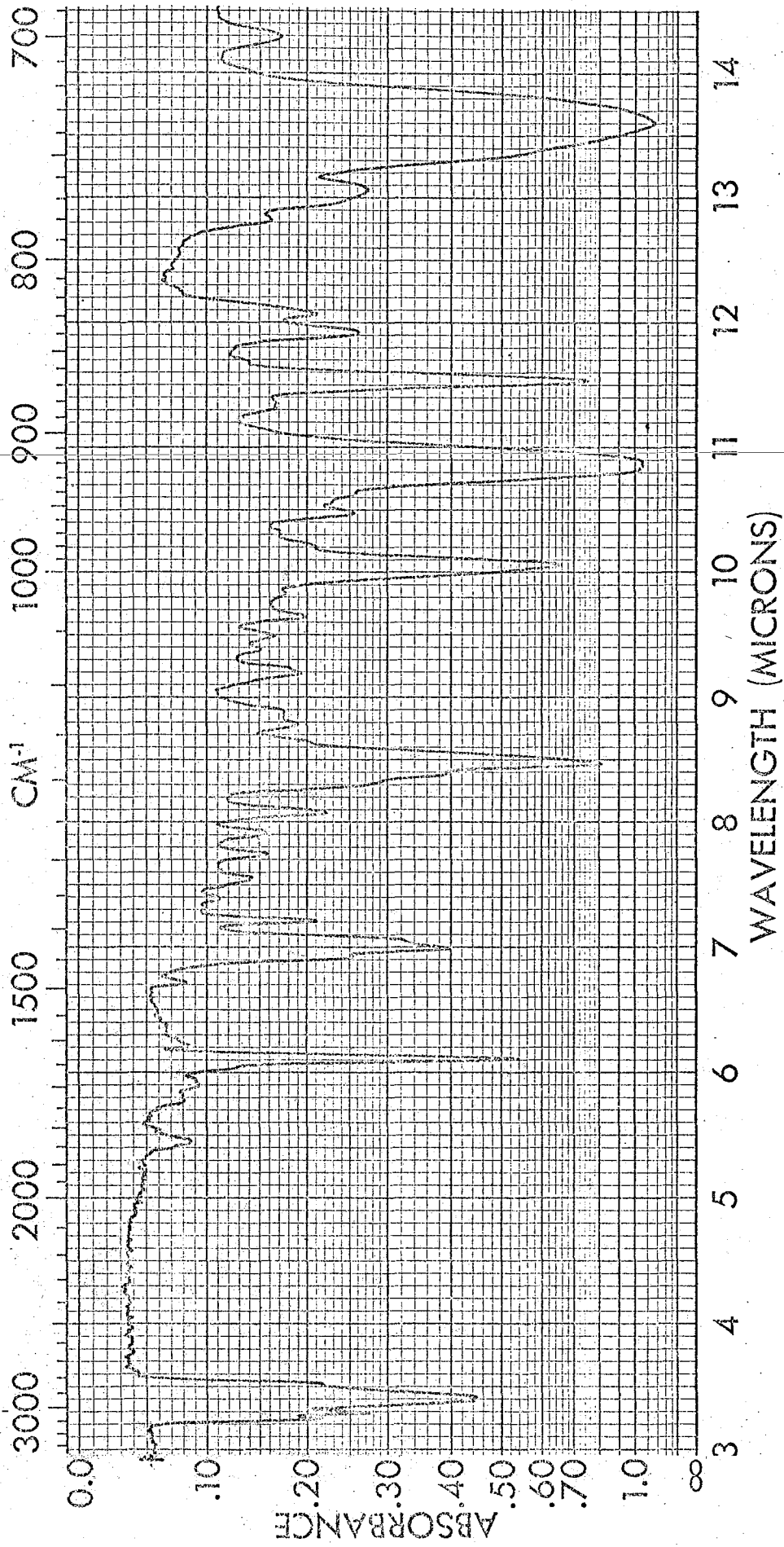
Fig. 6-1   Infrared absorption of liquid 4-bromo-4-vinylcyclohexene

37
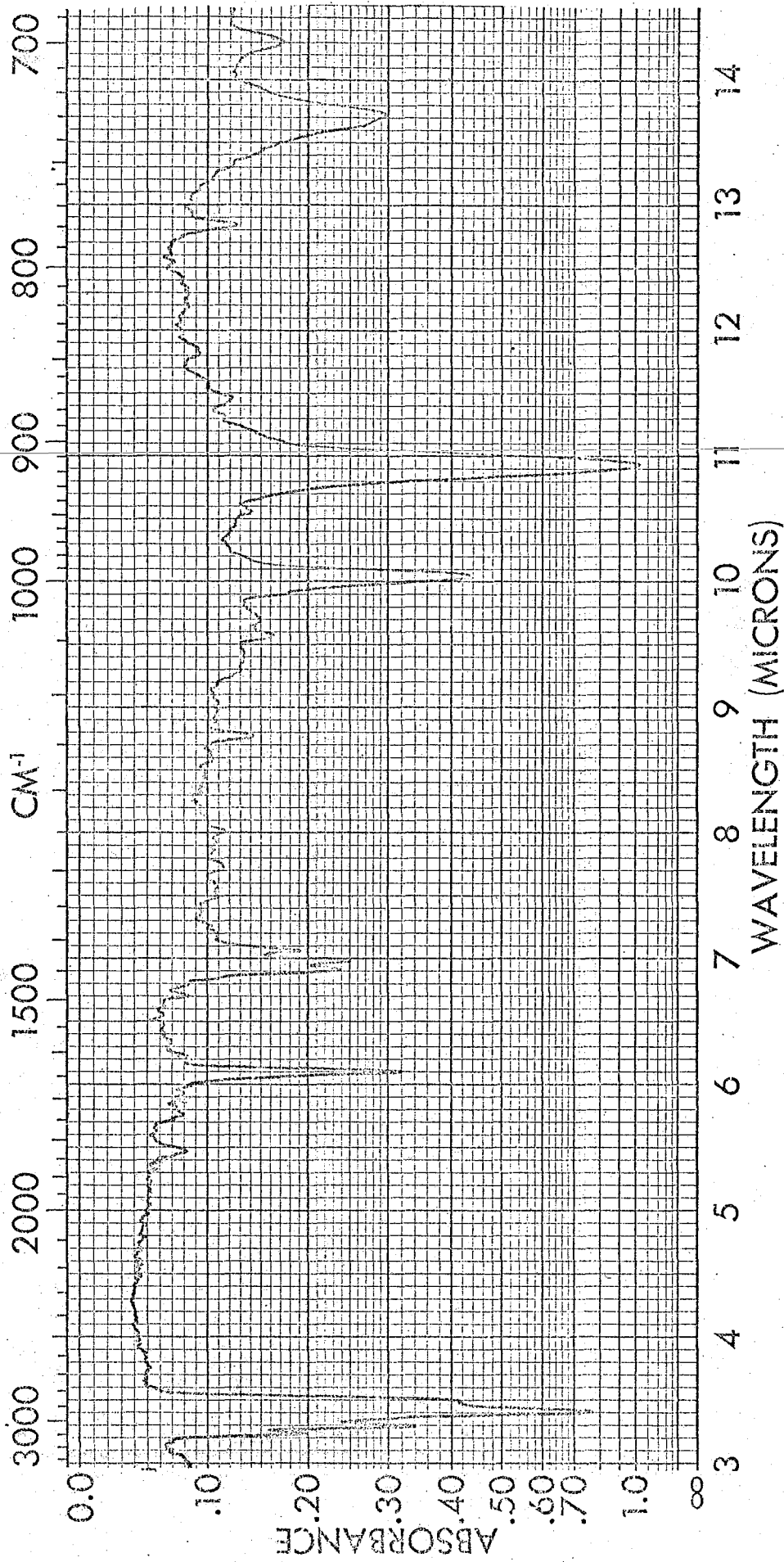
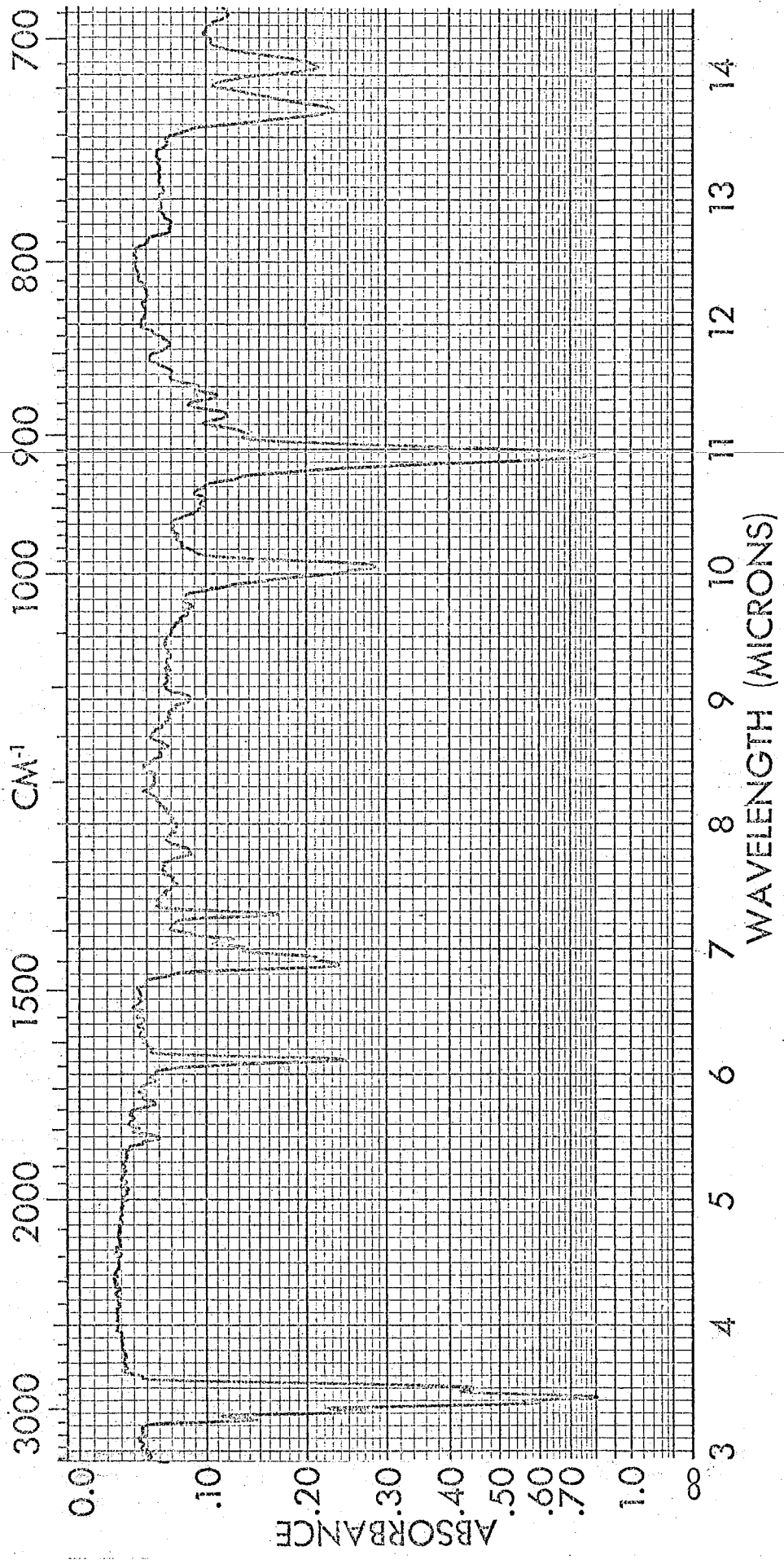Fig. 6-2   Infrared absorption of recovered liquid 4-vinylcyclohexene

38
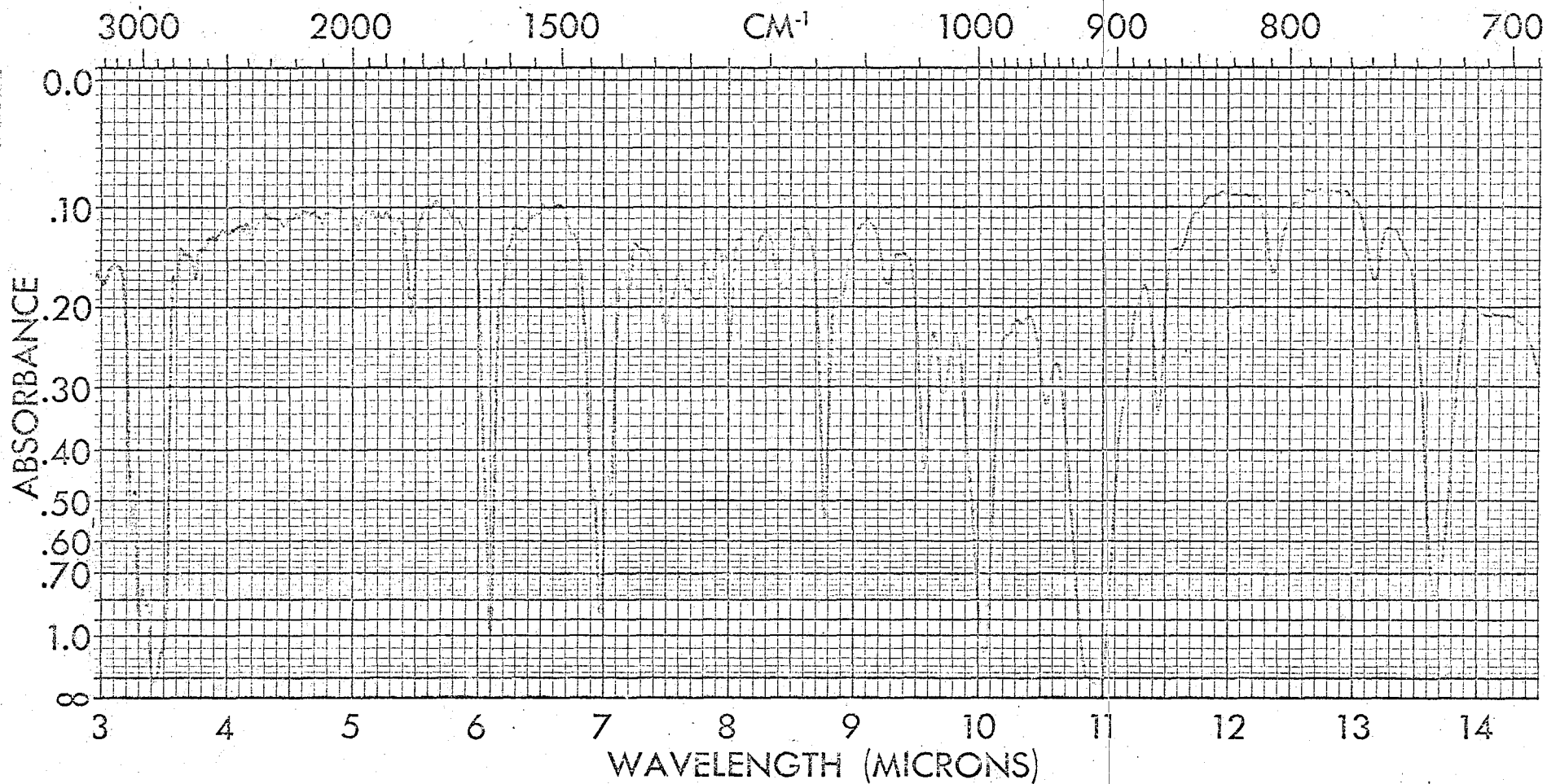
Fig. 6-3   Infrared absorption of liquid 4-vinylcyclohexene
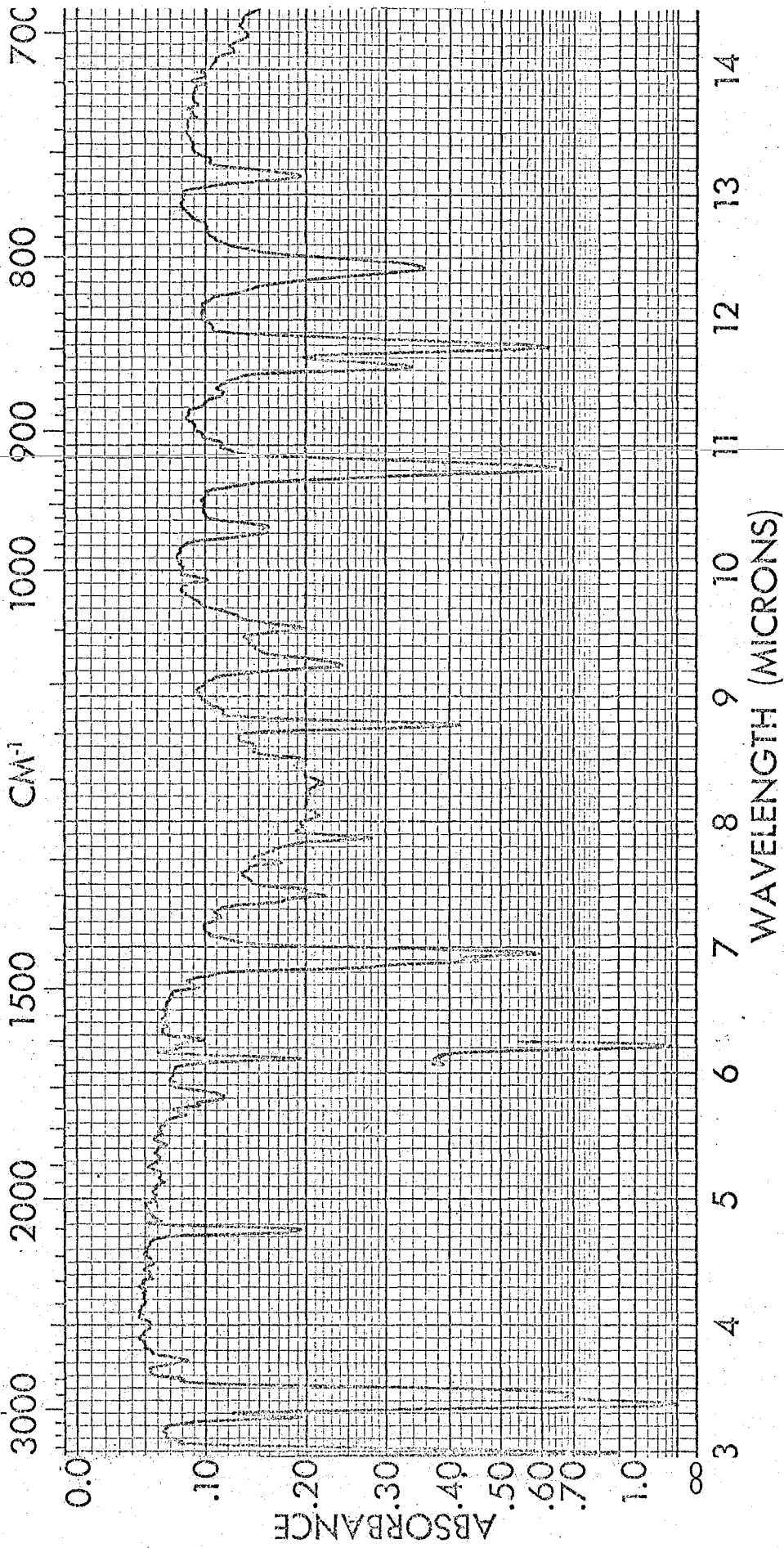
Fig. 6-4   Infrared absorption of liquid 1-ethynylcyclohexene

40
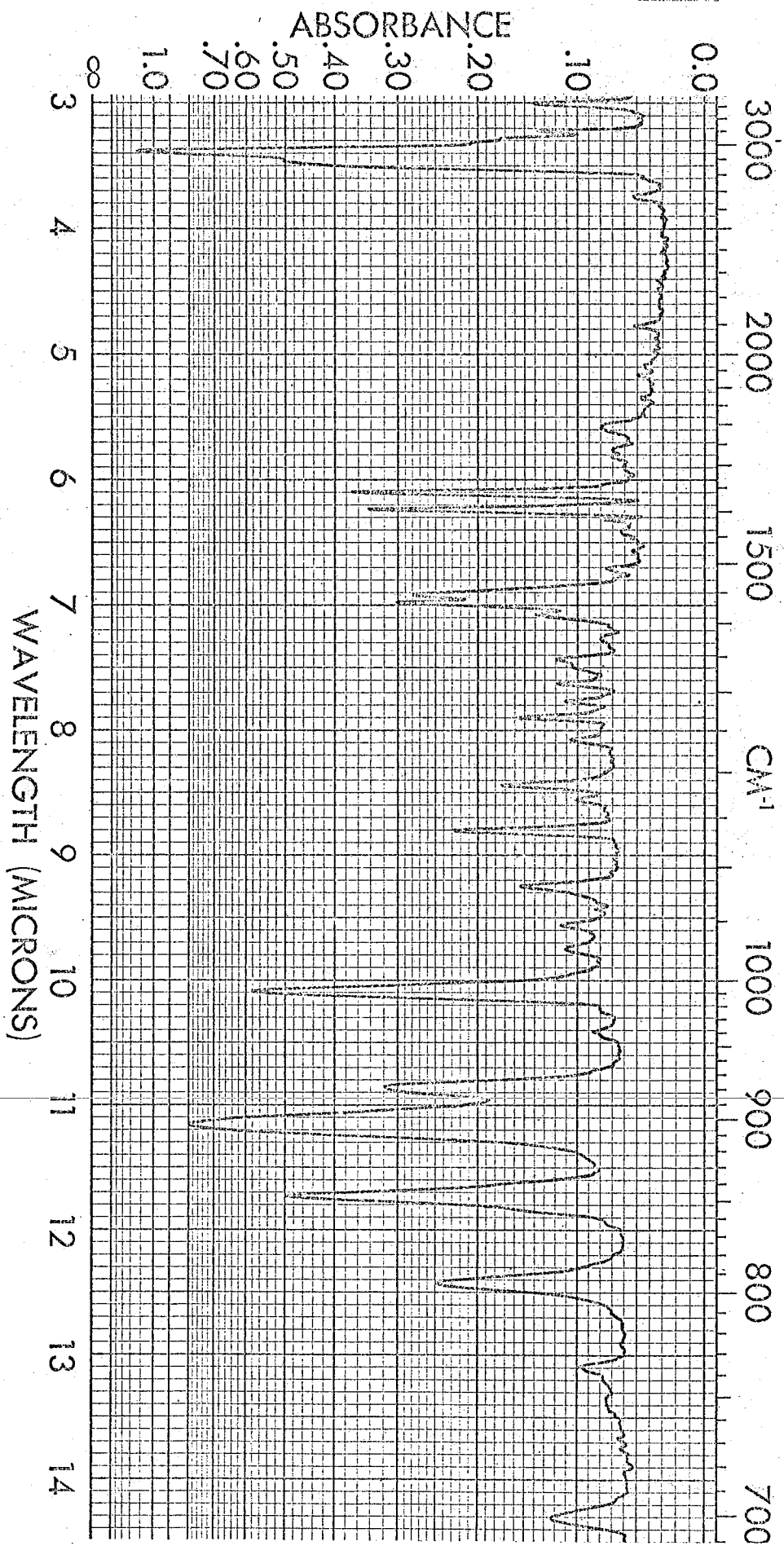
Fig. 6-5 Infrared absorption of liquid 1-vinylcyclohexene
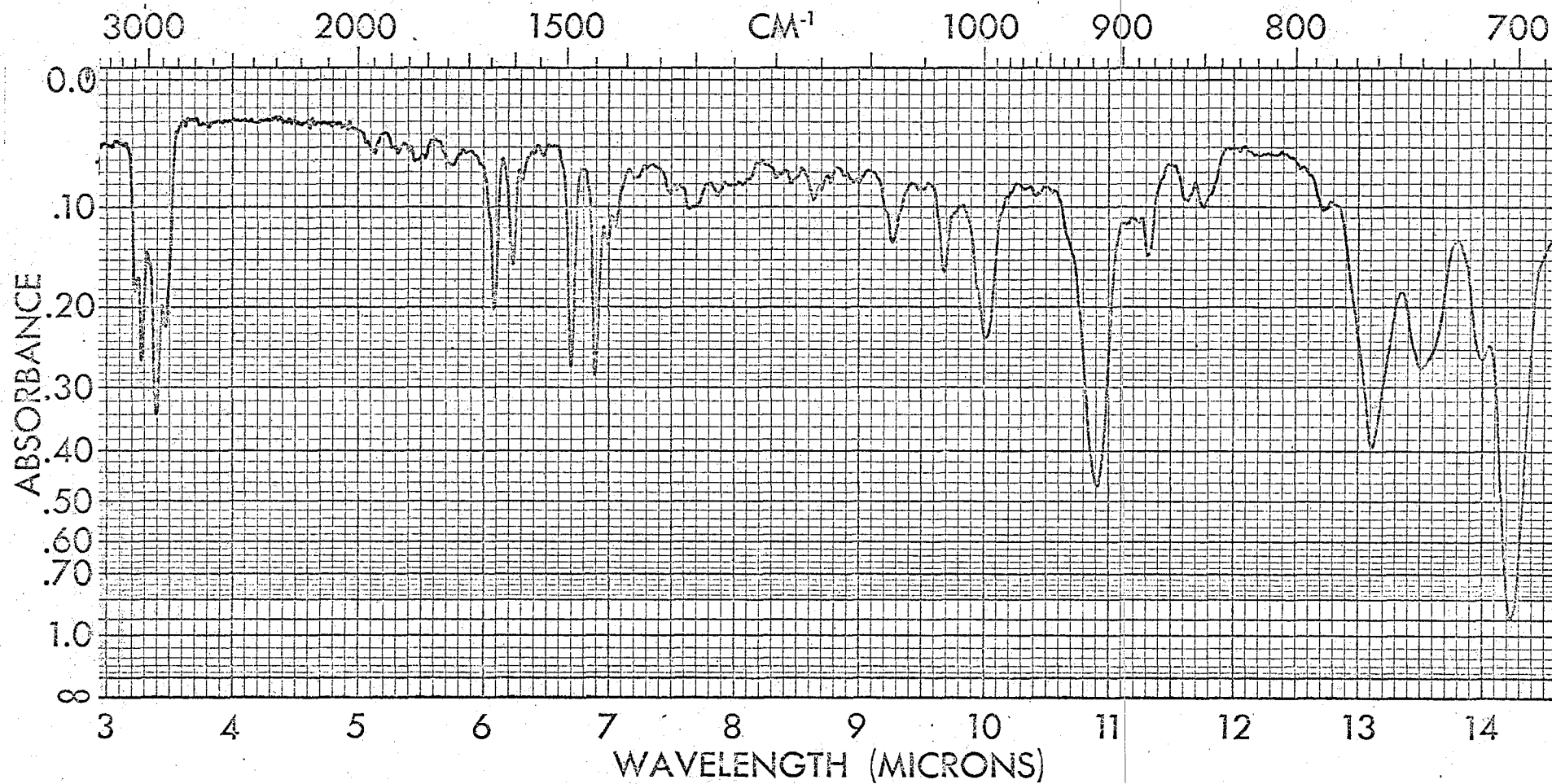
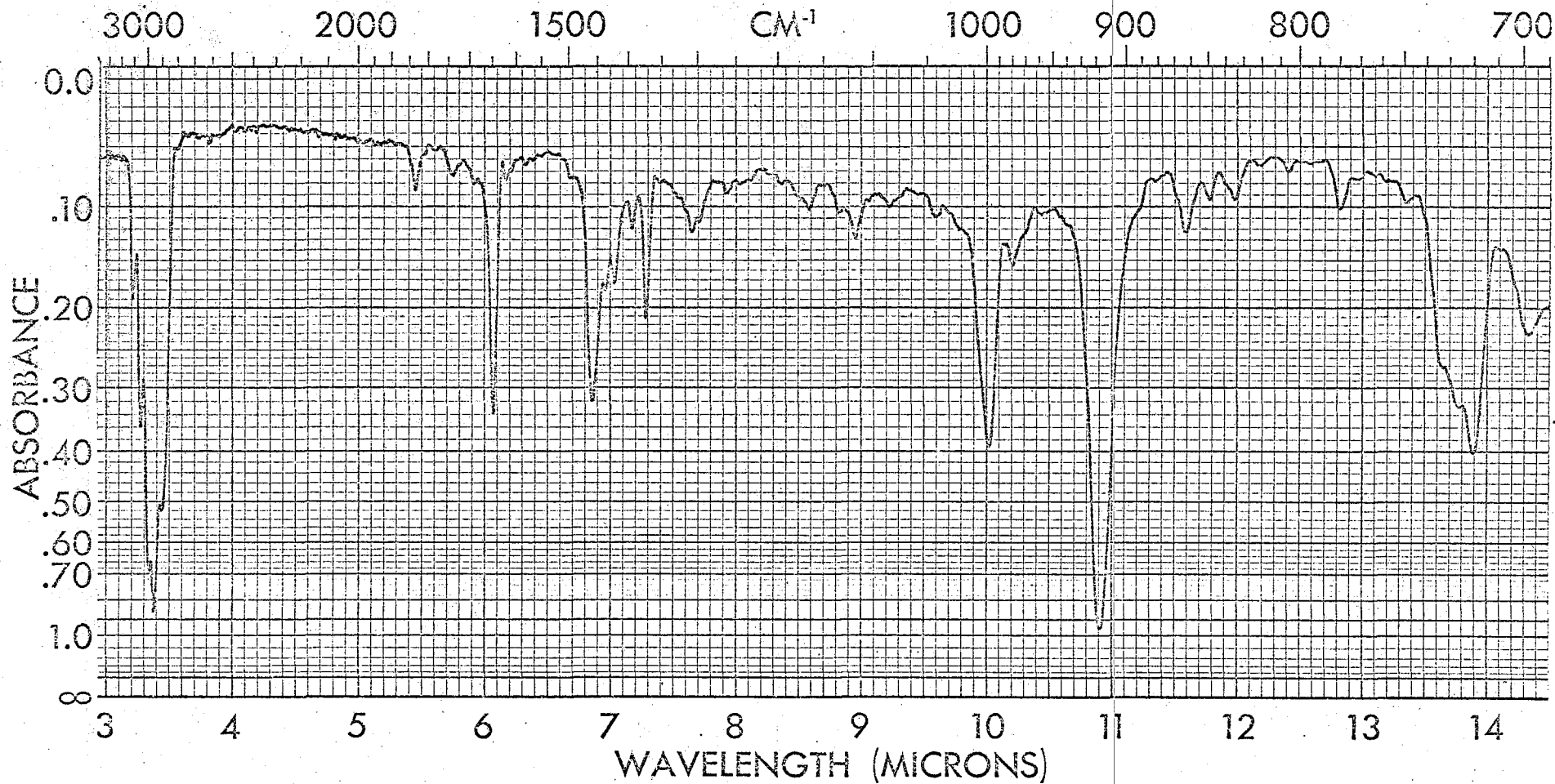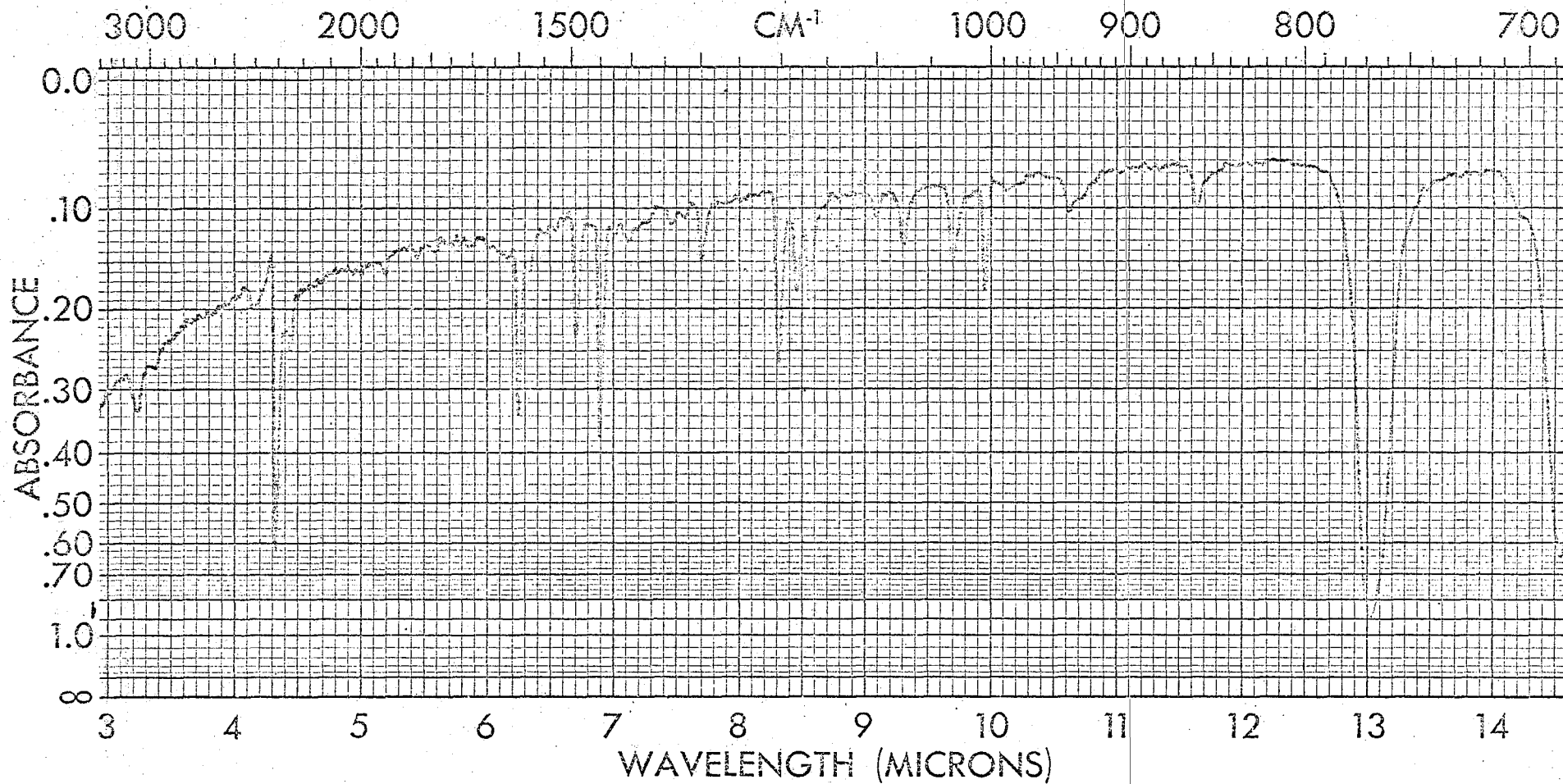Fig. 6-6   Infrared absorption of liquid 4-phenyl-4-vinylcyclohexene
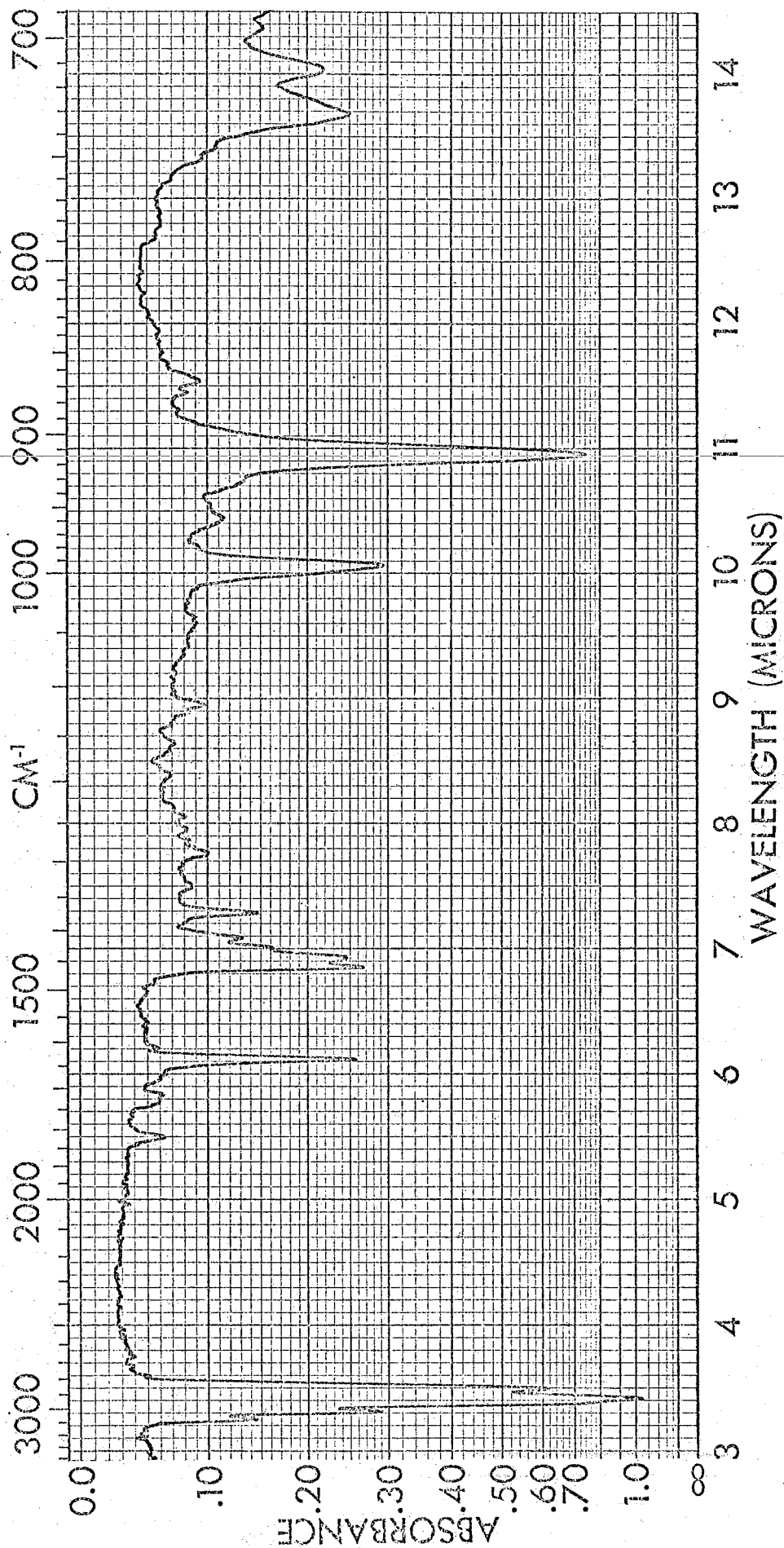
Fig. 6-7   Infrared absorption of liquid 4-butyl-4-vinylcyclohexene

43

Fig. 6-8   Infrared absorption of liquid 4-ethyl-4-vinylcyclohexene

44

Fig. 6-9   Infrared absorption of liquid 4-methyl-4-vinylcyclohexene

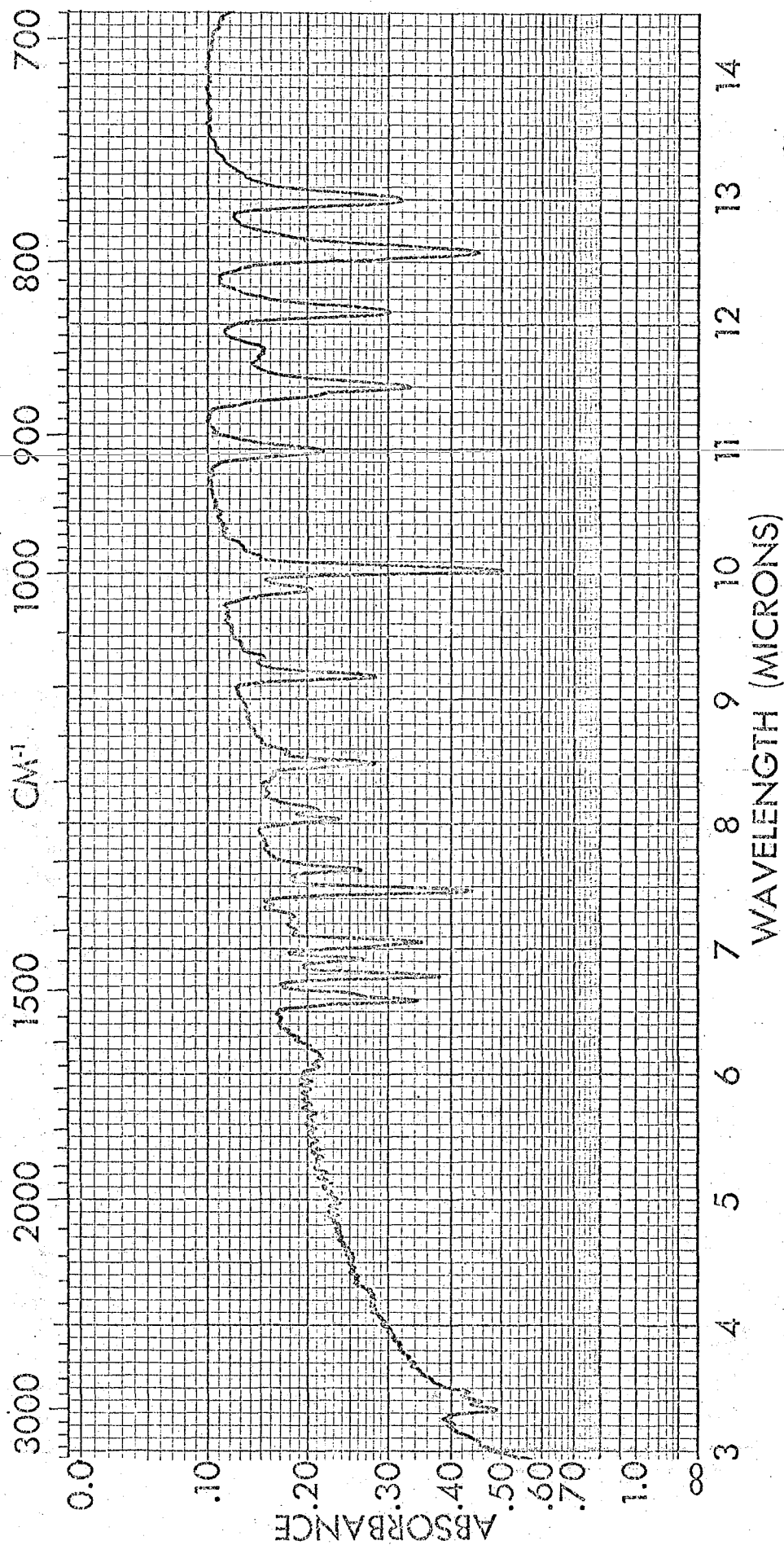Fig. 6-10   Infrared absorption of bis(benzonitrilo)palladium(II) chloride

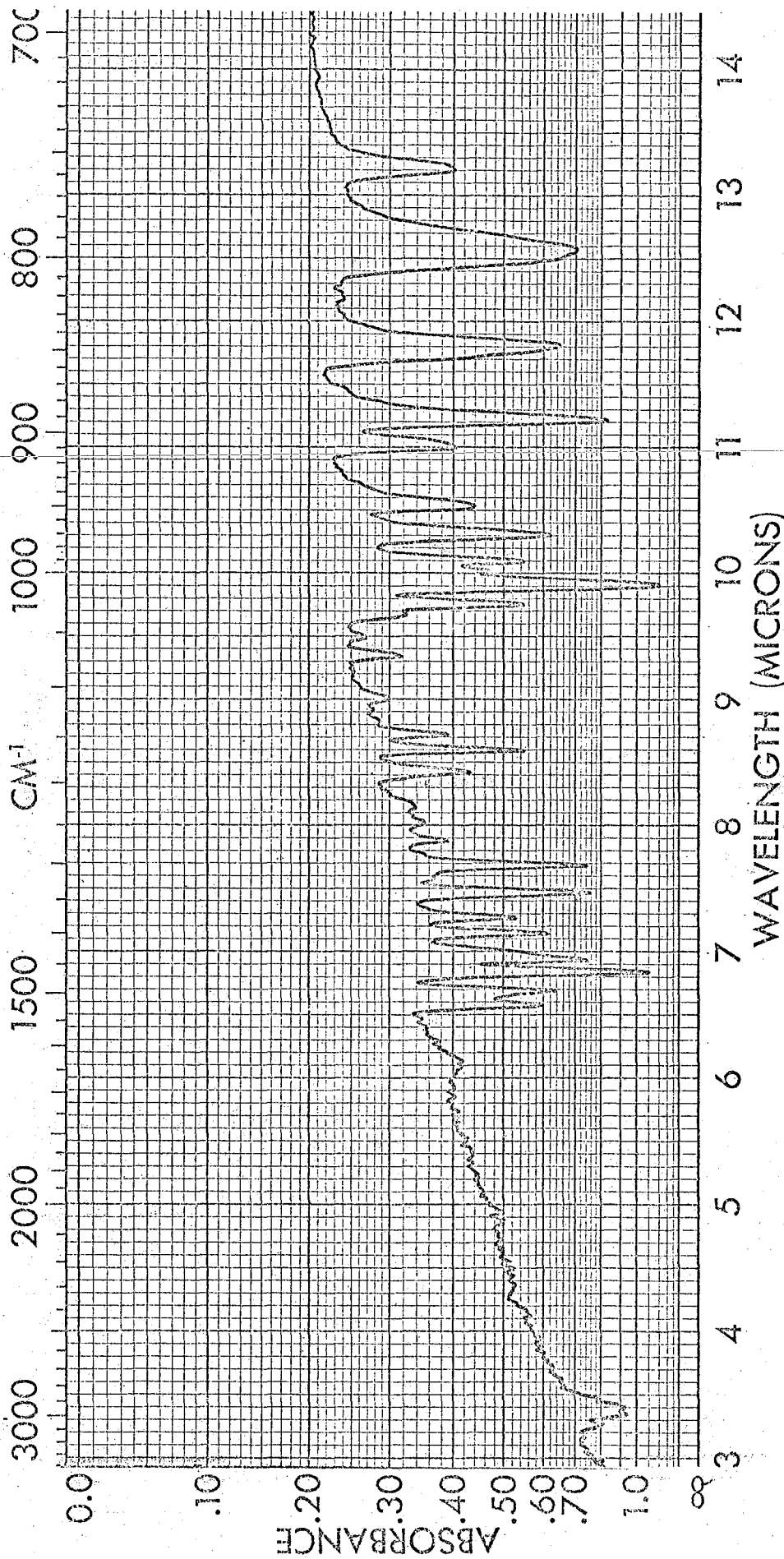Fig. 6-11   Infrared absorption of 4-vinylcyclohexene palladium(II) chloride

47

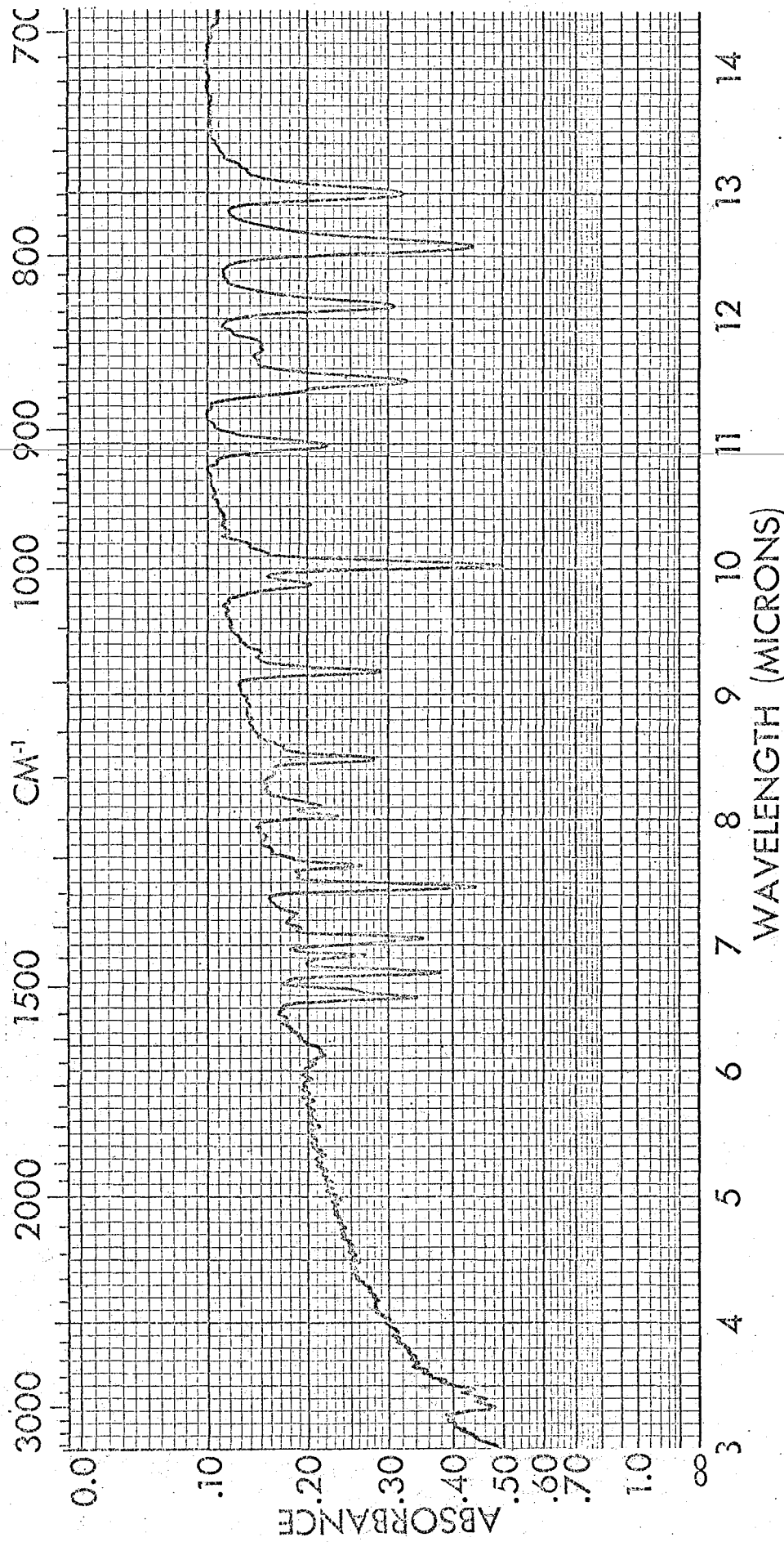Fig. 6-12   Infrared absorption of 4-vinylcyclohexene platinum(II) chloride

48

Fig. 6-13   Infrared absorption of 1,5-cyclooctadiene palladium(II) chloride
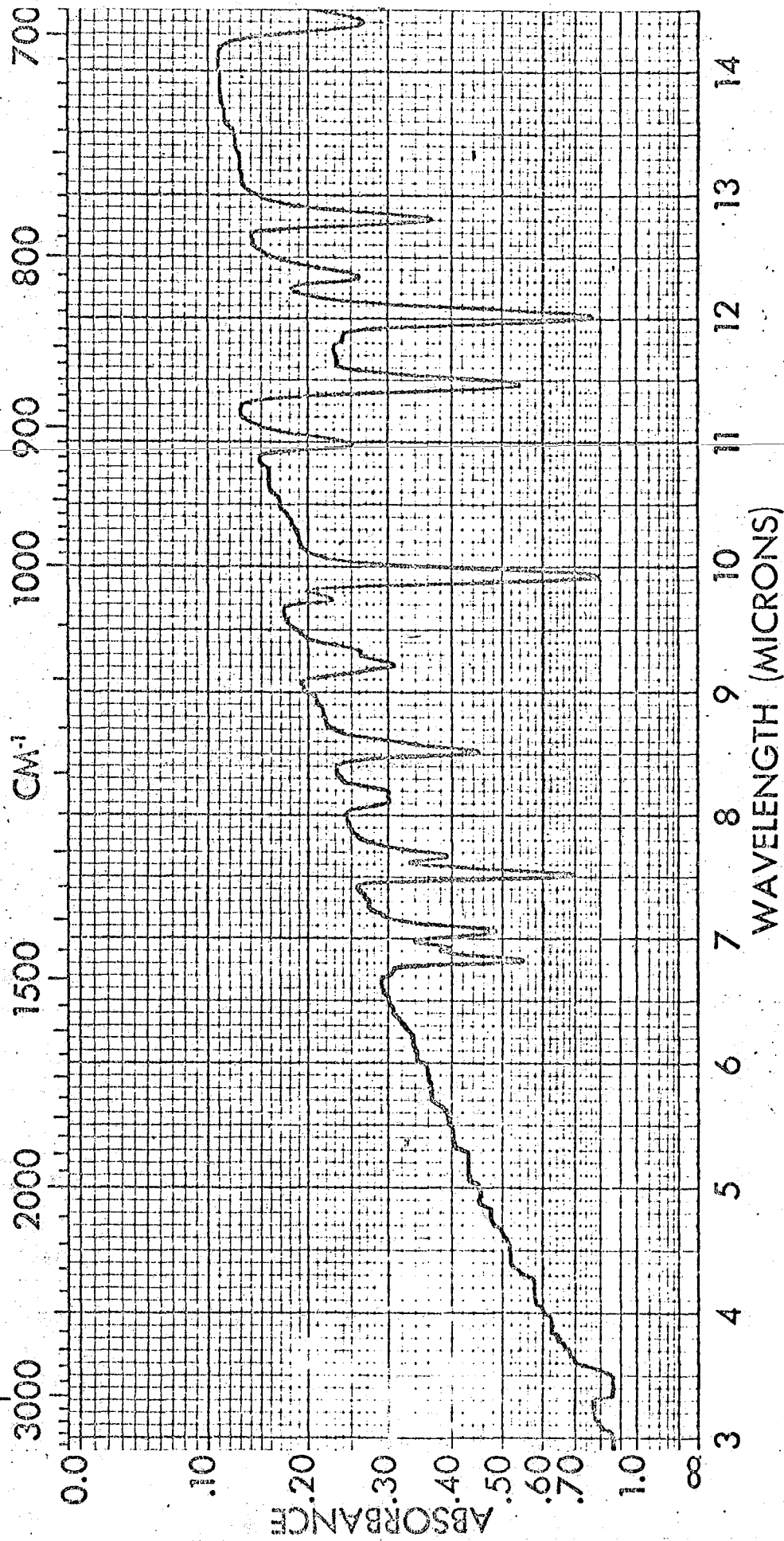
49

Fig. 6-14   Infrared absorption of 1,5-cyclooctadiene platinum(II) chloride
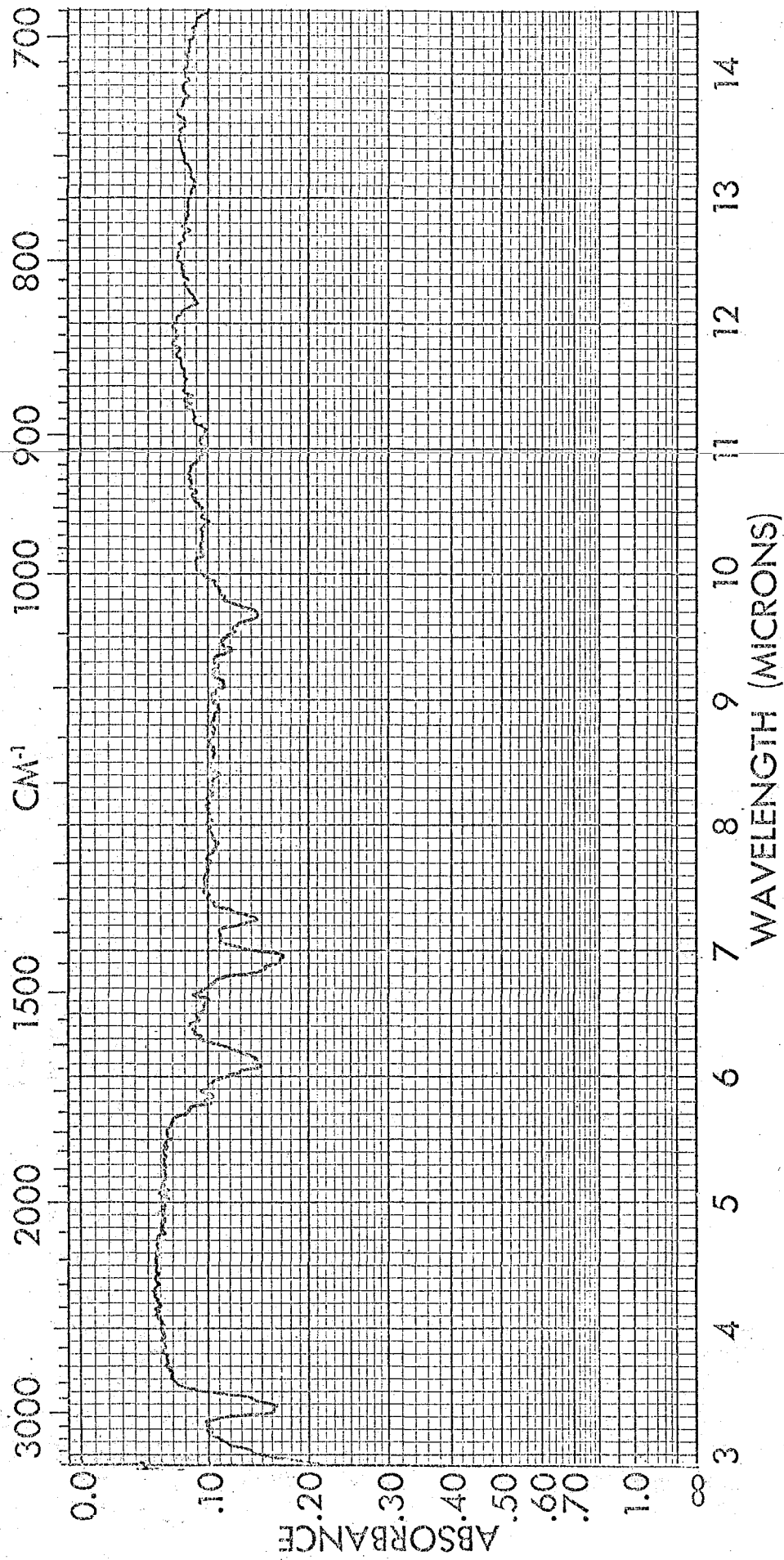
50

Fig. 6-15   Infrared absorption of d-limonene palladium(II) chloride
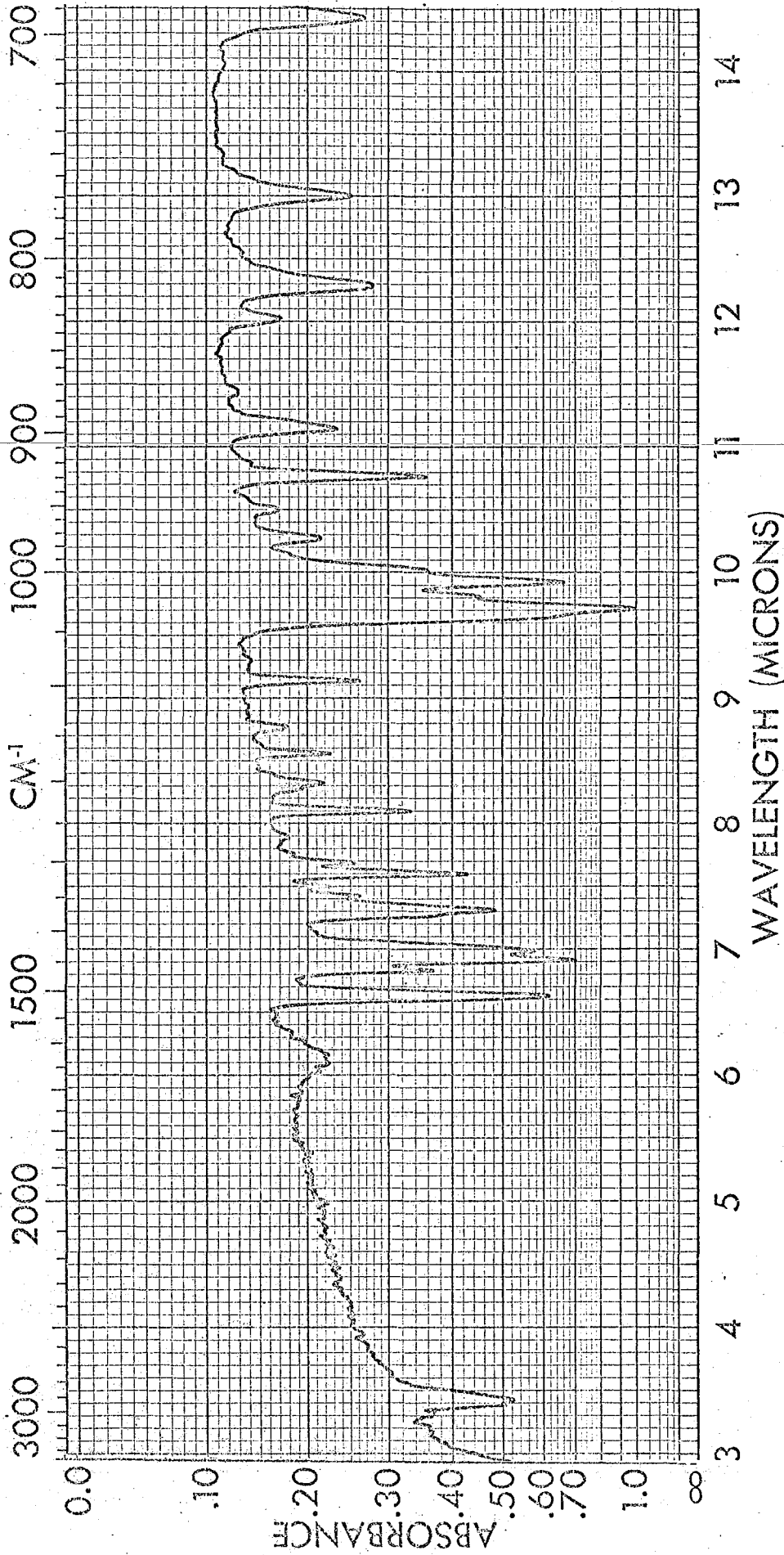
Fig. 6-16   Infrared absorption of d-limonene platinum(II) chloride
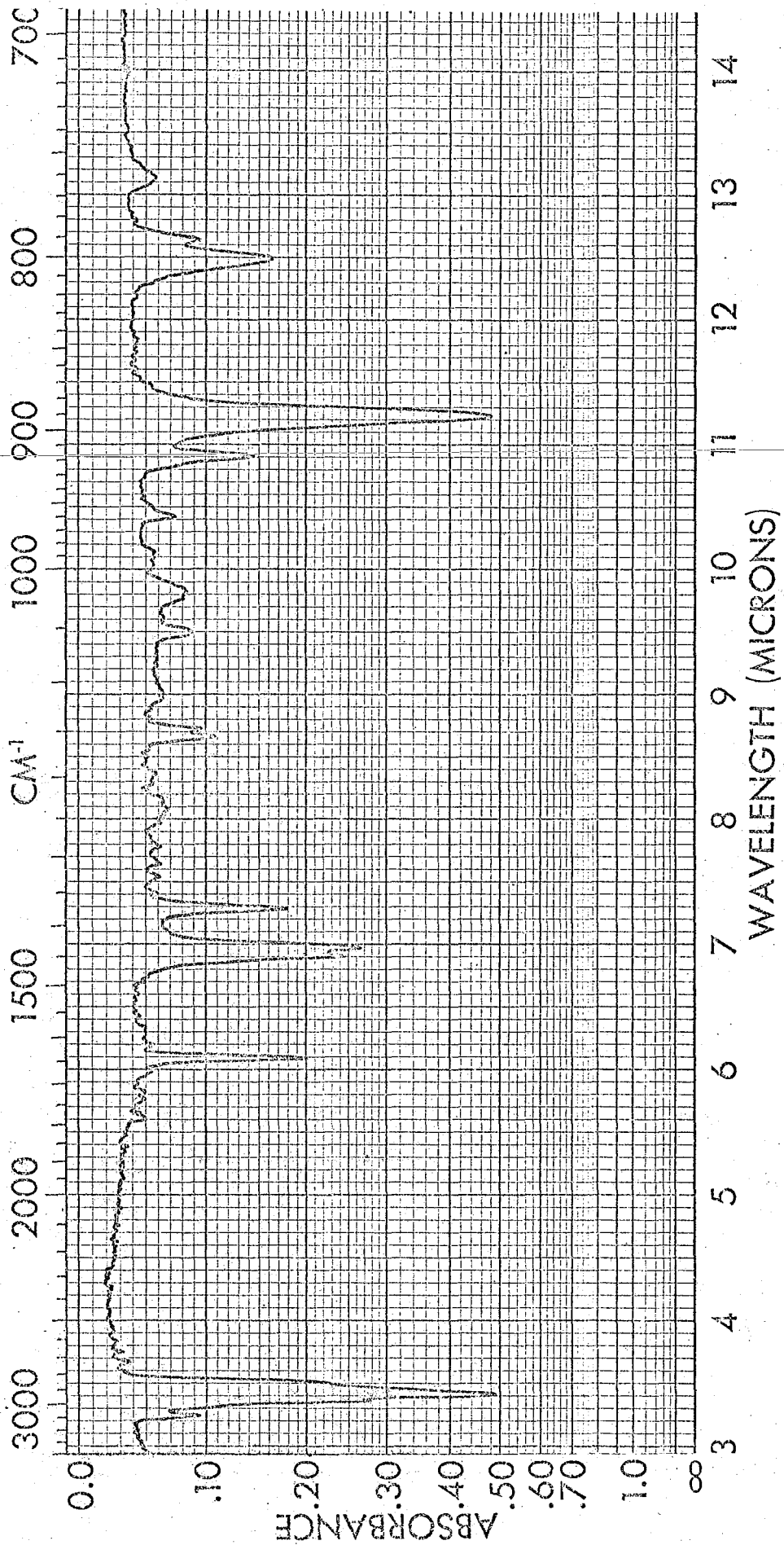
52

Fig. 6-17   Infrared absorption of liquid d-limonene

53

Fig. 6-18   Infrared absorption of 1-vinylcyclohexene palladium(II) chloride

54

Fig. 6-19   Infrared absorption of 1-vinylcyclohexene platinum(II) chloride

55

Fig. 6-20 Infrared absorption of 4-phenyl-4-vinylcyclohexene palladium(II) chloride

56

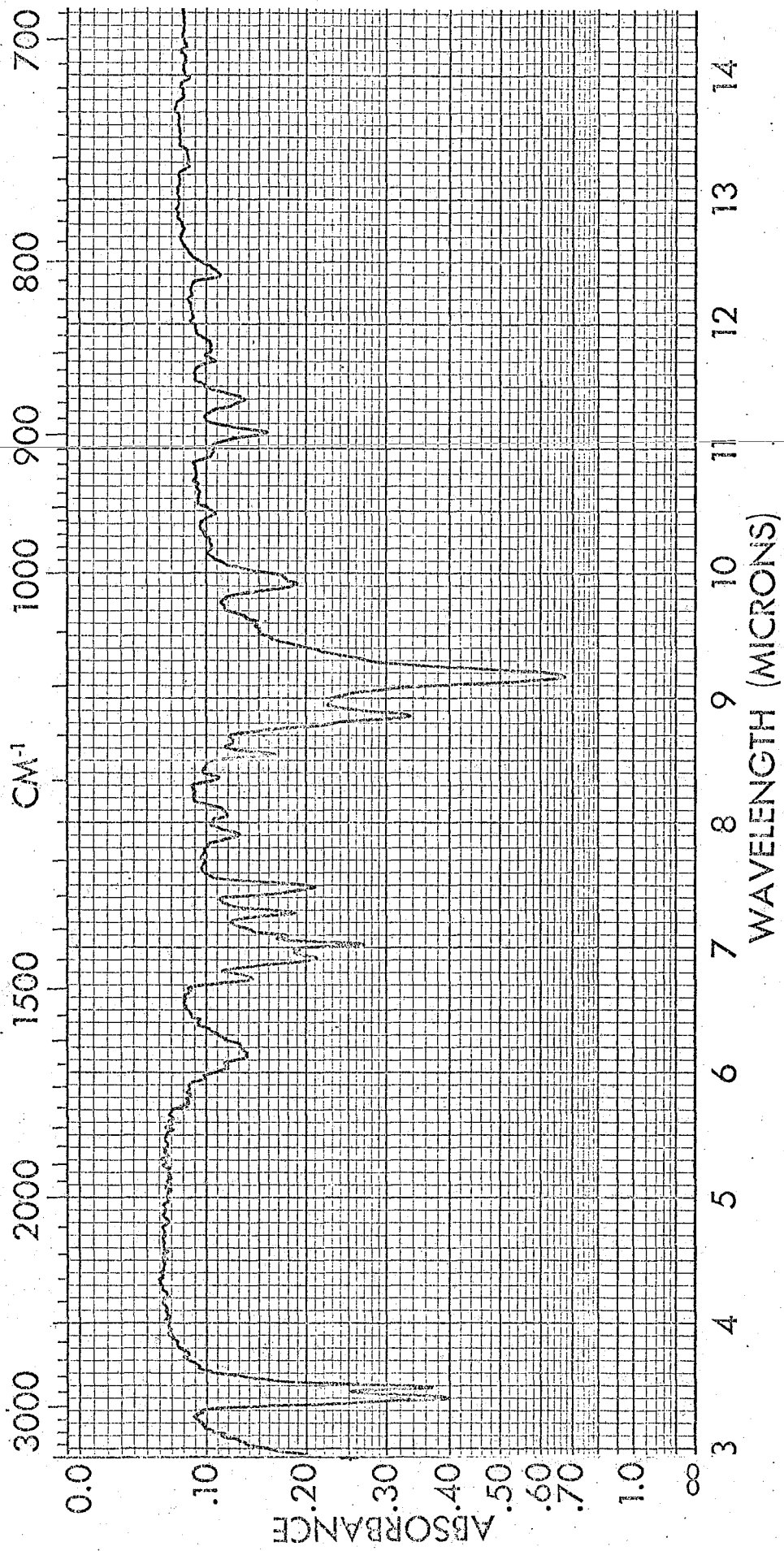Fig. 6-21   Infrared absorption of 4-phenyl-4-vinylcyclohexene platinum(II) chloride

Fig. 6-22　Infrared absorption of 4-butyl-4-vinylcyclohexene palladium(II) chloride
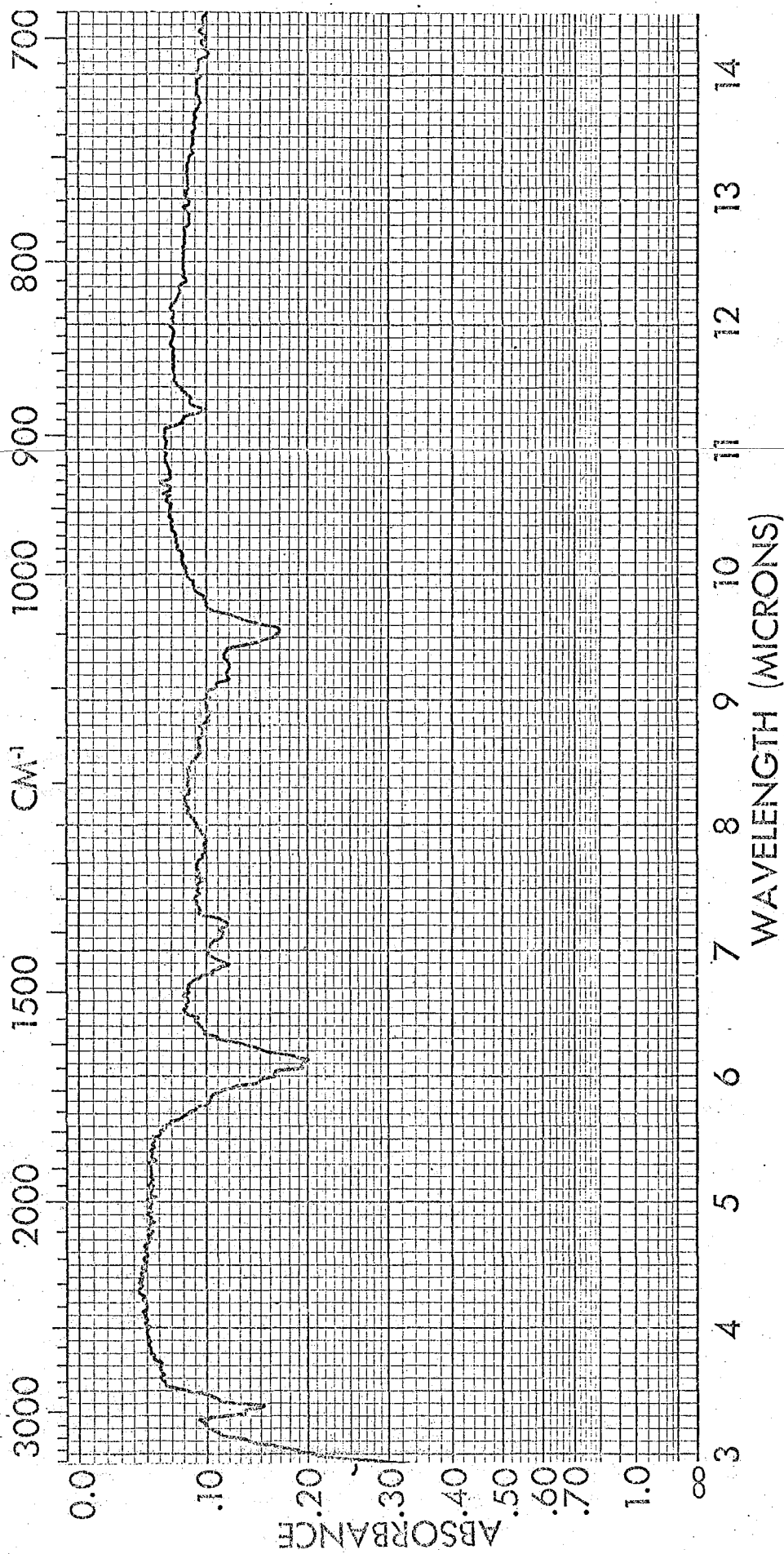
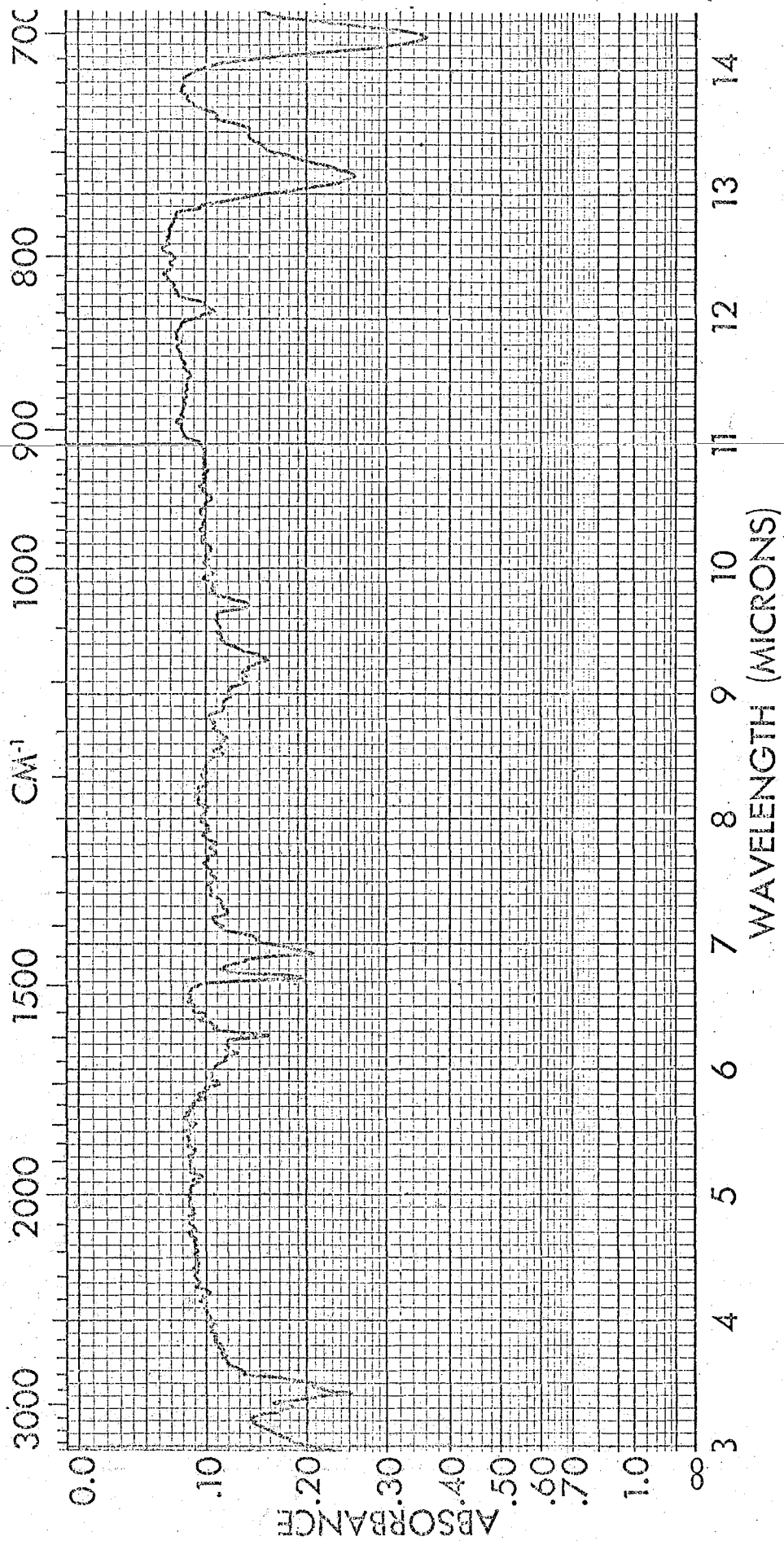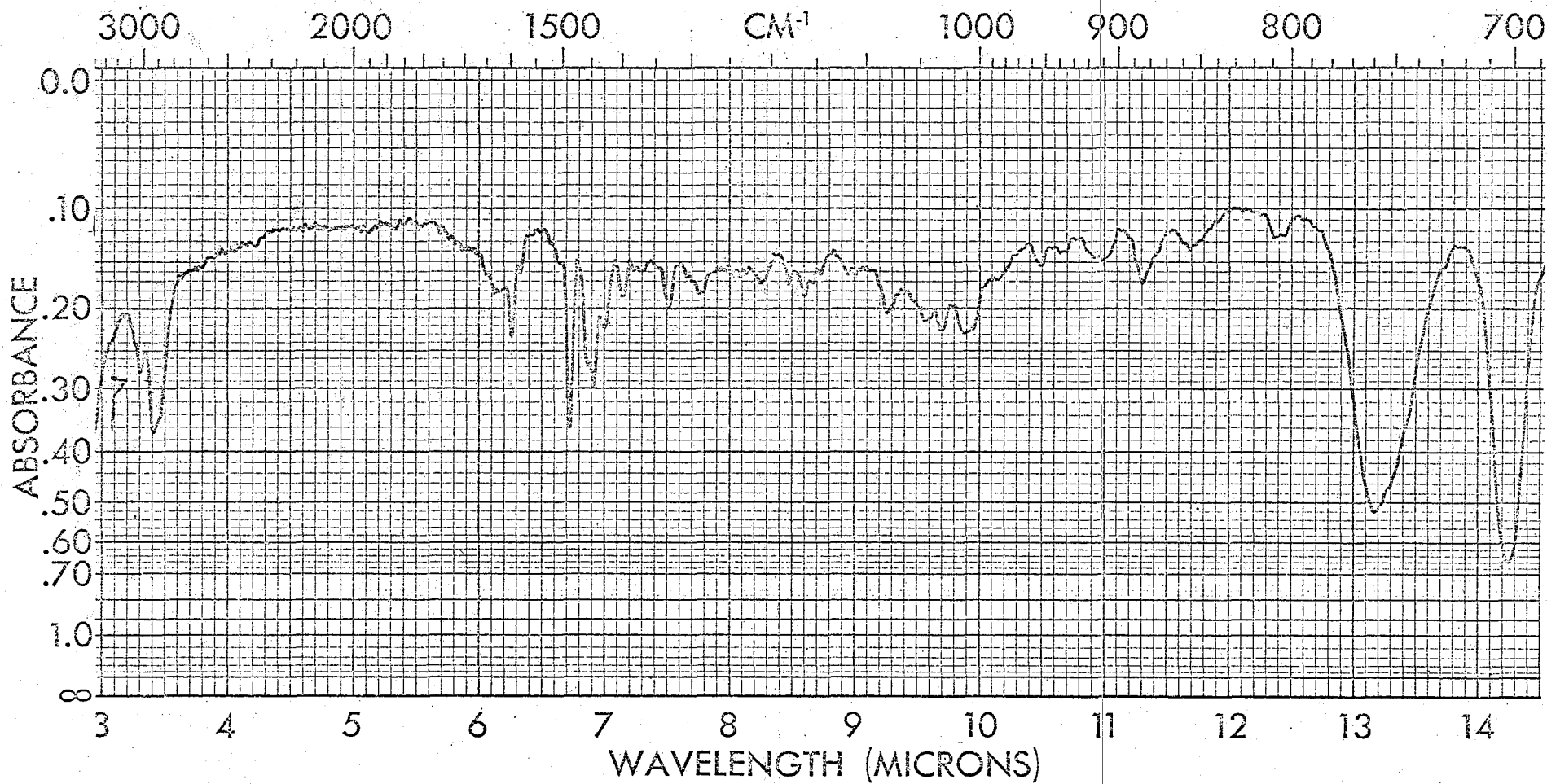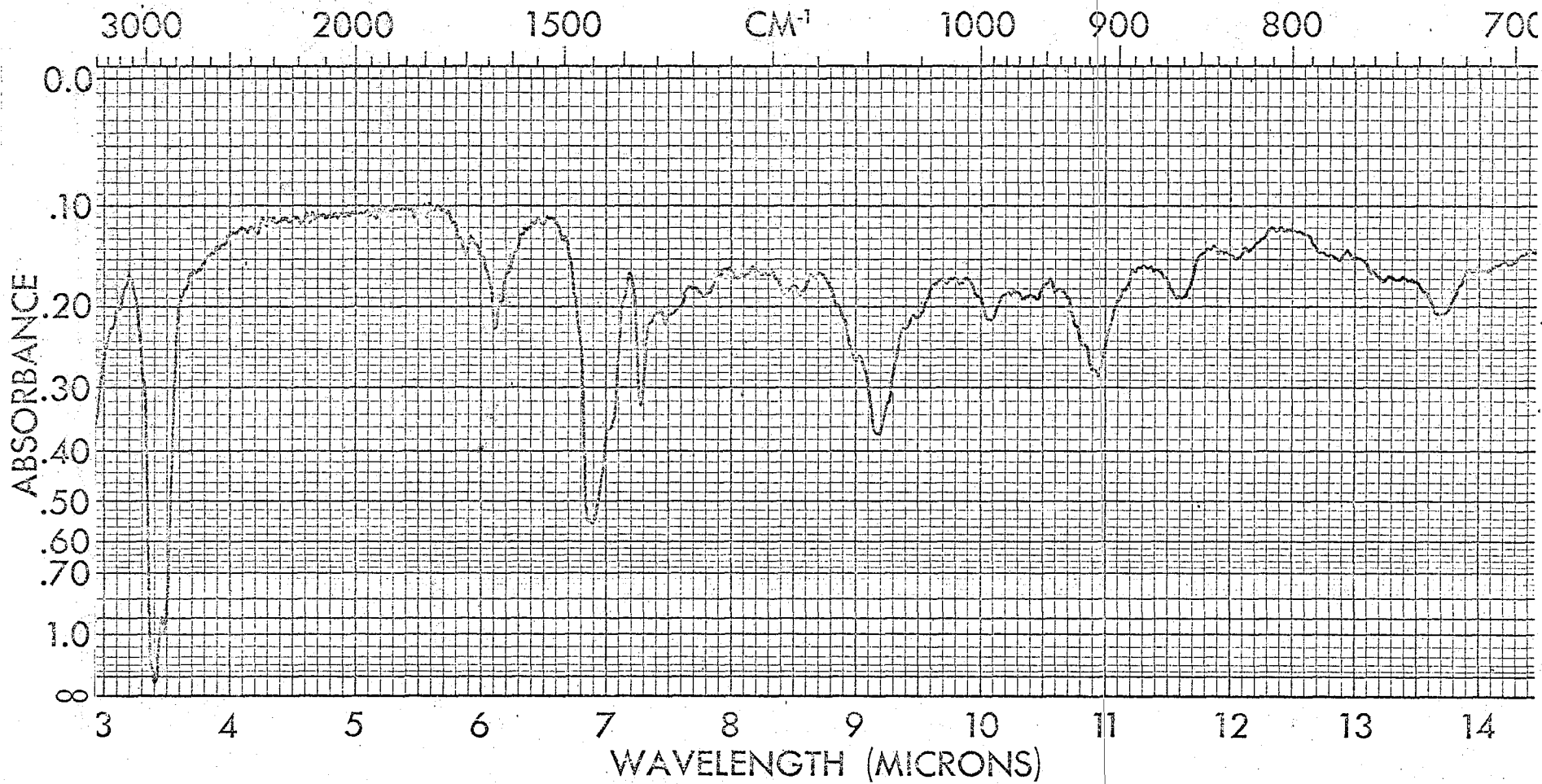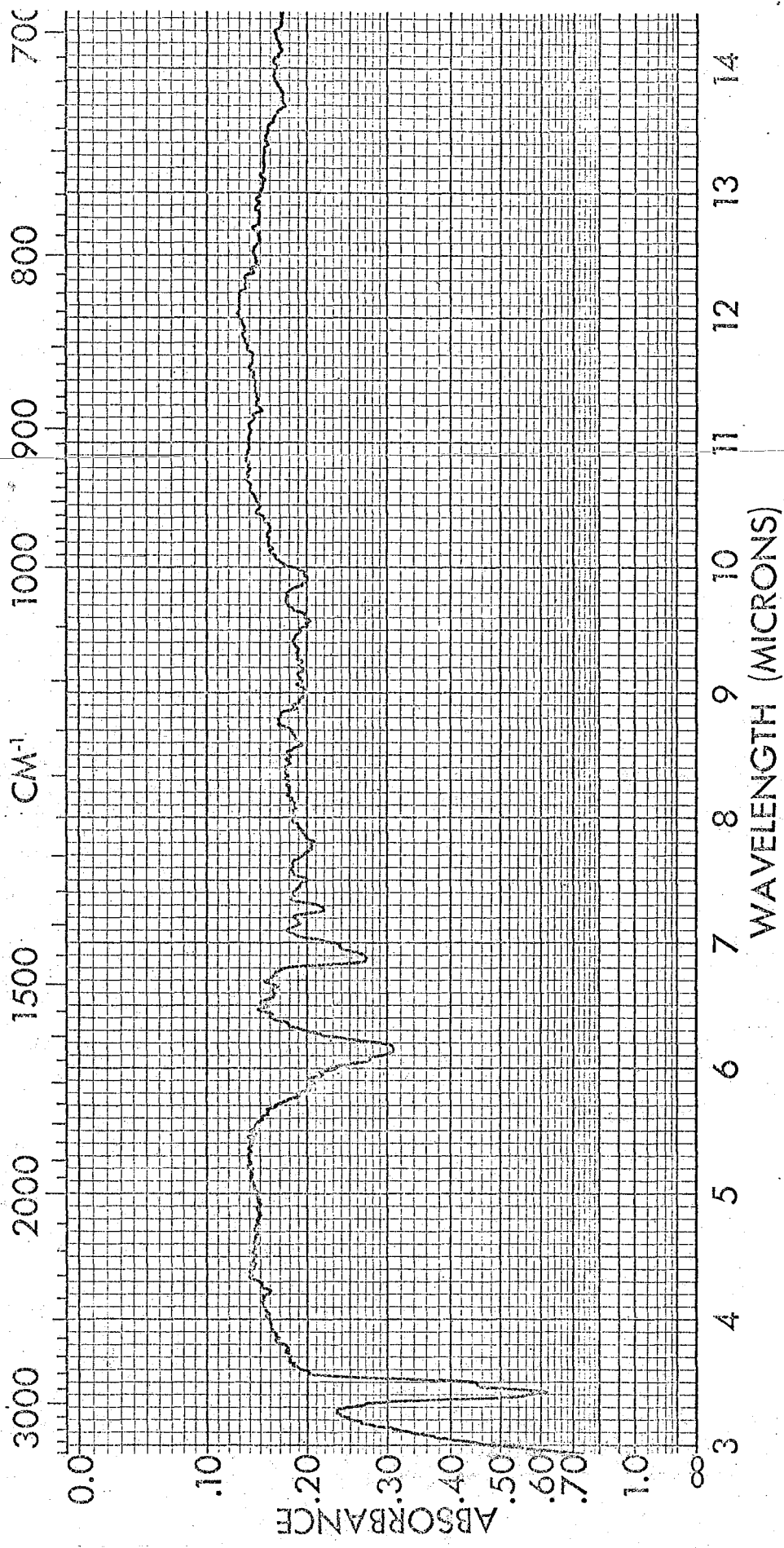Fig. 6-23   Infrared absorption of 4-butyl-4-vinylcyclohexene platinum(II) chloride
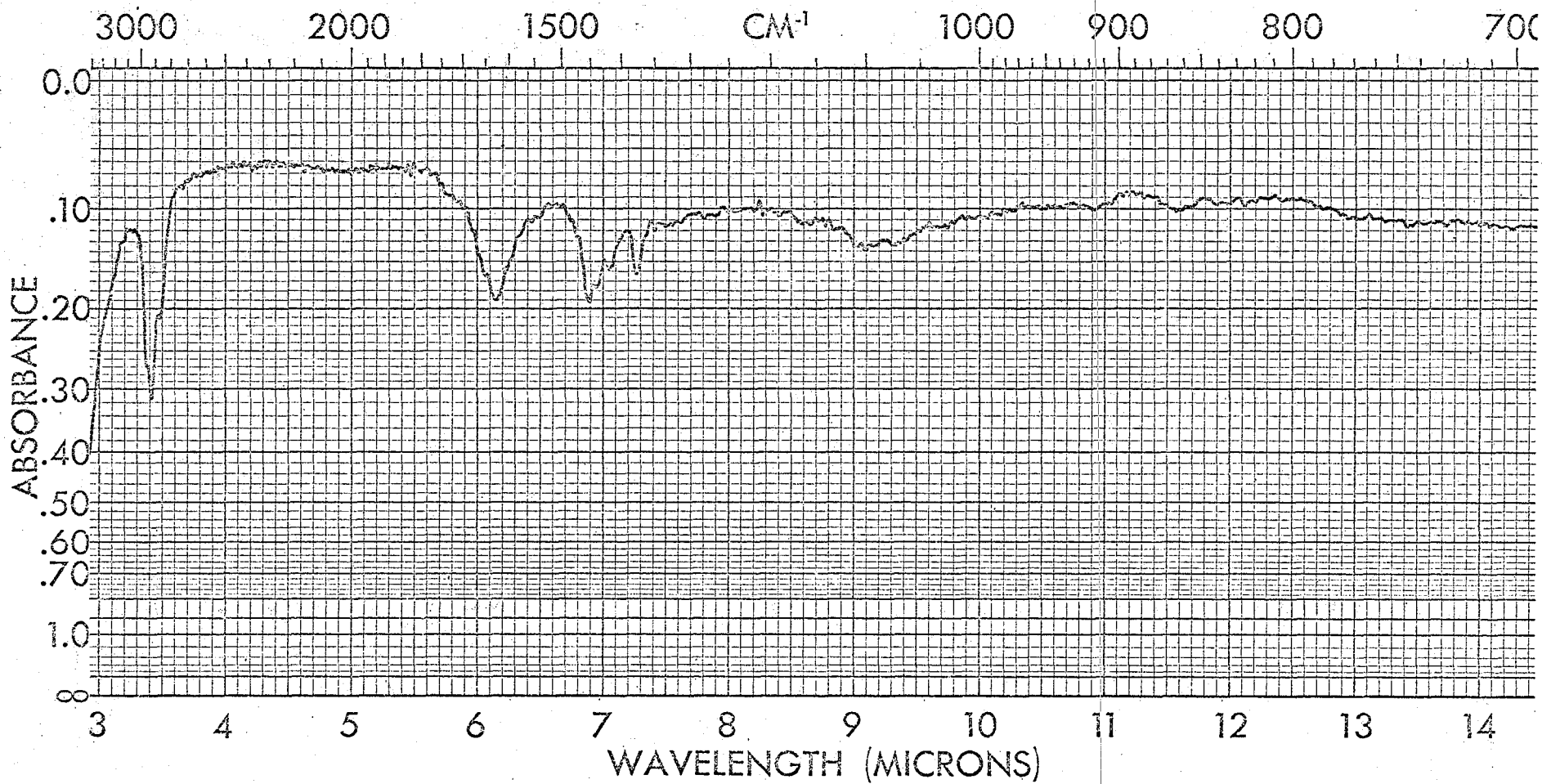
59

Fig. 6-24   Infrared absorption of 4-ethyl-4-vinylcyclohexene palladium(II) chloride
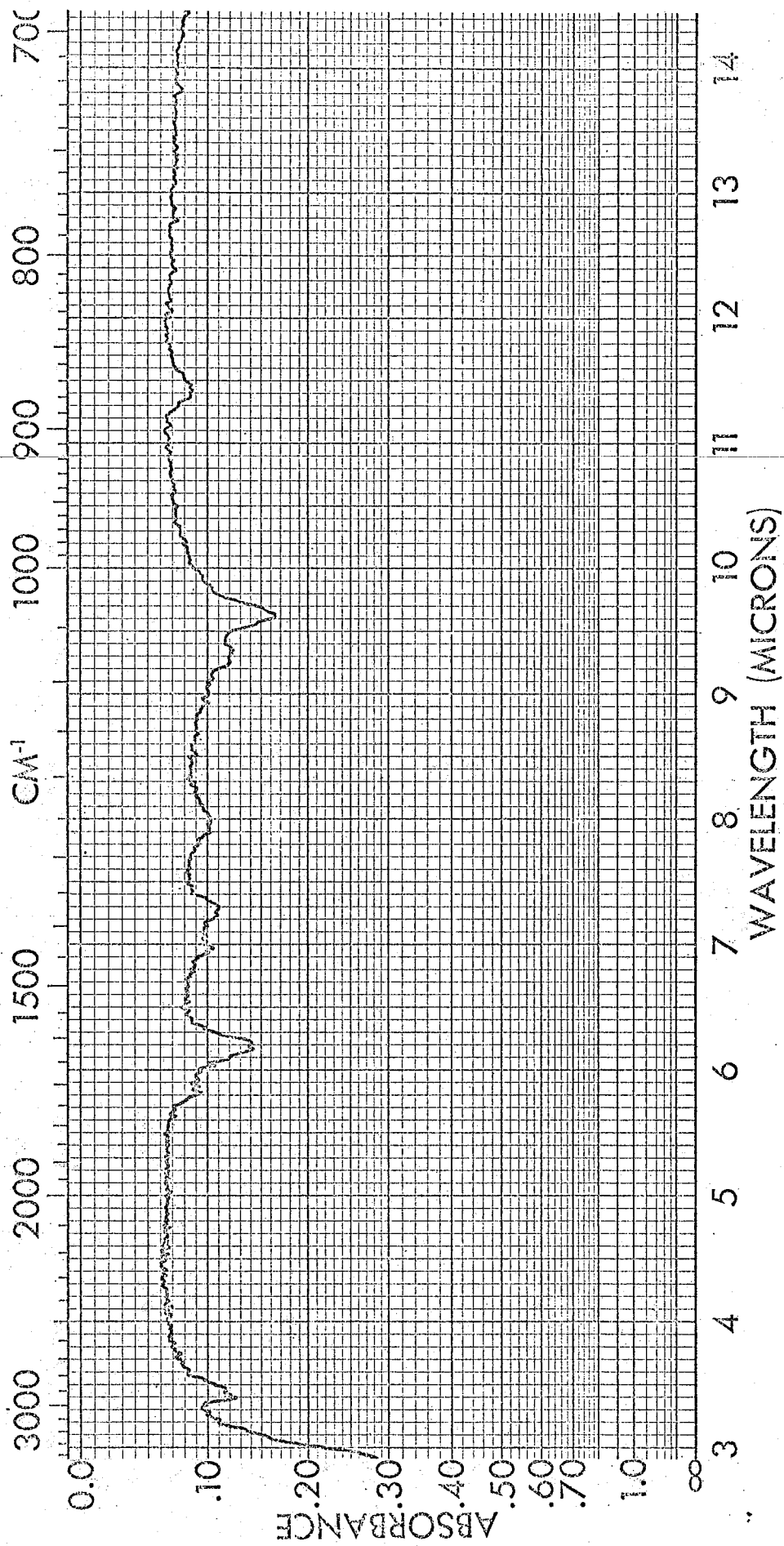
Fig. 6-25   Infrared absorption of 4-methyl-4-vinylcyclohexene palladium(II) chloride

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CHAPTER V

DISCUSSION AND SUMMARY

In the study of 4-vinylcyclohexene complexation with palladium(II) and platinum(II) chlorides, it has been noted that the palladium(II) complex was in fact the 1,5-cyclooctadiene complex rather than the normal pi complex product as was observed with the platinum(II) complex.

The preparation of 4-vinylcyclohexene palladium(II) chloride was repeated with alcoholic solution of palladous sodium chloride. The yield was more quantitative as compared to previous procedure. The results were the same; 1,5-cyclooctadiene palladium(II) chloride was the product observed. Infrared spectra indicated the identical product. See figure 6-11 and 6-13.

The platinum(II) complex of 4-vinylcyclohexene was prepared without any difficulty. Yellowish green granular crystals formed and were identified with previous information. Infrared spectra of this compound was compared with the spectra of 1,5-cyclooctadiene platinum(II) chloride. See figure 6-12 and 6-14. As before in literature observation, no rearrangement occurred.

1-Vinylcyclohexene was prepared according to literature information. The yield was less than predicted by literature due to the purity of the reagents and a slight modification

in the procedure. Elemental analyses showed the correct molecular formula and infrared spectra data showed the characteristic carbon-carbon double bond stretching of the conjugated system at 1600 cm^{-1} and 1650 cm^{-1}. Boiling point of 1-ethynylcyclohexene and 1-vinylcyclohexene seemed to correspond to the literature values. Complexation of 1-vinylcyclohexene with palladium(II) and platinum(II) chlorides were relatively unsuccessful. In both cases, the product observed seemed to be the oxide of the metal. The melting point was above 250°C and infrared spectra showed poor resolution of the characteristic peaks of the ligand. However, the palladium(II) complex infrared spectra showed better evidence of complexation than the platinum. The conjugated system, which evidently did not undergo rearrangement, was relatively stable and possibly did not provide the stereospecific requirement of perpendicularity bonding to either palladium and platinum chlorides. The possibility of complexation should not be completely eliminated since this research limited the complexing agent with the use of only Na$_2$PdCl$_4$ and Na$_2$PtCl$_4$.

The structure of d-limonene provided a methyl group attached to the vinyl carbon. See figure F. The electron donation of the methyl group directly into the pi system stablized the structure as evident of no rearrangement during complexation with either palladium(II) and platinum(II). The platinum complex of d-limonene was prepared by reacting

it with alcoholic solution of platinous sodium chloride. A
yellow crstalline product was obtained. Elemental analyses
and melting point corresponded to literature value. Infrared
spectra showed the absence of carbon-carbon stretching fre-
quency, characteristic of complexation. The structure of the
platinum(II) complex of d-limonene was described by Baenziger,
Medrud and Doyle (1) where coordination about the platinum
metal was square planar with the two chloride atoms occupying
cis position. The two double bonds of the olefin occupied
the remaining two coordinating position. The planes of the
two double bonds were oriented perpendicular to the platinum
chloride plane and to the platinum dsp^3 orbital.

In the preparation of the palladium(II) complex of
d-limonene, bis(benzonitrilo)palladium(II) chloride and
alcoholic solution of palladous sodium chloride as complexing
agent were used with little success. A brown precipitate
was recovered in small yield with melting point about $147^{\circ}C$
with decomposition. The infrared spectra showed the absence
of the carbon-carbon double bond stretching region. However,
the yield was too small after recrystallization for further
analyses. There was no literature report as to the prepara-
tion of this complex. It was suspected that the complex would
be the usual pi complex where the orientation would be similar
to the structure of the platinum complex. If rearrangement
had occurred, the complex would be relatively stable and

analyses would indicate this.

Substitution of an aryl and an alkyl group on the parent compound, 4-vinylcyclohexene, began with the free radical allylic bromination and followed by the Grignard reaction using the appropriate reagent. The difficulty confronted in this synthesis path was the possibility of isomerization during the substitution reactions.

Elemental analysis indicated the monobrominated rather than any multiple substituted product. Infrared spectra showed the presence of the olefinic group not in conjugation which eliminated other possibilities. Also in carbon-hydrogen bending region, 990 cm^{-1} and 920 cm^{-1} indicated monosubstituted (vinyl) alkene. See figure 6-1. The choice of the probable product of allylic bromination was narrowed down to two resonance form intermediate. See figure I.
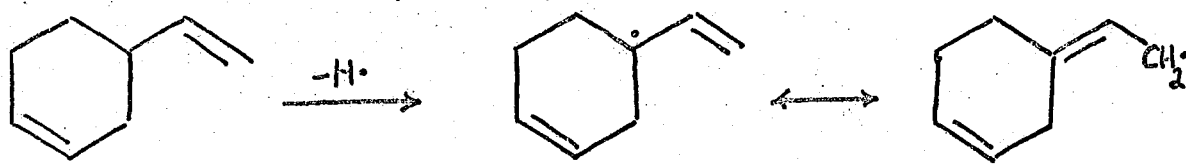

Figure I

The mechanism by which the bromination occurred followed a free radical intermediate, where the most probable attack was at the vinyl group. Nuclear magnetic resonance data seemed to rule out bromination in the cyclohexene ring. See figure

6-26. Spectra data showed no peaks at $\delta = 3.60$ ppm. indicating no hydrogen on carbon attached to a bromide group. From the evidence accumulated, the most probable isomer product derived at the present was 4-bromo-4-vinylcyclohexene. See figure J.
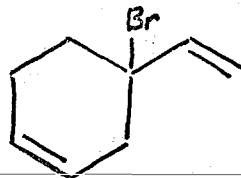

Figure J

Experimental work had been repeated numerous times with the same results obtained. In all cases, the boiling point and refractive index as well as infrared spectra verified the same isomeric product in 60-75% yield. Vapor phase chromatograph indicated that one major isomer was obtained.

4-Bromo-4-vinylcyclohexene was treated with lithium aluminum hydride in tetrahydrofuran and the results of this hydrogenolysis was isolated and compared with 4-vinylcyclohexene. The refractive index value was 1.4680 at 26°C as compared to 1.464 at 20°C for 4-vinylcyclohexene. Boiling points of both compound were similar but not exact. Infrared spectra of the recovered product of hydrogenolysis showed similarity to the spectra of 4-vinylcyclohexene. See figure 6-2 and 6-3.

4-Bromo-4-vinylcyclohexene underwent alkyl substitution by appropriate grignard reagent. 4-Phenyl-4-vinylcyclohexene

was prepared from the Grignard reaction with bromobenzene
and 4-bromo-4-vinylcyclohexene. The product was obtained
without any difficulty and vapor phase chromatography showed
95% purity of the major isomer product. Elemental analyses
indicated the product as monomeric when complexed with
palladium(II) and platinum(II) chlorides. The melting point
was relatively low compared to the unsubstituted 4-vinylcyclo-
hexene complexes and the rate of formation of the oxide
indicated the instability of the complexes. See figure K.
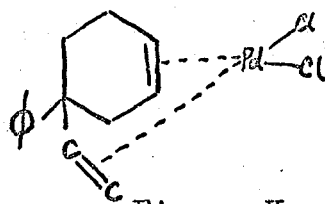

Figure K

4-Butyl-4-vinylcyclohexene posed additional problem
because of the length of the chain. The yield of the complex
formed was small. The rate of formation for the palladium
complex was reasonable but the platinum complex took several
days for completion. The ethyl subsituted product followed
similar experimental approach and the complexes were study.

4-Methyl-4-vinylcyclohexene was prepared by similar
method using methyl iodide and 4-bromo-4-vinylcyclohexene.
Nuclear magnetic resonance data was taken for this compound.
The methyl group hydrogen was shown at $S = 0.95$ ppm. The
methylene hydrogen of the cyclohexene ring was at $S = 1.8$ ppm.
The olefinic protons was located at $S = 5$ to 5.5 ppm.

The data seemed to support previous assignment of structure
for 4-bromo-4vinylcyclohexene. However, the N.M.R spectra
showed a splitting of the methyl hydrogen which was unexplain-
able at this time.

As has been observed in many previous papers on the
complexation of palladium and platinum metals, this research
has indicated that the platinum complex, even though more
difficult to obtain, was more stable than the palladium com-
plex of the same hydrocarbon. As for 4-vinylcyclohexene, the
behavior toward palladium and platinum may be attributed to the
radial dimension of platinum(II) and palladium(II) which
reflected in their bond strength. Platinum complex was capable
of forming well-defined compounds. Palladium(II) merely
served to act as a catalyst in the conversion of 4-vinylcyclo-
hexene to 1,5-cyclooctadiene complex.

A brief investigation into the literature concerning
metal catalyzed isomerization was made inorder to possibly
assign a particular mechanism to the rearrangement of 4-vinyl-
cyclohexene. One of the most popular mechanism used by
numerous workers involved a pi allylic intermediate.
Trebellas, Olechowski, and Jonassen (31) proposed this
intermediate in their study of 1,5-cyclodecadiene. They
illustrated their mechanism as:
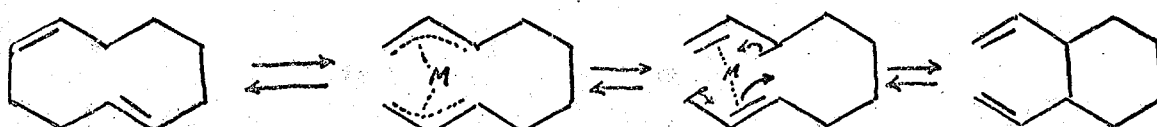
However, allylic intermediate itself has not been isolated. The preparation of such complexes as palladium π-cyclohexenyl (12) and the di (π-allyl) complex and intermediate prepared by Wilke and coworker (32) seemed to support the pi allyl intermediate.

Another mechanism that metal-catalyzed isomerization process may proceed was through a pi-allylic hydrido or a hydrido alkyl intermediate. Nicholson and Shaw (27) have proposed this mechanism for the isomerization of cyclooctadiene catalyzed by noble metal salts. Frye, Kuljian, and Viebrock (14) favored this mechanism for the ligand rearrangement of 1,3 to 1,5-cyclooctadiene by palladium(II) and platinum(II) complexes.

Harrod and Chalk (17), working with the isomerization of 1-Hexene by platinum(II) complex illustrated the double migration by the formation of metal hydride intermediate. See figure L

Figure L
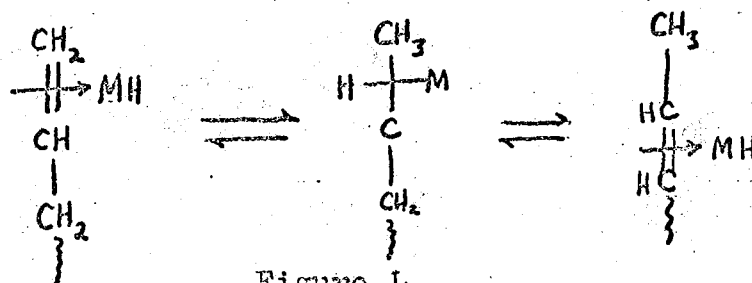
The source of the hydride ion seemed to originate from a co-catalyst. In the case of palladium, where no cocatalyst was required, hydride ion originated from the olefin.

Davies (8) preferred not to used the pi allylic hydride intermediate but instead proposed that the olefin passed through a coordinated carbene stage. See figure M.
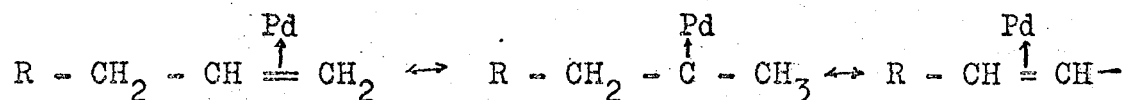
$$R - CH_2 - CH \xrightarrow{Pd} CH_2 \longleftrightarrow R - CH_2 - \overset{Pd}{C} - CH_3 \longleftrightarrow R - CH \overset{Pd}{=} CH-$$

Figure M

The mechanism for the rearrangement of 4-vinylcyclo-hexene would involve ring cleavage and expansion to accomo-date the vinyl group and thereby giving the energetically stable 1,5-cyclooctadiene system. One possible mechanism may be shown as going through a pi allylic intermediate. See figure N.
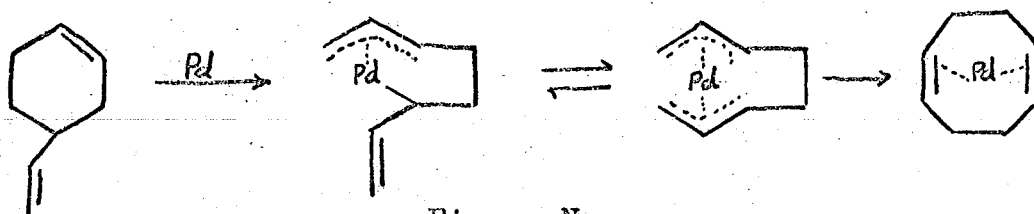

Figure N

The driving force for the molecular rearrangement could be the tendency of the cyclic diene system to achieve the greater molecular stability. In view of the ability of palladium to form olefin complexes and further the tendency of these to give pi-allylic complexes implied the labilization of one of the hydrogen on the olefin.

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