

6-1970

Photochemical reduction of benzophenone by 2-butyne-1, 4-diol and photochemical solvolysis reactions of beta-phenethyl compounds

Kenneth Lawrence Gordon
Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

Recommended Citation

Gordon, Kenneth Lawrence, "Photochemical reduction of benzophenone by 2-butyne-1, 4-diol and photochemical solvolysis reactions of beta-phenethyl compounds" (1970). *Honors Theses*. 1799.
<https://digitalworks.union.edu/theses/1799>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

The Photochemical Reduction of Benzophenone

by 2-Butyne-1,4-diol

and

Photochemical Solvolysis Reactions of

β -Phenethyl Compounds

by

Lawrence
Kenneth Gordon U.C. 1970

* * * * *

Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE

May, 1970



g
UN82
G663p ✓
1970
C.2

This Thesis
Submitted by

Kenneth Lawrence Gordon

to the

Department of Chemistry of Union College
in partial fulfillment of the requirements of the degree of
Bachelor of Science with a Major in Chemistry
is approved by

Alan L. Maycock

ABSTRACT

GORDON, KENNETH

The Photochemical Reduction of Benzophenone by 2-Butyne-1,4-diol. Department of Chemistry, May 1970.

The irradiation of a dioxane solution of benzophenone in the presence of 2-butyne-1,4-diol leads to reduction of the ketone rather than addition across the triple bond of the alkyne. However, great difficulty was encountered in identifying the product due to the formation of an organic complex involving benzopinacol and the dioxane. Nuclear magnetic resonance and ultraviolet spectral data confirm the presence of the complex.

Photochemical Solvolysis Reactions of β -Phenethyl Compounds. Department of Chemistry, May 1970.

An attempt was made to induce a known ground state reaction by photochemical means. This ground state reaction is known to proceed through an ethylene phenonium ion intermediate. Both β -phenethyl bromide and β -phenethyl-trimethylammonium tetrafluoroborate were irradiated in alcoholic solvents, but no reaction was observed.

CONTENTS

Abstract	page iii
List of Figures	page v
Part I: The Photochemical Reduction of Benzophenone by 2-Butyne-1,4-diol	
Introduction	page 1
Discussion	page 3
Conclusion	page 7
Experimental	page 10
Part II: Photochemical Solvolysis Reactions of β -Phenethyl Compounds	
Introduction	page 14
Discussion	page 15
Conclusion	page 17
Experimental	page 19
References	page 21
Figures	page 22

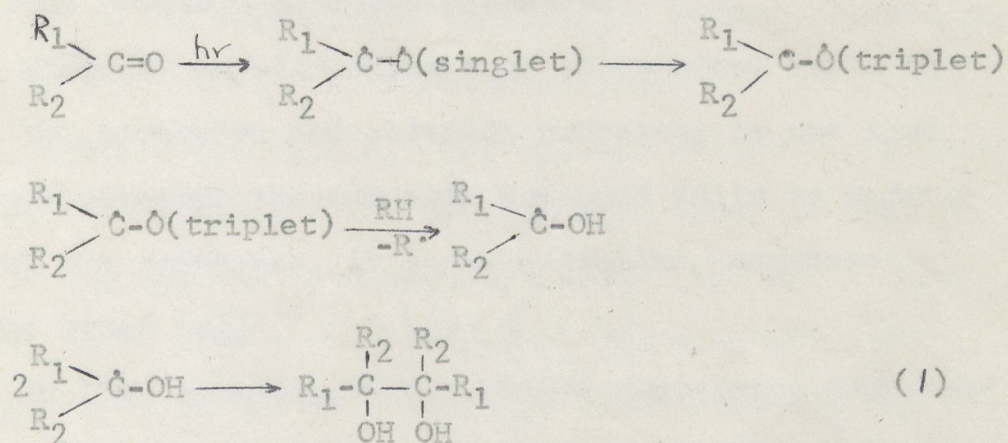
List of Figures

Infrared Spectrum of Product I	page 22
Nuclear Magnetic Resonance Spectrum of Product I	page 25
Mass Spectrum of Product I	page 26
Ultraviolet Spectrum of Product I	page 27
Ultraviolet Spectrum of Benzopinacol	page 28
Nuclear Magnetic Resonance Spectrum of Thermal Product	page 29
Infrared Spectrum of Product I after Repeated Recrystalization and Drying	page 30
Infrared Spectrum of Benzopinacol	page 33
Nuclear Magnetic Resonance Spectrum of a Mixture of Benzopinacol and Dioxane	page 36
Infrared Spectrum of Melted Product I	page 37

Part I:
The Photochemical Reduction of Benzophenone
by 2-Butyne-1,4-diol

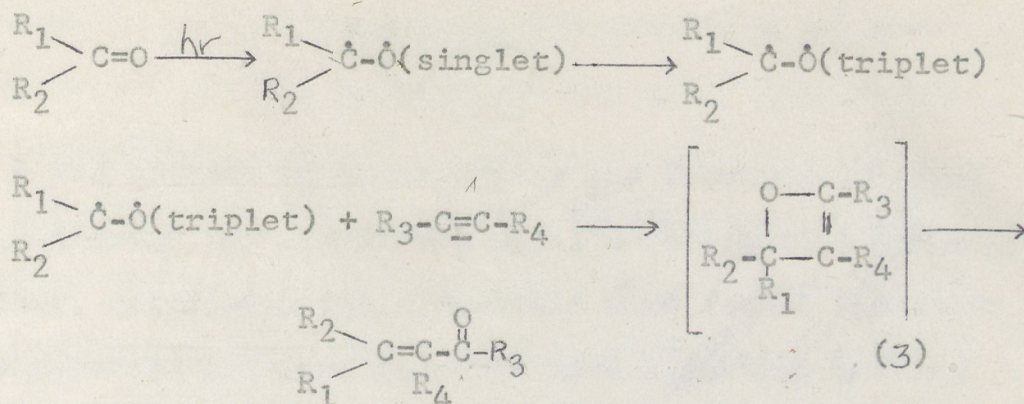
INTRODUCTION

One of the classic photochemical reactions of organic chemistry is the reduction of benzophenone to benzopinacol in the presence of a hydrogen atom donor. Studies have shown that this reaction is extremely general and can be observed with aliphatic and aromatic ketones and aldehydes alike (1). The reaction proceeds via the triplet state, and in its generalized form may be visualized as follows:



Among the compounds that may be employed as hydrogen donors, alcohols figure most predominately.

A much more obscure reaction that has been studied by G. Büchi is the light initiated addition of carbonyl compounds to substituted acetylenes (2). The products, α,β -unsaturated carbonyl compounds, probably arise via unstable oxetene intermediates (3). Again, in a generalized form, a possible mechanism may be visualized as follows:



(In the products, R_1 and R_2 may be interchanged as may be R_3 and R_4 depending upon the orientation of the molecules during the reaction. This being so, there are four possible isomeric products.)

There is an indication that the excited state in both the reduction and addition processes is the same because whenever the carbonyl compound fails to undergo one of the processes, it shows a similar inertness to the other (4).

In this investigation carbonyl containing compounds were exposed to ultraviolet radiation in the presence of a difunctional compound possessing both an acetylenic linkage and a primary hydroxyl group. The reaction was studied in great detail to discover whether it would proceed by reduction or by addition to the triple bond followed by rearrangement.

DISCUSSION

A 1:1 mixture of benzophenone and 2-butyne-1,4-diol in 1,4-dioxane was irradiated until a substantial quantity of clear, colorless, cubic crystals were formed (Reaction I). These crystals (I) were found to have a maximum melting point of 216° , well above that of benzopinacol ($188-189^{\circ}$ (5)), thus seeming to eliminate this as a possible reaction product.

The infrared spectrum of I (Figure I) contained a multitude of absorptions including a hydroxy absorption, but the most useful information obtained was the lack of a carbonyl absorption. The nuclear magnetic resonance spectrum of I (Figure II) contained an aromatic peak at 7.6 ppm and two up-field singlets at 4.2 and 3.5 ppm in the ratio 10:4:1 respectively. The smallest peak was found to be due to a hydroxyl group since it was not observed in d_6 -acetic acid. The mass spectrum of I (Figure III) showed a parent peak having a molecular weight of 182 (benzophenone?) and base peak of molecular weight 105, $\text{Ph}\overset{+}{\text{C}}=\text{O}$. However, this information proved useless because it was found that the product decomposes upon melting as it may have in the mass spectrum (Reaction II). The ultraviolet spectrum of I (Figure IV) was strange. Rather than showing one continuous absorption as was observed for benzopinacol (Figure V), there appeared to be several absorptions superimposed upon each other.

Yet when this data obtained from instrumental results was combined, it was insufficient for the determination of a structure.

To aid in the identification of this photochemically generated product, it was necessary to determine from which combination of reactants the product was formed. To this end tetrahydrofuran and diethyl ether were substituted for the dioxane. (Reactions III and IV). In the case of the former (Reaction III), minute quantities of a product were formed. This product had a lower and less distinct melting point than I, 173-176°, and a slightly different nuclear magnetic resonance spectrum, showing the same aromatic and hydroxy shifts and ratios, however a smaller and farther down-field third peak. This information along with the fact that less product was formed, seemed to indicate a solvent was involved in the reaction. The ether reaction mixture (Reaction IV) also produced a product, but in such low yield that it was only evident by the fact that a white solid could be seen in the reaction vessel at temperatures as high as 80°, well above the melting points of the reactants.

It seemed obvious that the solvent and benzophenone were participating in Reaction I, but as yet there was no indication that the 2-butyne-1,4-diol was a participant. Solutions of benzophenone in dioxane and benzophenone in tetrahydrofuran were irradiated to investigate whether

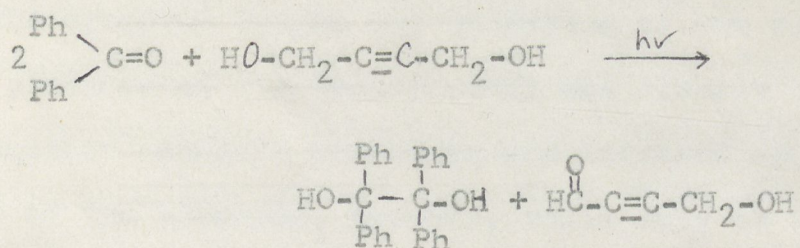
a product would be generated in the absence of the alkynediol (Reactions V and VI). The results of this were inconclusive because in both reaction vessels such minute quantities of product were formed that it was impossible to isolate and study them.

There still existed the possibility that these reactions were not photochemically initiated, but rather thermally, the heat being generated by the irradiating lamps. To decide upon this matter, a solution similar to the original one containing the benzophenone and 2-butyne-1,4-diol in dioxane was prepared, refluxed (Reaction VII), and examined. Nuclear magnetic resonance (Figure VI) demonstrated the existence of a product different from I, but it was not fully characterized.

Due to the almost complete lack of success in identifying the photo-product, it was deemed necessary to send the product for analysis and molecular weight determination. A highly purified sample was prepared by repeated recrystallization from chloroform and drying. However, the melting point of this material, 188-189^o, was observed to be different from that of product I. Further investigation revealed that the infrared spectrum (Figure VII) had also been drastically altered. Comparison of Figures I and VII demonstrated this plainly. A nuclear magnetic resonance spectrum of this new product revealed an aromatic peak and one, lone, up-field singlet due to a hydroxyl group in the ratio 10:1. This is

what might be expected for benzopinacol, one of the originally hypothesized products. To confirm this an infrared spectrum of a known sample of benzopinacol (Figure VIII) was compared with Figure VII and found to be identical.

If benzopinacol was to be formed by abstracting the hydrogen alpha to the hydroxyl group on the 2-butyne-1,4-diol according to the following reaction



an aldehyde might be a by-product. (The reaction could also produce the dialdehyde.) Its presence was suggested by a positive fuchsin-aldehyde reagent test (Reaction VIII), although attempts to isolate the aldehyde were futile.

CONCLUSION

There can be no doubt that a major product formed when benzophenone and 2-butyne-1,4-diol are irradiated with ultraviolet light is benzopinacol. This reaction must proceed by attack of an excited triplet state benzophenone upon a hydrogen in a position alpha to the hydroxyl group of the diol resulting in the reduction of the aromatic ketone and oxidation of the alcohol. The presence of the benzopinacol was clearly demonstrated by nuclear magnetic resonance and infrared spectroscopy. That of the aldehyde, however, could only be inferred by wet qualitative analysis since the compound is not isolable due to its instability. The reaction was shown to involve these two reactants by a series of experiments (Reactions V and VI) in which it was found that much less product was produced when the 2-butyne-1,4-diol was omitted. It was also shown, though, that replacing 1,4-dioxane, the solvent, with another ether reduces the yield (Reactions III and IV). This indicates that the dioxane reacts in some manner to form benzopinacol, whereas other ethers react to a lesser extent. An article by Rosenthal and Elad confirms this (6).

This paper might simply be terminated now if it were not for a number of curious observations that lead to an unusual conclusion. It is the opinion of the author that an organic complex was formed involving the benzopinacol

and 1,4-dioxane resulting in the difficulty of identifying the product. When first isolated the crystalline product was found to have a sharp melting point indicating a high degree of purity. However, the temperature at which the substance melted was higher than that of pure benzopinacol, thus eliminating the possibility of a simple mixture of the compounds, and causing doubt as to the true nature of the product. The nuclear magnetic resonance spectrum of the product (Figure II) was readily reproducible, crystals from each reaction vessel showing the same pattern. The ratio of hydrogen atoms in this spectrum, if the peak at 4.2 ppm is attributed to the dioxane, is that which might be expected for a 1:1 complex of benzopinacol and the dioxane. If dioxane, however is added to a chloroform solution of benzopinacol, it is found to have a shift at 3.7 ppm as expected (Figure IX) (7). The 0.5 ppm down-field shift is then attributed to a deshielding effect of the complex. Furthermore, this same nuclear magnetic resonance spectrum was obtainable after the reaction product had been recrystallized in chloroform, but not dried, indicating a strong attraction of the two compounds for each other.

The most striking evidence, however, for the existence of a dioxane - benzopinacol complex is the ultraviolet spectrum obtained from the product (Figure IV). If this so-called complex were no more than a trapping of the ether in the benzopinacol crystalline lattice,

when placed in an appropriate solvent for ultraviolet work, the spectrum would be only that of benzopinacol since the 1,4-dioxane absorbs at a much shorter wavelength. However, rather than displaying this simple spectrum, a much more complexed one was obtained. Hence, one must conclude that the aromatic diol, benzopinacol, and the cyclic diether, 1,4-dioxane, form an unusual organic complex with each other.

EXPERIMENTAL

Reaction I

One g (0.012 moles) 2-butyne-1,4-diol (recrystallized from diethyl ether; melting point 55-56°) and 2.1 g (0.012 moles) benzophenone (recrystallized from diethyl ether; melting point 47-48°) were mixed and melted. To this heterogeneous mixture sufficient 1,4-dioxane (made peroxide free by shaking with a saturated solution of ferrous sulfate and 5% sulfuric acid, extracting the aqueous layer, and refluxing for 12 hrs with sodium metal to remove the water; boiling point 101°) was added to effect solution. This solution was irradiated in a Rayonet Photochemical Reactor containing a circular bank of 16 lamps emitting maximum radiation at 300m μ for 42 hrs with the formation of 0.1 g of I after recrystallizing from chloroform. Each of these crystals had a distinct melting point, each melting between 196 and 216°. There was this great range of melting points because the product changed its crystalline structure just before melting. From this product the infrared spectrum (Figure I), nuclear magnetic resonance spectrum (Figure II), mass spectrum (Figure III), and ultraviolet spectrum (Figure IV) were obtained.

Reaction II

A sample of I was melted and the infrared spectrum (Figure X) obtained from the melt showed the development

of a strong carbonyl absorption. When this is considered along with the fact that the parent peak in the mass spectrum of I (figure III) was at 182, the molecular weight of benzophenone, it becomes a reasonable conclusion that I decomposes to benzophenone when melted.

Reaction III

The same procedure was followed as in Reaction I but tetrahydrofuran (boiling point 64°) was substituted for the dioxane. After 70 hrs of irradiation less than 0.05 g of product was obtained, melting point $173-176^{\circ}$.

Reaction IV

The same procedure was followed as in Reaction I but using diethyl ether (boiling point 34°). A Product was known to exist after 70 hrs irradiation only because solid remained in the reaction mixture up to a temperature of 80° , well above the melting point of any of the reactants.

Reaction V

Six g benzophenone were placed in 3.0 ml dioxane and irradiated for 68 hrs with the appearance of very minute quantities of a product.

Reaction VI

Benzophenone (6.6g) was placed in 3.0 ml tetrahydrofuran and irradiated for 68 hrs with the same results as Reaction V.

Reaction VII

Four g (0.047 moles) 2-butyne-1,4-diol, 8g (0.044 moles) benzophenone and 4 ml dioxane were refluxed

for 4 hrs. A product was observed as the center spot on an alumina thin layer chromatographic plate using chloroform as the solvent. This product was separated on an alumina chromatographic column again using chloroform as the moving phase. The nuclear magnetic resonance spectrum shown in Figure VI was obtained.

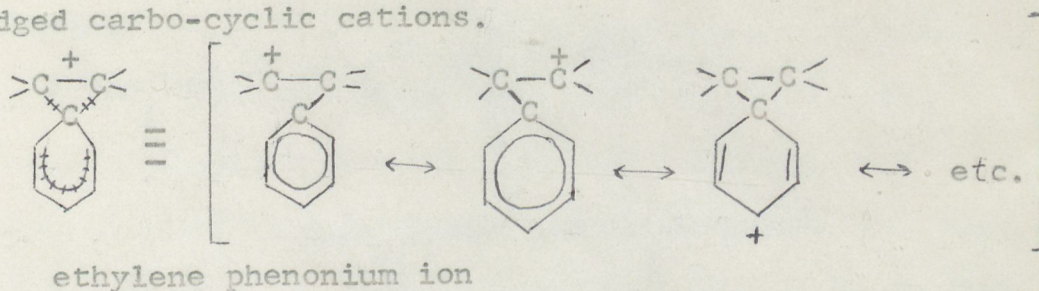
Reaction VIII

A few drops of the supernatant liquid from Reaction I was added to the fuchsin - aldehyde reagent, producing the characteristic violet - purple color diagnostic of the presence of an aldehyde.

Part II:
Photochemical Solvolysis Reactions
of β -Phenethyl Compounds

INTRODUCTION

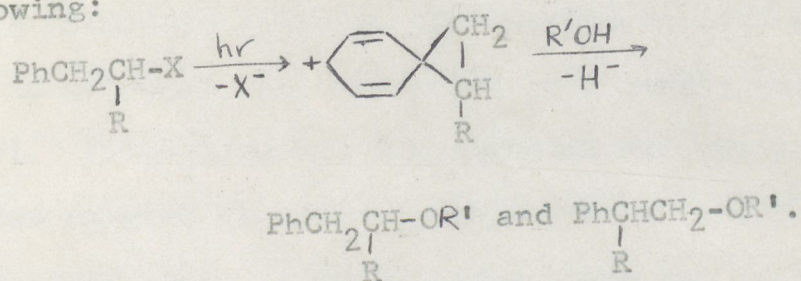
The case for the existence of ethylene phenonium ions as a discrete class of reaction intermediates in certain Wagner - Meerwein rearrangements has been presented by Donald J. Cram (8). His study of the kinetic and stereochemical course of these 1,2-rearrangements has provided direct evidence for the existence of these bridged carbo-cyclic cations.



Cram has examined only those reactions that proceed in the ground state. This paper explores the possibility of photochemically inducing similar excited state reactions.

DISCUSSION

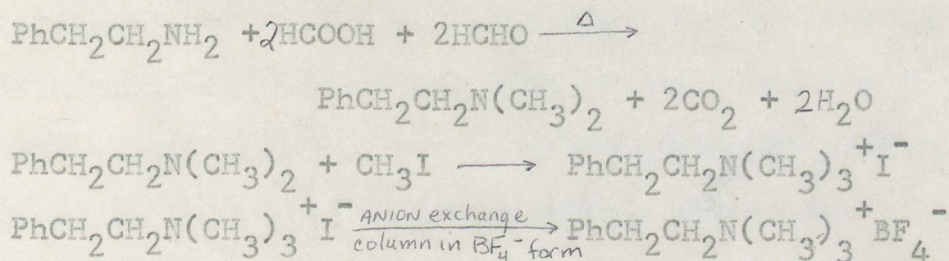
The approach used in this study was to investigate the possibility of photochemical solvolysis reactions in β -phenethyl compounds. If such reactions were found to occur, then appropriately substituted compounds would be employed to check for rearrangement. The solvents used were alcohols and the reaction examined was the following:



(If R is hydrogen then rearrangement yields the same product.)

A solution of β -phenethyl bromide in ethanol was irradiated in a quartz reaction vessel and the progress of the reaction followed by vapor phase chromatography. After 25 hrs of irradiation a blackening of the reaction mixture was observed and small amounts of two low boiling products were detected. Continued irradiation, however, did not increase the amounts of product. For this same time period, no reaction was observed in the absence of light. Thus it seemed that some photochemically induced reaction had taken place, but the yields were minute.

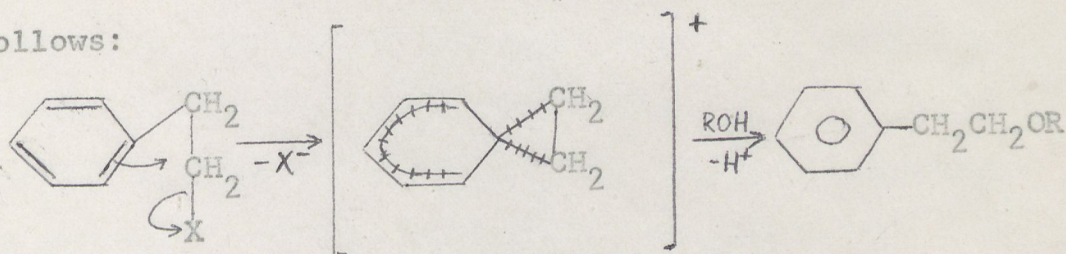
β -Phenethyltrimethylammonium tetrafluoroborate, prepared as shown in the following scheme, was also studied.



A saturated solution of this quaternary ammonium salt in methanol was irradiated in a quartz reaction vessel. Intermittently the reaction was halted and samples removed to follow its progress. After more than two hundred hours of irradiation there was no indication of any ether soluble product. The only products that formed during irradiation were water soluble oils. Again no reaction was observed in the absence of light.

CONCLUSION

It is clear that neither the solvolysis reactions of β -phenethyl bromide nor β -phenethyltrimethylammonium tetrafluoroborate can be initiated by exciting the aromatic ring. However, if these reactions did occur, it is unlikely that it would be due to a transfer of the excitation energy from the phenyl group through the sigma bond system to the heteroatom - carbon bond. It is more likely that an intramolecular nucleophilic substitution reaction would occur in which the α -carbon would approach the junction carbon of the aromatic system. If this occurred, the excitation energy of the ring could be transferred directly to the α -carbon and supply the energy necessary to break the bond to the heteroatom. The hypothesized mechanism may be pictured as follows:



There are at least two possible reasons why the expected reaction did not occur in the systems under investigation. First, it is possible that the excited state, be it singlet or triplet, has such a short lifetime that the α -carbon does not have enough time to approach the ring juncture. Secondly, the negative charge density

at the ring juncture carbon may be too small to attract the α -carbon. Either of these would hinder the formation of the ethylene phenonium ion intermediate. To overcome these difficulties it may be possible to place proper substituents on the aromatic ring that would increase the excited state lifetime and/or increase the negative charge density at the juncture carbon.

EXPERIMENTAL

A 9:3:1 mole solution of ethanol, distilled β -phenethyl bromide and hexadecane, respectively, was prepared and irradiated in a quartz vessel using a Rayonet Photochemical Reactor containing a circular bank of 16 lamps emitting maximum radiation at 254m μ . After 25 hrs of irradiation a sample of the blackened solution was removed and injected into a silicon gum vapor phase chromatographic column at 200°. In addition to the ethanol peak (after 30 sec), the β -phenethyl bromide peak (after 5 min), and the internal standard, hexadecane peak (after 10 min), two low boiling products were observed (after 90 sec and 100 sec). An additional 47 hrs of exposure to the ultraviolet light failed to change the contents of the reaction mixture. A darkened reaction vessel containing the same reactants showed no reaction during this same time period.

β -Phenethyldimethylamine (II) was prepared according to the procedure outlined by Icke and Wisegarver (9) from β -phenethylamine, formic acid and formaldehyde solution (45% yield). II was then converted into the quarternary ammonium iodide (III) using methyl iodide (65% yield). The iodide was then exchanged for tetrafluoroborate employing ion exchange techniques. A column containing excess Dowex 1-X8 in the chloride form was prepared and converted to the tetrafluoroborate

form using an excess sodium tetrafluoroborate. Through this an aqueous solution of III was passed yielding β -phenethyltrimethylammonium tetrafluoroborate (IV), recrystallized from water (melting point 155-157°).

A saturated solution of IV in methanol was irradiated as above for more than 200 hrs. Periodically samples of the reaction mixture were removed, extracted with ether, evaporated to almost dryness, and injected into a silicon gum vapor phase chromatographic column at 170°. Not ever after 200 hrs was there any indication of product.

REFERENCES

1. Kan, Robert O., Organic Photochemistry. New York City: McGraw - Hill Book Co., (1966).
2. Büchi, G., etal., "The Addition of Aromatic Carbonyl Compounds to a Disubstituted Acetylene," Journal of the American Chemical Society 78, 876 (1956).
3. Calvert, Jack G., and Pitts, James W., Jr., Photochemistry. New York City: John Wiley and Sons, Inc., (1967).
4. Turro, Nicholas J., Molecular Photochemistry. New York City: W. A. Benjamin, Inc., (1965).
5. Fieser, Louis F., Organic Experiments. Boston: D. C. Heath and Co., (1966).
6. Rosenthal, I., and Elad, P., "Photoalkylation of Cyclic Ethers," Tetrahedron 23, 3193 (1967).
7. Bhacca, N. S., etal., N. M. R. Spectra Catalog. Palo Alto, California: Varian Associates, (1963).
8. Cram, Donald J., "Phenonium Ions as Discrete Intermediates in Certain Wagner - Meerwein Rearrangements," Journal of the American Chemical Society 86, 3767 (1964).
9. Horning, E. C., Organic Synthesis. New York City: John Wiley and Sons, Inc., (1955).

00 3000 2500 2000 1800 1600

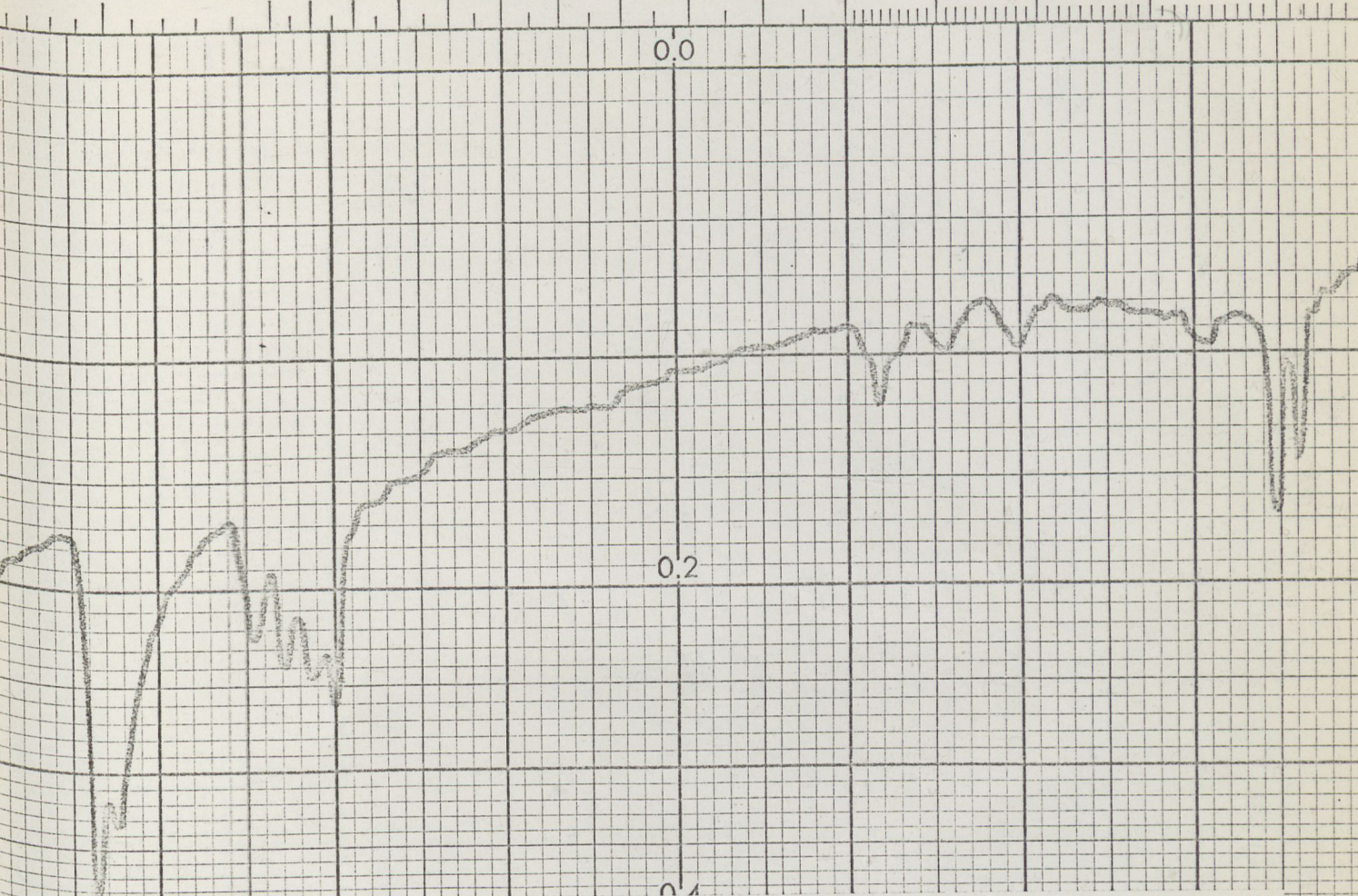


FIGURE I
Infrared Spectrum of Product I
(continued next two pages)

(22)

3 4 5 6

FREQUENCY (CM⁻¹)

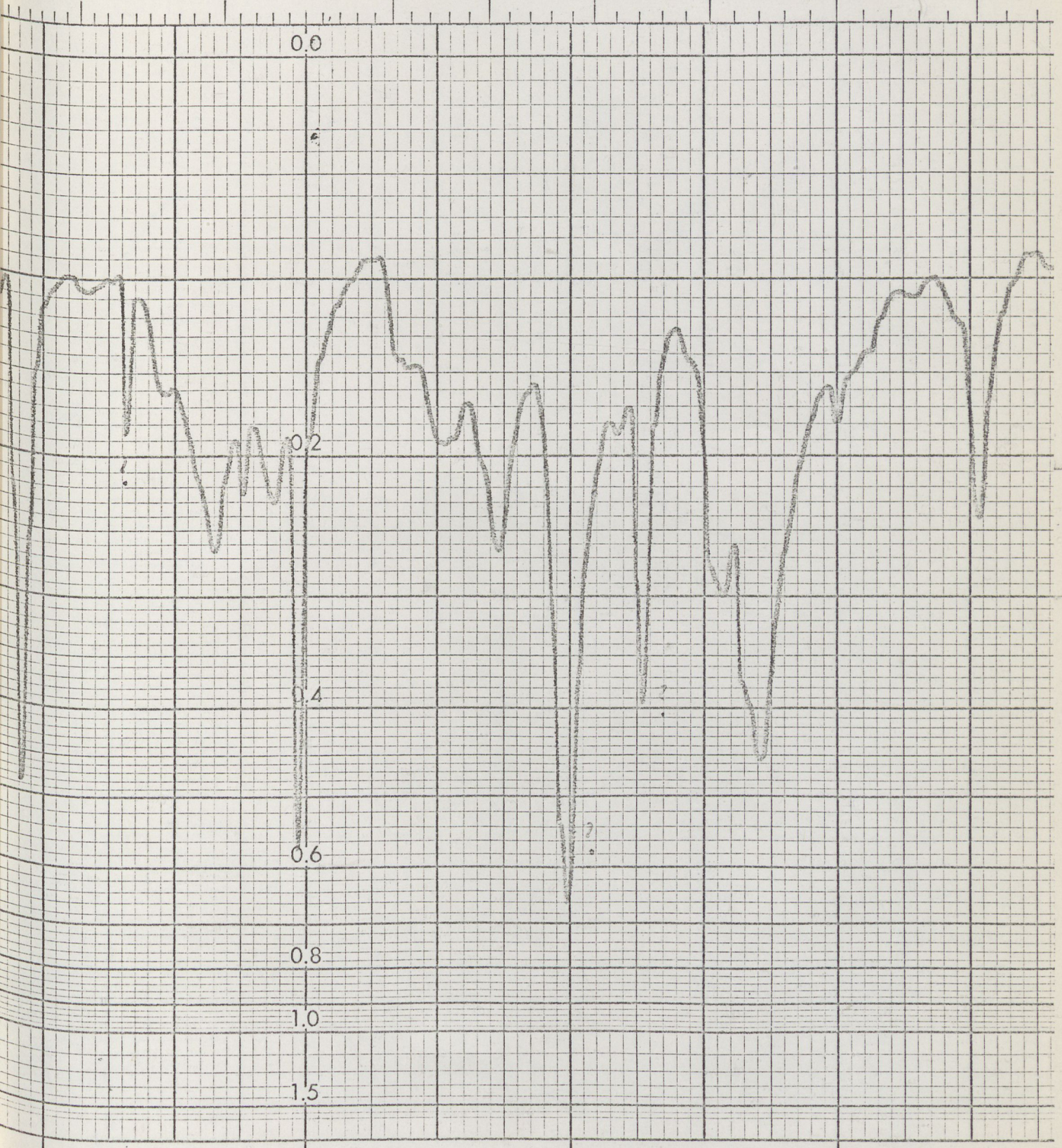
1400

1200

1100

1000

950



7

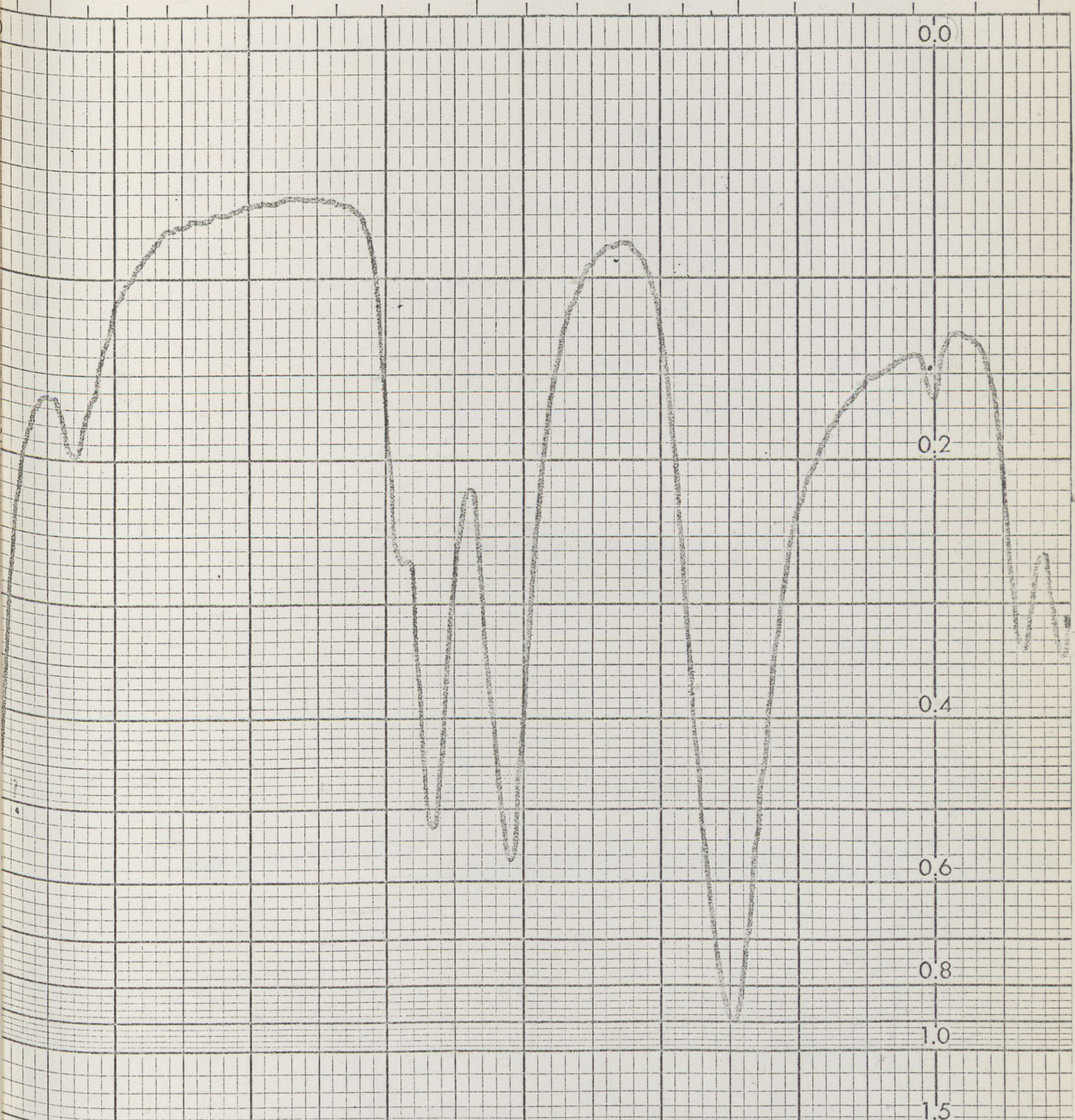
8

9

10

WAVELENGTH (MICRONS)

850 800 750 700 650



THE PERKIN - ELMER CORP., NORWALK, CONN.

12

13

14

15

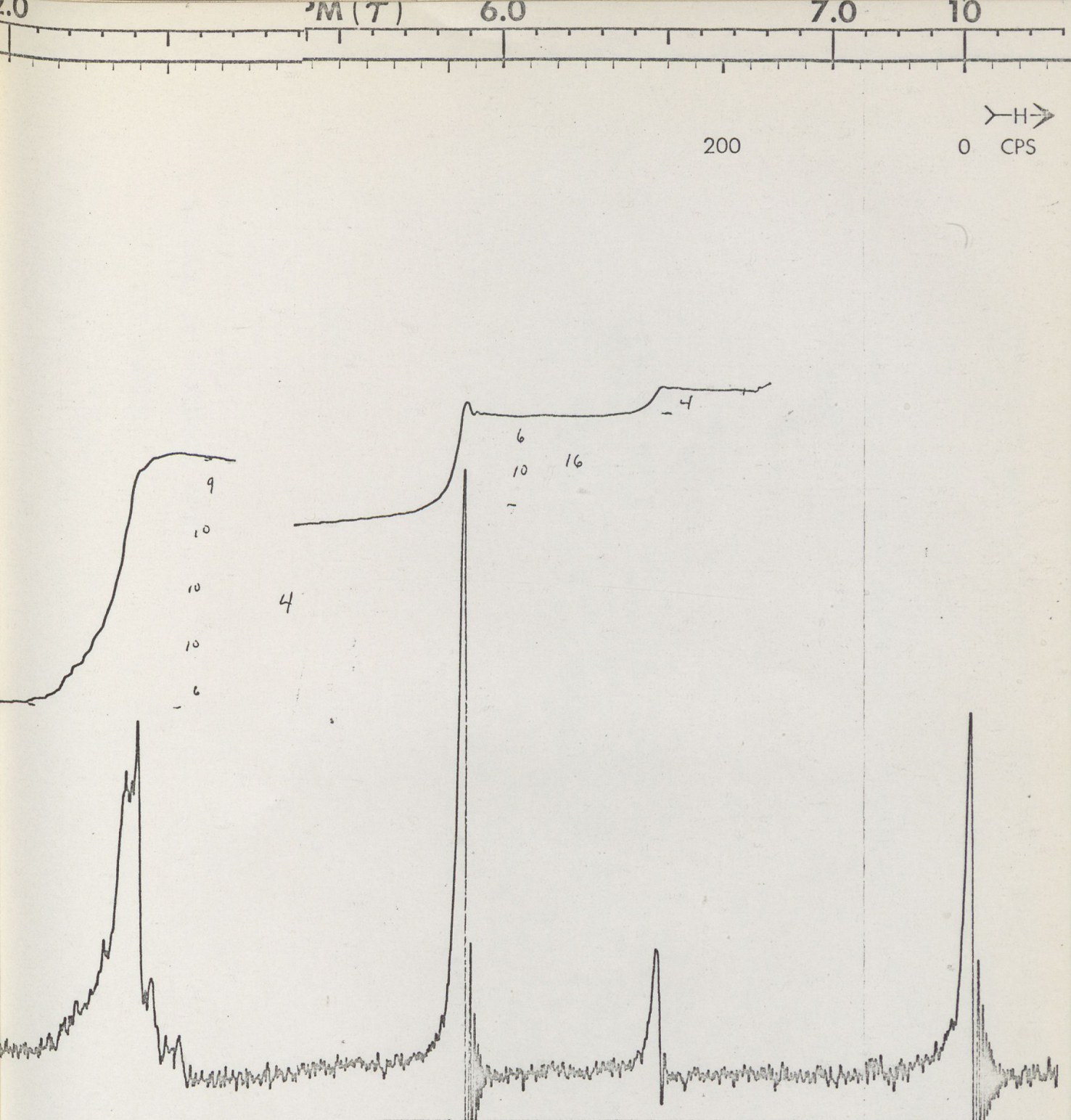


FIGURE II
Nuclear Magnetic Resonance
Spectrum of Product I

(25)

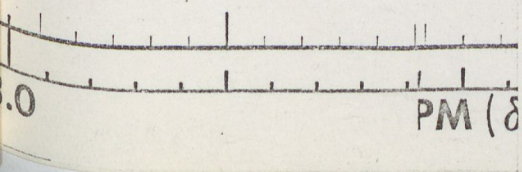
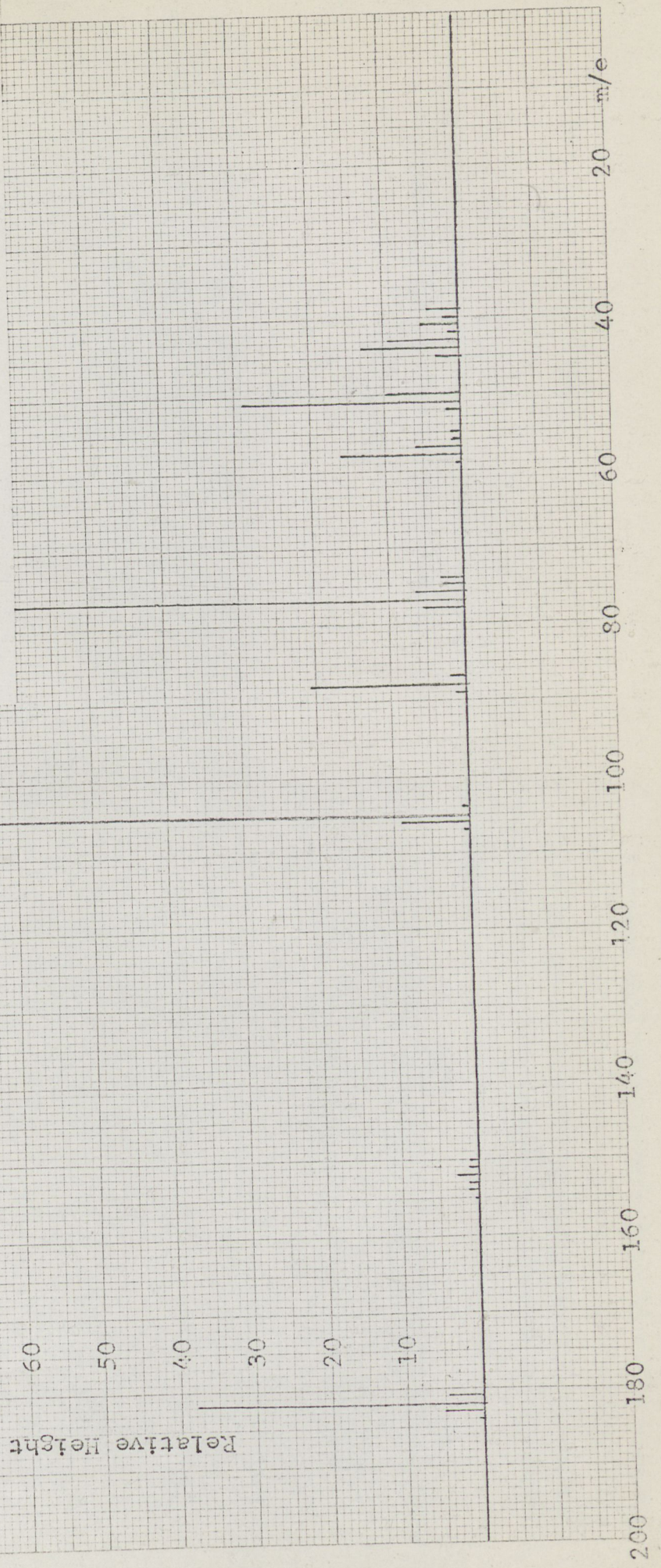


FIGURE III

Mass Spectrum of Product I

(26)



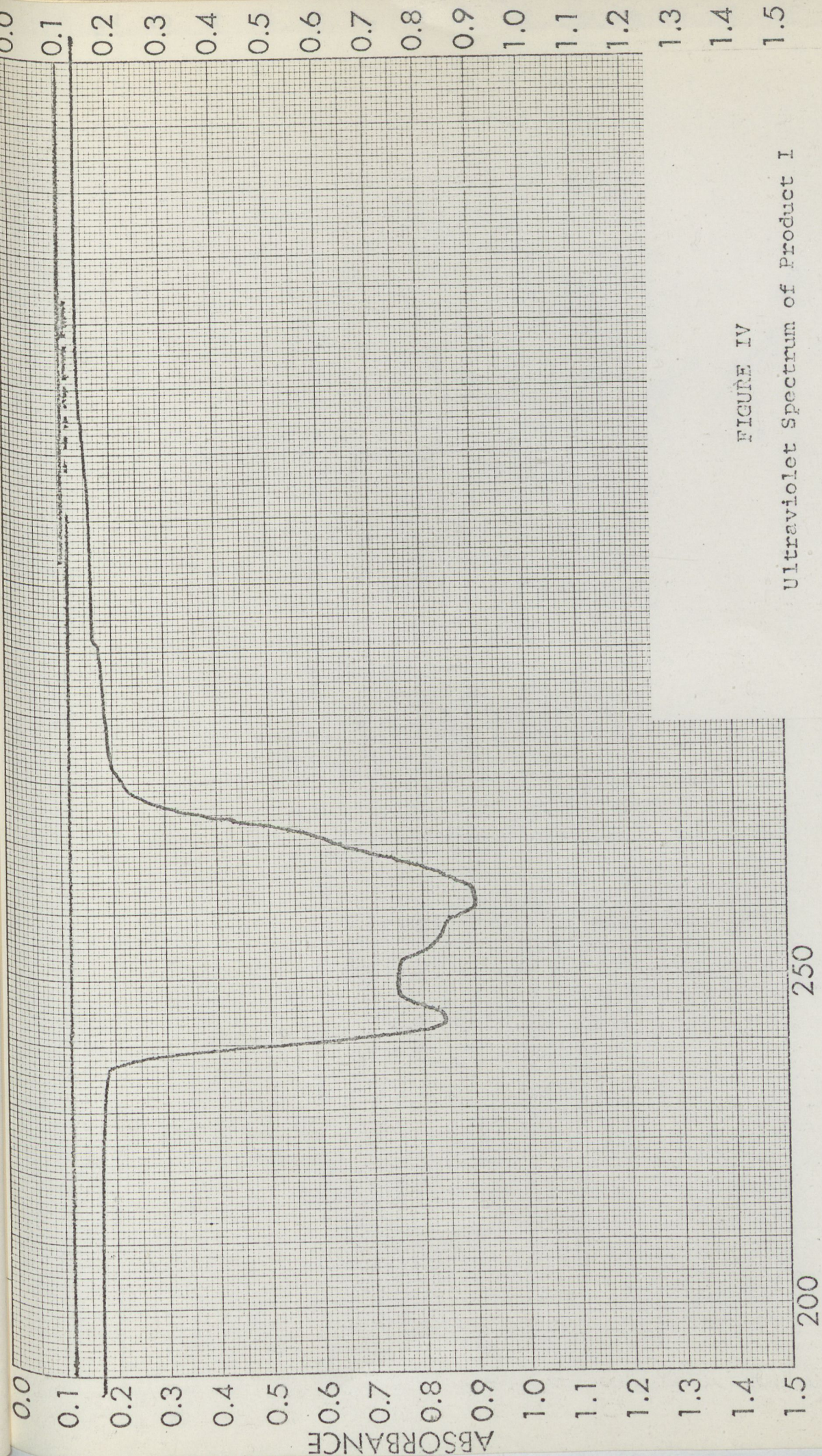


FIGURE IV

Ultraviolet Spectrum of Product I

SAMPLE	<i>Product Product</i>	CURVE NO.	<i>2</i>
ORIGIN		CONC.	
SOLVENT	<i>CHCl₃</i>	CELL PATH	
		REFERENCE	<i>CHCl₃</i>

(27)

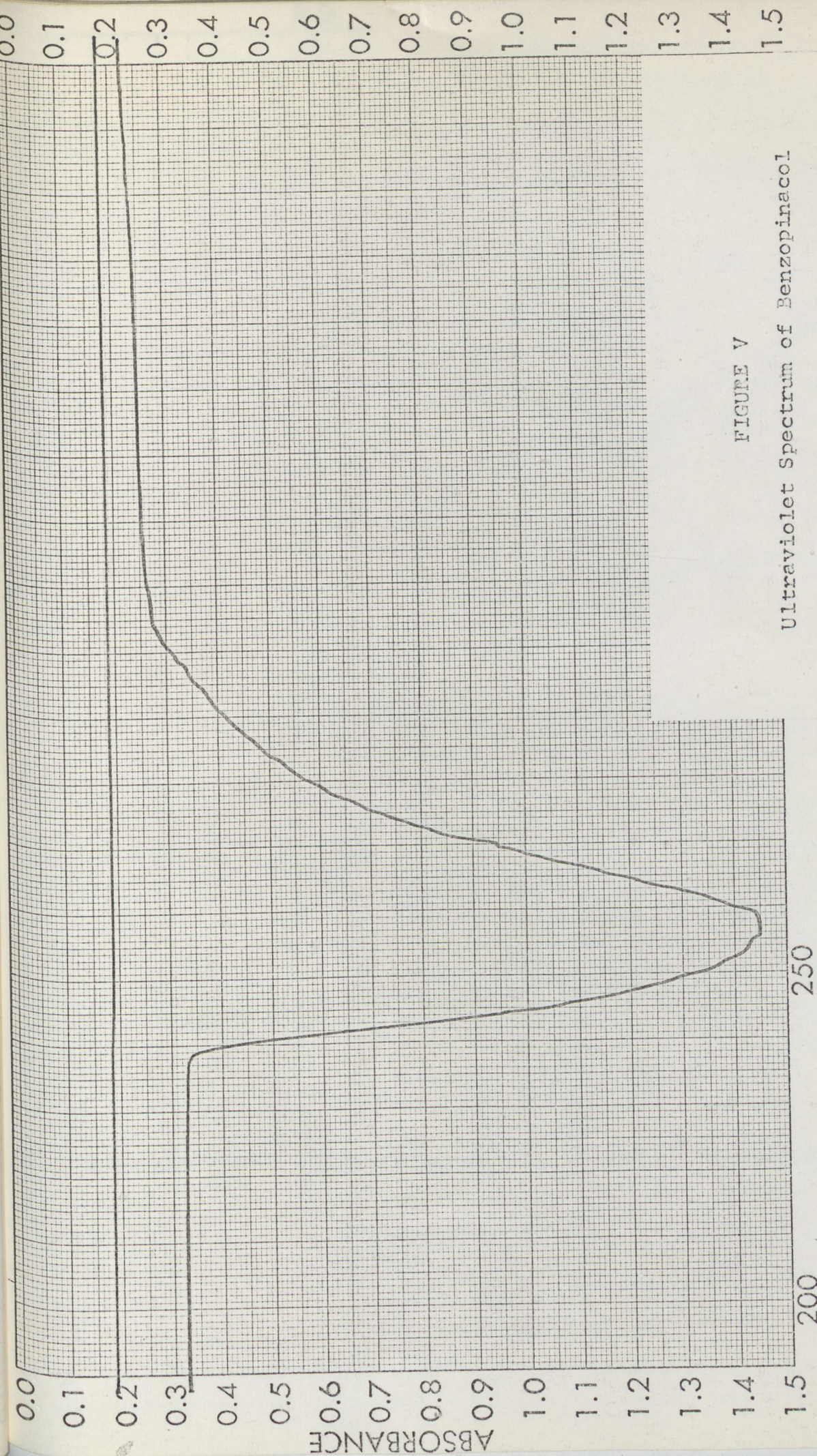


FIGURE V

Ultraviolet Spectrum of Benzopinacol

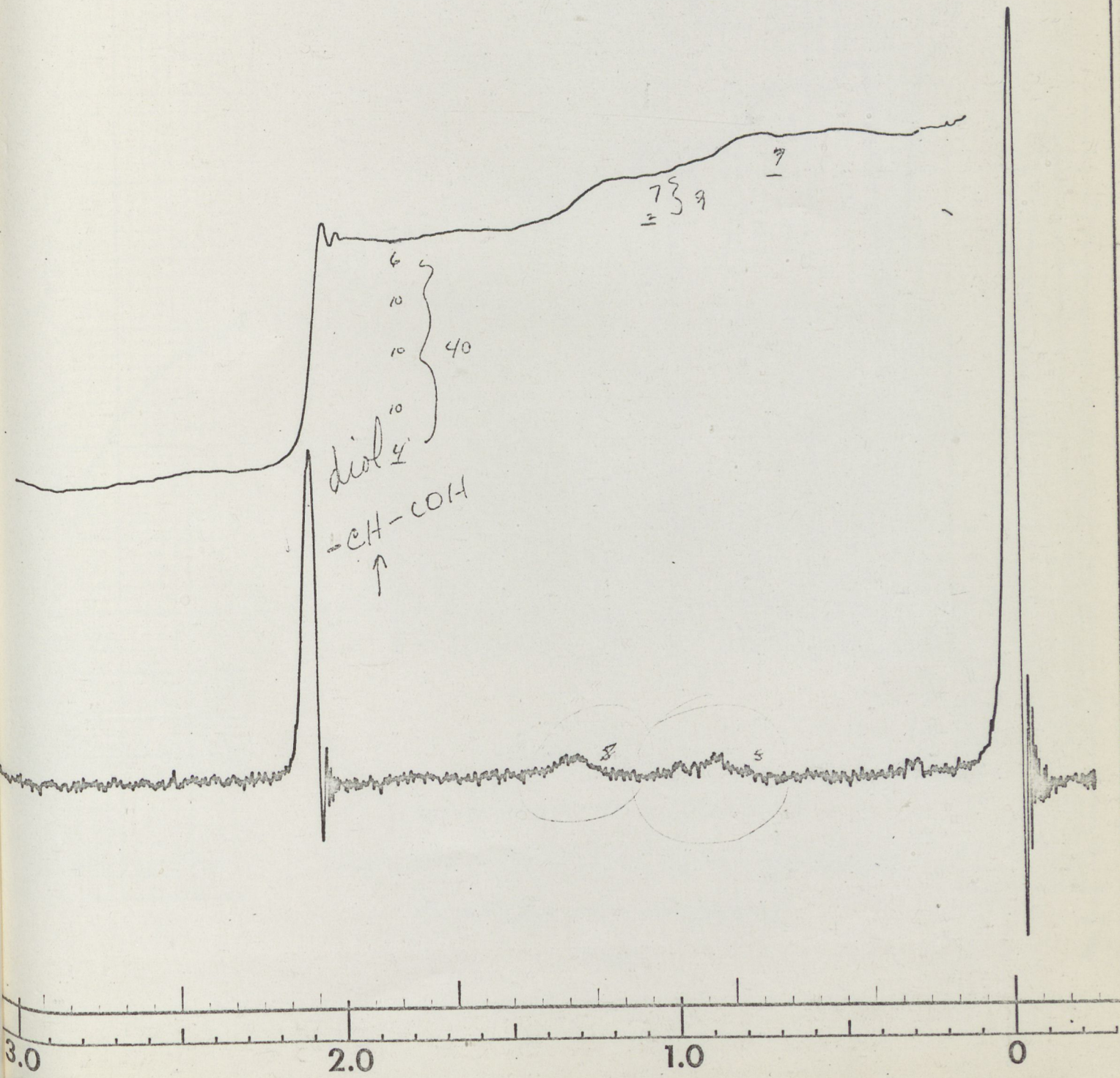
(28)

SAMPLE <u>Reacted mixture "B"</u>	CURVE NO. _____
ORIGIN _____	CONC. _____
SOLVENT <u>CHCl₃</u>	CELL PATH _____
	REFERENCE <u>CHCl₃</u>

0 8.0

FIGURE VI
Nuclear Magnetic Resonance
Spectrum of Thermal Product

(29)



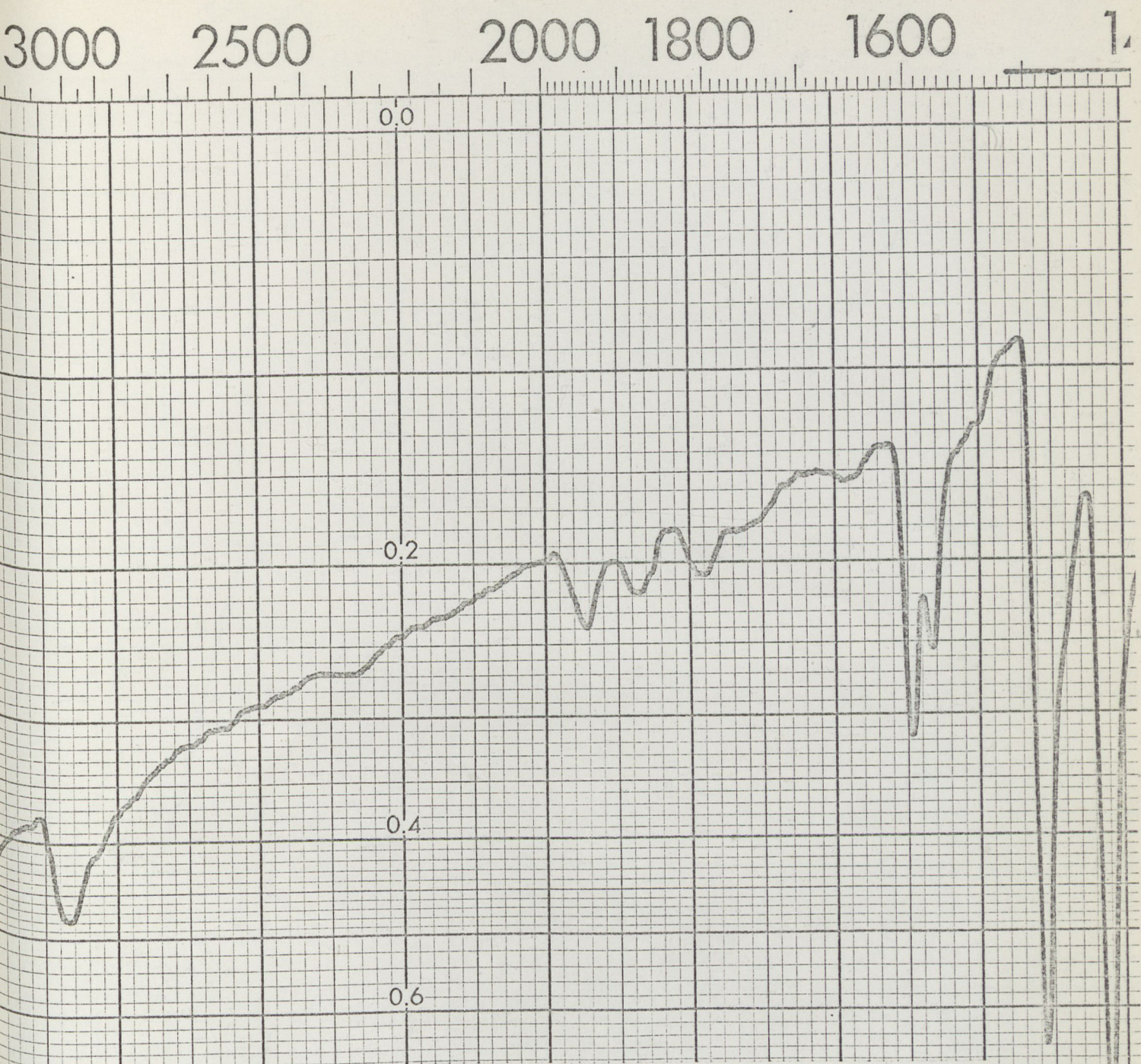
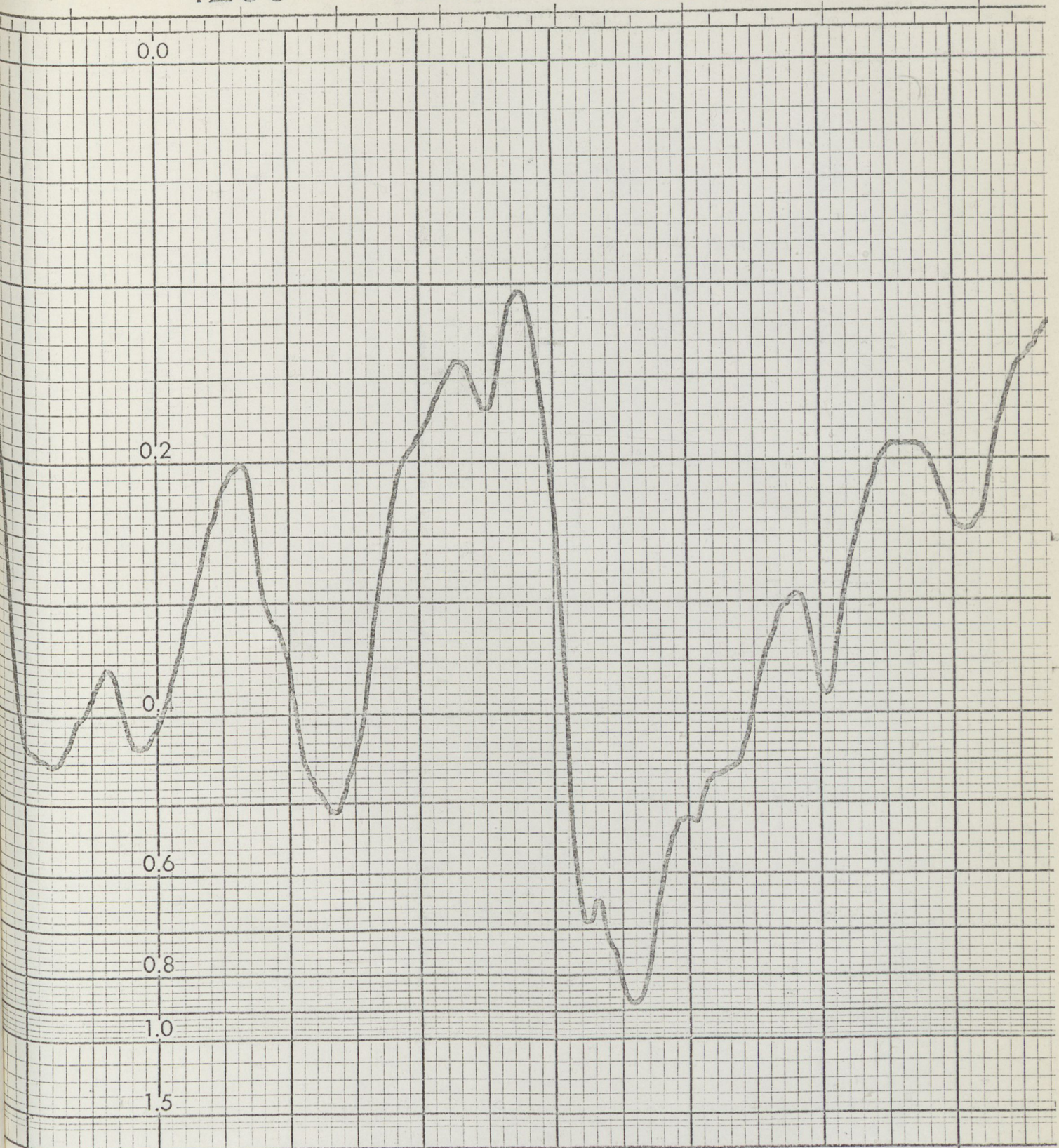


FIGURE VII
Infrared Spectrum of Product I
After Repeated Recrystallization and Drying
(continued next two pages)

FREQUENCY (CM⁻¹)

(31)

1200 1100 1000 950 900



WAVELENGTH (MICRONS)

850 800 750 700 650

0.0

0.2

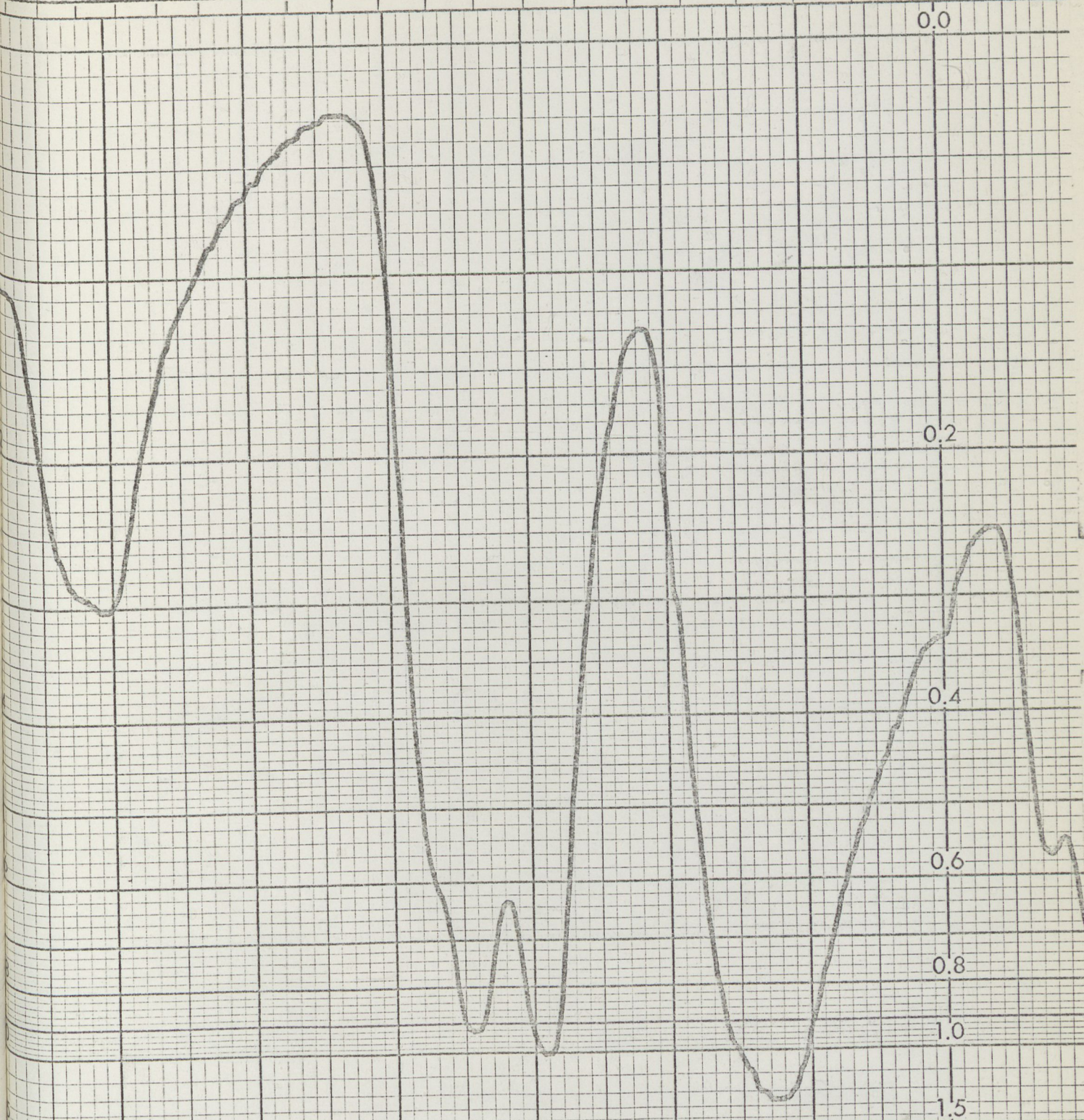
0.4

0.6

0.8

1.0

1.5



THE PERKIN - ELMER CORP., NORWALK, CONN.

12

13

14

15

3000 2500 2000 1800 1600

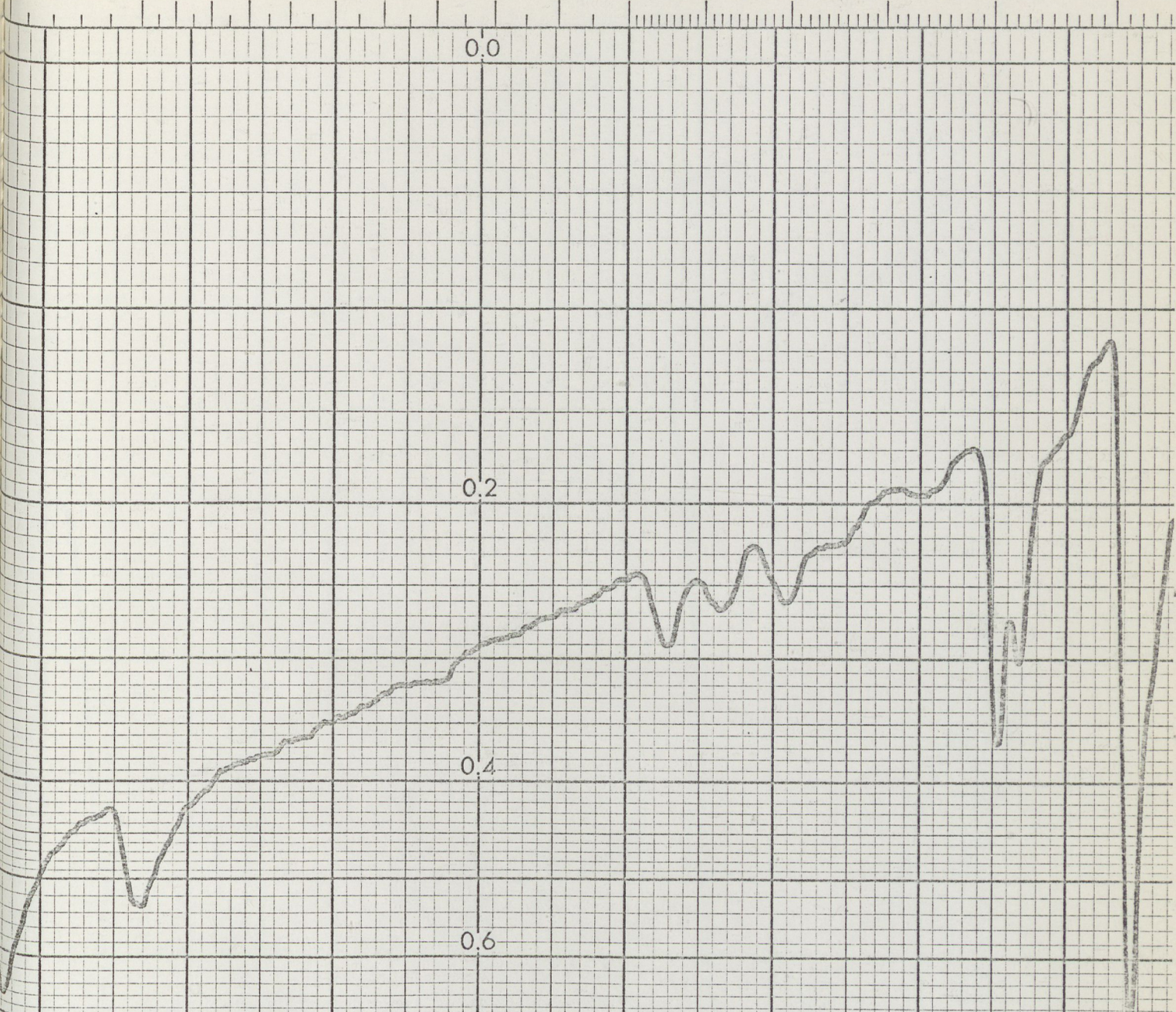
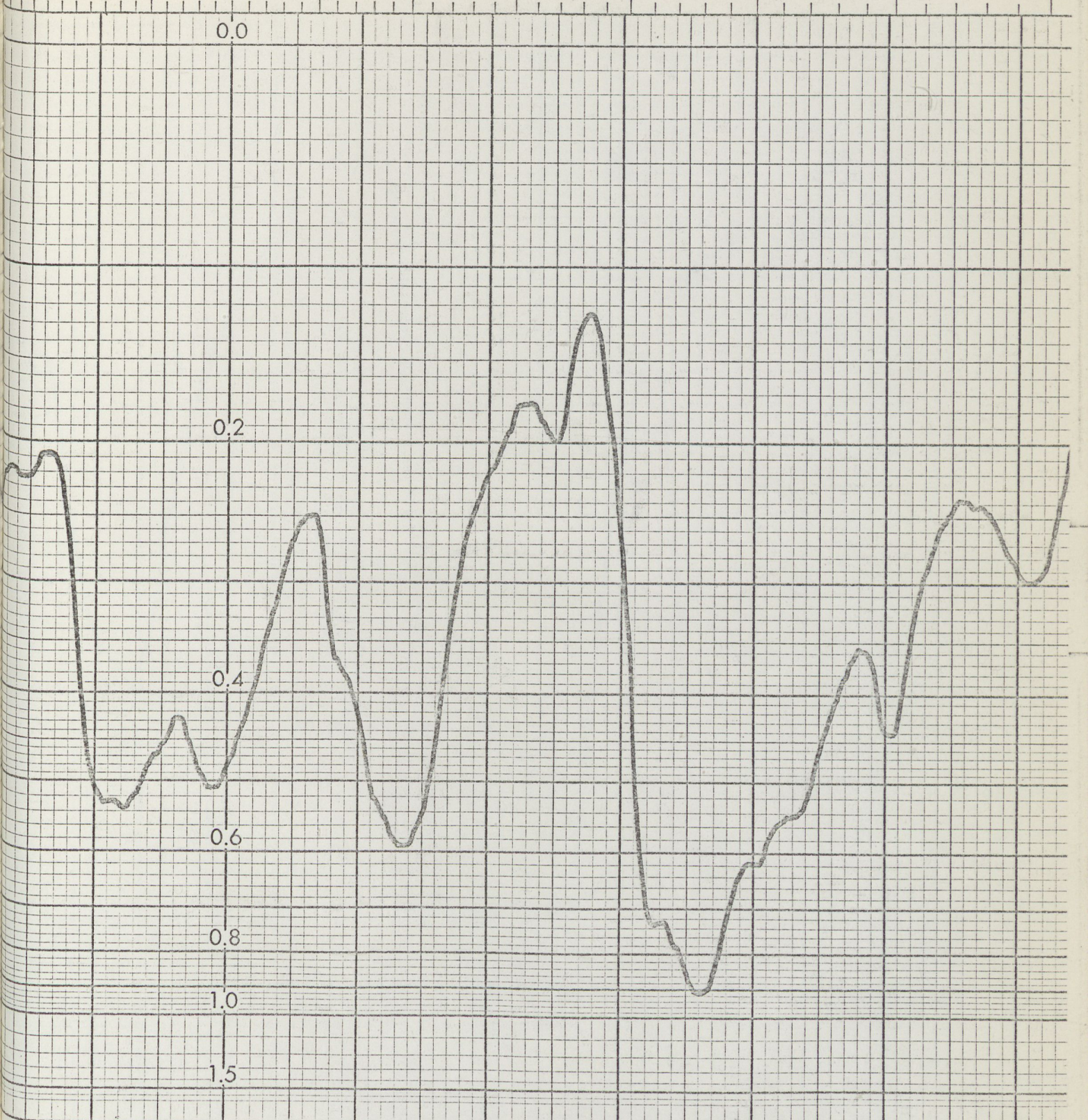


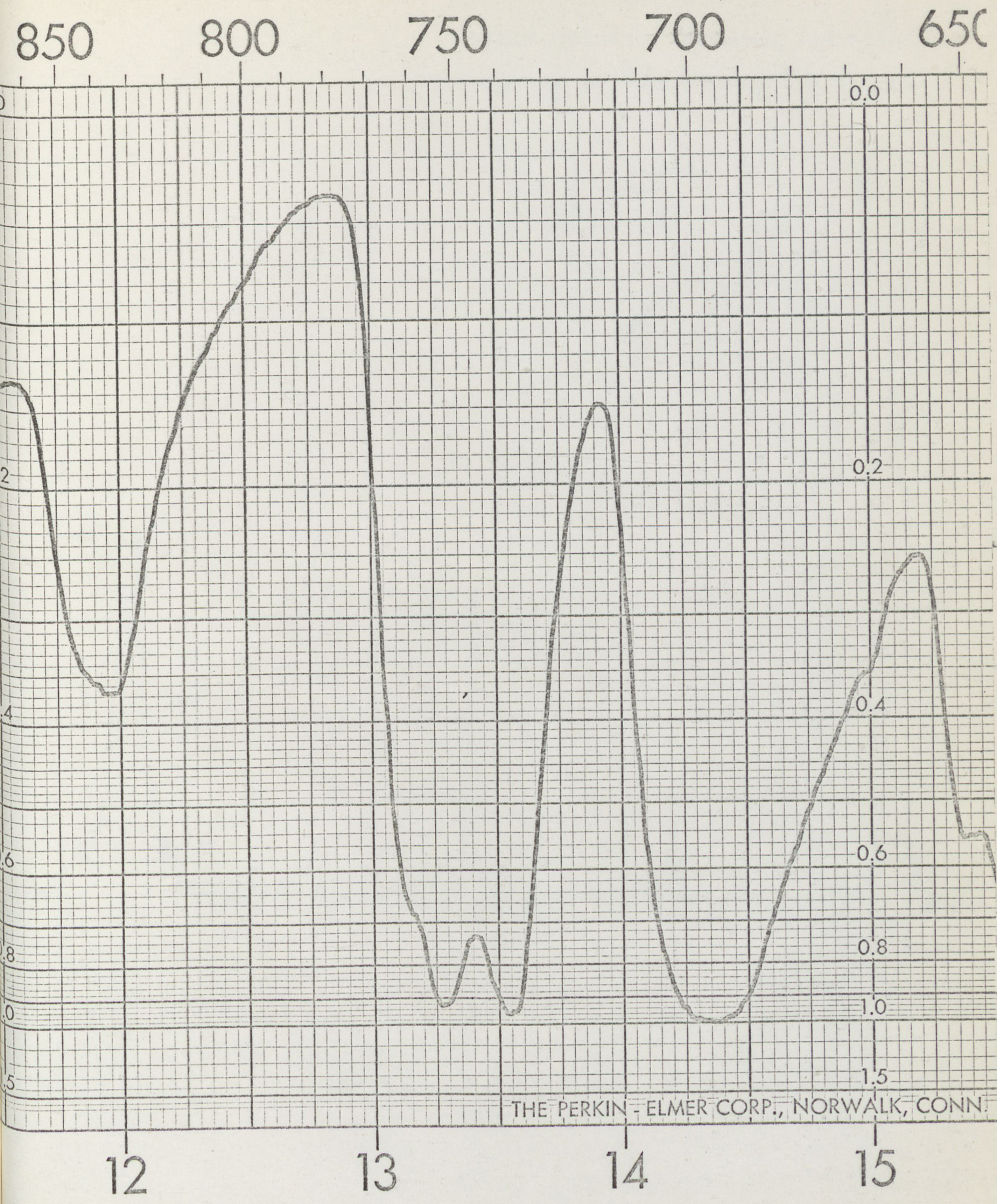
FIGURE VIII
Infrared Spectrum of Benzopinacol
(continued next two pages)

FREQUENCY (CM⁻¹)

1200 1100 1000 950 900



WAVELENGTH (MICRONS)



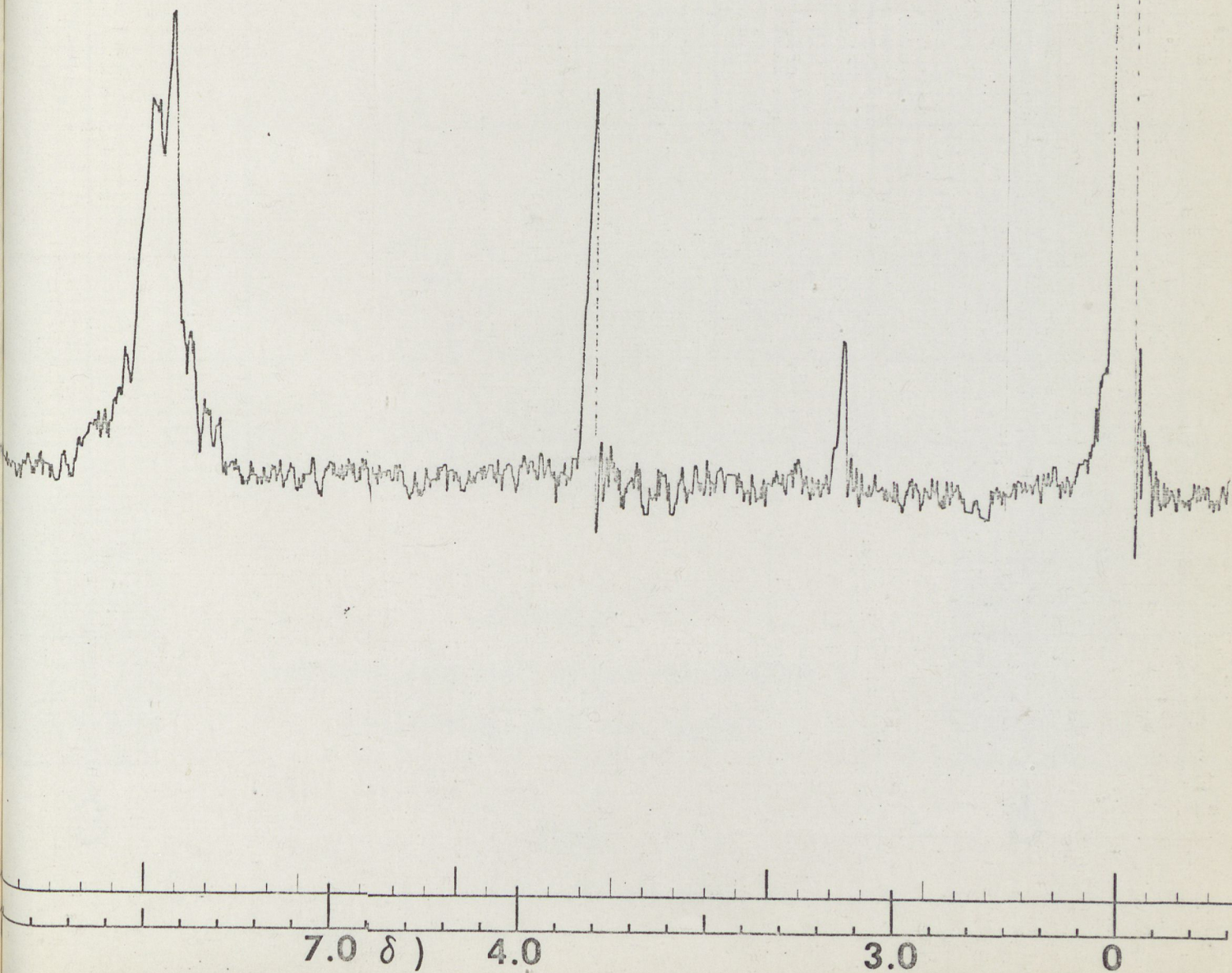
THE PERKIN - ELMER CORP., NORWALK, CONN.

3.077

FIGURE IX

Nuclear Magnetic Resonance Spectrum
of a Mixture of Benzopinacol and Dioxane

(36)



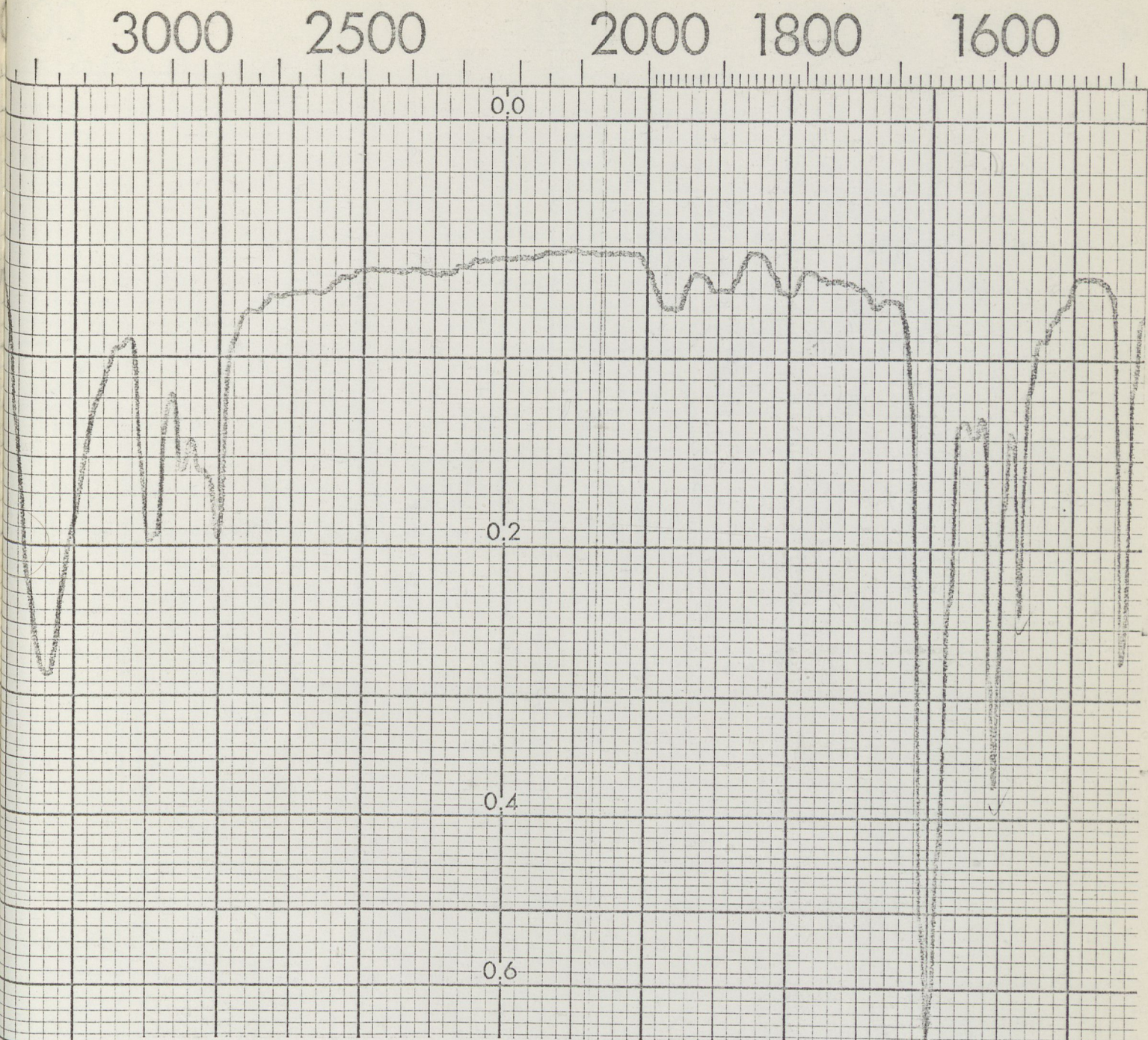


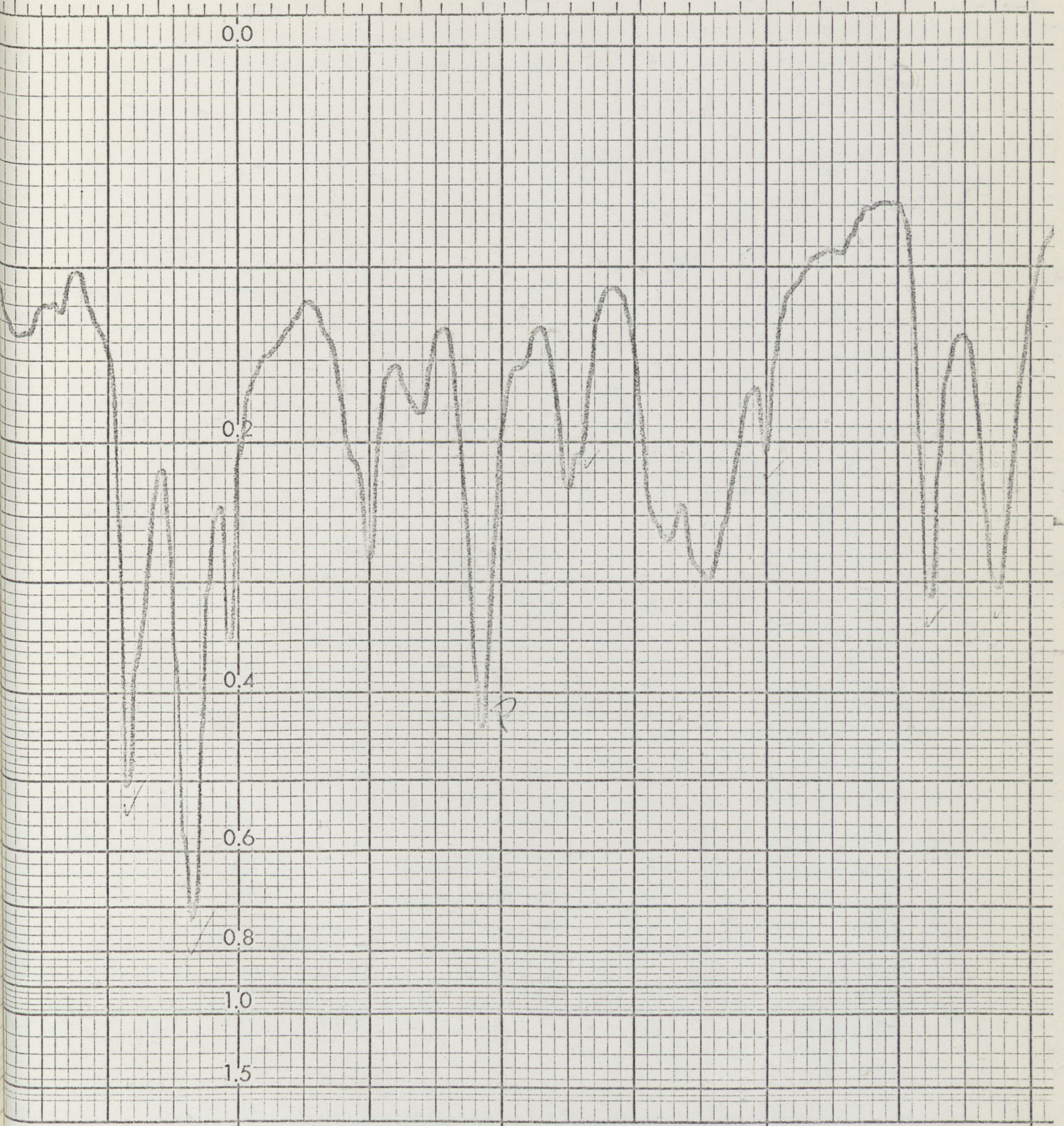
FIGURE X

Infrared Spectrum of Melted Product I

(continued next two pages)

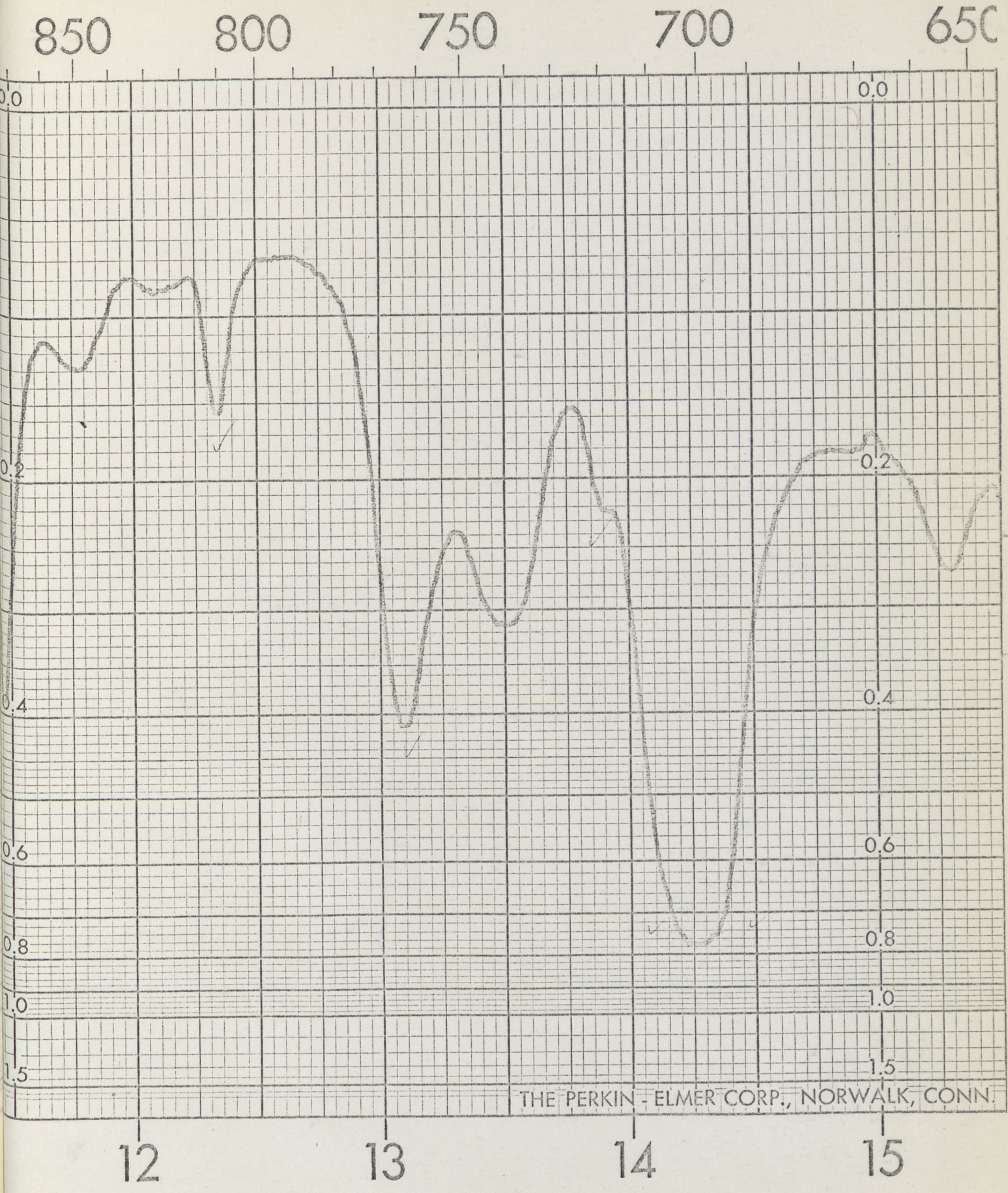
FREQUENCY (CM⁻¹)

1400 1200 1100 1000 950 900



WAVELENGTH (MICRONS)

8 9 10 11



THE PERKIN-ELMER CORP., NORWALK, CONN.