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## Preparations and Reactions of Two Aldoketenes: t-Butyl and Benzyl

Donna E. Loeffler

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PREPARATIONS AND REACTIONS OF TWO ALDOKETENES:

t-BUTYL AND BENZYL

Donna E. Loeffler

April 30, 1976

Submitted to the faculty of Ursinus College  
in partial fulfillment of the requirements for  
Departmental Honors in Chemistry

Submitted:

Donna E. Loeffler

Approved:

Allyn P. Stagner

Ronald E. Hess

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### ACKNOWLEDGEMENTS

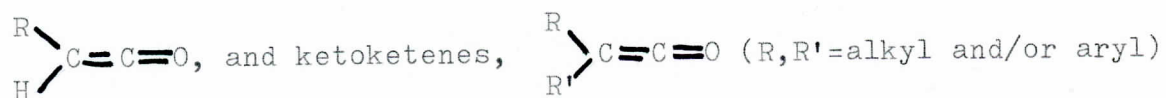
I would like to take this opportunity to express my appreciation to the Vansandt Fund for financial assistance, and to Dr. Claude Yoder of Franklin and Marshall College for providing the nmr spectra.

I would like also to thank the members of the Chemistry Department for their encouragement and advice throughout this project. I especially thank Dr. Roger Staiger for his efforts.

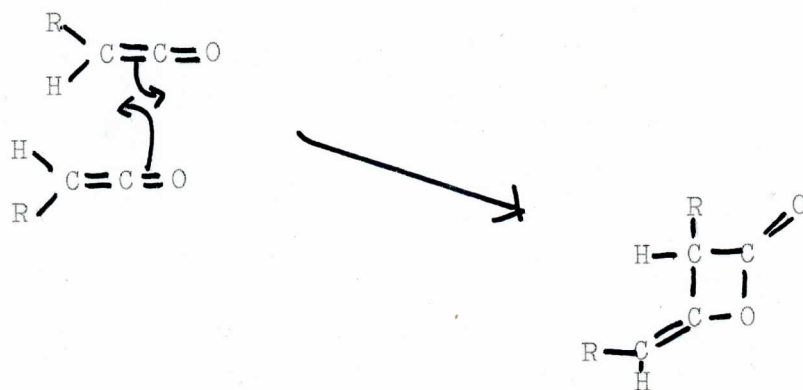
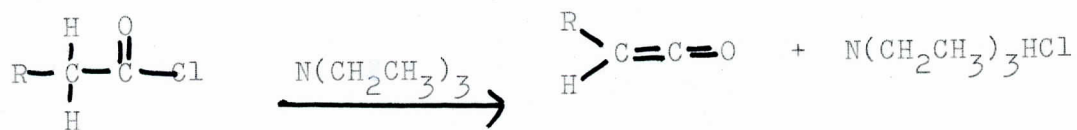
The most heartfelt and sincere appreciation and acknowledgement goes to Dr. Ronald E. Hess, for all the time, effort, and encouragement that he contributed. Thank you!

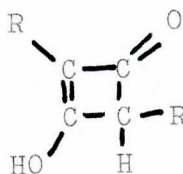
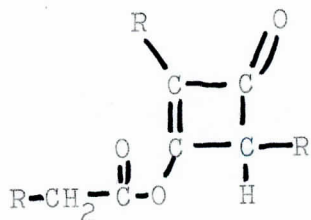
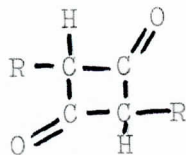
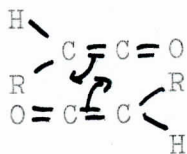
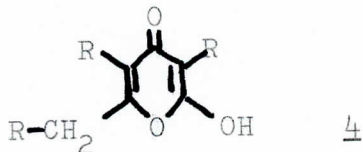
INTRODUCTION

Ketenes are compounds containing the functional group  $\text{>C=C=O}$ . There are two types of ketenes, aldoketenes,



ketenes can be prepared by reacting an acyl chloride with a tertiary amine. Aldoketenes are very reactive compounds; they will polymerize in several ways, as illustrated below, forming  $\beta$ -lactone dimers 1, 3-hydroxycyclobutenone dimers 2, acylated cyclobutenone trimers 3, and pyrone-type trimers 4.

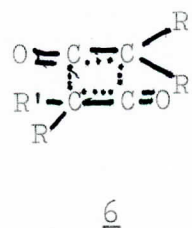
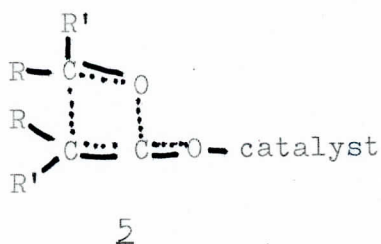


32

4

This method of preparation of B-lactone dimers, 1, and acylated cyclobutenone trimers, 3, has been shown to yield the dimer as a major product where  $R = \text{CH}_3, \text{CH}_2\text{CH}_3$ <sup>1</sup>; this contrasts with the case where aldoketenes are prepared by other methods. For example, Enk and Spes<sup>2</sup> found that in a reaction in which aldoketenes were prepared by dehydration of carboxylic acids, the major product was the trimer, 3, or the dimer, 2 (when  $R = \text{CH}_3$ ).

The mechanism suggested for the formation of the  $\beta$ -lactone dimer involves the presence of a catalyst (here, triethylamine or its hydrochloride). It has been suggested that there is a concerted cyclization with a skewed transition state, 5, the catalyst lending stability to the O-C-O bonds forming; this allows the C-C bond to form while maintaining the proper molecular orientation.



The extra bulk possessed by ketoketenes requires that a strong Lewis acid, such as  $\text{AlCl}_3$ , to act as a catalyst. Because there is less steric hindrance in the case of the aldoketenes, triethylamine or its hydrochloride provides sufficient catalysis. The competing reaction, which leads eventually to the formation of the cyclobutenone trimer in the case of aldoketenes, has a transition state, 6, which is effectively free of steric hindrance.<sup>1</sup>

It has been shown<sup>1,2</sup> that at higher temperatures, or in solvents in which triethylamine or its hydrochloride is less

soluble, more trimer is formed; this is similar to uncatalyzed polymerizations. It was therefore hypothesized that the trimer/dimer ratio will increase with the bulk of the R group of the aldoketene, because the additional bulk will cause more steric hindrance in the already skewed transition state leading to the formation of the B-lactone dimer.

Two compounds were chosen for study: (1) t-butyl ketene. The trimer/dimer ratio for the polymerization of t-butyl ketene has already been ascertained. The hypothesis stated above was supported by experimental data. The trimer/dimer ratio for t-butyl ketene is 0.75<sup>3</sup>, in contrast to the ratio for the methyl ketene, 0.38-0.42.<sup>1</sup> The objective in working with it again was to isolate the cyclobutenone trimer in pure form, as earlier results had been determined by nmr analysis of a contaminated product.

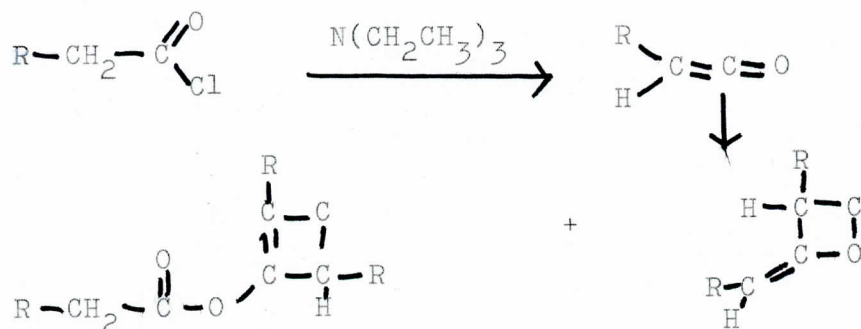
(2) Benzyl ketene. Hydrocinnamic acid chloride (1-phenylpropanyl chloride) was dehydrochlorinated to form benzyl ketene. This compound was chosen due to the bulky nature of the benzyl group. It was predicted that the cyclobutenone trimer (3, R= $\phi$ -CH<sub>2</sub>) would be formed in higher yields than in the case where R=CH<sub>3</sub>. Another objective of this study was, therefore, to seek further confirmation of the previously mentioned mechanistic hypothesis regarding the bulk of the R group.



DISCUSSION

Hydrocinnamic acid chloride could not be obtained commercially, so it was synthesized from hydrocinnamic acid. 1.0 parts acid were combined with 1.5 parts thionyl chloride, and the mixture was refluxed for one hour, in a synthesis similar to that of cinnamic acid chloride (1-phenyl propenyl chloride)<sup>4</sup>. Excess thionyl chloride was removed by distillation and the acid chloride isolated by vacuum distillation.

the reactions of t-butyl acetyl chloride and hydrocinnamic acid chloride were carried out under identical conditions. Equimolar amounts of triethylamine and acid chloride were combined.

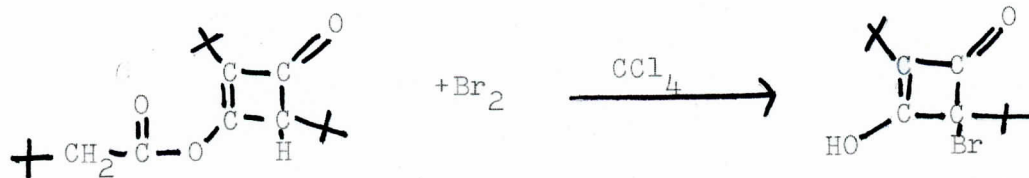


The triethylamine was added dropwise (one drop per second) to a refluxing solution of acid chloride in methylene chloride (200 ml per mole acid chloride). After the addition was completed, the mixture was refluxed for an additional five hours.

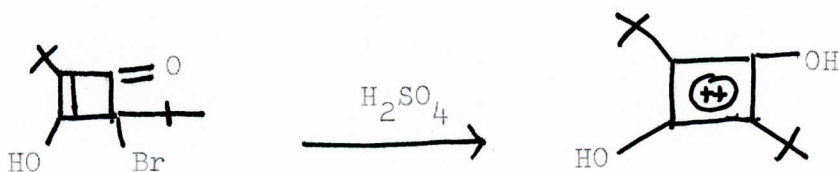
Vigorous stirring was effected during the addition and subsequent reflux. The solid triethylamine was removed by suction filtration and solvent was removed by distillation.

In the case of the reaction of t-butyl acetyl chloride, isolation of the products was accomplished via vacuum distillation. The trimer fractions were redistilled, again under a vacuum, to obtain further purity. The trimer thus isolated crystallized when refrigerated. The solid formed was a whitish-yellowish waxy substance which melted to an oil at about room temperature. Infrared and nmr analyses were consistent with the product structures postulated. Although the nmr spectrum of the trimer showed some contamination with the dimer, the proportion of dimer was so small that the percentage could not be determined from the integration. The nmr spectrum of the dimer did not show contamination.

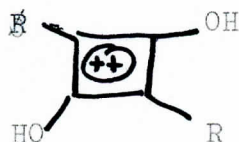
The trimer was further reacted with bromine in carbon tetrachloride. Equimolar amounts of trimer and  $\text{Br}_2$  were combined and the mixture stirred magnetically for two hours. The crystals formed were isolated by suction filtration. The product was isolated as



very fine white crystals. An infrared spectrum (IR #3) was consistent with the proposed structure. The wide band from 3-5 $\mu$  is typical of enolic-type structures. The carbonyl stretch is at 5.77 $\mu$ , and the absorbances at 8.06 $\mu$  and 8.28 $\mu$  are indicative of a t-butyl function. This compound is of theoretical interest as a possible precursor to a cyclobutadiene dication, a unique aromatic species.



The dication could possibly be prepared by a reaction with sulfuric acid. This type of compound was prepared in the phenyl series, but was not observed where  $R = \text{CH}_3$ .<sup>5</sup>



When the solvent was distilled from the benzyl reaction mixture, the mixture became extremely viscous. Additional solvent was removed under vacuum, but upon heating, no vaporization occurred. Heating was discontinued due to danger of decomposition. An infrared spectrum (IR #4) of the reaction mixture indicated that no B-lactone dimer was formed. The B-lactone dimer has characteristic peaks at approximately 5.4 and 5.8 $\mu$ . (Compare with

IR #1.) Since distillation, even under vacuum did not seem to be a viable method of purification, alternate methods were explored. Crystallation from mixed solvents was tried first. The mixture was soluble in ether, but not in ligroin. Attempts to obtain crystals from ether-ligroin systems were not successful; they resulted in the formation of oils. Purification with column chromatography was also attempted. Material with a spectrum similar to that of the reaction mixture was obtained by elution with benzene or benzene-ligroin mixtures. (See IR #5) The column was packed with Florisil. Subsequent elution with ether, and later, acetone, produced small amounts of material with similar infrared spectra. (See IR# 6.) There is evidence of decomposition in the form of a broad band at about  $3\mu$  and a generally less definitive spectrum. It is thus obvious that some purification has been accomplished. All material isolated, however, is still in the form of an oil. The material isolated by column chromatography is lighter in color, being a light orange as compared with a brown.

EXPERIMENTALPreparation of B-lactone dimer and cyclobutenone trimer of t-butyl ketene.

In a 3-liter, 3-necked round bottom flask equipped with a water cooled Freidrich condenser, carrying a calcium chloride drying tube, and a motor-driven centrifugal stirrer with a polyethylene paddle, methylene chloride (150 ml) and tertiary-butyl acetyl chloride (99.8g, 0.741 moles) wererefluxed employing a heating jacket. Vigorous stirring was initiated at the beginning of heating. Triethylamine (79.3 g, 0.784 moles) was added dropwise, over a period of one hour, from a pressure-equalized dropping funnel. When formation of solid triethylamine hydrochloride blocked passageways, methylene chloride was used to rinse. When the addition was complete, the funnel was replaced with a stopper. The mixture was refluxed for an additional 4.5 hours. Triethylamine hydrochloride was isolated with suction filtration. Methylene chloride was removed by distillation. More triethylamine hydrochloride was collected, bringing the total to 106.4 g; this represented a reaction completion of 104%. Two approximately equal fractions were distilled under vacuum. Fractions collected are summarized below.

Separation of the B-lactone dimer and cyclobutenone trimer of t-butyl ketene by fractional distillation.

<u>Fraction</u>	<u>Temp., °C</u>	<u>Press., mm Hg</u>	<u>Description</u>	<u>Amt., ml</u>
1A	22-22	0.250	orange liquid	trace
2A	46-47	0.35	clear light yellow liquid	1-2
3A	47-51	0.35-0.33	clear, almost colorless liquid	2
4A	51-54	0.33	clear, colorless liquid	2
5A	54-55	0.32-0.30	clear colorless liquid	15
6A	55-54	0.33-0.35	clear, colorless liquid	3
7A	54-105	0.35-0.40	clear light yellow liquid	4
8A	105-111	0.33-0.40	clear, light yellow liquid	3
9A	111-112	0.38-0.35	clear, light yellow liquid	5
1B	23	0.65	orange liquid	1
2B	50-53	0.45-0.47	clear, light yellow liquid	1
3B	54-56	0.47-0.45	clear, almost colorless liquid	2
4B	56-55	0.50-0.52	clear colorless liquid	9
5B	55-54	0.50-0.40	clear, colorless liquid	3
6B	50-103	0.44-0.48	clear, light yellow liquid	1-2
7B	103-110	0.50-0.42	clear, light yellow liquid	3
8B	110-111	0.50	clear, light yellow liquid	4
9B	111-108	0.50	clear, light yellow liquid	1

The infrared spectrum of the dimer (a representative spectrum is of fraction 4B, IR #1) shows  $\lambda_{\text{max}}^{\text{neat}}$  5.41, 5.55, and 5.85  $\mu$ . The nmr spectrum shows  $\uparrow$  5.31 (weakly coupled doublet,  $J=1.5$  Hz, area 1.0), 6.26 (weakly coupled doublet,  $J=1.5$  Hz, area 1.0), 8.87 (singlet, area 9.67), and 8.96 (singlet, area 8.95). Fractions 8A, 9A, 7B, 8B, and 9B solidified upon refrigeration, producing yellowish-whitish waxy material which melted to a light yellow oil at approximately room temperature. These fractions were combined and redistilled under vacuum. All fractions collected were a clear, light yellow liquid.

<u>Fraction</u>	<u>Temp, °C</u>	<u>Press, mm Hg</u>	<u>Amt, ml</u>
1	108-110	0.50	1
2	110-113	0.65-0.30	3
3	113	0.60-0.50	6
4	113-118	0.50	2

Fractions 2, 3, and 4 solidified upon refrigeration to produce crystals of the type previously described. The infrared spectrum showed  $\lambda_{\text{max}}^{\text{neat}}$  5.64, 5.71, and 6.10  $\mu$  (IR #2). The nmr spectrum showed  $\uparrow$  6.39 (singlet, area 1.0), 7.59 (singlet, area 2.0), 8.84 (singlet, area 11.0), 8.91 (singlet, area 7.1), and 9.08 (singlet, area 8.0). (nmr #2).

Preparation of 4-bromo-3-hydroxy-2,4-di-t-butyl cyclobutenone from the t-butyl ketene trimer.

In a 250 ml Erlenmeyer flask, with a calcium chloride drying tube, bromine (1.1g, 0.0068 moles) in 6 ml  $\text{CCl}_4$  was added to t-butyl ketene trimer (2.0g, 0.0068 moles) in 6 ml  $\text{CCl}_4$ . The mixture was stirred

magnetically for two hours. The bromine color faded rapidly and a white solid was produced. Fuming with an odor of HBr was noticed upon opening the flask. The crystals were suction filtered and washed with  $\text{CCl}_4$ . 1.7 g product was isolated (96.5% yield). The crystals had a melting point of  $175-8^\circ\text{C}$ . Decomposition with an orange color indicating bromine was noticed upon melting. The infrared spectrum showed

$\lambda_{\text{max}}^{\text{KBr}}$  5.77, 6.30, 8.06, 8.28  $\mu$ . (IR #3)

Preparation of hydrocinnamic acid chloride (3-phenyl propanoyl chloride).

In a 1-liter, 3-necked round bottom flask equipped with a water-cooled Freidrich condenser, carrying a calcium chloride drying tube, and a motor driven centrifugal stirrer with a polyethylene paddle,  $\text{SOCl}_2$  (122.6g, 1.03 moles) was added rapidly through a pressure-equalized dropping funnel to hydrocinnamic acid (98.9g, 0.658 moles). The funnel was then replaced with a stopper, and the mixture was refluxed, employing a heating jacket, for 1 hour. Excess  $\text{SOCl}_2$  was removed by distillation and 103.1g clear, light yellow liquid was collected by vacuum distillation (b.p.  $88-90^\circ\text{C}$ , 1.5-2.0 mm Hg). This represents a 92.9% yield.

Reaction of hydrocinnamic acid chloride with triethylamine.

In a 1-liter, 3-necked round bottom flask, equipped with a water-cooled Freidrich condenser carrying a calcium chloride drying tube, and

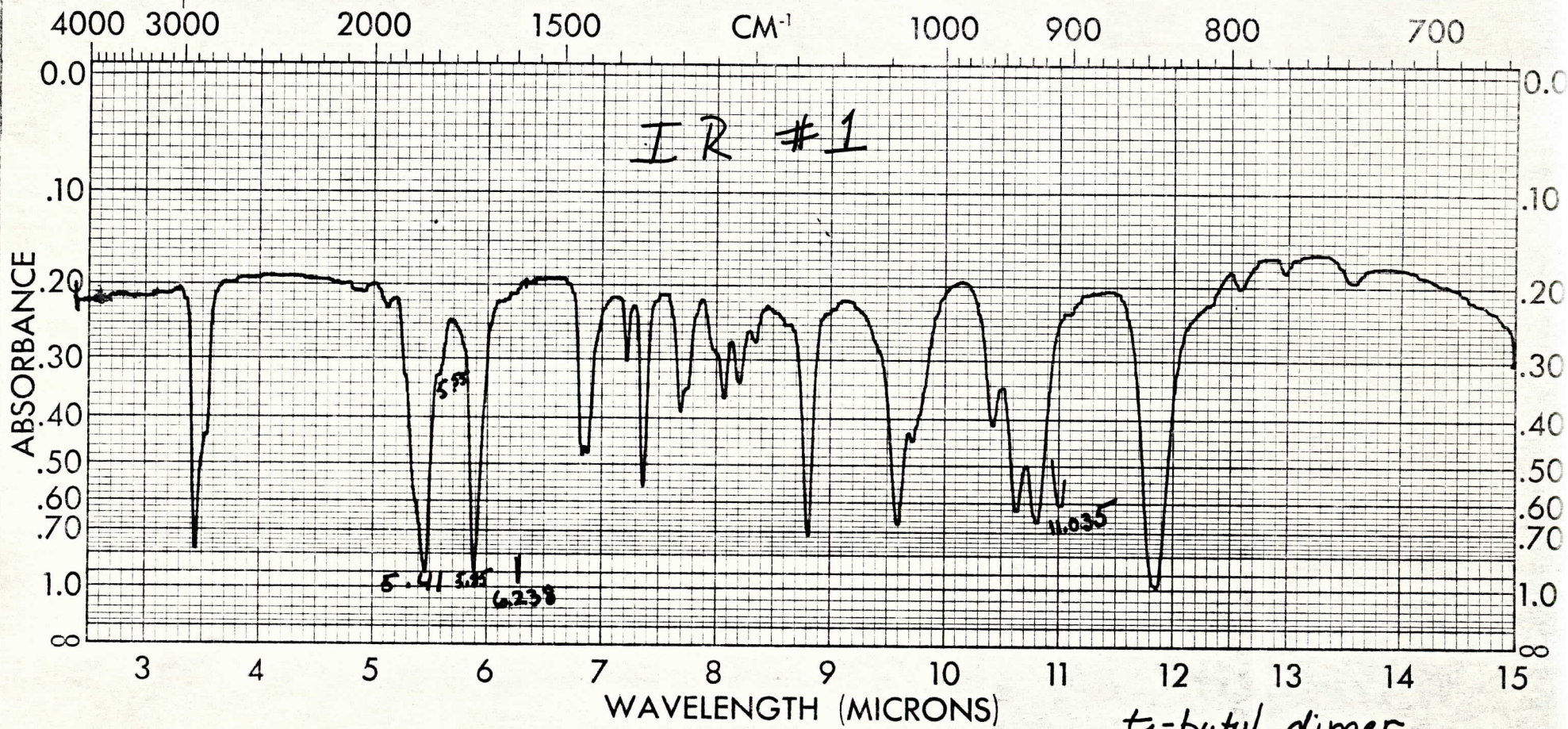


a motor driven centrifugal stirrer with a polyethylene paddle, methylene chloride (125 ml) and hydrocinnamic acid chloride (103.1g, 0.611 moles) were refluxed employing a heating jacket. Vigorous stirring was initiated at the beginning of heating. Triethylamine (67.0g, 0.662 moles) was added dropwise, over a period of 45 minutes, from a pressure-equalized dropping funnel. When formation of solid triethylamine hydrochloride blocked passageways, methylene chloride was used to rinse. When the addition was complete, the funnel was replaced with a stopper. The mixture was refluxed for an additional five hours. Triethylamine hydrochloride was isolated by suction filtration (86.5 g, which indicates 103% reaction completion). Methylene chloride was removed by distillation and vacuum distillation. No product vaporized during vacuum distillation. Heating was discontinued due to danger of decomposition. The infrared spectrum of the reaction mixture showed  $\lambda_{\max}^{\text{neat}}$  5.66, 5.80, 6.09, 6.24, 6.36, 6.68, 6.88  $\mu$ . (IR #4) Attempts to crystallize the substance from ether-ligroin systems were unsuccessful. Chromatography on a Florisil column, with benzene or benzene-ligroin solutions as elutants, yielded an oil upon solvent evaporation.  $\lambda_{\max}^{\text{neat}}$  5.69, 5.84, 6.10, 6.24, 6.36, 6.70, and 6.89  $\mu$ . (IR #5) Later elution with ether and then acetone resulted in small amounts of oil whose spectrum is described in the discussion section. (IR #6)

SPECTROSCOPIC DATA

The infrared spectra were recorded on a Perkin-Elmer Infracord Spectrometer at room temperature using sodium chloride plates, except in the case of IR #3, which utilized a KBr pellet.

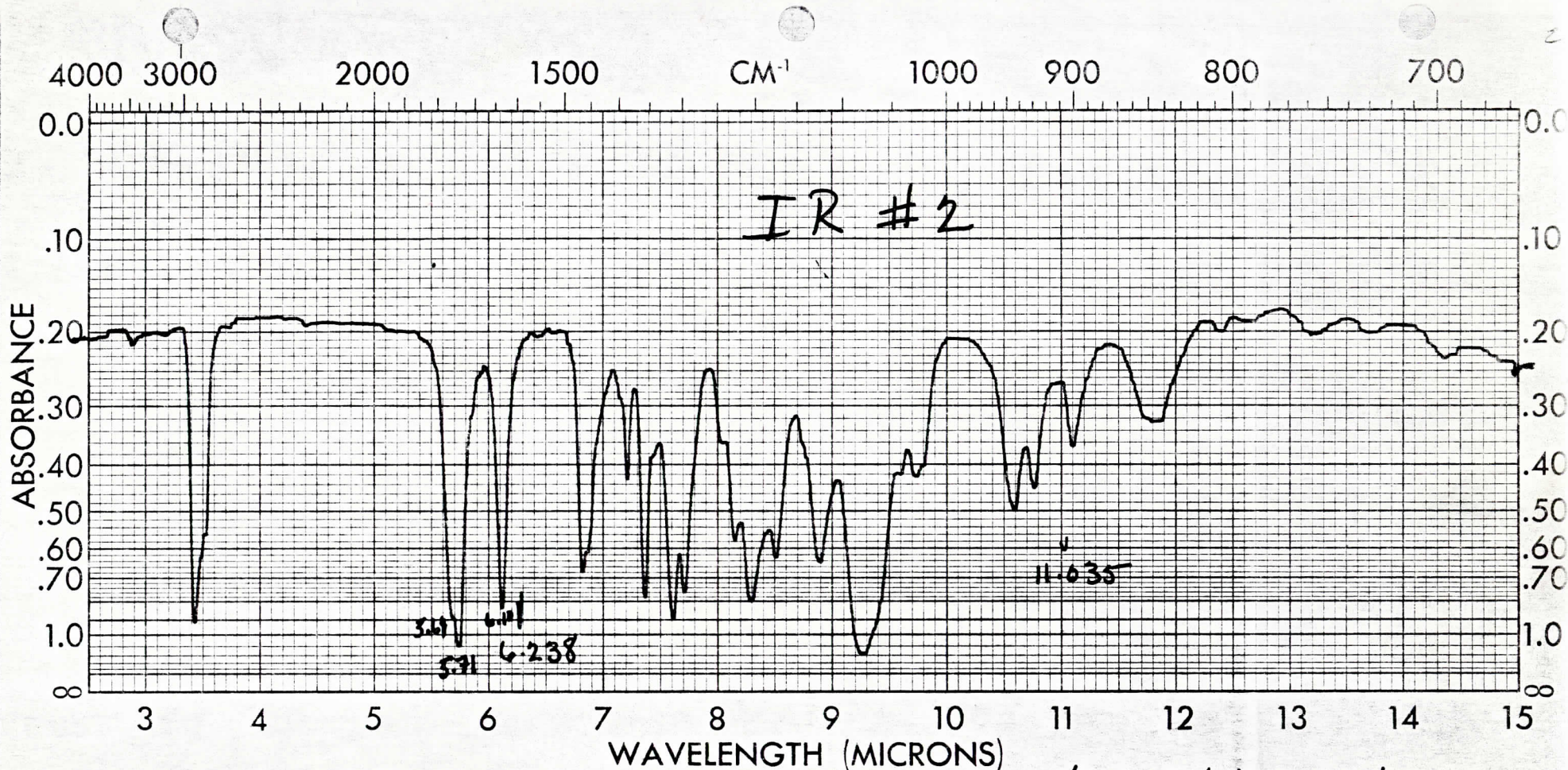
The nmr spectra were traced at Franklin and Marshall College using a Varian A-60D NMR Spectrometer. Tetramethyl silane was added as an internal standard. The sweep was with a constant 500 Hz.



*t*-butyl dimer

SPECTRUM NO <u>IR#1</u>	ORIGIN <u>dest. of 4/13/76</u>	LEGEND _____	REMARKS <u>t-butyl dimer</u>
SAMPLE <u>4F</u>	PURITY _____	1. _____	$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_3 - \text{C} - \text{CH}_3 \\    \\  \text{H} - \text{C} - \text{C} = \text{O} \\    \quad   \\  \text{C} \quad \text{O} \\    \\  \text{H} - \text{C} \\    \\  \text{CH}_3 - \text{C} - \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $
	PHASE _____	2. _____	
	THICKNESS _____	DATE <u>4/20/76</u>	
		OPERATOR <u>D. Staffler</u>	

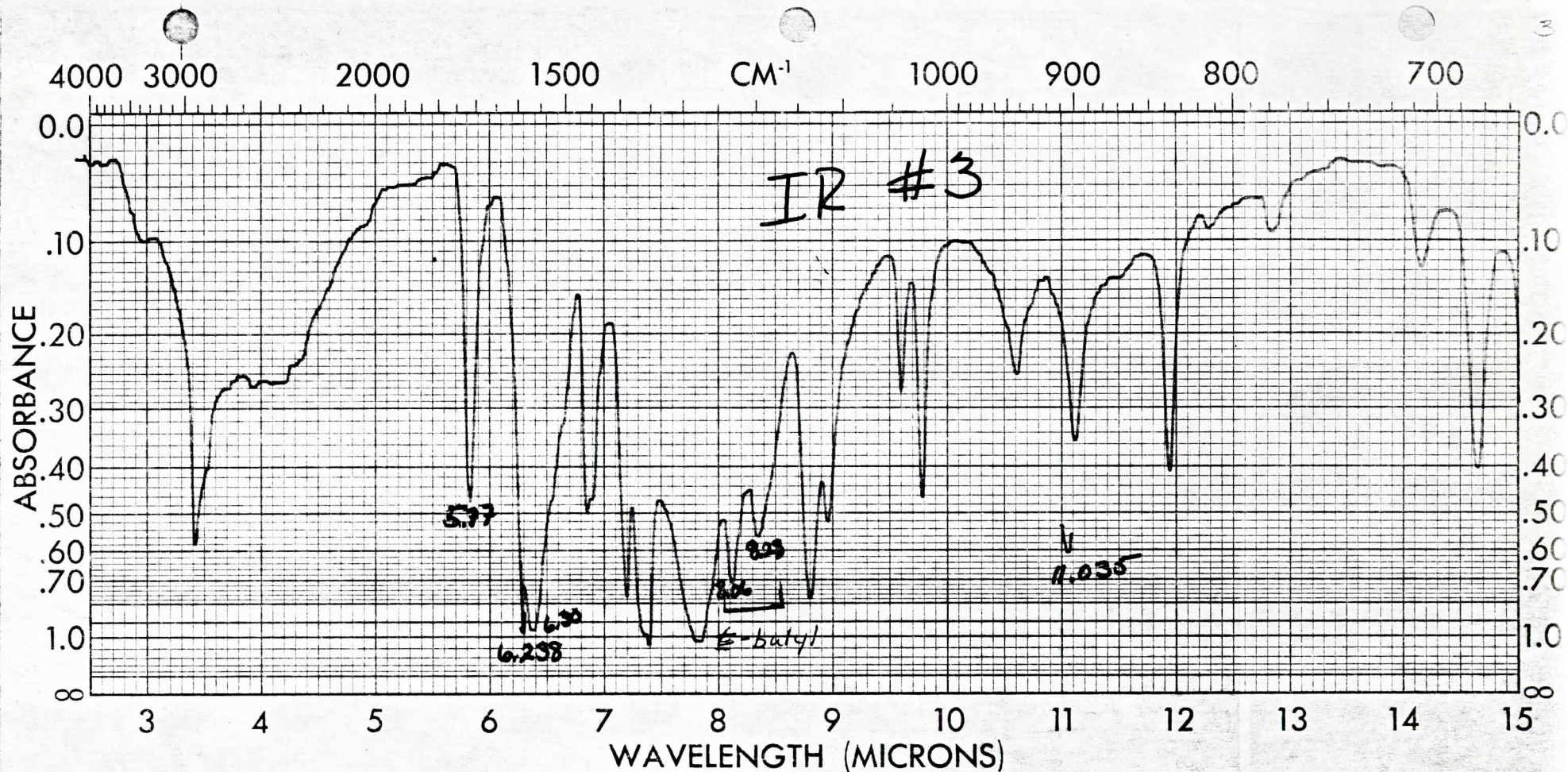
PERKIN-ELMER INC. JKT  
 SAMPLE 4F

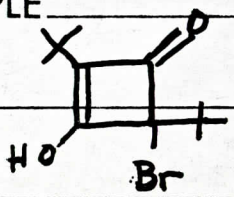


*t*-butyl ketene trimer

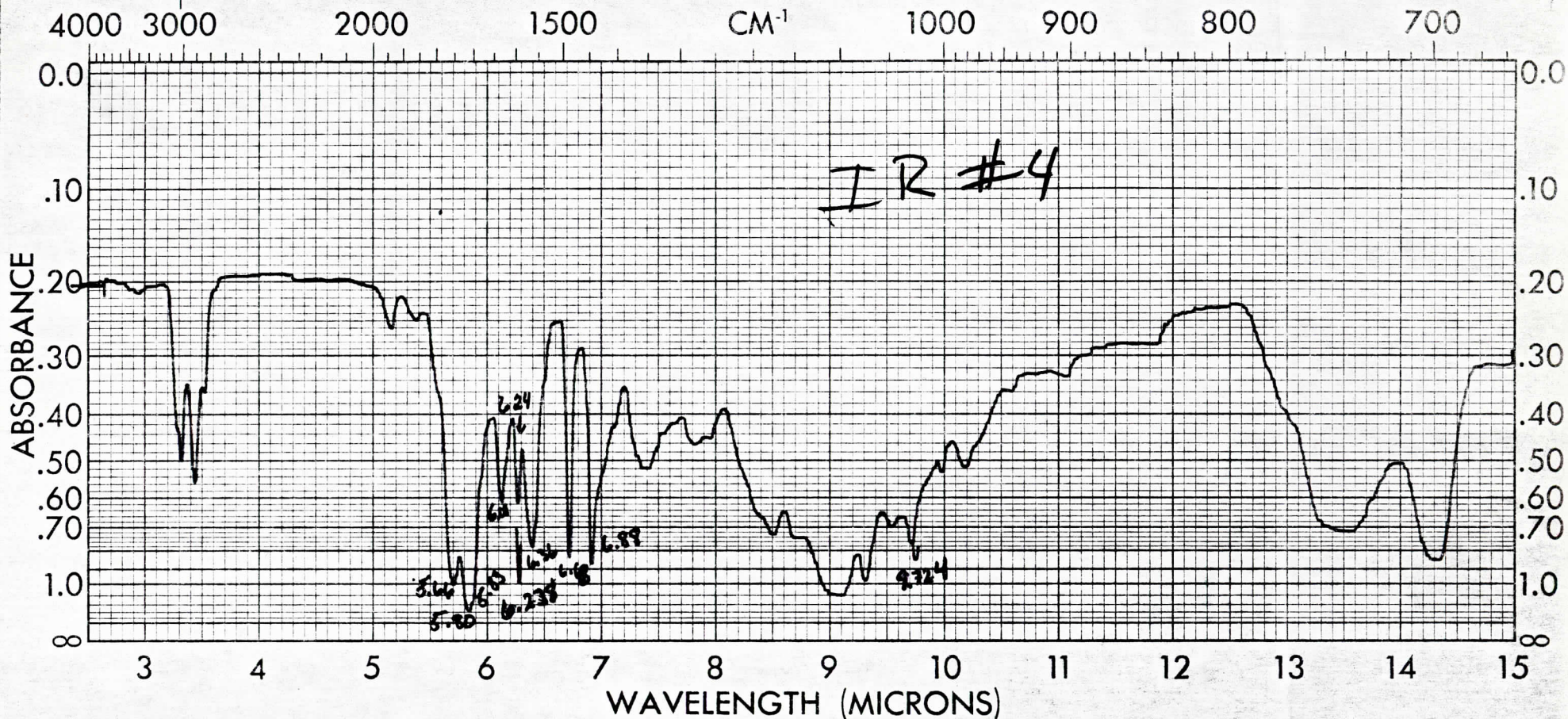
SPECTRUM NO. <u>IR#2</u>	ORIGIN <u>dist. of 4/15/76</u>	LEGEND _____	REMARKS <u>+ butyl trimer</u>
SAMPLE <u>fraction 3H</u>		1. _____	
<u>bp. 113°C, 0.6-0.5 mmHg</u>	PURITY <u>twice distilled</u>	2. _____	
	PHASE _____	DATE <u>4/20/76</u>	
	THICKNESS _____	OPERATOR <u>D. Zaepfel</u>	

SAMPLE NO. 3H



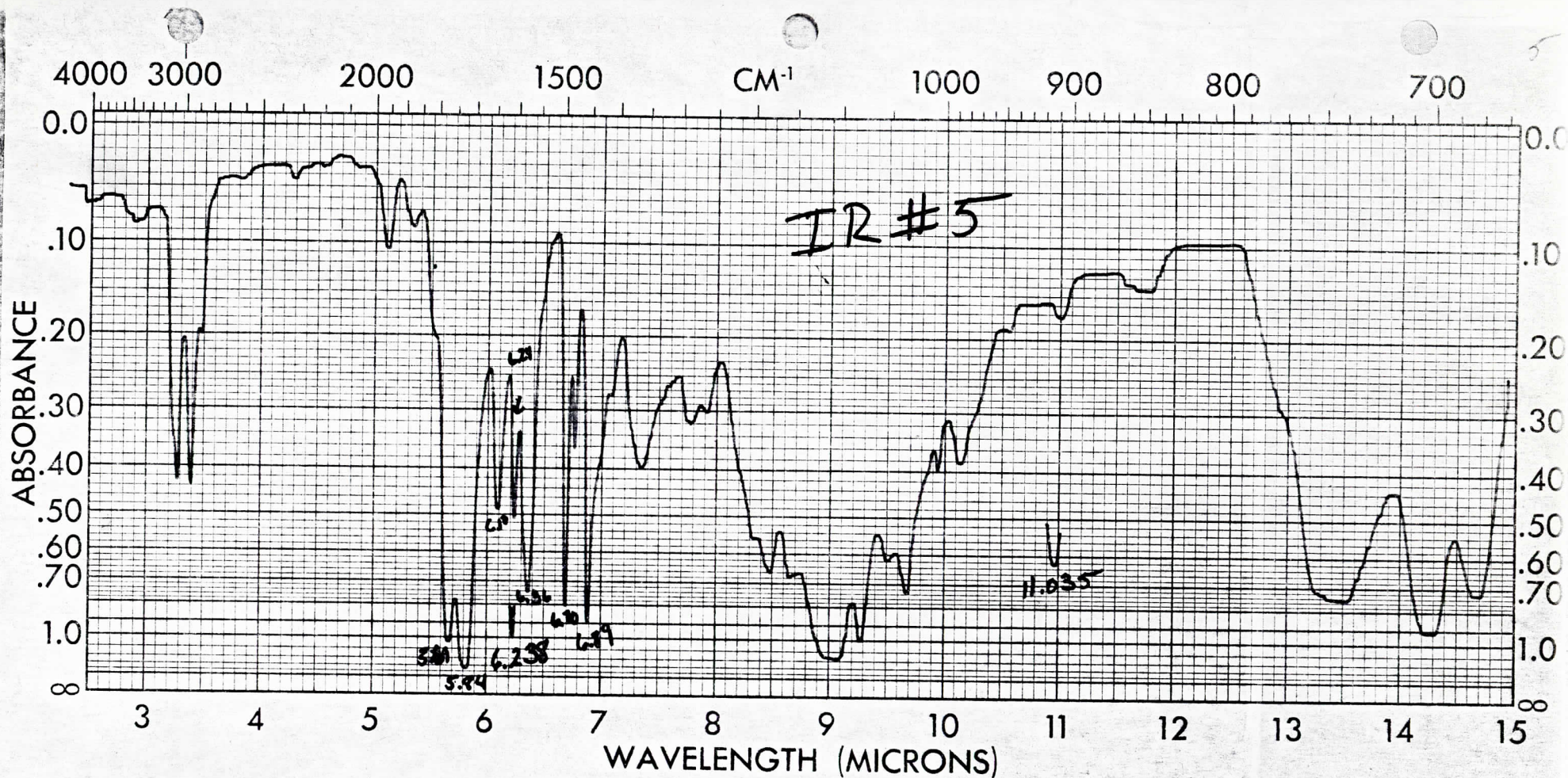
SPECTRUM NO. <u>IR#3</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE _____	PURITY _____	1. _____	<u>KBr pellet</u>
	PHASE _____	DATE <u>4/29/76</u>	
THICKNESS _____	OPERATOR <u>D. Loeffler</u>		

SAMPLE



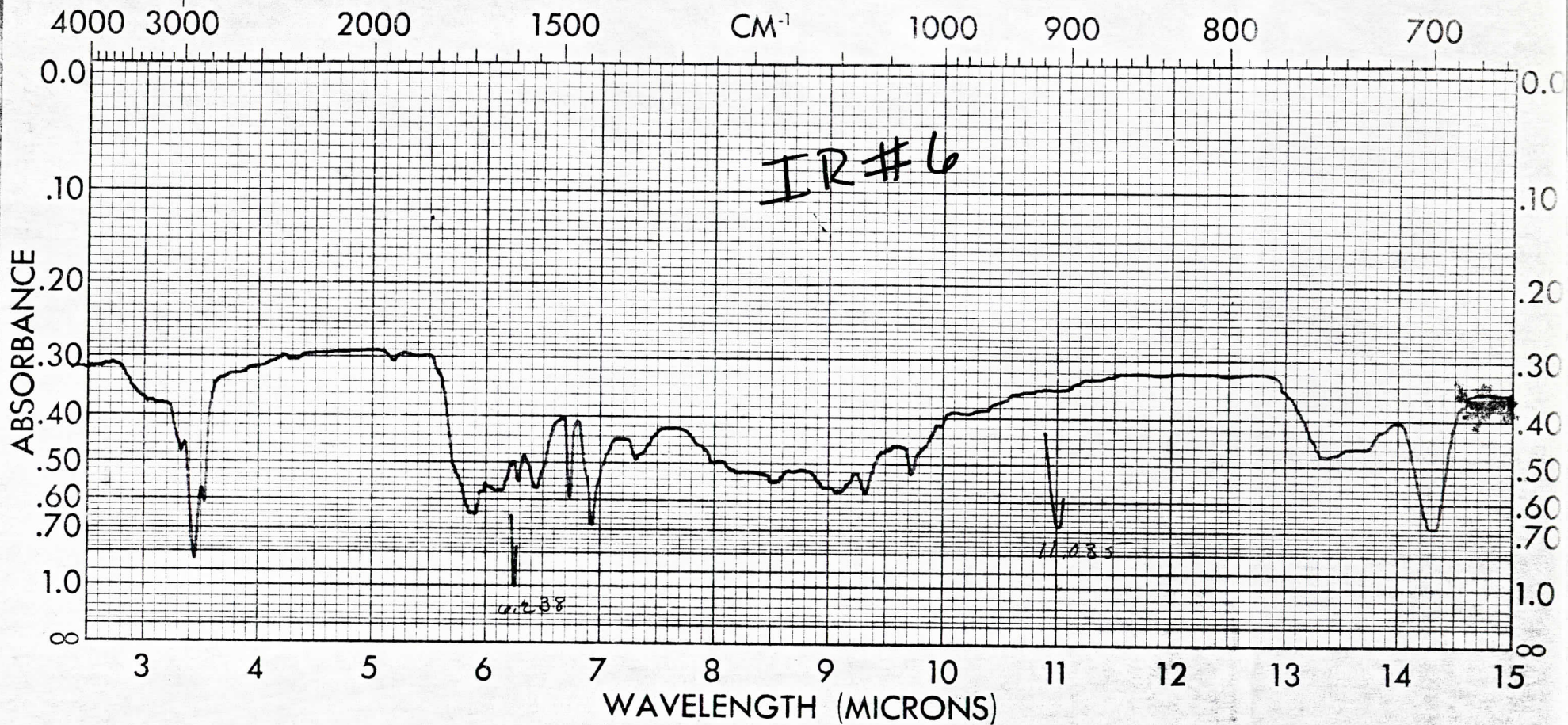
SPECTRUM NO. <u>IR#4</u>	ORIGIN <u>rxn of 4/15/76</u>	LEGEND _____	REMARKS _____
SAMPLE <u>Acrolein mix</u>	PURITY _____	1. _____	<u>Benzyl ketene</u>
<u>(Hydrocinnamyl rxn)</u>	PHASE _____	2. _____	<u>Polymerization,</u>
THICKNESS _____	DATE <u>4/22/76</u>	OPERATOR <u>D. Joepfle</u>	<u>Reaction mixture</u>

SAMPLE SPECTRUM NO. 4477 (19)



SPECTRUM NO. <u>IR #5</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>Hydrocinamic Res</u>		1. _____	<u>Benzyl Ketene</u>
<u>eluted from Florisil</u>	PURITY _____	2. _____	<u>Polymerization.</u>
<u>with Benzene</u>	PHASE _____	DATE <u>4/28/76</u>	<u>Eluted from Florisil</u>
	THICKNESS _____	OPERATOR <u>D Lauffe</u>	<u>with Benzene.</u>
			<u>Some benzene</u>
			<u>contamination</u>

SAMPLE NO. 101-1280



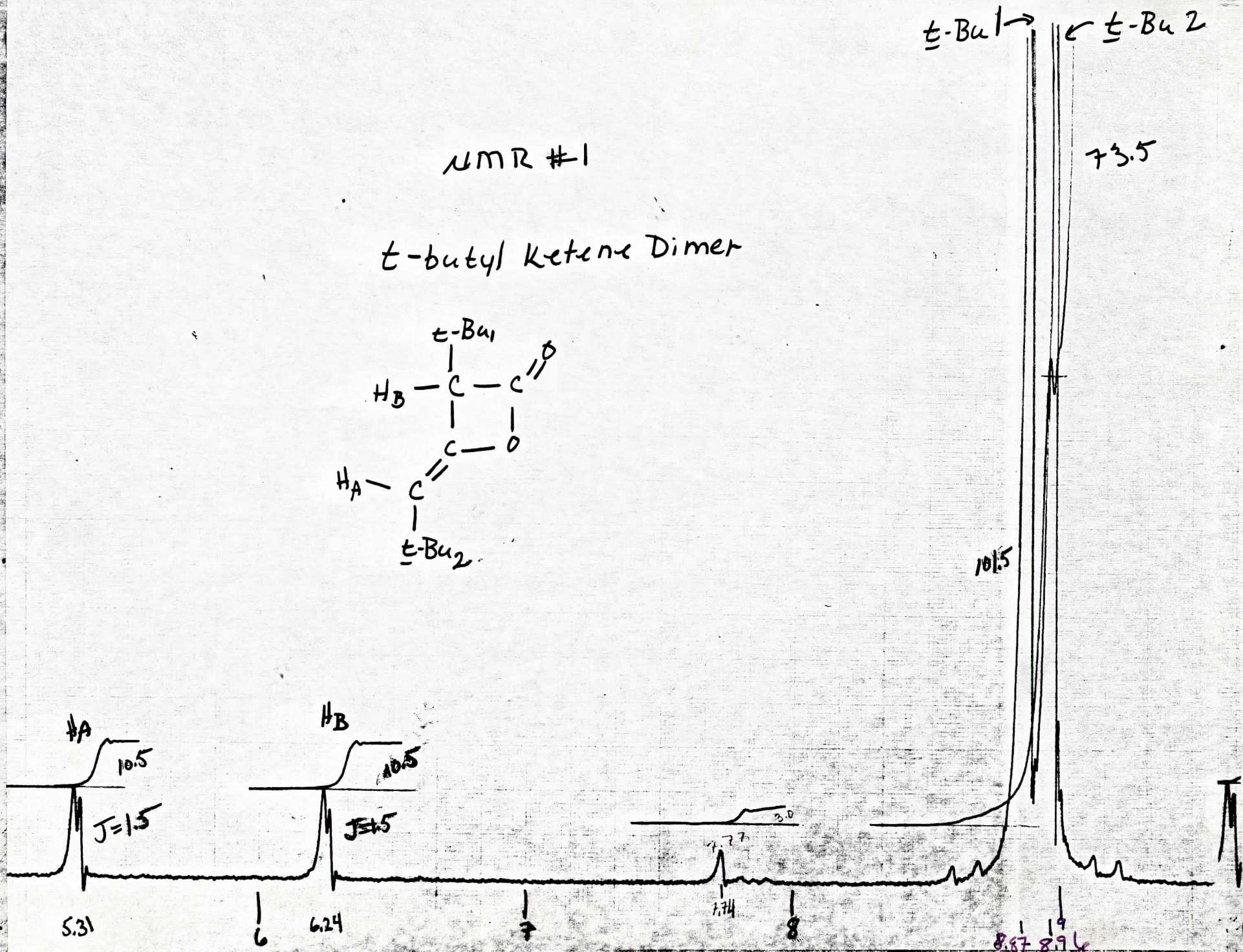
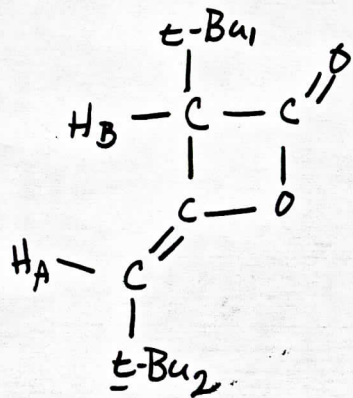
SPECTRUM NO. <u>IR #6</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>Hydrocinamic Rx</u>	_____	1. _____	<u>Eluted from</u>
<u>eluted from Florisil</u>	PURITY _____	2. _____	<u>Florisil with</u>
<u>with acetone</u>	PHASE _____	DATE <u>4/28/76</u>	<u>acetone.</u>
_____	THICKNESS _____	OPERATOR <u>D. Laeffler</u>	_____

PERKIN-ELMER CORPORATION, NORWALK, CONNECTICUT

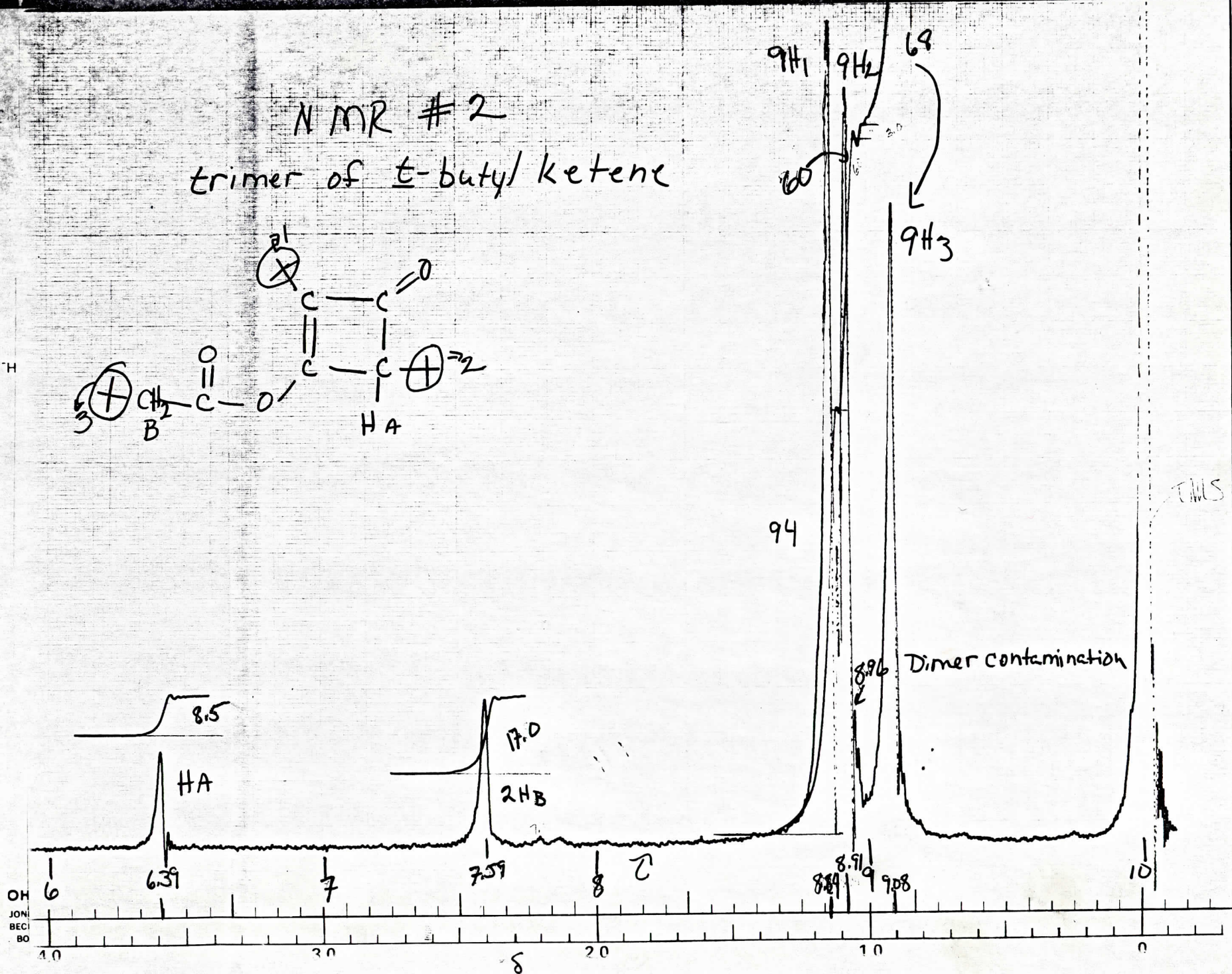
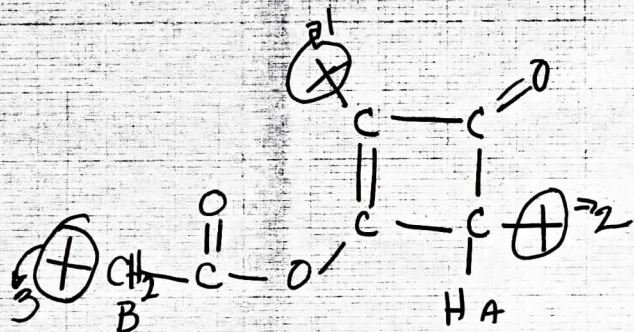


NMR #1

*t*-butyl Ketene Dimer



NMR #2  
 trimer of *t*-butyl ketene



TO  
 9 J  
 2 B  
 .O.

SOLV  
 TEMP  
 FILTER  
 R.F. F  
 SWEE  
 SWEE  
 SWEE  
 SPECT  
 INTEC  
 REMA

(Handwritten initials)

SUMMARY OF RESULTS AND FUTURE WORKResults

The cyclobutenone trimer of t-butyl ketene was obtained in a purer form, and spectral analyses were obtained.

4-bromo-3-hydroxy-2,4-di-t-butyl cyclobutenone was prepared. As far as it can be ascertained, this compound was previously unreported in the literature.

The reaction of hydrocinnamic acid chloride with triethylamine was carried out and the product was analyzed via column chromatography.

Future Work

4-bromo-3-hydroxy-2,4-di-t-butyl cyclobutenone, as mentioned previously, is the possible precursor to an unusual aromatic species, the 2,4-di-t-butyl-1,3-dihydroxy cyclobutadiene di-cation. The bromide will be further purified and its nmr spectrum in concentrated sulfuric acid will be determined in an effort to observe the di-cation.

The reaction of hydrocinnamic acid chloride with triethylamine will be carried out in other solvent systems, for example, diethyl ether, in an attempt to isolate the cyclobutenone trimer.

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