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# The decomposition of phenyl-benzoyl-diazamethane and its relevance to alkyne ozonolysis

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THE DECOMPOSITION OF PHENYL-BENZOYL-DIAZAMETHANE AND ITS  
RELEVANCE TO ALKYNE OZONOLYSIS

by

Joy A. Sawyer

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

UNION COLLEGE

March, 1977

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ABSTRACT

Name: Joy A. Sawyer  
Title: The Decomposition of Phenyl-Benzoyl-Diazomethane  
and its Relevance to Alkyne Ozonolysis  
Department: Chemistry  
Date: April 7, 1977

The thermal or photolytic decomposition of diazo compounds is known to produce a carbonyl oxide in the presence of oxygen. Analogously,  $\alpha$ -diazoketones should produce acyl carbonyloxides. This intermediate is identical to one proposed for the ozonolysis of alkynes and its substantiation is the purpose of this study. By examining the products of the thermal, copper catalyzed phenylbenzoyldiazomethane decomposition, one should be able to determine the intermediate's presence. Benzoic anhydride, benzil and methyl diphenylacetate have been identified as products and tetraphenylglycolide is also thought to be present. Methyl diphenylacetate is the result of Wolff rearrangement, while the other three are proposed to be derived from oxygen addition to a ketocarbene, i.e. the acyl carbonylacetate. The product's formation is speculated to be connected to the triplet and/or singlet nature of the intermediate. The triplet state is thought to produce tetraphenylglycolide exclusively, while the singlet yields benzil and benzoic anhydride. These latter two products are also produced for diphenylacetylene ozon-

olysis; a noted singlet process. The presence of the singlet state is attributed to intersystem crossing promoted by the copper catalyst as the singlet's attributed products are not found in the non-catalyzed runs.

DEDICATION

I would like to dedicate this work to Professor Robert Schaefer and Professor Leslie Hull in appreciation of their help and guidance.

#### ACKNOWLEDGEMENTS

I would like to thank the Petroleum Research Fund and the Union College Chemistry Department for supporting this project.

"Nothing in the world can take the place of persistence. Talent will not; nothing is more common than unsuccessful men with talent. Genius will not; unrewarded genius is almost a proverb. Education will not; the world is full of educated derelicts. Persistence and determination alone are omnipotent. The slogan 'Press On' has solved and always will solve the problems of the human race".

- Calvin Coolidge

## TABLE OF CONTENTS

	<u>Page</u>
Abstract.....	ii
Dedication.....	iv
Acknowledgements.....	v
Quotation.....	vi
Index of Figures and Tables.....	viii
Introduction.....	1
Experimental.....	17
Results.....	22
Discussion.....	40
Future Work.....	52
References.....	53
Appendix I.....	57
Appendix II.....	61
Appendix III.....	62



## INDEX OF TABLES AND FIGURES

### I. Figures

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Resonance Structures of Ozone	1
2	Criegee Clefin Mechanism	2
3	Carbonyl Oxide Resonance Structures	4
4	Stereoisomeric Forms of Carbonyl Oxide	4
5	Rearrangement Reaction Mechanism	6
6	Storr Aldehyde-Interchange Mechanism	8
7	Criegee-Lederer Alkyne Mechanism	9
8	2-Eutyne Epoxidation	10
9	Dezora Alkyne Ozonolysis Mechanism	11
10	Hull Alkyne Ozonolysis Mechanism	12
11	Dioxetene	14
12	Proposed Azitenzil Decomposition	15
13	Addition of ethanol to Diphenylketene	24
14	Tetraphenylglycolide	33
15	<u>Bis-benzilketenine</u>	33
16	Diphenylketene Reaction with Benzene	37
17	Molff Rearrangement	40
18	Ketene Reactions	41
19	Chenide Formation from Diphenyldiacetylene	44

I. continued

<u>Number</u>	<u>Title</u>	<u>Page</u>
20	Tetraphenylglycolide	46
21	Stereochemistry of Acyl Carbonyl Oxide	50
22	Formation of a Cyclic Anhydride Intermediate	50

## II. Tables

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Percent Yield of Benzil and Benzoic Anhydride	25
2	Benzil Production after Variation in Times of Ozone Addition and Trapping Agent Addition	25
3	Nitrogen Atmosphere Azilenzil Decomposition	27
4	Run #44 - Two Atmospheres Oxygen	31
5	Methyl Benzoate versus Methyl Diphenylacetate	35
6	Decomposition Product Treated with Base and Methanol	36
7	Decomposition Product Plus Methanol	39
8	Standardization Curve of Dodecane and 1-Decene	52
9	Ozone Production	52
10	Coolant Paths	60
11	Standardization of Benzil and Benzoic Anhydride via the Infrared Spectrometer	60
12	Data from Oxygen Azilenzil Decompositions	63

## INTRODUCTION

Ozonation is a general term referring to a substrate's reaction with ozone. Since it was first studied in 1855 by Schobőin, ozonation has been shown to be a versatile method for bond cleavage. Utilization of ozonation in this manner is referred to as ozonolysis. Ozone, as a reagent, is versatile and energetic. This may be attributed to the high energy oxygen-oxygen bonds as shown by the following resonance structures.<sup>1</sup>

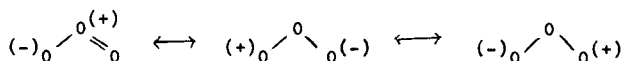


Figure 1: Resonance Structures of Ozone

The attack of ozone on an organic molecule can occur in five possible fashions:<sup>2</sup> 1) an electrophilic attack on a nucleophilic atom, resulting in the formation of a sigma complex or a similar species, 2) production of a pi complex by an electrophilic attack on a carbon-carbon double (or triple) bond, 3) a four-centered reaction on a carbon-carbon double bond, 4) a nucleophilic attack on an electrophilic atom and 5) a radical attack on specific saturated groups. The exact nature of ozone's attack depends on a variety of conditions, including substrate and solvent.

The Criegee olefin ozonolysis mechanism is considered to be the most acceptable proposal to date.

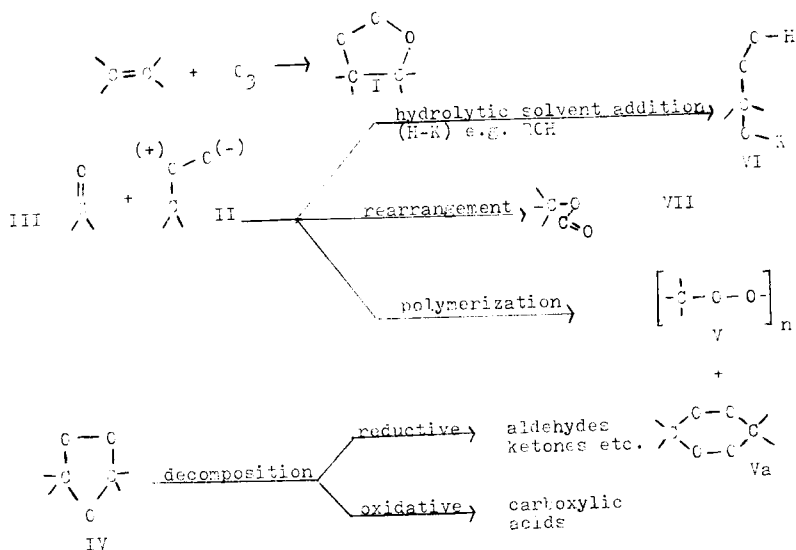


Figure 2: Criegee Olefin Mechanism

The initial ozone attack has been indicated by kinetic data to be a concerted 1,3-dipolar addition.<sup>3,4</sup> This form of addition reaction results in the formation of a 1,2,3-trioxolane, I. (also referred to as a primary ozonide or a molozonide). This structure is thermodynamically unstable, though low ring strain and a lack of formal charge have allowed its isolation in some cases.<sup>5</sup> Bailey has further confirmed

the 1,2,3-trioxolane structure by low temperature ( $-110^{\circ}\text{C}.$ ) NMR spectroscopy.<sup>6</sup> Utilizing the molozone from trans di-*t*-butyl ethene, the NMR spectrum indicated the equivalence of the chemical environments around the carbon atoms, thus confirming the ring structure. The primary ozonide occurs primarily in cases where steric hindrance is low. In cases where bulky groups are present, partial cleavage occurs. Epoxide formation is the result of this reaction. Studies have indicated that a sigma complex is the most likely path to the epoxide. Such an intermediate presents a major source of competition to the molozone production.<sup>3</sup>

Once formed, the 1,2,3-trioxolane undergoes a synchronous decomposition to produce a carbonyl compound, III, and a zwitterion (i.e. carbonyl oxide), II.<sup>7</sup> In this decomposition, the oxygen-oxygen and carbon-carbon bonds cleave while the stronger carbon-oxygen bonds remain intact.<sup>8</sup> The zwitterion formed depends on the substituents of the original carbon-carbon double bond. Electron-releasing groups are more capable of stabilizing the developing positive charge. Such stability is accomplished by increasing the electron density in the region of the potential zwitterionic carbonium ion via inductive and mesomeric effects.<sup>9</sup> Thus, the preferred zwitterions are the ones with the strongest electron-releasing substituents.

Structurally, the carbonyl oxide is isoelectronic with ozone. Consisting of a pi system with four pi electrons,

two main resonance forms occur.<sup>1,10</sup>

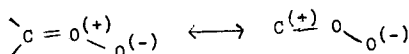


Figure 3: Carbonyl Oxide Resonance Structures

The zwitterion may also exist in two stereoisomeric forms:<sup>11</sup>

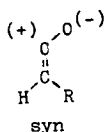
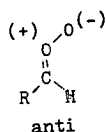


Figure 4: Stereoisomeric Forms of Carbonyl Oxide

These stereoisomers were added to the original mechanism to account for deviations in the 1,2,4-trioxolane's (IV) cis-trans ratio.

The evidence for the zwitterion's presence comes primarily from the isolation of ozonolysis products. Work done with  $\text{O}^{18}$  labeling, is a major contributor. The label's incorporation, via a free aldehyde in the ozonolysis reaction mixture, showed that the carbonyl group is utilized in forming the 1,2,4-trioxolane's ether linkage. This indicates the presence of a species containing peroxide linkages, i.e. the zwitterion. The actual generation of the zwitterion comes from a source analogous to ozonolysis. Diazo compounds have been known to produce 1,2,4-trioxolanes upon photo-oxidation. Murray isolated products from a short-lived carbonyl oxide from this type of reaction, thus providing verification that

such intermediates do exist.<sup>10</sup> Other experimental validation comes from the fact that when styrene undergoes ozonolysis, polystyrene is not yielded. Such would be the case if a free radical was present in the mechanism.<sup>12</sup> Having suggested experimental grounds for believing in the zwitterion's existence, a correlation between the zwitterion and the rest of the mechanism is required. The carbonyl oxide provides a means through which the formation of ozonide and non-ozonide products may be deduced.

Ozonolysis products may be produced via one of four carbonyl oxide reactions: 1) addition of a free aldehyde or ketone, 2) rearrangement, 3) polymerization and 4) hydroxylic solvent addition. The first of these, addition, is characterized as a concerted 1,3-dipolar addition. This is analogous to step one, a logical conclusion when one considers that ozone and the carbonyl oxide are isoelectronic. The products of the addition are ozonides, IV. Existing in two forms, normal and crossed, the 1,2,4-trioxolane's isolation provides evidence for the zwitterion's occurrence. A cross-ozonide is formed when the substituents on the primary ozonide are dissimilar. The assymetrical molozonide can decompose into two zwitterions and two carbonyl groups. These may recombine to produce three ozonides: two whose substituents are identical and one whose substituents are not identical.<sup>8</sup> The latter is referred to as a cross-ozonide.<sup>18</sup> When a foreign carbonyl is incorporated into the ozonolysis reaction mixture the pro-



duction of cross-ozonides provides evidence that not only an addition reaction is occurring but also that a zwitterion is present in the mechanism. It should be noted that there is a limitation to the addition reaction. Specifically, most ketones sterically hinder the addition, either to the extent that it doesn't go at all or is slowed up sufficiently to allow a significant portion of alternative competing reactions to occur.

Polymerization occurs when the carbonyl oxide recombines with itself. This type of reaction is prevalent primarily amongst olefins containing four substituents at the carbon-carbon double bond.<sup>8</sup> The products produced are either the polymer, V, or a diperoxide; the dimer Va.

Rearrangement is a slightly more complicated reaction than either addition or polymerization. Here ozonolysis leads to both the rupture of the double bond and the adjacent carbon-carbon single bond, an "anomalous ozonization".<sup>8</sup> The mechanism involved may be explained in terms of a peroxide rearrangement of the carbonyl oxide.<sup>8</sup>

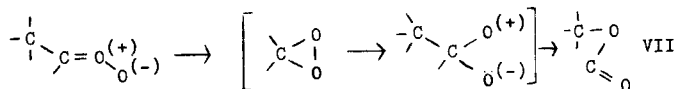


Figure 5: Rearrangement Reaction Mechanism

The products produced from rearrangement are primarily esters, lactones and carboxylic acids.

The presence of a protic solvent in solution offers the main source of competition to the 1,2,4-trioxolane formation. The solvent readily donates its protons in solution. The latter, being small and electron deficient, move rapidly through solution towards the zwitterion and are easily incorporated. This is attributed to the zwitterion's charge separation. The products produced by solvent addition depend on the solvent, though for alcohols the main product is an alkoxyhydroperoxide, VI.

Criegee's mechanism is not without opposition. The main arguments raised are those dealing with the 1,2,4-trioxolane stereochemistry. The original mechanism had no provisions for stereochemical effects, nor could it predict whether reunification of carbonyl and carbonyl oxide fragments would produce cis ozonides, trans ozonides or a combination of the two.<sup>7</sup> Three modifications of the existing mechanism were developed to account for the observed inconsistencies. The first consisted of Criegee allowing the zwitterion to exist in syn and anti forms. (see figure 4) Bauld and Bailey also worked along these lines, while Story developed an entirely different approach.

The Bauld-Bailey mechanism proposed a zwitterion intermediate that existed in both the syn and anti forms. These zwitterions were responsible for determining the overall reaction's stereochemistry. A series of rules were formulated to predict the stereochemical transformations via which the

conformations of the primary and the secondary ozonides would occur.<sup>13</sup> These rules, and the assumptions behind them composed the main objections to the mechanism. Criegee holds that the assumptions are faulty, while work done by Lattimer et al. indicates that the mechanism is good only for bulky substituents.<sup>8,11</sup> Despite the objections raised this mechanism has not been totally refuted.

The Story aldehyde-interchange mechanism was developed to accommodate the same objections as the Bauld-Bailey and to account for the presence of  $O^{18}$  in 1,2,4-trioxolane's peroxide linkages. (indicated by \* below)

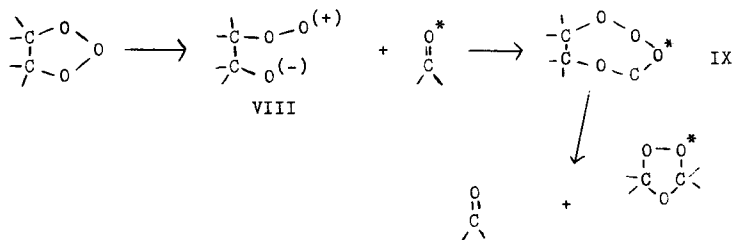


Figure 6: Story Aldehyde-Interchange Mechanism

According to Story, molozonide decomposes to yield species VIII which then combines with a free carbonyl to produce a seven-membered carbon-oxygen ring, IX. This ring undergoes decomposition to yield a new carbonyl plus a 1,2,4-trioxolane. The problems with this mechanism are multi-fold. First of all, species IX is extremely improbable both from a bonding and a

thermodynamic point of view. To achieve the desired ring structure, a 2+2 concerted addition is required.<sup>14</sup> Such a pathway is unfavorable and would account for the fact that no such ring has ever been isolated, either from ozonolysis or from a complimentary reaction. Further contradiction of Story's mechanism comes from the inability to reproduce his experiments, particularly the ones involving  $O^{18}$  labeling. The latter have been conclusively disproved and the mechanism is no longer under consideration.<sup>10</sup>

The ozonolysis of alkynes has been suggested to follow a mechanism analogous to that for olefins. Accordingly Criegee and Lederer have proposed the following combination.<sup>20</sup>

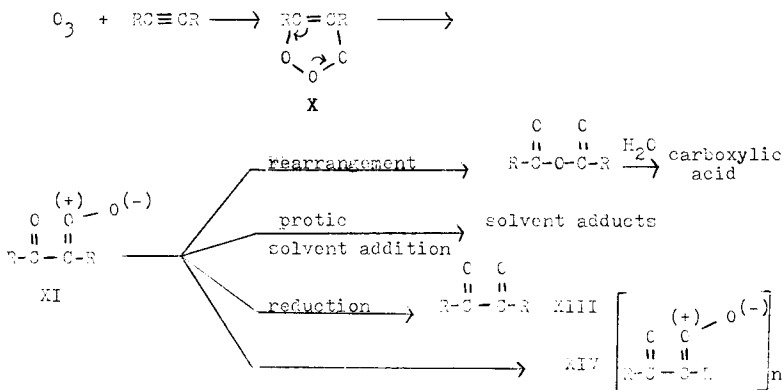


Figure 7: Criegee-Lederer Alkyne Mechanism

The production of a 3,4,5-trioxolene, X, in step one, is analogous to that in Criegee's olefin mechanism.<sup>15</sup> The existence of X has been indicated by DeMore and Lin and by Hamilton and Keay.<sup>15,16</sup> The former observed a strong infrared absorption band at  $1740\text{ cm}^{-1}$ , during the ozonolysis of 1-butyne, 2-butyne and 1-propyne. This band was attributed to the carbonyl stretching of an anhydride precursor. (presumably XI) The carbonyl stretching tentatively rules out a cyclic intermediate. However, it was noticed that the amount of anhydride produced was greater than that of the intermediate. This indicates that a cyclic form may also be present and be responsible for the greater anhydride production. Hamilton and Keay further strengthened this hypothesis by their work with epoxides produced from 2-butyne.

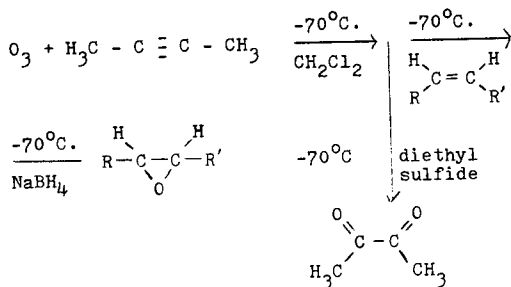


Figure 8: 2-Butyne Epoxidation

They observed that: a) lower yields of epoxide occurred if the solvent's methanol concentration was increased, b) epoxi-

dations were almost, but not completely stereospecific and c) trapping with diethyl sulfide yielded 2,3-butanedione.<sup>15</sup> All of this points to a possible acyl carboxyloxy intermediate, XI, or its cyclized tautomer, X. The former probably arises from the latter as bond energy considerations indicate that the 3,4,5-trioxolene is slightly favored thermodynamically.<sup>15</sup>

The production of species X or XI is slower than the analogous step in the Criegee olefin mechanism. This is attributed to a high activation energy. DeMore has calculated such an energy as being 10.8 kcal/mole for acetylene.<sup>17</sup> In the same ozonolysis series, using acetylene, dimethylacetylene, methylacetylene and ethylacetylene in the gaseous phase, DeMore calculated the Arrhenius preexponential factor as being  $10^3$  times greater than that for olefins. The size of this factor fails to accommodate a cyclic intermediate as the initial ozone addition product and therefore excludes the possibility of a concerted addition. DeMore proposed a 1,3 dipolar addition with an open chain intermediate to accommodate the above observations.<sup>17</sup>

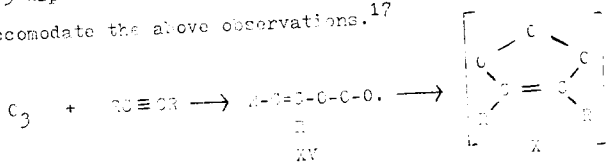


Figure 9: DeMore Alkyne Ozonolysis Mechanism  
The above mechanism has been proposed for the gas phase.

Later work by DeMore has not produced the isolation of XV nor has there been any denial of the aforementioned's existence.<sup>16</sup>

Returning to the Criegee-Lederer mechanism, notice should be taken of the role that the acyl carbonyloxyde, XI, plays. This intermediate is assumed to undergo four basic types of reactions, all of which are analogous to those undergone by carbonyl oxide. These reactions are: 1) polymerization, 2) reduction, 3) protic solvent addition and 4) rearrangement. Hamilton and Keay based a portion of their results on the third of these, the protic solvent addition. For our purposes the last of these reactions, rearrangement, is of primary interest.

Hull and coworkers have proposed the following alkyne ozonolysis mechanism:<sup>40</sup>

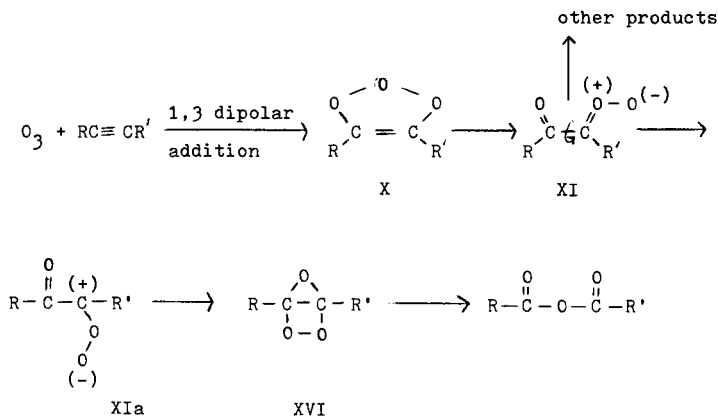


Figure 10: Hull Alkyne Ozonolysis Mechanism

The above mechanism is a literal translation of Criegee's olefin ozonolysis mechanism into one for alkynes. The mechanism's principal features are species XIa and XVI. The former is produced by rotation of the carbon-carbon single bond in XI. This form is a logical configuration provided that there is no steric hindrance of rotation. Hamilton and Keay have presented evidence for species XI probable existence.<sup>30</sup> When a 50% methanol solution is added to 2-butyne during ozonation a 75% decrease in alkene epoxidation is observed. The same procedure at  $-70^{\circ}\text{C}$ . gave a 9% yield of  $\alpha$ -diketone, while reaction at  $-15^{\circ}\text{C}$ . gave a 90% yield. The above experimental results indicate that one is dealing with an intermediate that is prone to protic solvent trapping at low temperatures but may also act as an oxygen transfer reagent. Hamilton and Keay suggest that such behavior is within reason for a acyl carbonyloxy intermediate, given its structure and the variety and nature of the products produced during ozonolysis.

The existence of dioxetenes as proposed by Turro et. al., (see figure 11) provides evidence that compounds similar to XVI can exist as isolable materials.<sup>29</sup> Turro has noted the presence of a stable intermediate between  $-90^{\circ}\text{C}$ . and  $-30^{\circ}\text{C}$ . upon the reaction of 1-thio-3,3,6,6-tetramethylcyclohept-4-yne and singlet oxygen. The dioxetene has been identified as this stable intermediate. Such an intermediate exhibits a ring strain similar to that expected in



XVI and thus is an indication of such a specie's probable existence. The formation of XVI may be considered to be comparable to carbonyloxide's addition to a carbonyl group. The only dissimilarity is the fact that both the carbonyl group and the carbonyloxide are joined by a carbon-carbon single bond. Once produced, the species is thought to be concertededly rearranged into an anhydride. The exact process involved is indicated in figure 9 by arrows.

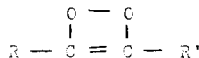
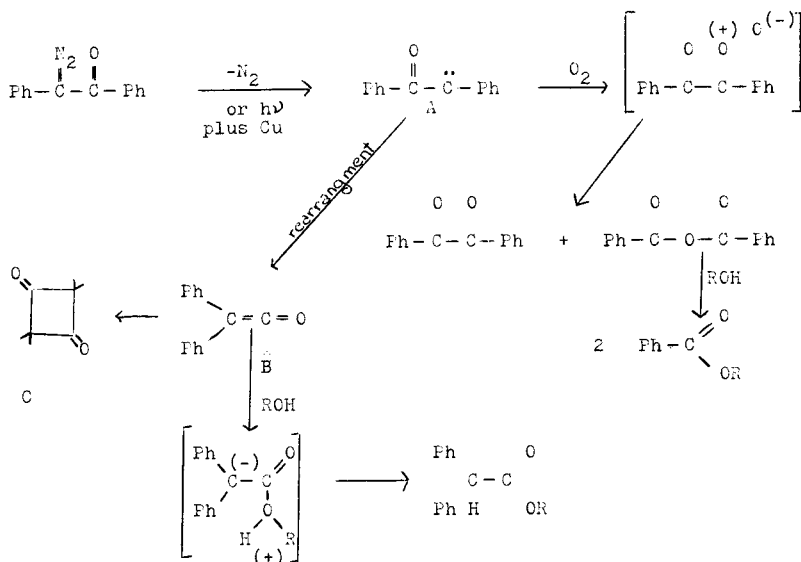


Figure 11: Dioxetene

This investigation will utilize the decomposition of azibenzil (phenylbenzoyldiazomethane) to elucidate the presence of the acyl carbonyloxide.

Figure 12: Proposed Azibenzil Decomposition

When azibenzil undergoes decomposition, (i.e. loses nitrogen) two possible paths may be taken after the formation of the carbene: Wolff rearrangement to the ketene (B) or formation of the acyl carbonyloxide in the presence of oxygen. The ketene may react to form the dimer (C), or if treated with methanol to give methyl diphenylacetate. The acyl carbonyloxide, on the other hand, would be expected to form benzoic



anhydride and benzil, which if subsequently treated with methanol would give methyl benzoate leaving the benzil untouched. Each of the expected products is sufficiently different in molecular weight so as to provide an adequate separation on the gas chromatograph. By analyzing the products and the proportions in which they are produced, we will hopefully be in a position to further substantiate the acyl carbonyloxyde's existence.

### EXPERIMENTAL

#### Determination of Benzil and Benzoic Anhydride Production from the Ozonolysis of Diphenylacetylene

One millimole of diphenylacetylene was dissolved in 10 milliliters acetone and allowed to equilibrate to the desired temperature. ( $-42^{\circ}\text{C}$ . or  $0^{\circ}\text{C}$ .) Ozone was then passed through the mixture for 30 minutes and a trapping agent (one milliliter diphenylsulfide in eight milliliters acetone) added after a one minute wait.<sup>47,48</sup> The reaction mixture was brought up to room temperature and evaporated to remove the acetone. Carbon tetrachloride was added to the residue, evaporated off, and more added to bring the reaction mixture to a desired volume. An infrared spectrum was taken of the final solution.<sup>49</sup> The absorbance at  $1800\text{ cm}^{-1}$  and  $1680\text{ cm}^{-1}$  were measured and compared to a standardization curve to determine the relative amounts of benzoic anhydride and benzil respectively.

#### Benzil Production after Variation in Times of Ozone Addition and Trapping Agent Addition

The procedure used here was identical to that mentioned above. The only notable changes were that the runs were conducted at  $-42^{\circ}\text{C}$ . and  $-62^{\circ}\text{C}$ . as well as variation in ozonation and trapping reagent addition times.

#### Benzil Monohydrazone Preparation:<sup>33</sup>

0.75 moles of 85% hydrazine hydrate are slowly dropped,

with stirring, into a hot solution of benzil (0.75 moles) and ethanol (300 milliliters). The product begins to separate from the solution after approximately three quarters of the hydrazine hydrate has been added. At the completion of the addition the mixture is refluxed for five minutes and then cooled to 0°C.. The monohydrazone is filtered off and washed twice with 100 milliliter portions of cold ethanol. An additional washing may be necessary if traces of yellow benzil are present in the off-white benzil monohydrazone. The yield is 140 grams or 93% of the theoretical.

The product's melting point is 149-51°C. with decomposition and its structure was confirmed utilizing NMR (spectrum #1), IR (spectra #2 and 3) and UV-Vis (spectrum #4) spectroscopy.<sup>41,50</sup>

#### Azibenzil (phenylbenzoyldiazomethane) Preparation.<sup>32</sup>

Benzil hydrazone (0.134 moles), yellow mercuric oxide (0.28 moles) and anhydrous calcium sulfate (0.110 moles) are mixed together thoroughly in a mortar and pestle. The mixture is then introduced to a 500 milliliter stoppered bottle and covered with 200 milliliters of absolute ethyl ether. Ten milliliters of a saturated, alcoholic solution of potassium hydroxide is then added to catalyze the reaction, and the mixture is shaken vigorously for ten to fifteen minutes. The solution is filtered off and the residue washed several times with absolute ether until the filtrate is only

slightly colored. The combined ethereal extracts are evaporated to dryness on a rotoevaporator with heating at a temperature not greater than  $40^{\circ}\text{C}$ . Caution: The material may explode if the evaporation is carried out at atmospheric pressure on the steam bath. The yellow-orange crystalline material is recrystallized from anhydrous ether, dried and stored in the refrigerator in an amber bottle to prevent decomposition. The yield was 19.3 grams, or 65% of the theoretical.

The product melts at approximately  $79^{\circ}\text{C}$ . with decomposition and has been characterized by NMR, IR and UV-Vis spectroscopy.<sup>50</sup> (Spectra #5-9)

Methyl Diphenylacetate Preparation Utilizing the Fischer Esterification Technique:<sup>59</sup>

To a solution of 2.5 moles methanol and 0.5 moles diphenylacetic acid, 10 milliliters of concentrated sulfuric acid catalyst are added. The solution is refluxed overnight (approximately 18 hours) and cooled to room temperature. Sodium bicarbonate (0.206 moles) is then slowly added and 75-100 milliliters of methanol distilled off. The residue is diluted with 50 milliliters of water and the organic phase is extracted three times with 50 milliliter portions of methylene chloride. A check of the inorganic phase shows it to be neutral. The combined organic phase is dried over magnesium sulfate, filtered and distilled to remove the methylene chloride (B.P.  $40^{\circ}\text{C}$ .) and the remainder of the methanol. A final vacuum distillation is utilized to obtain

the final product. It should be noted that the product is a low melting solid (60°C.) and care must be taken to maintain the temperature of the condenser above this level. The yield of product was 39.2 grams or 37% of the theoretical.

Structural determination of the ester was carried out using infrared and NMR spectroscopy.<sup>50</sup> (spectra #10-12)

#### Azibenzil Decomposition

##### A. General

0.3 grams copper powder was added to 30 milliliters of a 0.45 M. azibenzil and benzene solution. The reaction vessel, after the addition, was immersed in a 50°C. water jacket to maintain a constant temperature. The mixture was then placed under nitrogen and stirred to maintain an even copper distribution. At the end of two hours, the solution was filtered free of copper and analyzed on a Glow Mac series 550 gas chromatograph using a DC-200 column.<sup>43,45</sup> A series of four control runs were set up and run on the gas chromatograph. Each sample consisted of six milliliters of the decomposition product, plus four milliliters of the appropriate solvent. Two microliters of the sample were injected into the gas chromatograph, followed by two microliter injections from a series of standards. This permitted the results to be quantified. The controls utilized were: 1) decomposition product, 2) decomposition product treated with methanol and

refluxed for 30 minutes under nitrogen, 3) decomposition product treated with oxygen and then methanol, 4) decomposition product treated with sodium bicarbonate and then with methanol.

#### B. 0.2 and one atmosphere oxygen runs

The method and apparatus used was identical to the above with one exception: the reaction mixture was not placed under nitrogen. Instead oxygen gas (one atmosphere) or dry air (0.2 atmosphere oxygen) was bubbled through the reaction flask during the run. The gas chromatograph work up of the decomposition product was similar to that used in the control run. The following samples were analyzed: 1) decomposition product 2) decomposition product treated with methanol and refluxed for  $\frac{1}{2}$  hour, and 3) decomposition product stirred with a 15% sodium hydroxide solution for one hour, heated to boiling, separated, and added to methanol.

#### C. High pressure oxygen runs

The experimental set up used in these runs was a Parr Pressure Reaction Apparatus. The nature of this apparatus was such that the temperature maintenance ( $50^{\circ} \pm 5^{\circ}\text{C}.$ ) was accomplished via the use of heating tape wound around the reaction vessel. The work up of the decomposition product was identical to that used in section B.



RESULTS

The ozonolysis of diphenylacetylene is thought to follow the scheme in figure ten. This mechanism proposes an acyl carbonyl oxide intermediate which goes either to benzoic anhydride or to other products. The latter arise via rearrangement or through the loss of oxygen. Benzil is thought to be such a product. By comparing these two products yields, the mechanism's preferred route may be inferred.

Table 1: Percent Yield of Benzil and Benzoic Anhydride

The data from table one indicates that benzil and benzoic anhydride are the preferred products of diphenylacetylene's ozonolysis under conditions where some intermediate is trapped by diphenylsulfide. They account for  $75 \pm 2\%$  of all products at  $-42 \pm 1^\circ\text{C}$ . and  $52 \pm 2\%$  at  $0 \pm 1^\circ\text{C}$ . The yield of benzil in each case is larger than that for benzoic anhydride by a factor of 4.2 for the  $-42^\circ\text{C}$ . runs and 3.0 for the  $0^\circ\text{C}$ . runs. This preference for benzil suggests that it is the major product, where some intermediate can react with diphenylsulfide. Two additional observations should be noted: 1) the preference for benzil decreases as temperature increases; and 2) the preference of its formation is not absolute as the identity of the other products was not elucidated.

The effect of the trapping agent, diphenylsulfide, on benzil's production was also studied. Variations were made in the time of ozonation and the time elapsed before

Table 1:  
Percent Yield of Benzil and Benzoic Anhydride

Unknown	Spectra #	Temperature (°C) (+1°C)	Moles PhC≡CPh used ( $\pm 10^{-5}$ )	Benzil Absorbance (+0.02)	Moles Benzil ( $\pm 10^{-5}$ )	% Yield Benzil (+1%)	Benzoic Anhydride Absorbance (+0.02)	Moles Benzoic Anhydride ( $\pm 10^{-5}$ )	% Yield Benzoic Anhydride (+1%)	Total Yield (+2%)
1	I*	-42°C	$1.00 \times 10^{-3}$	0.376	$7.0 \times 10^{-4}$	70%	0.080	$1.2 \times 10^{-4}$	12%	82%
2	II	-42°C	$9.98 \times 10^{-4}$	0.330	$6.1 \times 10^{-4}$	61%	0.062	$9.0 \times 10^{-5}$	9%	70%
3	III	-42°C	$1.02 \times 10^{-3}$	0.287	$5.3 \times 10^{-4}$	52%	0.059	$8.8 \times 10^{-5}$	9%	61%
4	IV**	-42°C	$1.01 \times 10^{-3}$	0.331	$6.1 \times 10^{-4}$	60%	0.100	$1.5 \times 10^{-4}$	14%	74%
5	VI	-42°C	$1.00 \times 10^{-3}$	0.351	$6.4 \times 10^{-4}$	64%	0.116	$1.7 \times 10^{-4}$	17%	81%
6	VIII**	-42°C	$1.00 \times 10^{-3}$	0.309	$5.7 \times 10^{-4}$	57%	0.097	$1.4 \times 10^{-4}$	14%	71%
7	IX	0°C	$9.96 \times 10^{-4}$	0.254	$4.7 \times 10^{-4}$	47%	0.121	$1.7 \times 10^{-4}$	17%	64%
8	X	0°C	$1.01 \times 10^{-3}$	0.253	$4.7 \times 10^{-4}$	46%	0.117	$1.7 \times 10^{-4}$	10%	57%
9	XI	0°C	$9.99 \times 10^{-4}$	0.240	$4.4 \times 10^{-4}$	44%	0.079	$1.2 \times 10^{-4}$	12%	54%

\* done at 104 V. instead of 114 V.

\*\* benzoic acid present 1680 obscured

diphenylsulfide's addition. The results obtained are noted in table two. These indicate that the time of ozone exposure has little effect on the yield of benzil at  $-64^{\circ}\text{C}$ . and  $-42^{\circ}\text{C}$ .. Conversely, the elapsed time before trapping does have a significant influence. The longer the wait, the smaller the yield at both  $-42^{\circ}\text{C}$ . and  $-64^{\circ}\text{C}$ .. This last observation allows the conclusion that the yields of benzil in table one are maximums.

The catalytic, thermal decomposition of azibenzil (phenylbenzoyldiazomethane) occurs rapidly upon the addition of the copper catalyst. The reaction mixture remains orange in color throughout the decomposition, both in inert and oxygenated environments. Decomposition in the inert atmosphere proceeds through a carbene which rearranges to diphenylketene. (Wolff rearrangement) The diphenylketene may subsequently undergo reactions as indicated in figure twelve, page 15. The control runs mentioned in the experimental section, were designed to establish that the Wolff rearrangement is the only path followed in an inert atmosphere. Accordingly, when the decomposition product is treated with methyl alcohol, methyl diphenylacetate and any remaining diphenylketene should be the only products.

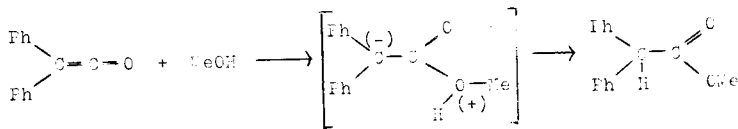


Figure 13: Addition of Methanol to Diphenylketene

Table 2:

Benzil Production After Variation in Times of Ozone Addition and Trapping Agent Addition

Sample #	Spectrum #	Temp. (+10C)	Ozonation Time (min+10sec)	Time Before Ph2S added(min) (+10sec)	Moles Ph2C≡C ( $\pm 10^{-5}$ )	Absorbance of Benzil (+0.01)	Moles of Benzil ( $\pm 10^{-5}$ )	% Yield of Benzil (+1%)	Amount of Benzilic Anhydride Present
10	XVIII	-42	10	2	$1.00 \times 10^{-3}$	0.305	$6.6 \times 10^{-4}$	66%	trace
11	XIX	-42	10	21	$1.01 \times 10^{-3}$	0.095	$1.8 \times 10^{-4}$	18%	~20% Benzil peak height
4	IV	-42	30	1	$1.01 \times 10^{-3}$	0.331	$6.1 \times 10^{-4}$	60%	substantial am't obscures Benzil peak
12	XX	-64	10	2	$9.95 \times 10^{-4}$	0.266	$4.9 \times 10^{-4}$	49%	trace
14	XXII	-64	10	21	$1.01 \times 10^{-3}$	0.174	$3.2 \times 10^{-4}$	32%	obscures Benzil peak
13	XXI	-64	30	1	$9.99 \times 10^{-4}$	0.239	$4.4 \times 10^{-4}$	44%	trace
acetone	XXIII	-42	10	2	-----	-----	-----	---	----

Treatment of the decomposition product with base should result in the diphenylketene forming a salt. (see figure 15) This would be evident by the disappearance of the diphenylketene peak from the gas chromatographic results.<sup>52</sup> The decomposition product's oxygen plus methanol treatment should result in the same product distribution as that from methanol treatment. This comes from the hypothesis that oxygen does not react with ketenes. Additional products may be observed however, in cases where the decomposition was not complete. Azibenzil would still be present and would be capable of carbene formation, which is then thought to react with oxygen to give benzoic anhydride and methyl diphenylacetate. (see figure 12) The gas chromatographic analysis of the above runs is presented in table three.

The identity of several peaks in table three may be specified. Peak four in run 54A is thought to be methyl diphenylacetate. This speculation is supported by a comparison of retention times with a pure sample and spiking with the same. Methyl diphenylacetate is also thought to be present in sample 51C, peak seven. This peak's area is substantially smaller in size than the comparable one in 54A. This result varies somewhat from the original hypothesis concerning base reaction with diphenylketene. The discrepancy may be accounted for by utilizing a longer base reaction time in this control.

Diphenylketene has been identified in all three of

Table 3

## Nitrogen Atmosphere Azibenzil Decomposition

51A - decomposition product

54A - decomposition product plus methanol

36B - decomposition product plus oxygen plus methanol  
(not listed due to irregularities in analysis procedures)

51C - decomposition product treated with 15% NaOH and methanol

<u>Run</u>	<u>Peak</u>	<u>Retention Time</u> (min $\pm$ 0.05)	<u>Area</u> (cm $^2$ $\pm$ 0.1)	<u>Content</u>
51A	1	0.62	trace	-----
	2	0.75	trace	-----
	3	1.50	trace	-----
	4	2.50	0.9	diphenylketene
	5	3.06	1.7	-----
	6	4.94	2.8	benzil
54A	1	0.62	0.3	-----
	2	0.69	0.2	methyl benzoate
	3	3.31	0.3	diphenylketene
	4	4.19	6.6	methyl diphenyl- acetate
	5	5.19	5.6	benzil
51C	1	0.56	trace	methyl benzoate
	2	0.62	trace	-----
	3	0.75	trace	-----
	4	1.50	0.2	-----
	5	2.69	0.2	diphenylketene

<u>Run</u>	<u>Peak</u>	<u>Retention Time</u> (min $\pm$ 0.05)	<u>Area</u> (cm <sup>2</sup> $\pm$ 0.1)	<u>Content</u>
510	6	3.0	3.3	-----
	7	3.91	.4	methyl diphenyl- acetate ?
	8	4.33	5.8	benzil ?

the above samples. The evidence supporting this conclusion is not absolute. Figure 13 shows the reaction between an alcohol and diphenylketone. The course of such a reaction may be followed by comparing samples 51A to 54A. The area of the designated diphenylketone peak in 51A undergoes a six-fold decrease upon the addition of methanol while at the same time a peak corresponding to methyl diphenylacetate is noted in 54A. These observations all serve to lend credibility to the diphenylketone assumption.

Peak four in 51A has been identified as benzil. This assignment comes from the comparison of the decomposition product's infrared spectrum (spectrum 13) with that of benzil.<sup>50</sup> (spectrum 14) Both spectra contain identical absorption bands. Further evidence comes from the comparison of the retention time of a pure benzil sample and spiking the decomposition product with the same. The former comparison has been extended to samples 54A and 51C. The result of this comparison is the conclusion that benzil is probably present in both samples.

The presence of benzil is inconsistent with the proposed inert atmosphere decomposition reaction. Two conclusions may be drawn from this: 1) the azibenzil synthesized has benzil as an impurity, or 2) oxygen is entering the reaction system during the decomposition. The former is not the case as a comparison of benzil's infrared spectrum with that of azibenzil indicates that benzil is not present



in the latter. (A 2% benzil impurity is estimated, see Appendix II, spectra 14 and 15.) The above "oxygen leak hypothesis" would also account for the presence of a methyl benzoate peak in 54A as determined by spiking and retention time comparison. Further evidence for this hypothesis comes from considering the products from run 36B. Although not listed due to irregularities in the gas chromatograph conditions, run 36B exhibits similar features to the "oxygen leak" run, 54A. Specifically, a benzil and a methyl benzoate peak are noted as being present due to unreacted azibenzil being in solution.<sup>53</sup>

Azibenzil decomposition performed under oxygen conditions gave results that differ from the nitrogen runs. Specifically, benzoic anhydride, (measured as methyl benzoate) and benzil were produced. This is a situation that should not occur in the uninterfered Wolff rearrangement. To illustrate this point observe the product distribution of run 744 performed under two atmospheres of oxygen.

Diphenylketene's, benzil's and methyl diphenylacetate's identification was accomplished through employing the proofs utilized for the control runs. Methyl benzoate has been identified in samples 441 and 443. This determination was yielded by comparing an original sample with the experimental run. Tanaka et. al. have suggested two additional azibenzil decomposition products.<sup>34</sup> The first of these is tetraphenylglycolide, a cyclic diether possessing a characteristic in-

Table 4: Run 44 - 2 atmospheres oxygen

44A - final product

44B - final product + MeCH (2x conc. of 44A and C)

44C - final product + MeCH + MeCH

44D - Benzil

44E - methyl benzoate

44F - methyl diphenylacetate

Run	Peak	Retention Time (min±0.05)	Area (cm <sup>2</sup> ±0.1)	Concentration (mole liter <sup>-1</sup> )	Content
44A	1	0.62	trace		
	2	1.44	trace		
	3	2.56	trace		
	4	3.00	1.4		diphenyl- ketene
	5	4.91	1.4		
	6	0.47	1.1	6.2x10 <sup>-3</sup>	benzil
44B	1	0.56	4.05	2.5x10 <sup>-2</sup>	methyl benzoate
	2	1.81	trace		
	3	2.56	0.7		diphenyl ketene
	4	2.91	2.4		
	5	3.81	3.3	1.7x10 <sup>-2</sup>	methyl diphenyl- acetate
	6	4.75	11.4	7.3x10 <sup>-2</sup>	benzil
44C	1	0.64	0.6	5.5x10 <sup>-3</sup>	methyl benzoate
	2	1.54	0.6		

<u>Run</u>	<u>Peak</u>	<u>Detection Time</u> (min $\pm$ 0.05)	<u>Area</u> (cm $\pm$ 0.1)	<u>Concentration</u> (mole liter $^{-1}$ )	<u>Content</u>
440	3	2.91	6.0		diphenyl- ketene
	4	3.25	1.1		
	5	4.10	1.5	$5.1 \times 10^{-3}$	methyl diphenyl- acetate
	6	5.25	7.0	$4.0 \times 10^{-2}$	Benzil
	7	6.61	0.2		?dimer?
440	1	4.80	27.0	0.442%	Benzil
447	1	3.80	111.6	0.5002%	methyl diphenyl- acetate
447	1	0.62	90.2	0.799%	methyl benzoate

frared absorption at  $1750\text{ cm}^{-1}$ .

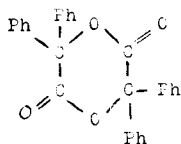


Figure 14: Tetraphenylglycolide

A  $1750\text{ cm}^{-1}$  absorption has been noted in the decomposition product's infrared spectrum. (appendix II, spectrum #1C) This suggests that tetraphenylglycolide may possibly be present. Bis-benzilketazine was the second decomposition product Tanaka et. al. suggested.<sup>34</sup>

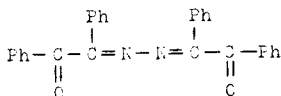


Figure 15: Bis-Benzilketazine

There are no literature references listing the spectra of the above compound, though it is known to exist.<sup>54</sup> The azibenzil decomposition analysis suggests that if the aforementioned compounds are indeed present, they probably have retention times corresponding to 1.5 and three minutes. Peaks with these retention times occur in every run with no change due to the addition of methyl alcohol or base. (see

appendix III) Considering the structures of the proposed compounds such an observation is not inconsistent with their presence.

As noted in table four, the decomposition product was worked up in two manners. The first, methanol addition, was utilized to facilitate the separation of the decomposition's various components. One notes that if the azibenzil decomposition follows the paths proposed in figure twelve, all the products obtained would be of comparable molecular weight. This molecular weight similarity would result in nearly identical retention times and thus a poor gas chromatographic separation. The methanol addition results are given in table six.

Table six shows that benzil, methyl benzoate and methyl diphenylacetate account for only  $38 \pm 1\%$  of the initial azibenzil concentration. This, plus the lack of identification of the other decomposition products, makes difficult any calculations with respect to the favored path for the oxygen atmosphere decomposition. However, tables five and six do indicate the presence of two trends.<sup>55</sup> There are methyl diphenylacetate's and methyl benzoate's dependence on pressure. As the pressure increases, the methyl benzoate concentration increases. Conversely, the methyl diphenylacetate concentration decreases as the pressure increases. There is no noticeable trend for benzil.

Table 5: Methyl Benzoate versus Methyl Diphenylacetate

Run	Oxygen Pressure (atm, $\pm 0.01$ atm)	Area Diphenylketene ( $\text{cm}^2$ , $\pm 0.1$ )	Area Methyl Benzoate ( $\text{cm}^2$ , $\pm 0.1$ )	Area Methyl Diphenylacetate ( $\text{cm}^2$ , $\pm 0.1$ )	Area Methyl Benzoate Area Diphenylketene + Area Methyl Benzoate ( $\pm 0.3$ )
51B	0	2.0	$\sim 0$	9.2	$\sim 0$
42B	0.2	0.3	2.4	9.2	0.25
48B	1.0	trace	3.1	3.1	1.0
45B*	2.0	0.6	5.1	2.9	1.5
47B	4.0	0.3	6.7	0.5	8.4

\* an average of runs 44B and 45aB

Table 6

## Decomposition Product Plus Methanol

Run	Pressure Oxygen (atm) (+0.01atm)	Concentration of Azibenzil Solution (mole liter <sup>-1</sup> ) (+0.0002)	Area of Diphenyl- ketone remaining (cm <sup>2</sup> , $\pm$ .1)	Concentration of Methyl benzoate (mole, liter <sup>-1</sup> ) (+0.0002)	Concentration of Benzil (mole, liter <sup>-1</sup> ) (+0.0002)	Concentration Methyl di- phenylacetate (mole, liter <sup>-1</sup> ) (+0.0002)	Sum of Products (mole, liter <sup>-1</sup> ) (+0.0006)
51E <sup>56</sup>	0.0	0.271	2.0	0.0	0.0	0.0485	0.0485
42E	0.2	0.2708	0.3	0.0147	0.0384	0.0476	0.1007
49E	1.0	0.2730	trace	0.0193	0.128	0.0158	0.1631
44E	2.0	0.2704	0.7	0.025	0.0731	0.0169	0.1150
45aE	2.0	0.2698	0.4	0.0375	0.0855	0.0129	0.1359
52E	3.0	0.2705	1.6	0.0216	0.0332	0.0034	0.0582
47E	4.0	0.2706	0.3	0.0410	0.0543	0.0025	0.0978

average concentration of azibenzil solution: 0.2709M  $\pm$  0.0002Maverage sum of products: 0.1027M  $\pm$  0.0006Mpercent known products comprise of initial solution: 38%  $\pm$  1%

The second decomposition product work up was treatment with a 15% sodium hydroxide solution. Addition of base to the decomposition product should result in diphenylketene and any acidic precursors forming their respective salts. This is the expected result, provided that the decomposition proceeds via the scheme presented in figure twelve. The following illustration depicts diphenylketene's reaction with base.

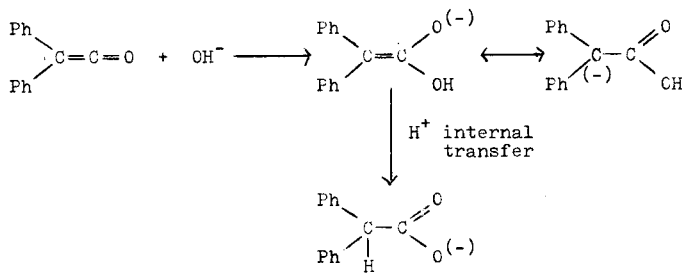


Figure 16: Diphenylketene reaction with base

Salt formation may be followed by observing the size of the peaks produced by gas chromatographic analysis. If a compound or its precursor forms a salt, there will be a decrease in the compound's peak area. The results for base addition to the decomposition product are presented in table seven.

Table seven indicates that substantial reductions do occur in the methyl benzoate and diphenylketene concentrations. Methyl diphenylacetate's concentration, on the other hand,



differs only slightly from that of the non-base treated samples. (see table seven) This last observation indicates that either the diphenylketene reacts slowly with base, or esterification is preferable to salt formation. The former may be remedied by allowing a longer reaction time or increasing the base's concentration. Returning to the methyl benzoate observations, there is indication that an acidic precursor is involved in its formation.

The precursor appears to be benzoic anhydride as infrared analysis has verified its presence in the decomposition product. (Appendix II, spectra #16 and #17) Additional evidence is provided by comparing the gas chromatographic separation of the decomposition product with that of the decomposition product plus methanol. **Anhydrides** are known to react with alcohols to produce esters. Methyl benzoate does not appear in the decomposition product, but does when the sample is treated with methanol. This observation aids the substantiation of the benzoic anhydride claim.

Table 7

Decomposition Product Treated with Base and Methanol<sup>55</sup>

Run	Oxygen Pressure (atm)	Concentration of Azibenzil Solution (mole, liter <sup>-1</sup> ) (+0.0002)	Area of Diphenylketene before base addition (cm <sup>2</sup> +0.1)	Area of Diphenylketene remaining (cm <sup>2</sup> +0.1)	Concentration of Methyl benzoate (mole liter <sup>-1</sup> ) (+0.0002)	Concentration of Benzil (mole liter <sup>-1</sup> ) (+0.0002)	Concentration of Methyl diphenylacetate (mole liter <sup>-1</sup> ) (+0.0002)
51C	0	0.2710	0.2	0.2	~ 0	~ 0	0.0076
42C <sup>60</sup>	0.2	0.2708	2.2	0.2	0.0022	0.0095	0.0088
48C	1.0	0.2730	3.7	0.2	0.0024	0.0882	0.0074
44C	2.0	0.2704	1.4	0.3	0.0052	0.0402	0.0051
45aE	2.0	0.2698	3.5	1.0	trace	0.0173	0.0051
52C	3.0	0.2705	0.2	0.2	0.0055	0.0455	0.0076
47C	4.0	0.2706	3.3	0.1	0.0018	0.0425	0.0073

### DISCUSSION

$\alpha$ -Diazoketone decomposition yields primarily rearranged products. These products are commonly ketenes (B) and the rearrangement process is referred to as the Wolff rearrangement.<sup>44</sup>

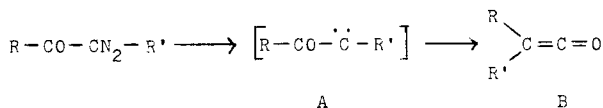


Figure 17: Wolff Rearrangement

Wolff rearrangement involves the loss of nitrogen followed by alkyl or aryl group migration.<sup>44</sup> Considerable work has been done to elucidate the exact nature of this mechanism since its 1912 introduction. Most agree that the pathway involves ketocarbene (A) formation followed by rearrangement to the ketene. (figure 17)

The use of carbene terminology exists primarily due to the lack of contrary evidence.<sup>44</sup> There is no recent literature refuting the ketocarbene intermediate and all appear to assume its existence. Davis and Preston as well as Murray and Suzui suggest that the carbene produced is in the triplet state for alkyl diazo cases.<sup>21,62</sup> The  $\alpha$ -keto-carbene intermediate is thought to be somewhat different. The presence of an adjacent carbonyl group to the electron deficient carbon, can cause perturbations to the carbene-alkyl orbital system. This may result in the preferred state being

the singlet rather than the triplet.

Ketene production from  $\alpha$ -diazoketones was first confirmed by diphenylketene's preparation from azibenzil.<sup>44,63</sup> Other stable ketenes have been similarly synthesized since this time.<sup>64</sup> Ketene production is thought to occur by the  $\alpha$ -ketocarbene undergoing an intramolecular reaction.<sup>44</sup> Ketenes are known to undergo a number of reactions. For example, reaction with alcohols yields esters, while with water acids are produced.<sup>44</sup>

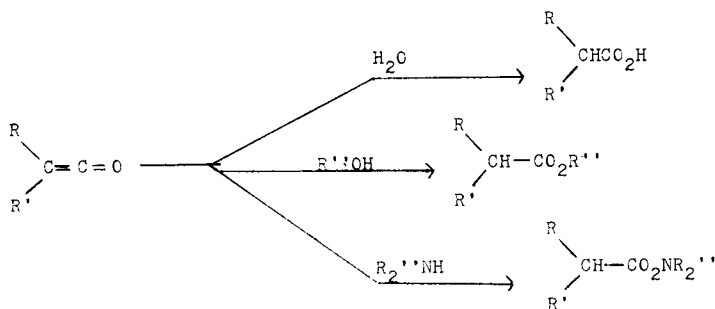
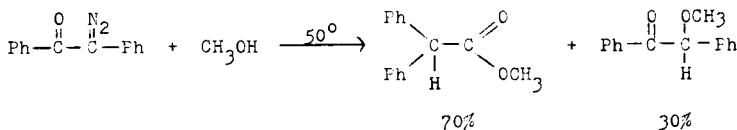


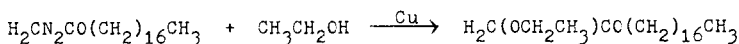
Figure 18: Ketene Reactions

Ketenes are the  $\alpha$ -diazoketone decomposition's primary product in a majority of cases. There are, however, instances in which Wolff rearrangement does not occur exclusively. The literature suggests two general categories in which the diazo group replacements occurs without rearrangement.<sup>44</sup> The first of these is in the presence of protic solvents at

moderate temperatures.<sup>44</sup> For example;



In the above case, methyl diphenylacetate is the rearranged product while methyl benzoin is the unrearranged product. The second category of incomplete rearrangement is in the presence of copper powder or salts.<sup>35</sup>



There is no rearranged product produced in the above example. Ethanol's and copper's presence are held responsible. The exact role that copper plays here has not been determined. However, it is recognized that copper does possess catalytic properties.

Contineau et. al. have proposed that nitrogen removal from the diazoketone is the decomposition's rate determining step.<sup>37</sup> Accordingly, Yates has suggested that copper may catalyze this removal through interaction with its available valence electrons.<sup>35</sup> It is not known whether or not the ketocarbene remains independent of the copper or is bound to it. In the latter situation, copper would serve to complete the octet around the electron deficient carbon, thus stabilizing it. Once formed, the ketocarbene may go

to either the rearranged or unrearranged products. Unrearranged product formation is thought to involve an attack of the ketocarbene (bound or unbound) by the unshared pair of electrons on a nucleophilic oxygen (or a similar molecule).

The introduction suggested that in an oxygen atmosphere  $\alpha$ -diazoketone decomposition may form an acyl carbonyl-oxide intermediate (figure 12). If such a formation occurs, it will provide precedent for the existence of a similar intermediate in alkyne ozonolysis. Carbonyl oxides, in analogous systems, are known to react to give dimeric ketone peroxides. Bartlett and Traylor have isolated a dimeric benzophenone peroxide.<sup>61</sup> This compound was produced by decomposing diphenyldiazomethane,  $\text{Ph}_2\text{CN}_2$ , via exposure to ultraviolet light or moderate temperatures. The dimeric benzophenone's presence indicates that alkyl diazo compound decomposition produces carbonyl oxides. Murray and Suzui also confirm this statement. They report the trapping of a ozonide from diphenyldiazomethane's photolysis in the presence of oxygen and aldehydes.<sup>21</sup> The ozonide is thought to be formed from the reaction of a carbonyl oxide with an aldehyde. In a later article, Murray and Suzui used isotope effect studies to confirm the carbonyl oxide's presence.<sup>60</sup> These studies were also utilized to refute the suggestion that a diradical interaction was involved in the ozonolysis mechanism. There is, however, no denial that the diradical may be present in the carbene case. In fact Murray and Suzui

hypothesize that the diradical species is formed first, with a portion going on to populate the dipolar form, as illustrated in figure 19.<sup>21</sup>

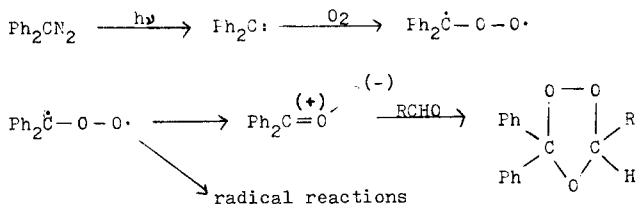


Figure 19: Czonide Formation from Diphenyldiazomethane

It should be recognized that the photodecomposition reaction results are generally assumed to resemble those of the thermal runs.<sup>34</sup> This generalization permits comparison between the above diazomethane systems and the  $\alpha$ -diazoketone one.

Azibenzil (phenylbenzoyldiazomethane) is the  $\alpha$ -diazoketone utilized in the following discussion. The experimental section indicates that analysis work was done on both the untreated decomposition product and that treated with methyl alcohol. The former's analysis yielded a five to six peak average. Benzil and diphenylketene have been identified as being two of these peaks. Additional analysis, using infrared spectrometry and basic studies, confirmed benzoic anhydride's presence in the untreated samples. A six peak average was yielded from the methyl alcohol treated decomposition product. Four of these peaks have been identified: benzil, di-

phenylketene, methyl benzoate and methyl diphenylacetate. Methyl diphenylacetate's presence confirms the diphenylketene designation, as ketenes form esters in an alcohol's presence. Similarly, methyl benzoate's presence helps substantiate benzoic anhydride's existence in the untreated sample. (see page 41)

The identification of the above compounds indicates that Wolff rearrangement is occurring as well as the production of non-rearranged materials. The latter is of concern, as it was noted that diphenylacetylene ozonolysis produced the same products: benzil and benzoic anhydride. The ozonolysis work indicates that the precursor involved is at a maximum concentration at  $-42^{\circ}\text{C}.$ , the temperature at which benzil and benzoic anhydride production is also at a maximum.<sup>40</sup> (73  $\pm$  2% yield) Hull and Jackson suggest that this ozonolysis intermediate is an acyl carbonyloxide or a acyclic dioxetene. Since diazo compounds yield analogous carbonyl oxides upon decomposition, one may arrive at the conclusion that the intermediate involved in both cases is similar, if not identical.<sup>21,60,61</sup>

Tanaka et. al. have done oxygen atmosphere decomposition studies on the azitenzil system without the use of a copper catalyst.<sup>34</sup> Three products were identified: tetraphenylglycolide 40%, diphenylacetic acid 21%, and big-benzilketazine 15%. Benzil and peroxides are specifically noted by Tanaka et. al. as not being present. Additionally there



is no diphenylketene or benzoic anhydride reported. Diphenylketene's absence may be accounted for by assuming complete reaction and that water was added to the system to isolate the diphenylketene as diphenylacetic acid. In identifying their products, Tanaka et. al. proposed a pathway via which the dimeric tetraphenylglycolide may be formed.<sup>34</sup> They suggest that a  $\text{Ph}\ddot{\text{C}}\text{COR}$  type ketocarbene, generated from the corresponding  $\alpha$ -diazoketone, reacts with molecular oxygen, followed by R migration. This mechanism does include an acyl carbonyloxy as a possible intermediate following the oxygen addition. There is however, no mention of any alternative reaction products from such an intermediate.<sup>34</sup>

The tetraphenylglycolide reported above was not identified in the copper catalyzed run, although it is suspected to be present.

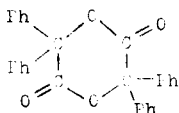


Figure 20: Tetraphenylglycolide

Conversely, benzil and benzoic anhydride were noted by us and not by Tanaka. This difference in products may be explained in terms of spin multiplicity. It has previously been suggested that the ketocarbene produced during azibenzil decomposition is in the singlet state. If this is the case,

then the triplet oxygen attack on the ketocarbene should yield a triplet, acyl carbonyloxy, due to spin multiplicity conservation. Triplets are known to behave like diradicals. Accordingly, dimerization is the preferred triplet reaction rather than internal bond formation. The predominance of dimerization amongst triplets is attributed to the triplet's nature. Triplets possess two unpaired electrons with the same spin. The Pauli Principle states that two unpaired electrons possessing identical spins may not occupy the same orbital. The implication here is that intramolecular coupling is prohibited unless intersystem crossing can occur. Intersystem crossing results in the transition from one energy state to another one, i.e. in this case from a triplet to a singlet. Heavy metals have long been known to promote this relaxation process. Accordingly, it may be hypothesized that the copper catalyst's presence allows singlet acyl carbonyloxy to be formed as well as triplet acyl carbonyloxy. Singlets are defined as having paired electrons of opposite spins. The spin difference permits the electrons to occupy the same orbital and therefore internal rearrangement may occur.

The preceding explanation of triplet versus singlet behavior accounts for the azibenzil decomposition products observed in both the catalyzed and non-catalyzed decomposition. Triplet acyl carbonyloxy is produced upon oxygen's reaction with the  $\alpha$ -ketocarbene. In the absence of any means for

intersystem crossing (i.e. the presence of a heavy metal) the triplet acyl carbonyl oxide will most likely dimerize. Tetraphenylglycolide thus, is the only expected product. When the decomposition is copper catalyzed, the copper provides a readily available means of intersystem crossing. Singlet and triplet acyl carbonyl oxide are thus both present. The latter should form tetraphenylglycolide while the former may undergo intramolecular reaction to form either benzil or benzoic anhydride. Further work needs to be done to ascertain whether tetraphenylglycolide is present in the catalyzed decomposition.

Benzil and benzoic anhydride were noted earlier as being diphenylacetylene's ozonolysis products. Czone's (a singlet) reaction with alkynes should yield a singlet intermediate. (probably acyl carbonyl oxide) This evidence supports the previous contention that a singlet intermediate is responsible for benzil's and benzoic anhydride's formation. No tetraphenylglycolide has been identified in the ozone reaction. The ozonolysis results also imply that the copper catalyst is probably responsible for providing an intersystem crossing mechanism. All this would help to explain the difference in results between Tanaka's and our system.

Bis-benzilketazine has not been identified from any azibenzil decomposition systems other than Tanaka et. al.<sup>34</sup> Contineau et. al. contend that a secondary reaction between the ketocarbene intermediate and an undecomposed molecule is

highly unlikely.<sup>27</sup> The evidence for this statement comes from thermal kinetic studies on azibenzil in the absence of a catalyst and oxygen. (The latter is the sole condition differing from Tanaka et. al., but considering the compound under discussion, should be of no significance.) Measurement of the moles of nitrogen produced during decomposition corresponds quantitatively to the theoretical value according to the stoichiometry of ketocarbene formation. These quantitative results lead to the above statement. No conclusion may be drawn from these contrary pieces of evidence, though intuitively the Contineau et. al. work seems to be more precise.

Benzil's, benzoic anhydride's and methyl diphenylacetate's formation warrants further consideration. As noted in an earlier section benzoic anhydride (in the form of methyl benzoate) production increases with oxygen pressure while that of methyl diphenylacetate decreases. These trends are significant by themselves, yet once the unidentified products are known and their concentration changes can be followed, the degree of preference for Wolff rearrangement may be determined more precisely. The actual benzil and benzoic anhydride production may be explained by their intermediate's stereochemistry.

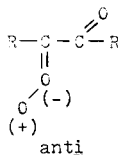
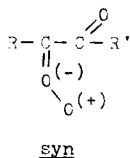


Figure 21: Stereochemistry of acyl carbonyloxide

The exact nature of benzoic anhydride's precursor is not known. Figure ten suggests that a bicyclic intermediate may be involved.<sup>40</sup> Figure 22 indicates that such a cyclized compound can only arise from the syn form of acyl carbonyloxide.

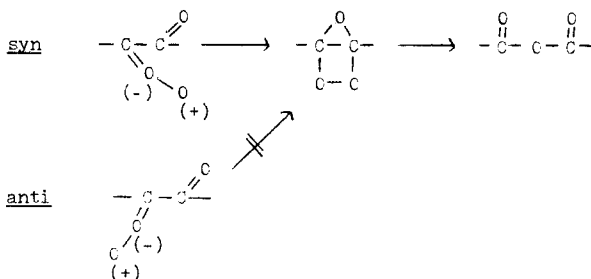


Figure 22: Formation of a cyclic anhydride intermediate

The syn isomer has its oxygens in close proximity to the carbonyl carbon, and thus may form a ring with a minimum amount of strain. Conversely, the anti acyl carbonyloxide possesses a configuration where cyclization is not possible

due to the large strain that would result in the ring. The predicted result is that the anti may lose an oxygen in preference to cyclization, forming benzil.

FUTURE WORK

A complete identification of azibenzil's decomposition products, from both thermal and photolytic decomposition, is necessary to clarify speculation concerning the intermediate. Specifically one needs to know whether or not tetraphenylglycolide is present and in what quantities. The latter will aid in defining the trends noted from increasing oxygen pressure as well as the extent of intersystem crossing promoted by copper. Intersystem crossing is of major significance, as it provides evidence for hypotheses concerning the intermediate's reactivity. Work utilizing both catalyzed and non-catalyzed conditions should further clarify this point. Decomposition utilizing singlet oxygen should be even more helpful, as the non-catalyzed case would be expected to produce only singlet products. This in turn may be compared to alkyne ozonolysis where the intermediate should also produce products resulting from a singlet state.

REFERENCES

1. J. Telew, "Oxidation," Marcel Dekker, New York, 1969, p. 259.
2. F. Bailey, E. Painthia and I. Auckire, J. Am. Chem. Soc., **22**, 1136 (1960).
3. F. Bailey and A. Lane, J. Am. Chem. Soc., **22**, 4473 (1967).
4. R. Huisgen, Angew. Chem., **2**, 565 (1960).
5. R. Criegee, Chem. Ber., **22**, 669 (1960).
6. S. Fliszar and J. Charles, Can. J. Chem., **47**, 3921 (1969).
7. R. Murray, Acc. Chem. Res., **1**, 319 (1968).
8. R. Criegee, Angew. Chem. Internat. Ed., **14**, 745 (1975).
9. S. Fliszar and W. Granger, J. Am. Chem. Soc., **22**, 3361 (1970).
10. R. Murray and D. Higley, J. Am. Chem. Soc., **25**, 7886 (1973).
11. R. Lattimer, R. Kuczkowski and C. Gillies, J. Am. Chem. Soc., **26**, 342 (1974).
12. R. Criegee, Rec. Chem. Progr., **12**, 111 (1957).
13. N. Pauld, J. Thompson, T. Hudson and I. Bailey, J. Am. Chem. Soc., **20**, 1822 (1968).
14. G. Klopman and D. Joiner, J. Am. Chem. Soc., **27**, 5287 (1975).
15. G. Hamilton and R. Reay, J. Am. Chem. Soc., **27**, 6876 (1975).
16. W. DeNore and C.L. Lin, J. Org. Chem., **32**, 925 (1973).
17. W. DeNore, Int. J. Chem. Kin., **3**, 161 (1971).
18. Cis-trans isomerization also occurs for a total of six products with 1,2 disubstituted alkenes.
19. D. Williamson and D. Cvatanovic, J. Am. Chem. Soc., **20**, 4248 (1968).
20. W. Lederer and R. Criegee, Ann., **11**, 454 (1959).
21. R. Murray and A. Suzui, J. Am. Chem. Soc., **25**, 2343 (1973).



22. F. Bailey and S. Lath, J. Am. Chem. Soc., **79**, 3120 (1957).
23. R. Criegee, Advances in Chemistry Series, **21**, 133 (1959).
24. F. Bailey, Y. G. Chang and M. Kwie, J. Org. Chem., **27**, 1193 (1962).
25. L. Durham and P. Greenwood, Chem. Commun., **16**, 844 (1967).
26. G. Klopman, "Chemical Reactivity and Reaction Path," John Wiley and Sons, New York, 1974, p. 142.
27. I. Story, J. Alford, M. Ray and J. Burgess, J. Am. Chem. Soc., **93**, 3044 (1971).
28. I. Story, J. Alford, J. Burgess and M. Ray, J. Am. Chem. Soc., **93**, 3042 (1971).
29. N.J. Furro, V. Ramanurthy, H.T. Liu, A. Krebs and R. Kempton, J. Am. Chem. Soc., **98**, 6758 (1976).
30. R.H. Keay and G.A. Hamilton, J. Am. Chem. Soc., **98**, 6578 (1976).
31. M. Regitz, Tetrahedron Letters, **22**, 1403 (1964).
32. A.H. Blatt, ed. "Organic Syntheses," Vol. 2., John Wiley and Sons, New York, 1943, p. 496.
33. A.H. Blatt, ed. "Organic Syntheses," Vol. 3., John Wiley and Sons, New York, 1955, p. 356.
34. Y. Tanaka, T. Nagai and F. Kohara, J. Org. Chem., **28**, 8, 1602 (1973).
35. F. Yates, J. Am. Chem. Soc., **74**, 5376 (1952).
36. J.C. Newman and F.R. Seal III, J. Am. Chem. Soc., **72**, 5161 (1950).
37. M. Pontineanu, T. Olgescu and R. Schindler, Rev. Roumaine de Chimie, **18**, 4, 577 (1973).
38. M. Pontineanu, T. Olgescu and R. Schindler, Rev. Roumaine de Chimie, **18**, 5, 753 (1973).
39. Langreke, "Theory and Practice in the Organic Laboratory," p. 362.
40. J.A. Hull and D. Jackson, J. Org. Chem., **41**, 3540 (1976).

41. All of the NMR work was done on a Hitachi-Perkin Elmer R24A, while the IR and UV-Vis were carried out on a Perkin Elmer 237 and a Cary 110 respectively.
42. A. L. Crozzolo, Acc. Chem. Res., **1**, 329 (1968).
43. In all of the below runs the conditions utilized were as follows: Column 1, 2 microliter injection, 200 amp bridge current, injector 250°C., detector 245°C., column 195°C., 1 inch per minute, attenuation x1, solvent: benzene.
44. J. Kirmse, "Organic Chemistry: A Series of Monographs," Vol. 1., A.T. Florquist ed., Academic Press, New York, 1964, p. 115.
45. The Column was four feet by 1/4 inch of 151 DC-200 on Chrom-F, 80/100 mesh, with a maximum temperature of 250°C.
46. F.S. Bailey, Chem. Rev., **52**, 925 (1958).
47. The rate of ozone production was  $5.9 \times 10^{-4}$  mole/min..
48. A 12.5% solution of diphenylsulfide was used as the trapping agent.
49. A PE-237 infrared spectrometer was used.
50. See appendix II.
51. 51A is 50% less concentrated than 54A.
52. Salts do not give rise to peaks in gas chromatographic analysis.
53. The significance and identification technique used for this peak will be explained at a later point.
54. J. Ritter and G. Niedeman, J. Am. Chem. Soc., **51**, 3583 (1929).
55. One important factor must be taken into consideration when reviewing this table. The temperature for the elevated pressure runs may vary by as much as 70°C from run to run. This is do to the nature of the heating tape used and therefore may result in inconsistencies in the data.
56. Assuming that in the case of no oxygen leak, the concentrations of benzil and methyl benzoate are zero.
57. Not stirred for one hour and heated.

58. F. Yates and T.J. Clark, Tetrahedron Letters, 13, 425 (1961).
59. R.T. Morrison and R.V. Boyd, "Organic Chemistry, 3rd Ed.," Allyn and Bacon, Inc., Boston, 1973.
60. R.W. Murray and A. Suzui, J. Am. Chem. Soc., 23, 4963 (1973).
61. F.D. Bartlett and T.G. Traylor, J. Am. Chem. Soc., 84, 3408 (1962).
62. H.G. Preston, Jr. and J.C. Davis, Jr., J. Am. Chem. Soc., 88, 1504 (1966).
63. G. Schroeter, Ber. deut. Chem. Ges., 42, 2336 (1909).
64. H. Staudinger and K. Hirzel, Ber. deut. Chem. Ges., 49, 2522 (1916).
65. V. Franzen, Ann., 614, 34 (1958).
66. M. Kirtse, L. Korner and K. Hoffmann, Ann., 614, 22 (1958).
67. The 10-900 gas chromatograph was equipped with a 6' x 1/8" column, made up of 10% K20F. The conditions utilized were: injector 200°C, manifold 200°C, flow 35, FID mode, attenuation x 64 and the amplifier range x 100. The program utilized was 70-125°C with a two minute initial, four minute final and a rate of 12°C per minute.

#### Appendix I Details of Ozonolysis

This appendix presents the details of diphenyl-acetylene ozonolysis as referred to in the experimental section.

#### Standardization of the Welbach Model T-408 Ozonator

The determination of the Welbach Ozonator's ozone production was accomplished via the use of a FE-900 gas chromatograph. Stock solutions of dodecane and 1-decene were injected into the gas chromatograph and their relative peak heights noted.<sup>67</sup> From this data a standardization curve was constructed to be utilized in the final determination of ozone production. A 0.146% dodecane and 1-decene solution was placed in the ozonator's reaction vessel and equilibrated to the desired temperature. Ozone was then run through the mixture for two minutes, after which the mixture was allowed to equilibrate to room temperature. A one microliter sample was injected into the gas chromatograph and the remaining amount of 1-decene calculated.<sup>49</sup> This procedure was varied by changing the reaction mixture's temperature and/or the ozonator's power or rate of flow. The production rate observed was calculated in moles per minute.

Table 8: Standardization Curve of Dodecane and 1-Decene

Sample	Concentration dodecane (mole/1.±5%)	Concentration 1-decene (mole/1.±5%)	Area dodecane (cm <sup>2</sup> , ±10%)	Area 1-decene (cm <sup>2</sup> , ±10%)	Area 1-decene area dodecane (±10%)
1	0.149	0.0149	7.13	0.59	0.0822
2	0.149	0.0298	6.65	0.93	0.140
3	0.149	0.0447	5.79	1.44	0.249
4	0.149	0.0596	6.46	2.10	0.325
5	0.149	0.0745	6.50	2.64	0.406
6	0.149	0.0894	5.84	2.75	0.471
7	0.149	0.104	5.18	2.91	0.562
8	0.149	0.119	4.11	2.67	0.650
9	0.149	0.134	6.11	4.61	0.754

UN82 SAWYER, J.A. THE DECOMPOSITION OF PHENYL-, etc.  
S271d/1977 Chemistry HRS. 3/77 2 of 2



Table 9: Ozone Production

Flow: 0.6	Units: mole/minute $\pm$ 10%			
Temperature power	-27°C.	-42°C.	-62°C.	Average
114V.	$6.4 \times 10^{-4}$	$7.0 \times 10^{-4}$	$4.5 \times 10^{-4}$	$5.9 \times 10^{-4}$
90V.	$5.9 \times 10^{-4}$	$3.9 \times 10^{-4}$	$5.1 \times 10^{-4}$	$4.8 \times 10^{-4}$
57V.	$1.9 \times 10^{-4}$	$1.1 \times 10^{-4}$	$1.9 \times 10^{-4}$	$1.6 \times 10^{-4}$
Power 114V. Flow				
0.6	$6.4 \times 10^{-4}$	$7.0 \times 10^{-4}$	$4.5 \times 10^{-4}$	$5.9 \times 10^{-4}$
0.2	$8.7 \times 10^{-4}$	$7.6 \times 10^{-4}$	$8.9 \times 10^{-4}$	$8.4 \times 10^{-4}$

Table 10: Coolant Baths

Temperature	Solvent	Coolant
$0^{\circ} \pm 1^{\circ}$	water	ice
$-42^{\circ} \pm 2^{\circ}$	acetonitrile	liquid nitrogen
$-64^{\circ} \pm 2^{\circ}$	chloroform	liquid nitrogen

Table 11: Standardization of Benzil and Benzoic Anhydride on I.R.

Absorption v.s. Concentration

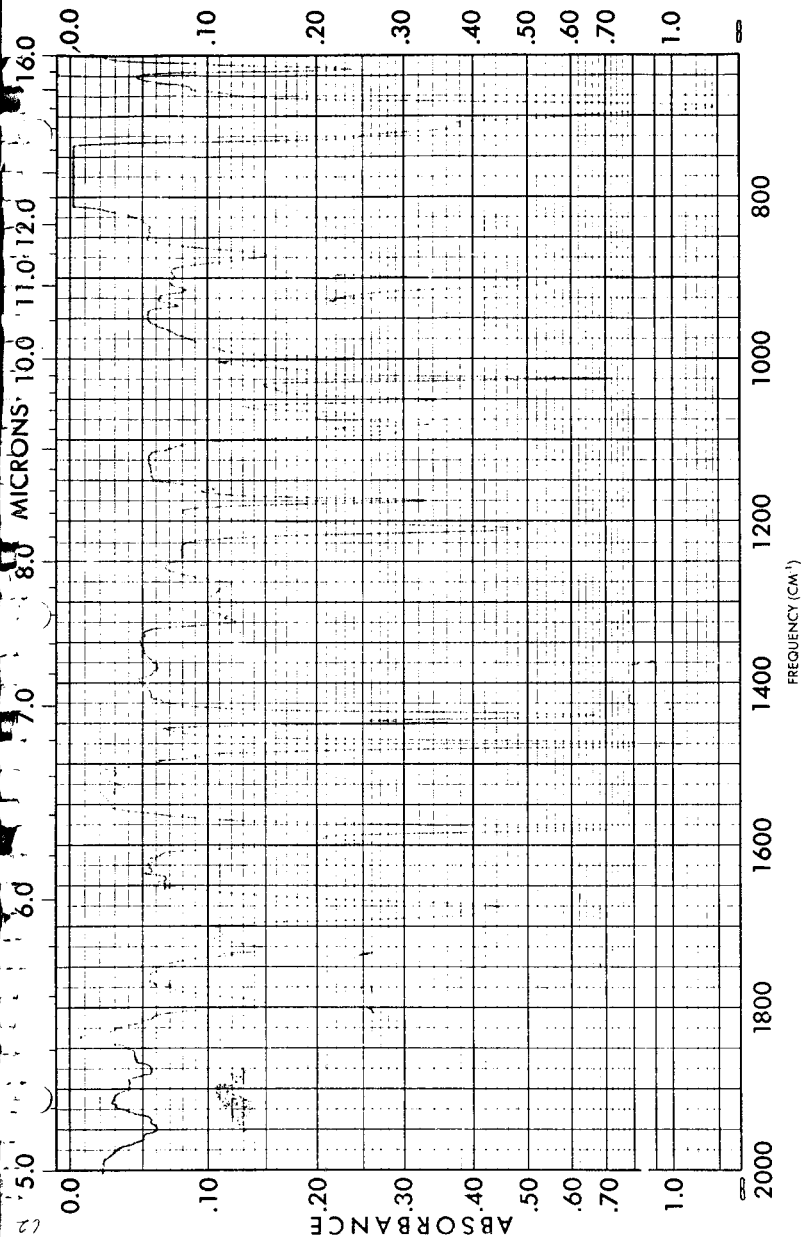
Substance	Concentration (mole/liter) $\pm 2\%$	Spectra #	Band $\text{cm}^{-1}$	Absorbance
Benzil	0.0501	2	1680	0.267
Benzil	0.0400	3,15	1680	0.197, 0.220
Benzil	0.0300	4	1680	0.171
Benzil	0.0200	5	1680	0.107
Benzil	0.100	13	1680	0.540
Benzoic Anhydride	0.0510	8	1800	0.348
Benzoic Anhydride	0.0408	9	1800	0.265
Benzoic Anhydride	0.306	10	1800	0.203
Benzoic Anhydride	0.0204	11	1800	0.138
Benzoic Anhydride	0.0102	12	1800	0.065
Benzoic Anhydride	0.107	14	1800	0.634



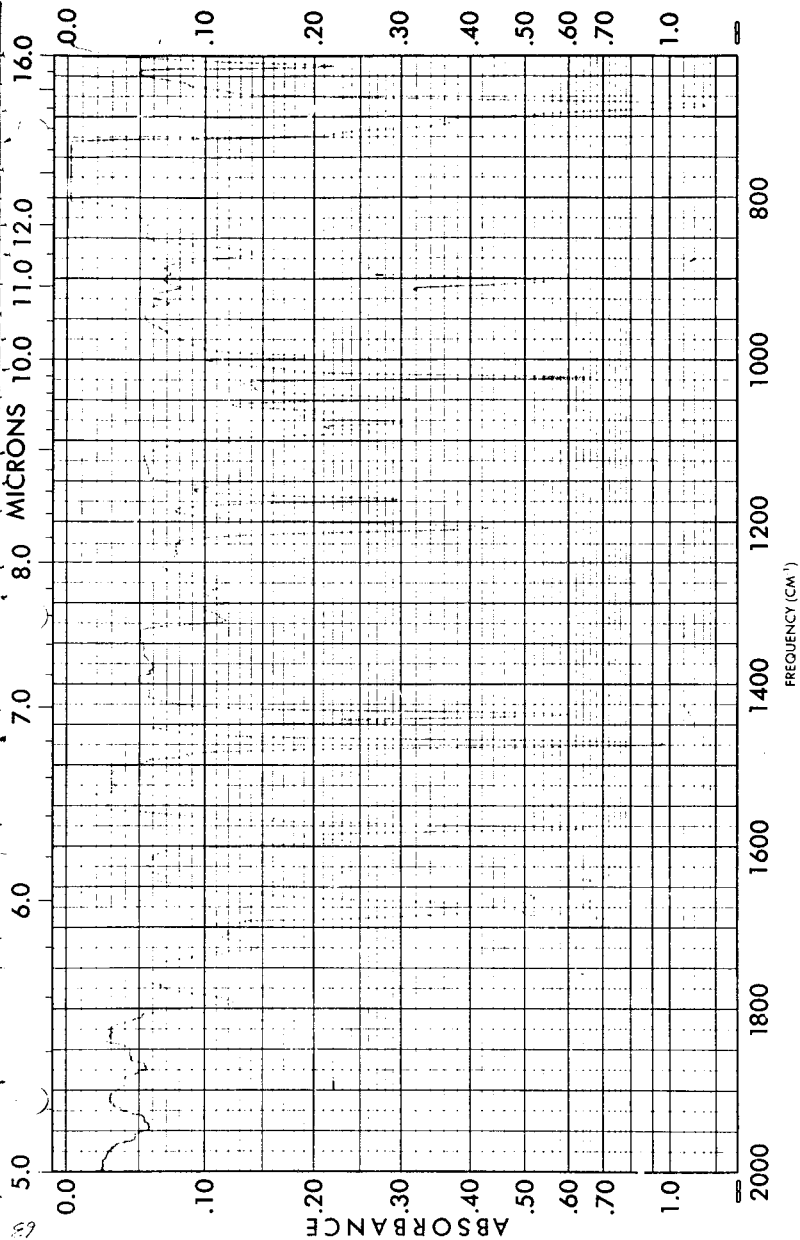
Appendix II Spectral Data

61

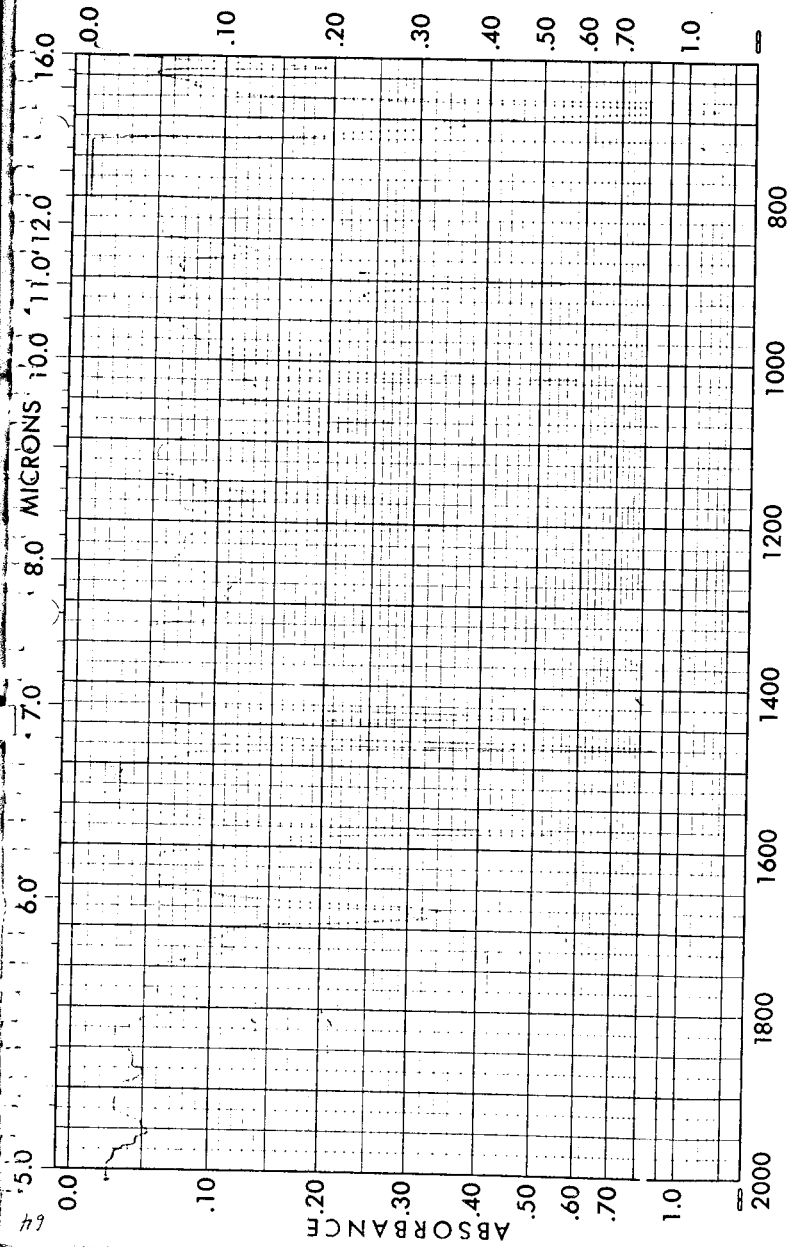
This appendix contains all spectra work done in the experimental section.



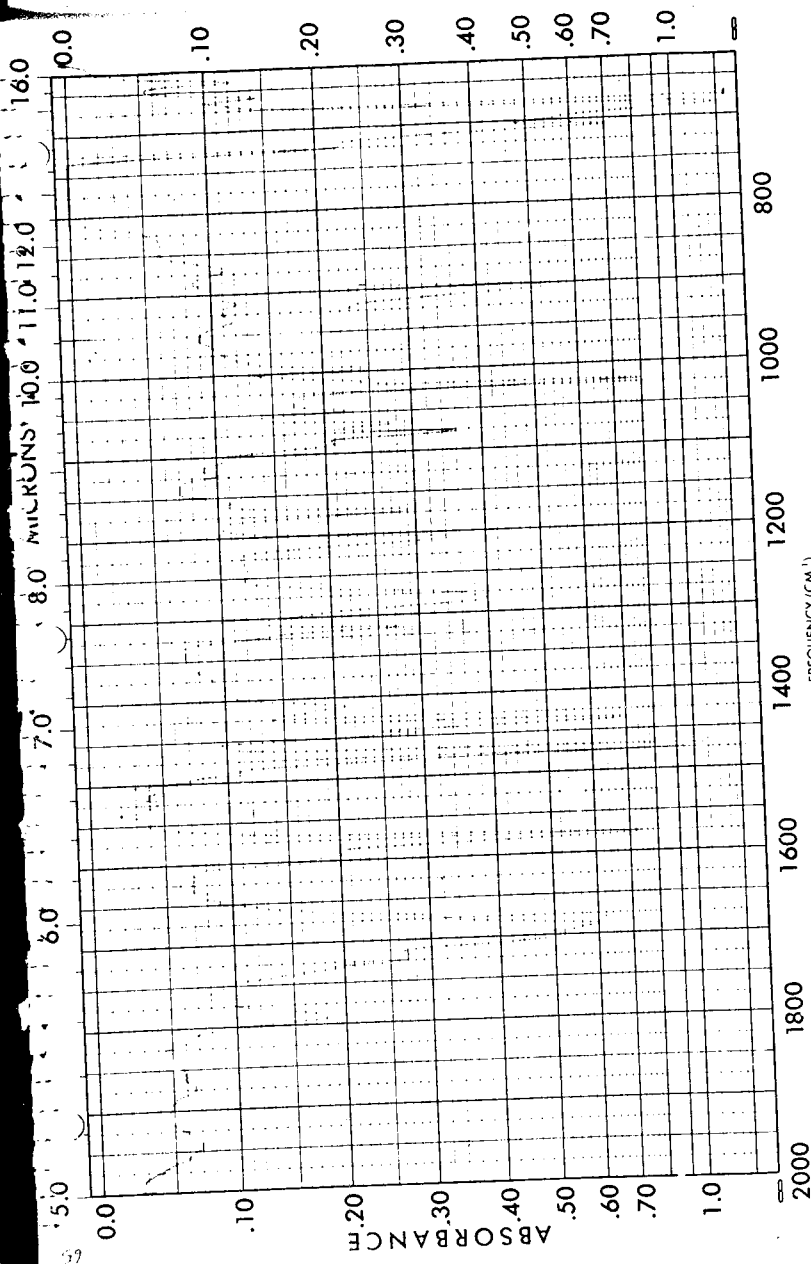
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ORIGIN Oxanolytic	CELL PATH 0.1 mm	REMARKS	
SOLVENT CCl <sub>4</sub>	REFERENCE 906.7		



SAMPLE	No. 2	CURVE NO. <u>III</u>	SCAN SPEED <u>Fast</u>		OPERATOR <u>AP</u>
			SUIT	DATE <u>5-12-76</u>	
ORIGIN	<u>o2nolupis</u>	CELL PATH	REMARKS		
SOLVENT	<u>CCl<sub>4</sub></u>	REFERENCE			



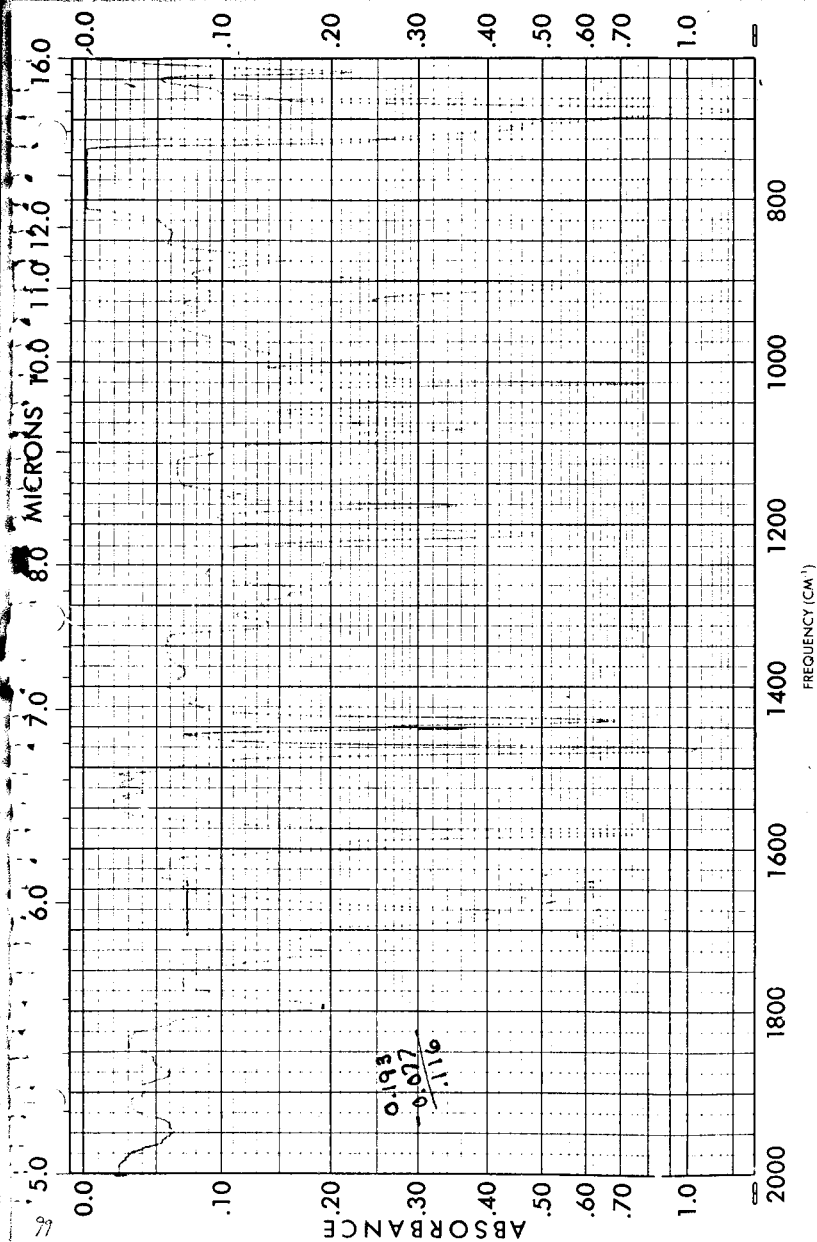
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	CONC. ....	SUIT <i>2530</i>	DATE <i>5-12-76</i>
ORIGIN <i>analysis</i>	CELL PATH <i>0.1 mm</i>	REMARKS	
SOLVENT <i>CCl<sub>4</sub></i>	REFERENCE <i>906.7</i>		



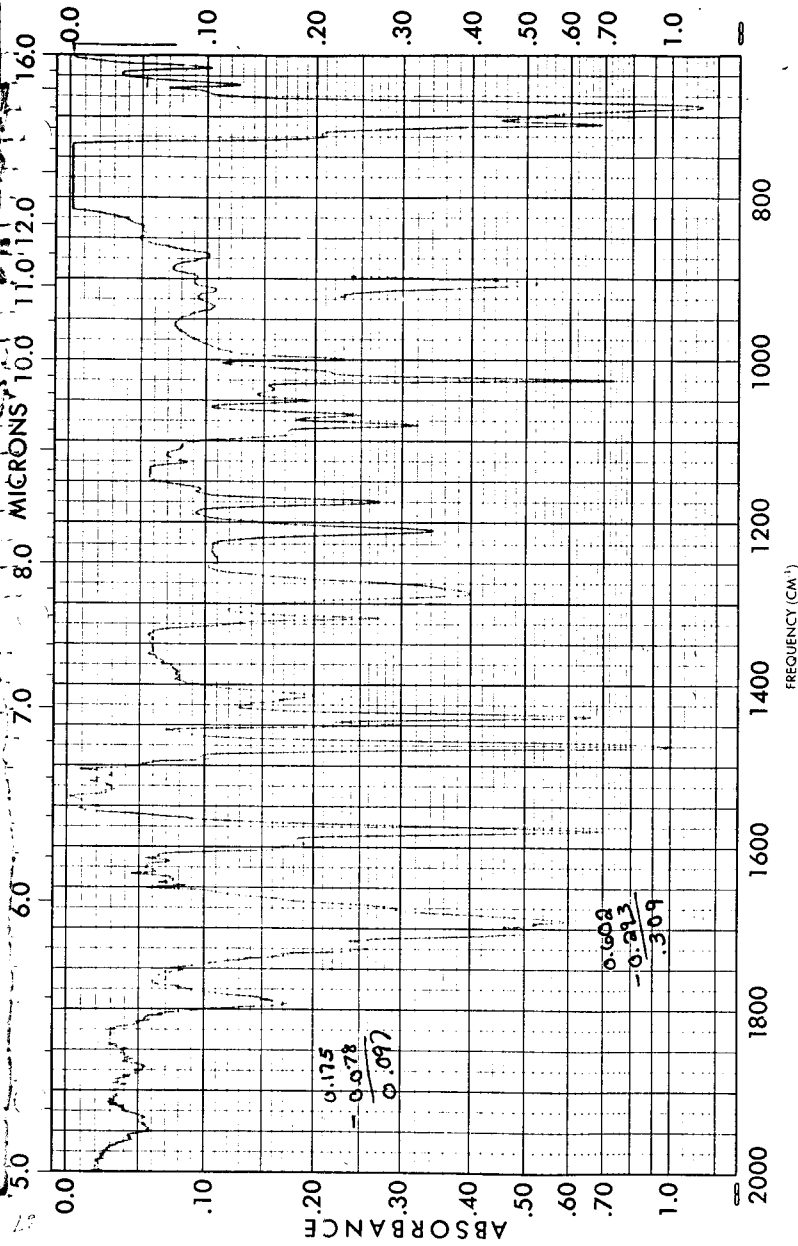
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		SLIT	DATE
ORIGIN SOLVENT	REMARKS		

No PR 18R (237-1033)

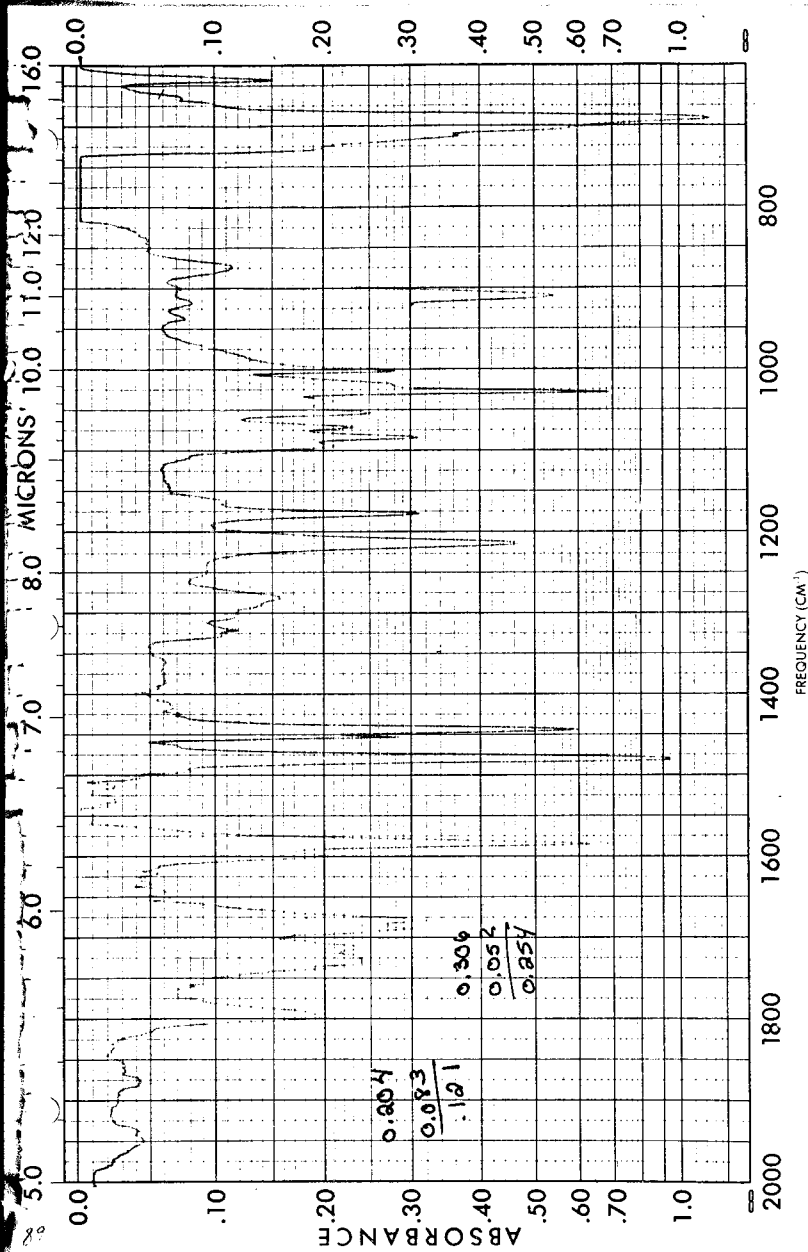
PREPARED BY: [illegible]



SAMPLE <b>No. 5</b>	CURVE NO. <b>VI</b>	SCAN SPEED <b>5530</b>	OPERATOR <b>SS</b>
		SPLIT <b>5530</b>	DATE <b>3/2/76</b>
ORIGIN <b>Ozoneolysis</b>	CONC. <b>0.1mm</b>	REMARKS	
SOLVENT <b>CCl<sub>4</sub></b>	CELL PATH <b>906.7</b>		

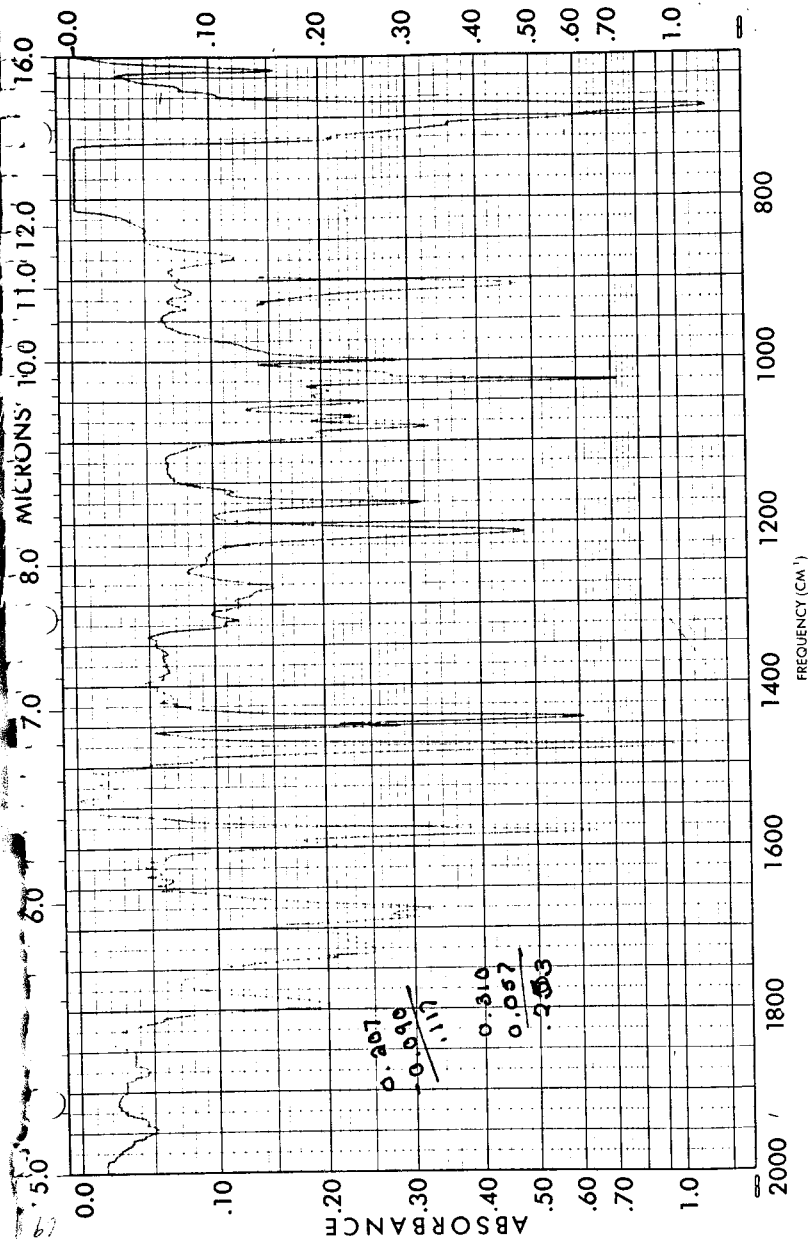


SAMPLE	Na <sub>2</sub> Co	CURVE NO.	VIII	SCAN SPEED	50+	OPERATOR	JD
				CONC.	2530	DATE	5-19-76
ORIGIN		CELL PATH	0.1mm	REMARKS			
SOLVENT	CCl <sub>4</sub>	REFERENCE	906.3				

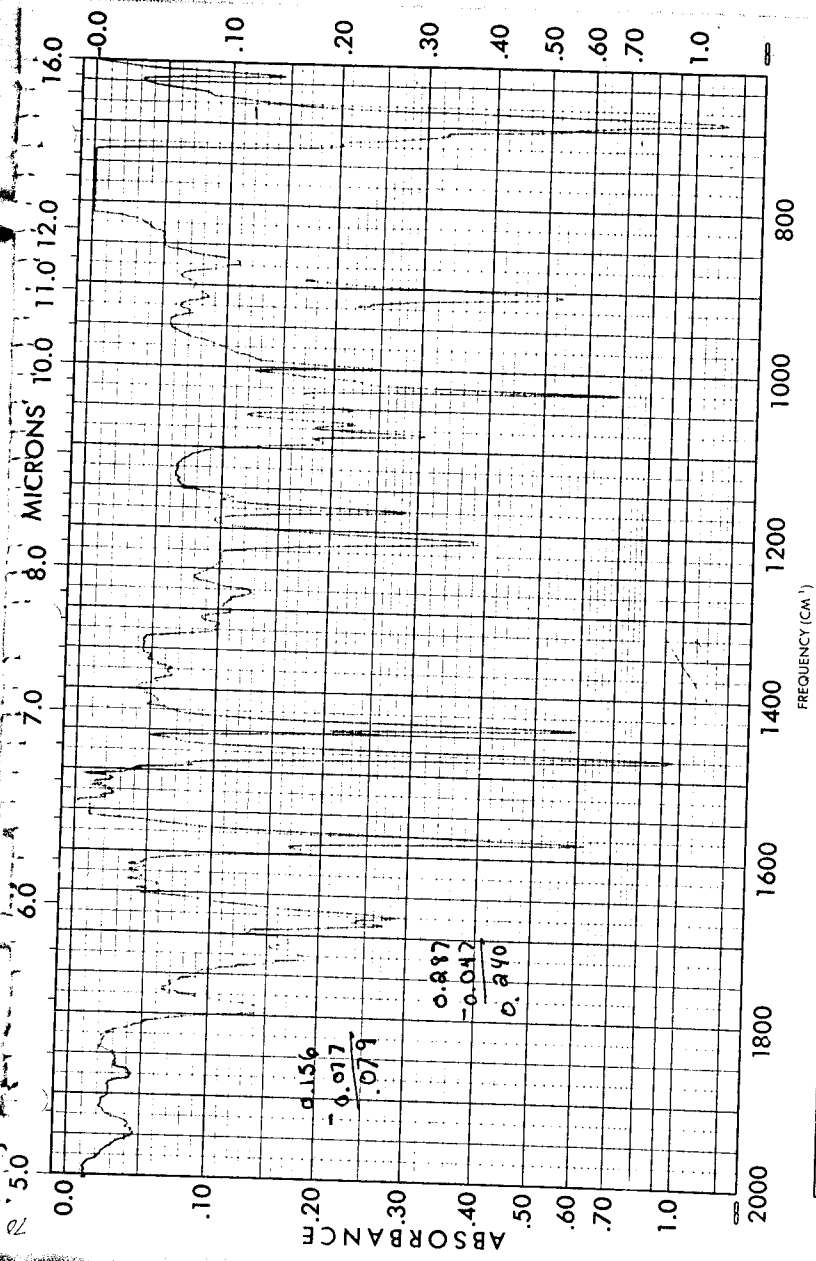


SAMPLE	No. 7	CURVE NO.	IX	SCAN SPEED	fast	OPERATOR	JS
				SUIT	8530	DATE	5-19-76
ORIGIN		CELL PATH	0.1mm	REMARKS	0°C		
SOLVENT	CCl <sub>4</sub>	REFERENCE	906.7				

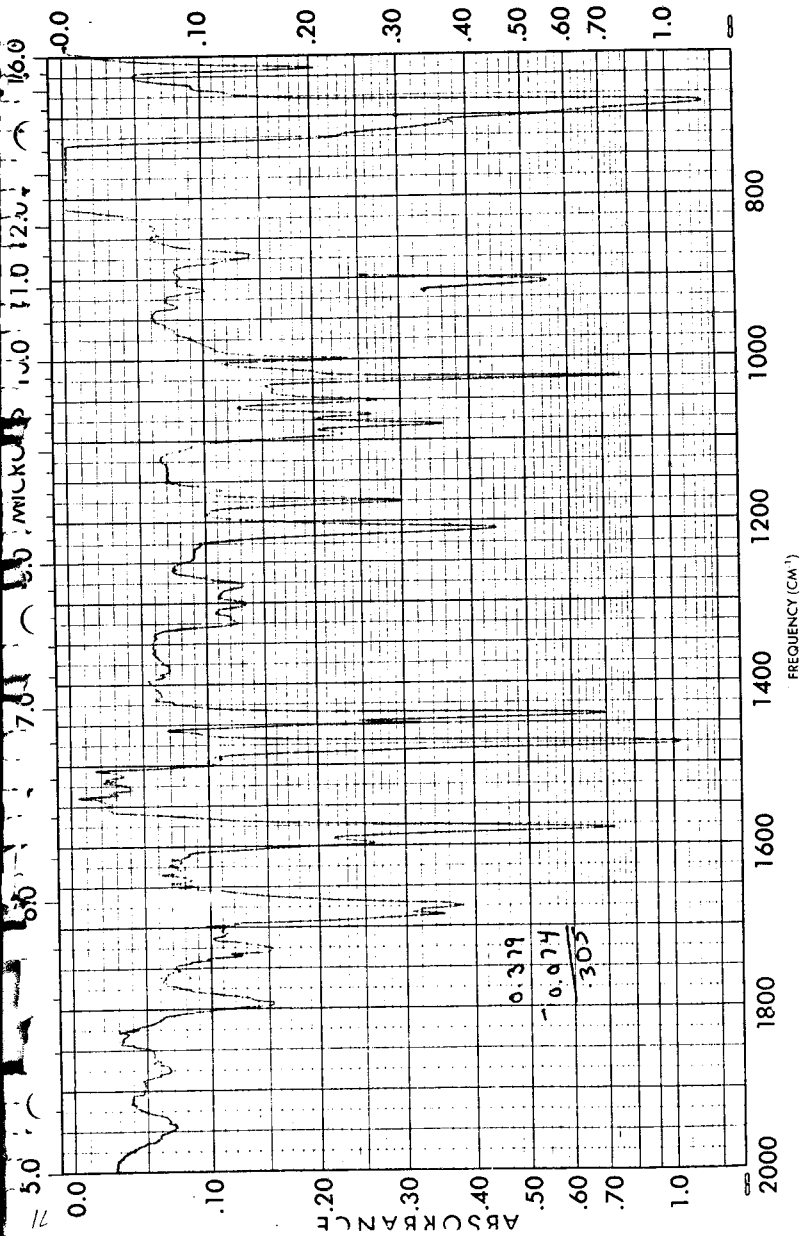




SAMPLE	No. 8	CURVE NO.	X	SCAN SPEED 585†	OPERATOR JS
ORIGIN		CONC.		SPLIT	2530
SOLVENT	CCl <sub>4</sub>	CELL PATH	0.1 mm	REMARKS	
		REFERENCE	90% 7		

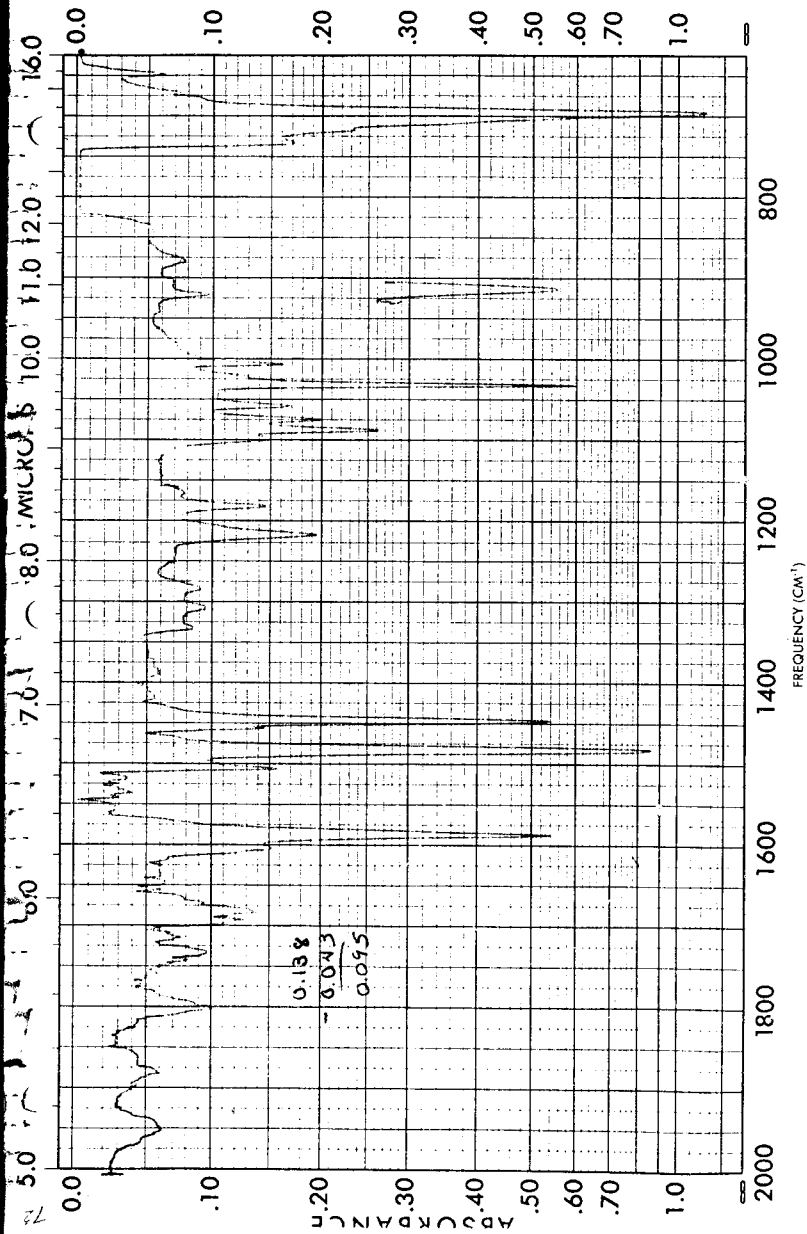


SAMPLE No. 9	CURVE NO. XI	SCAN SPEED	5000	OPERATOR	J.S.
		SPLIT	2530	DATE	5-19-76
ORIGIN	CELL PATH	REMARKS		0°C	
SOLVENT	CCl <sub>4</sub>	0.1mm		906.7	

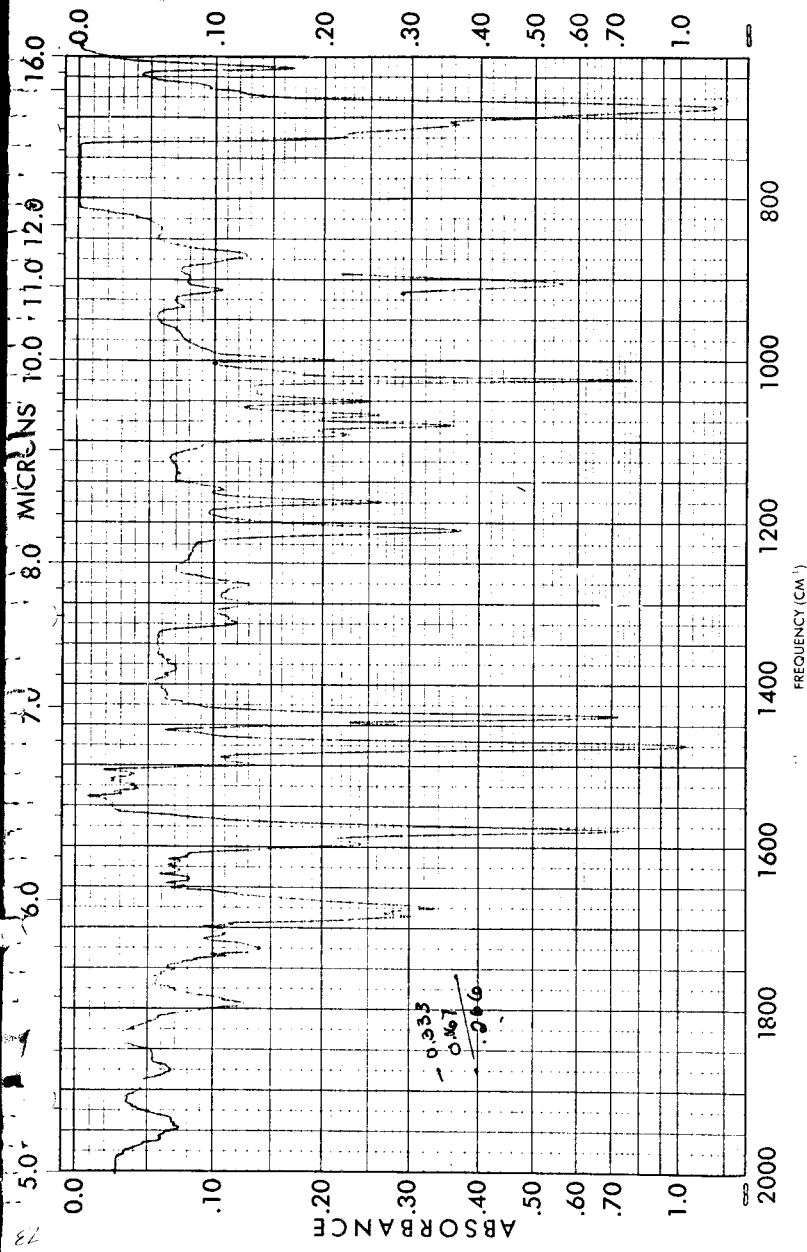


SAMPLE	10	CURVE NO.	XIII	SCAN SPEED	Fast	OPERATOR	JS
						DATE	5-28-76
ORIGIN		CONC.		SLOT	2530	REMARKS	2 min wait -40°C
SOLVENT	CCl <sub>4</sub>	CELL PATH	0.1 mm	REFERENCE	906.7		

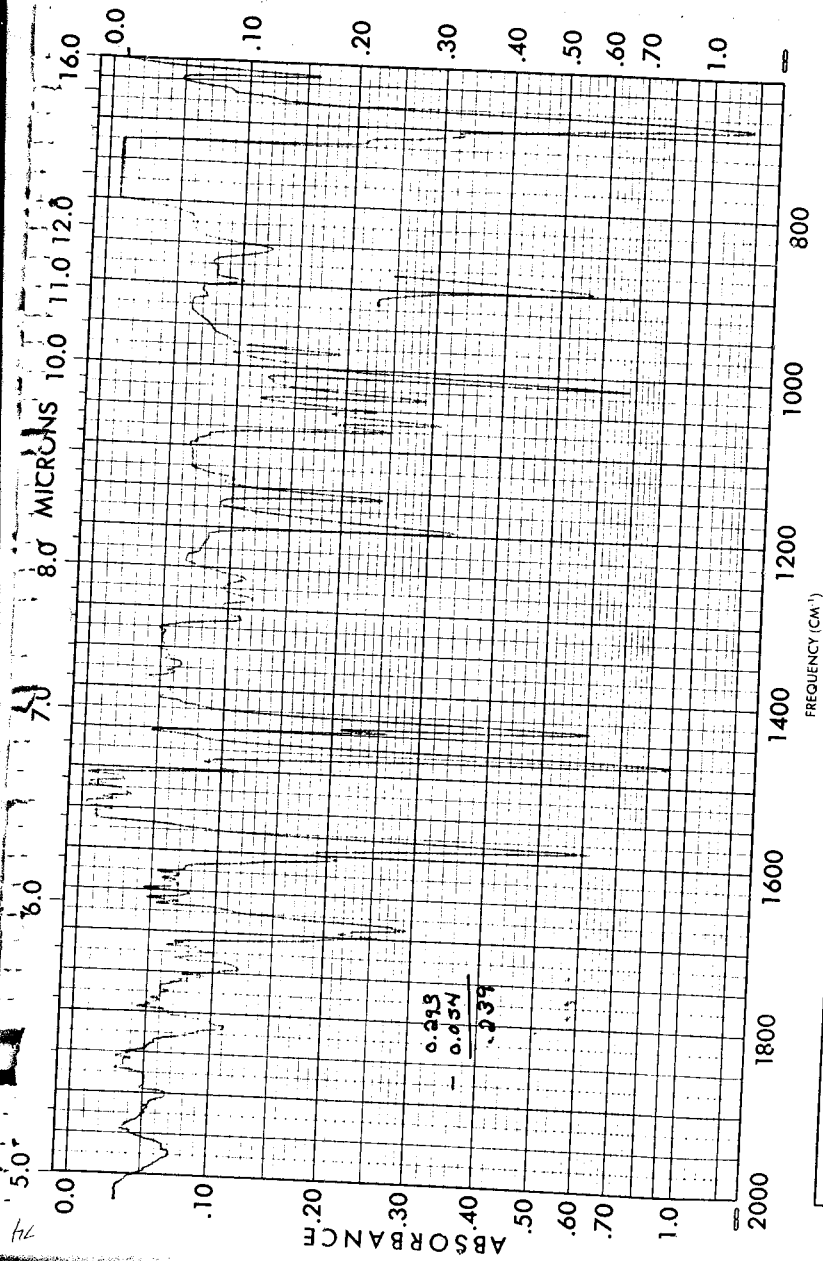
RECORDING CHARTS (GRAPHIC CONTROLS CORPORATION) BUFFALO, NEW YORK



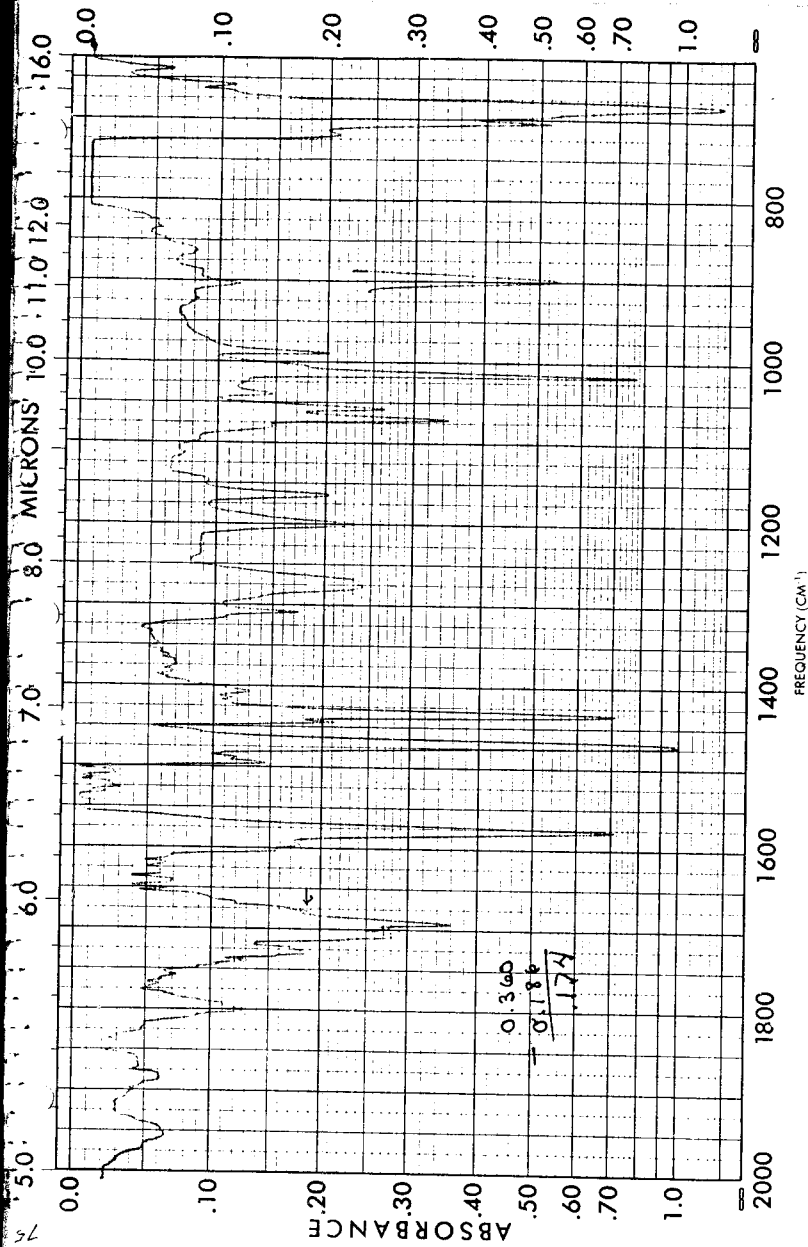
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ORIGIN		CONC.		SPLIT	25%	DATE	5/28/76
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		REFERENCE	96.7				



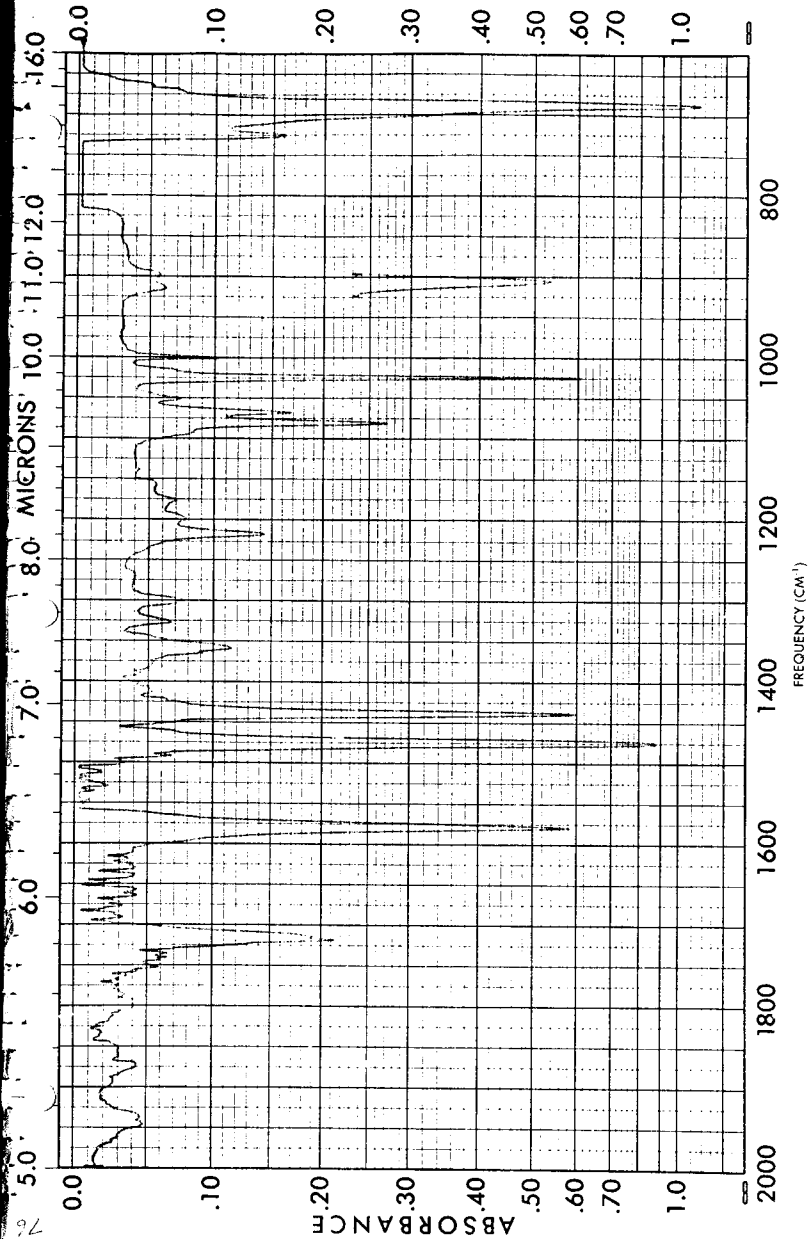
SAMPLE <u>16</u> ORIGIN SOLVENT <u>CCl<sub>4</sub></u>	CURVE NO. <u>88</u> CONC. CELL PATH <u>0.1 mm</u> REFERENCE <u>106.7</u>	SCAN SPEED <u>Fast</u> SLIT <u>253</u> REMARKS <u>2 min wait - 64°</u> <u>10 min equilibration</u>	OPERATOR <u>SS</u> DATE <u>5-28-76</u>
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SAMPLE	13	CURVE NO.	XXI	SCAN SPEED	Fast	OPERATOR	JS
ORIGIN	CC14	CONC.	diluted to 10 ml	SLIT	2580	DATE	5/31/76
SOLVENT	CC14	CELL PATH	0.1 mm	REMARKS	-60°	30 min operation	
		REFERENCE	906.7		1 min wait		



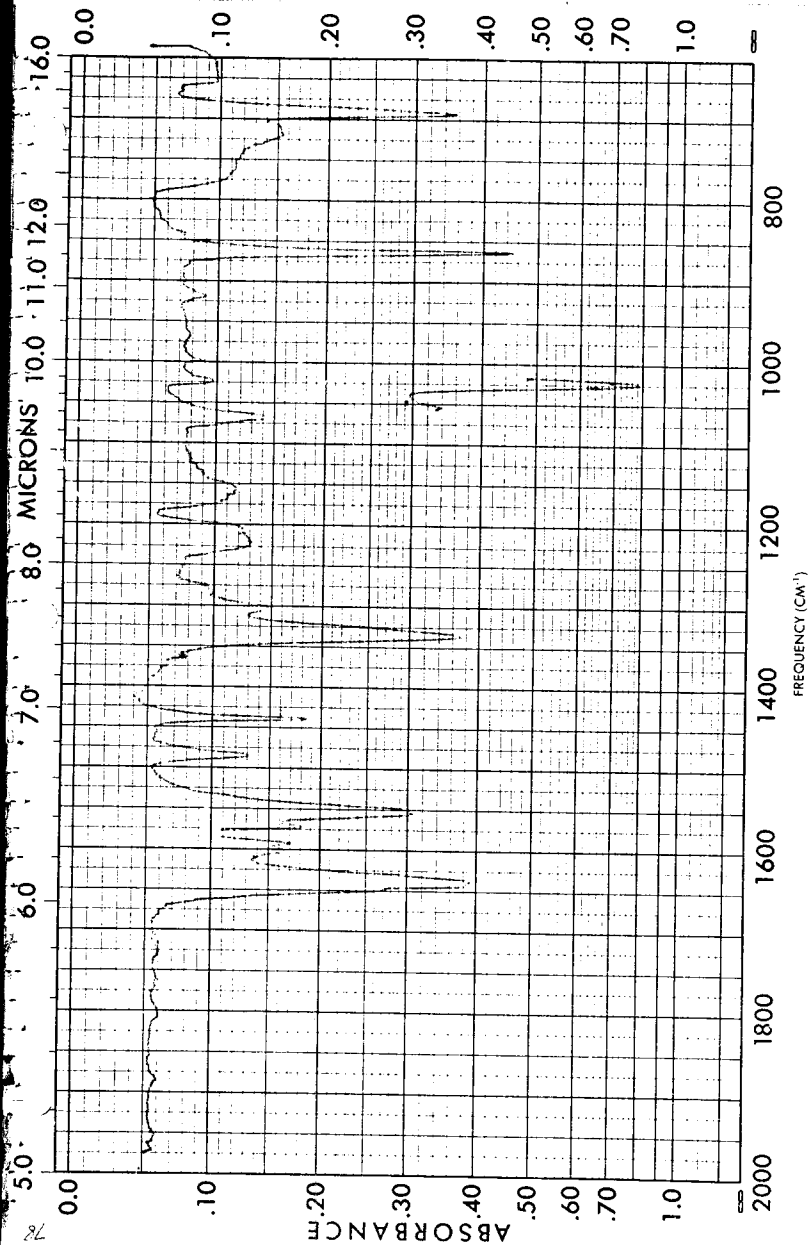
SAMPLE <b>14</b>	CURVE NO. <b>XXII</b>	SCAN SPEED <b>Fast</b>	OPERATOR <b>D</b>
	CONC. <b>diluted to 10ml</b>	SLIT <b>2530</b>	DATE <b>5/3/73</b>
ORIGIN	CELL PATH <b>0.1mm</b>	REMARKS <b>10 min. 02ms 21 min. wet</b>	
SOLVENT <b>CCl<sub>4</sub></b>	REFERENCE <b>.906.7</b>		



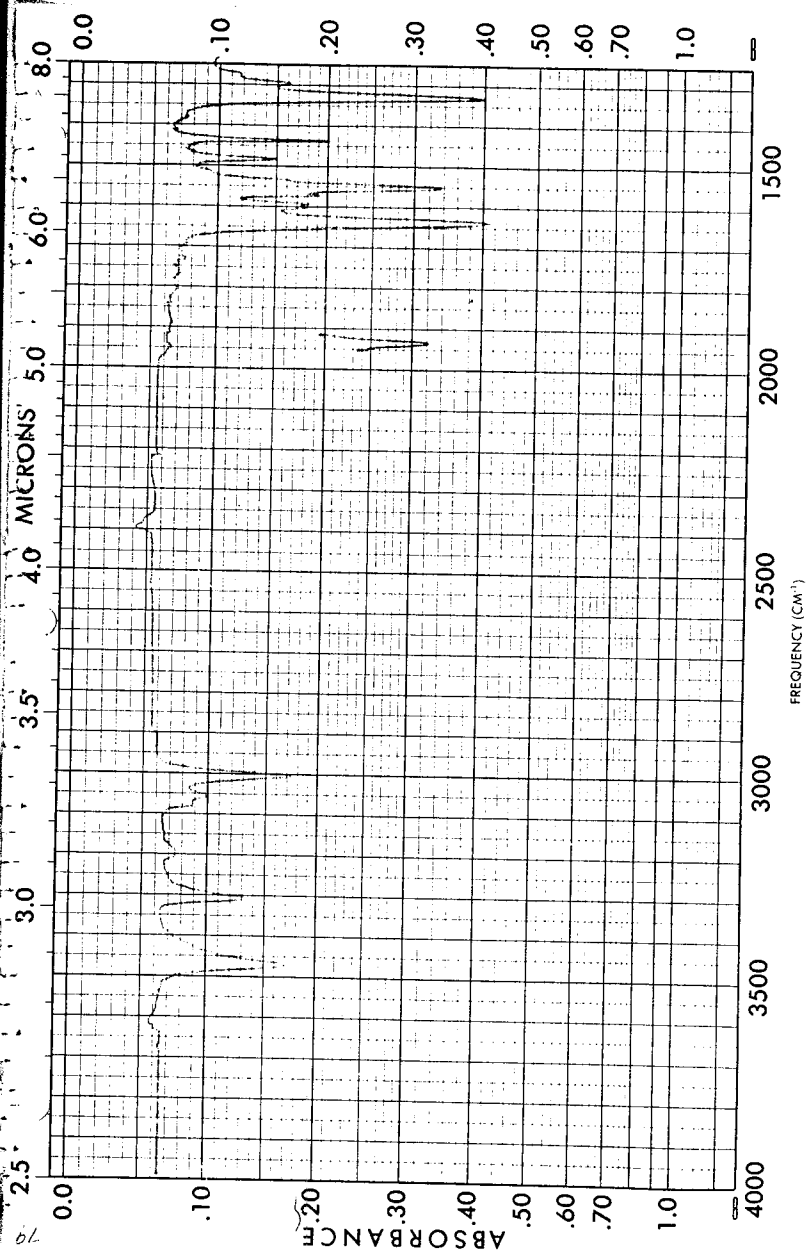
SAMPLE	15	CURVE NO.	XX111	SCAN SPEED	Fast	OPERATOR	JS
ORIGIN		CONC.	diluted to 10m	SLIT	2530	DATE	5-31-76
SOLVENT	CCl <sub>4</sub>	CELL PATH	0.1mm	REMARKS	Spec tone - ozone 10 min -		
		REFERENCE	906.7		welt 2 min		-42.6



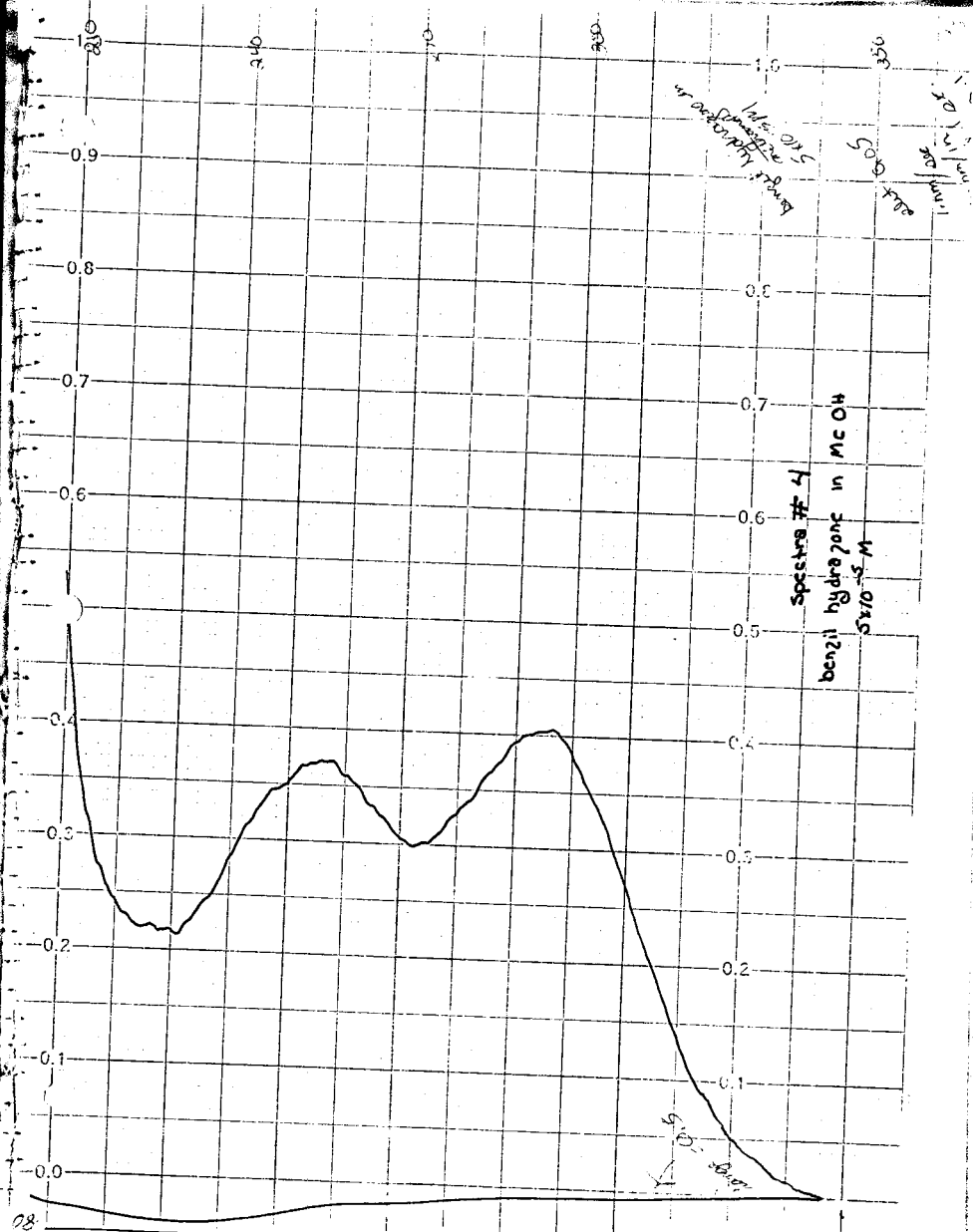




SAMPLE benzil hydrogen run#2	CURVE NO. 12	SCAN SPEED 500	OPERATOR JAS
ORIGIN JAS	CONC. saturated	SLIT 2535	DATE 11-17-76
SOLVENT CHCl <sub>3</sub>	CELL PATH 1	REMARKS	
REFERENCE 10380			



SAMPLE benzylhydrozone run #2		CURVE NO. 3		SCAN SPEED fast		OPERATOR JAS	
ORIGIN JAS	CONC. saturated	CELL PATH 1 cm	SUIT 2535	DATE 11-17-76	REMARKS		
SOLVENT CHCl <sub>3</sub>	REFERENCE 1444						

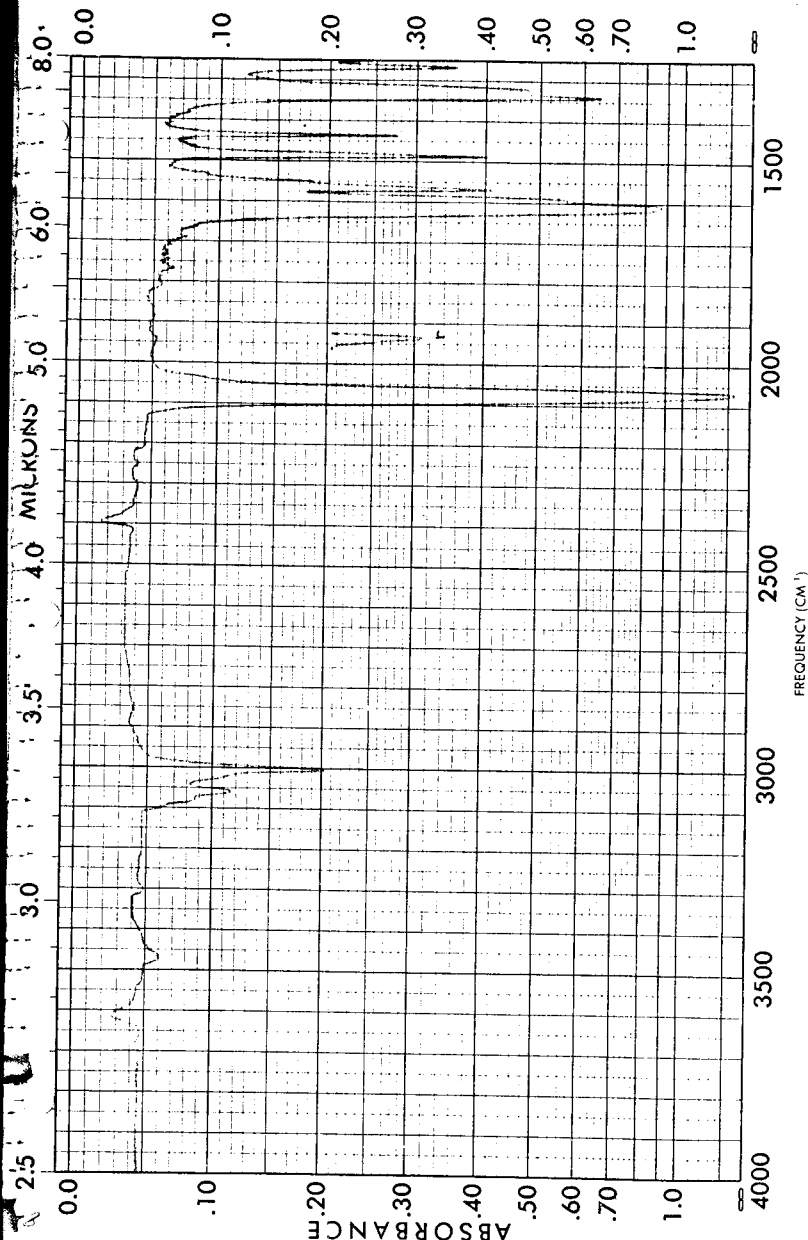


1.0  
 0.9  
 0.8  
 0.7  
 0.6  
 0.5  
 0.4  
 0.3  
 0.2  
 0.1  
 0.0

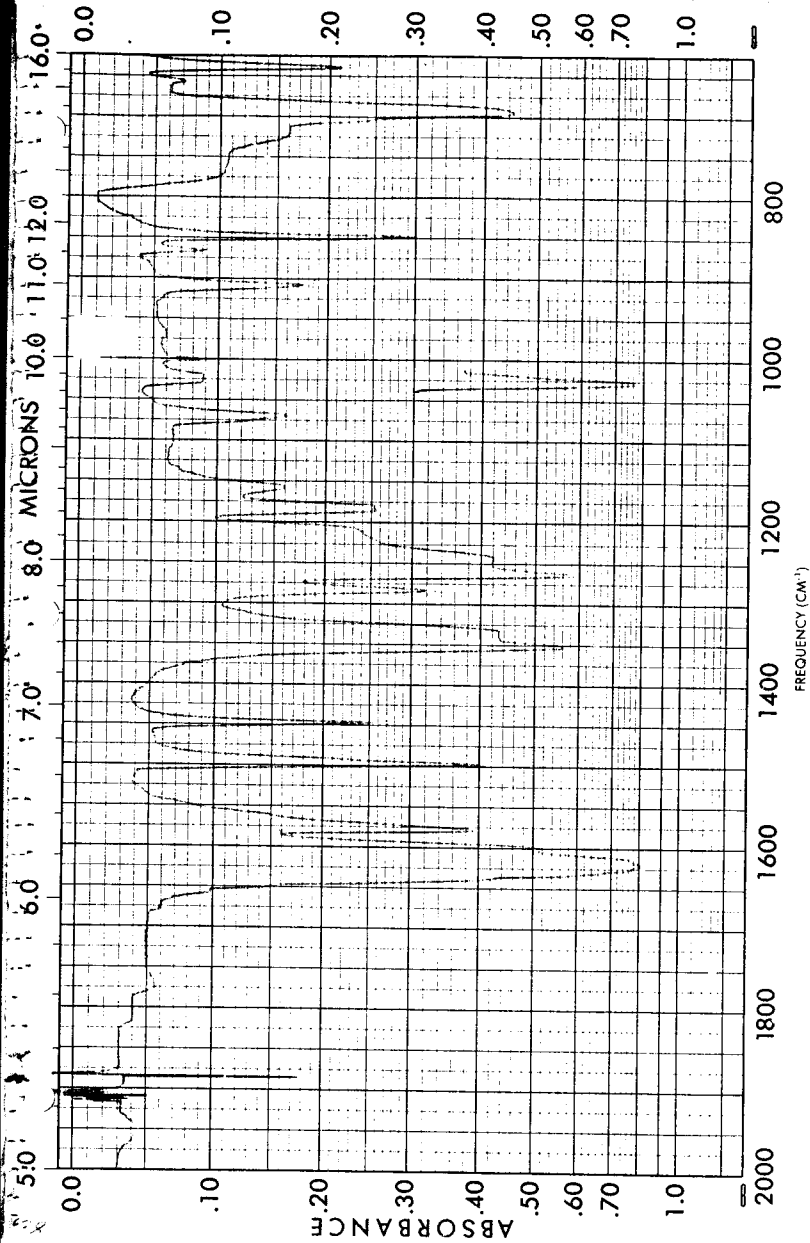
Spectra # 4  
 benzil hydrazone in MeOH  
 5x10<sup>-5</sup> M

200  
 210  
 220  
 230  
 240  
 250  
 260  
 270  
 280  
 290  
 300  
 310  
 320  
 330  
 340  
 350





SAMPLE <i>Quinone</i> run #4	CURVE NO. <i>6</i>	SCAN SPEED <i>fast</i>		OPERATOR <i>JAS</i>
		CONC.	SPLIT <i>2535</i>	DATE <i>11-3-76</i>
ORIGIN <i>JAS</i>	CELL PATH <i>10m</i>	REMARKS		
SOLVENT <i>CHCl<sub>3</sub></i>	REFERENCE <i>1944</i>			



SAMPLE <i>271benzyl</i>	CURVE NO. <i>7</i>	SCAN SPEED (cm/s)		OPERATOR
		SUIT <i>2535</i>		JAS
ORIGIN <i>JAS</i>	CONC.	REMARKS		DATE <i>11-3-74</i>
SOLVENT <i>CHCl<sub>3</sub></i>	CELL PATH <i>1cm</i>	REFERENCE <i>1028.0</i>		

NO PR 1BR (1237-1033)

RECORDING UNIT

DATE 11-3-74

$\epsilon = 0.551$   
 $\frac{1}{\text{cm} \cdot \text{M}} \left( \frac{\text{cm}^2}{\text{mol}} \right)$   
 $\text{measured } 5.5 \times 10^4$   
 $\lambda = 350 \text{ m}\mu$   
 $\text{measured } 5.5 \times 10^4$   
 $\lambda = 350 \text{ m}\mu$   
 $\text{measured } 5.5 \times 10^4$

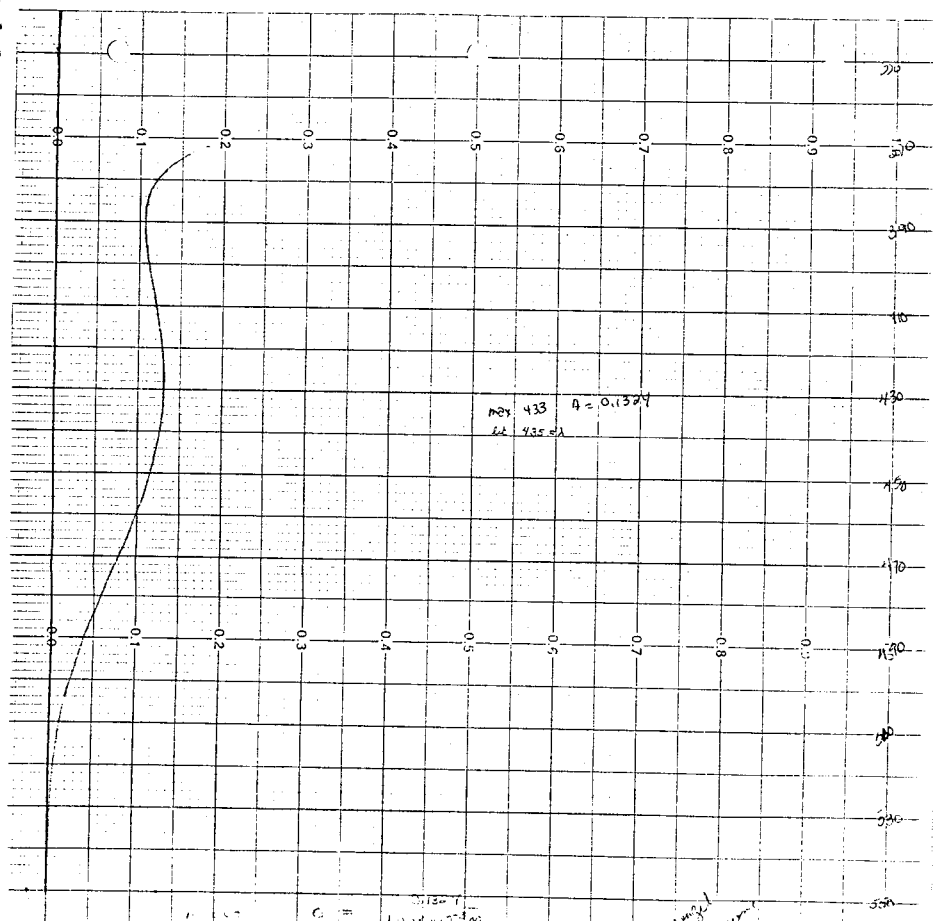
Spectrum #8  
 $10^{-5} \text{ M epibenzil in MeOH}$

2000-1800  
 2000-1800

2000-1800  
 2000-1800

$10^{-5} \text{ M epibenzil in MeOH}$   
 $\lambda = 350 \text{ m}\mu$   
 $2000-1800$   
 $2000-1800$   
 $2000-1800$



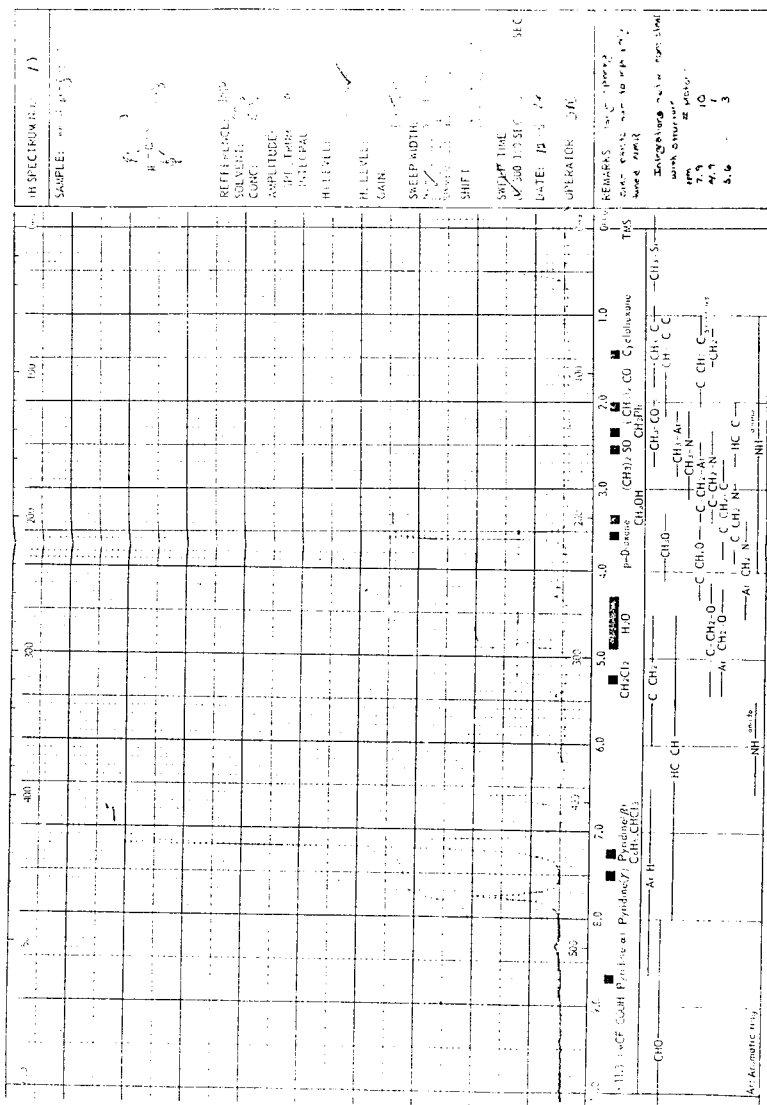


Spectrum # 9

$\frac{0.1524}{1.0 \times 10^{-2} \text{ m}}$   
 $= 1.524 \times 10^4 \text{ m}^{-1}$

*optimal  
 in benzene*

slit = 0.05  
 20 nm/sec in  
 2 nm/sec  
 range 1.0  
 400-600 nm



IN SPECTROMETER (1)

SAMPLE: 100-1000

REFERENCE: 100-1000  
SOLVENT: CH<sub>2</sub>Cl<sub>2</sub>  
CONC: 10%  
AMPLITUDE: 5  
PH: 1000  
DATE: 10/10/60

PH LEVEL: 100

GAIN: 100

SWEEP WIDTH: 100

SWEEP RATE: 100

SHIFT: 100

SWEEP TIME: 100

DATE: 10/10/60

OPERATOR: JAC

REMARKS: 100-1000

100-1000

100-1000

100-1000

100-1000

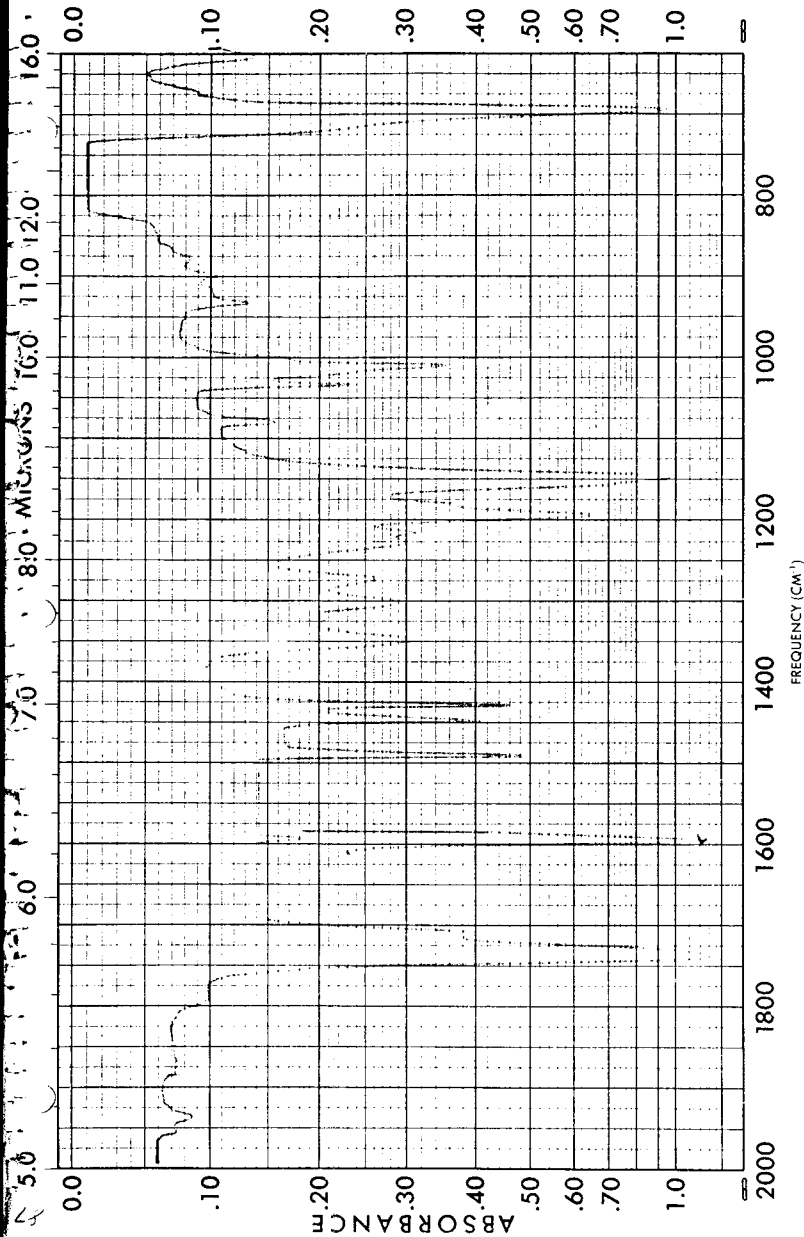
100-1000

100-1000

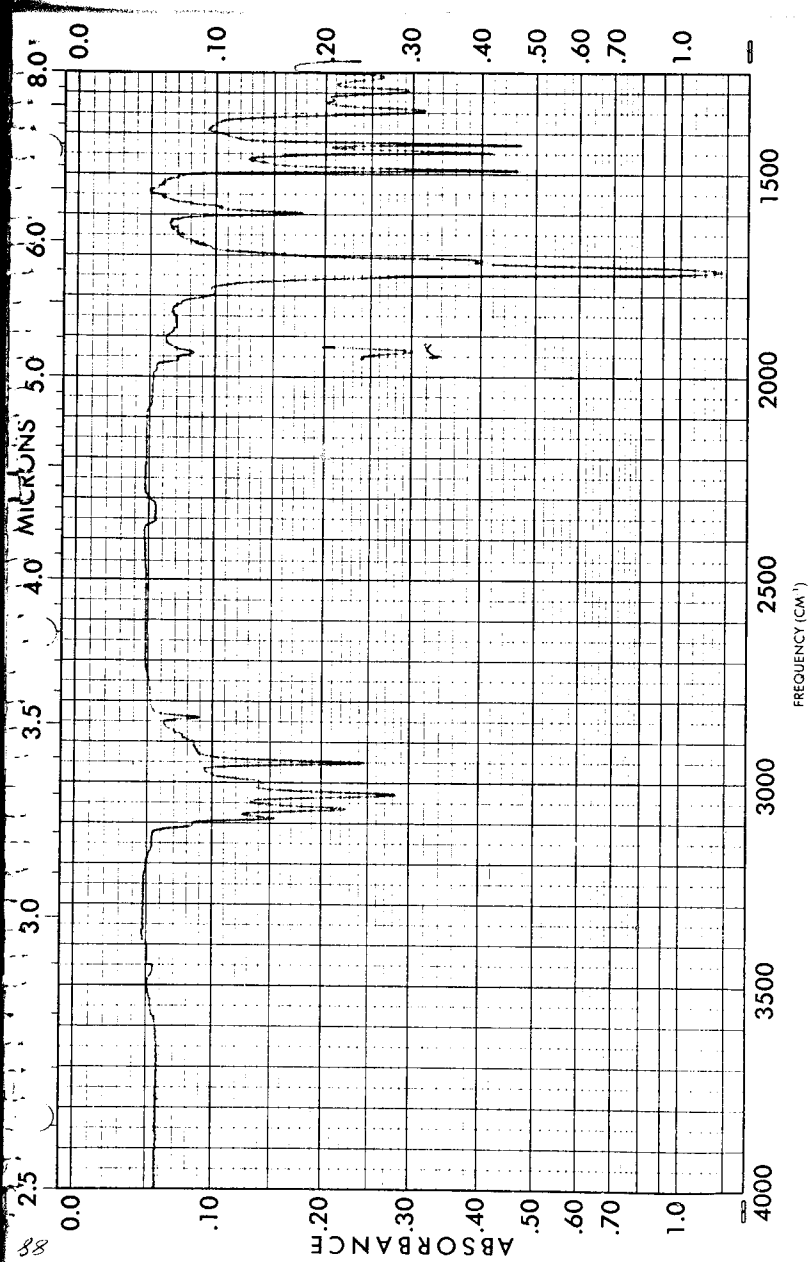
100-1000

100-1000

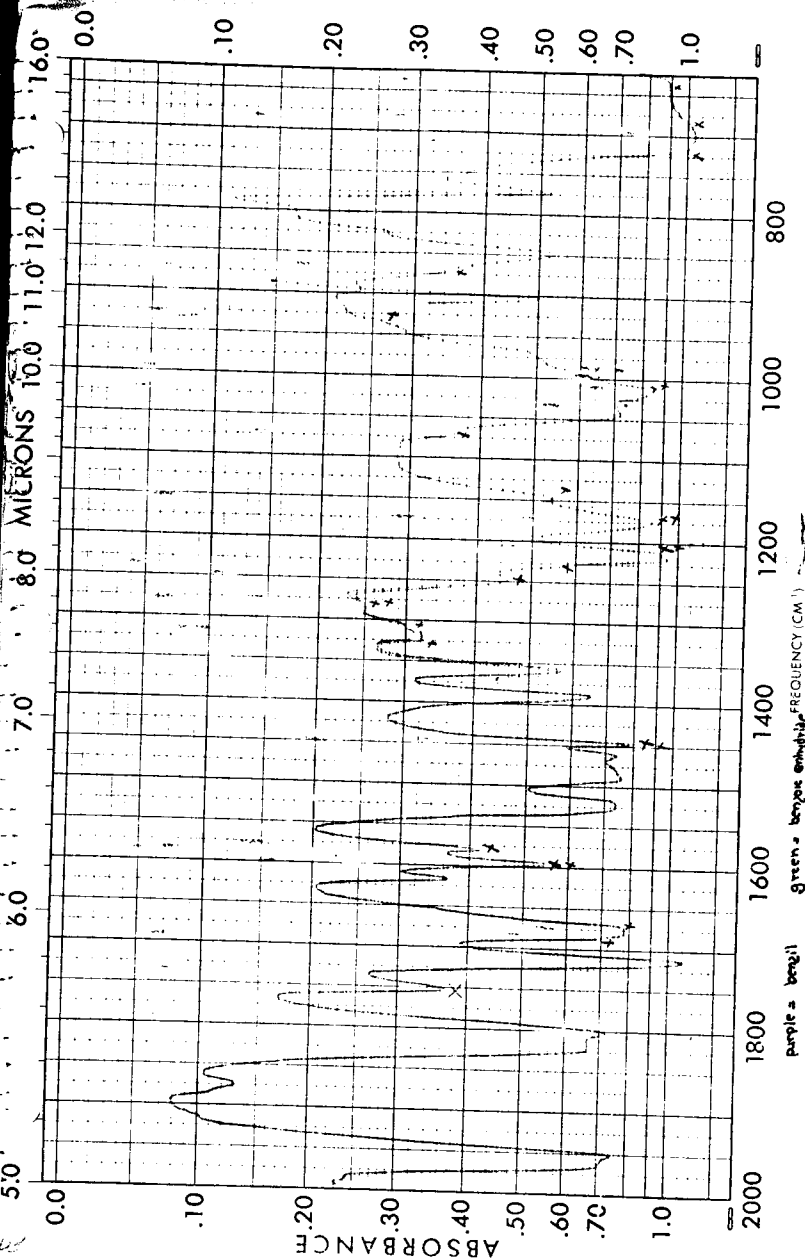
CHAPT. NO. 100-1000

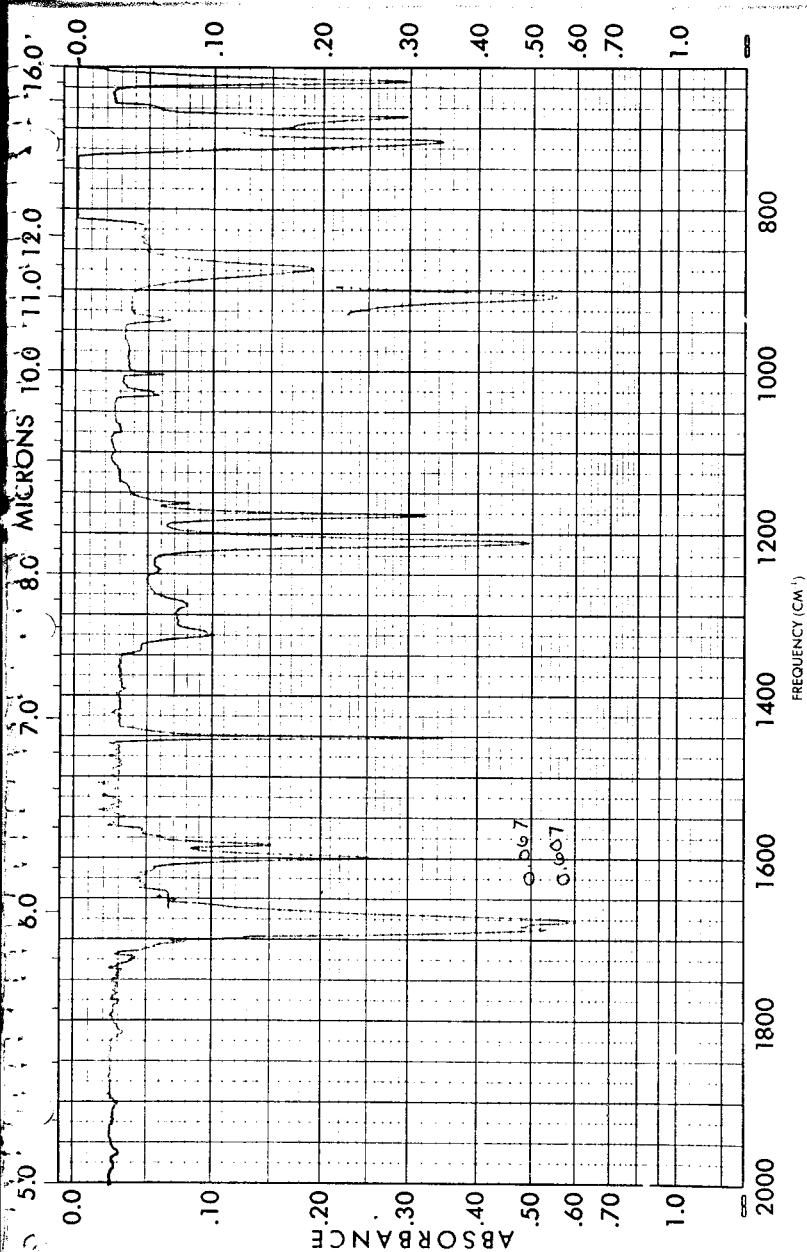


SAMPLE	melting styrene (solid)		CURVE NO.	11		SCAN SPEED	Fast	OPERATOR	JAG
ORIGIN	JAS		CONC.	0.4 M		SUIT	8535	DATE	8-5-76
SOLVENT	CCl <sub>4</sub>		CELL PATH	0.1 cm		REMARKS			
			REFERENCE	16014					

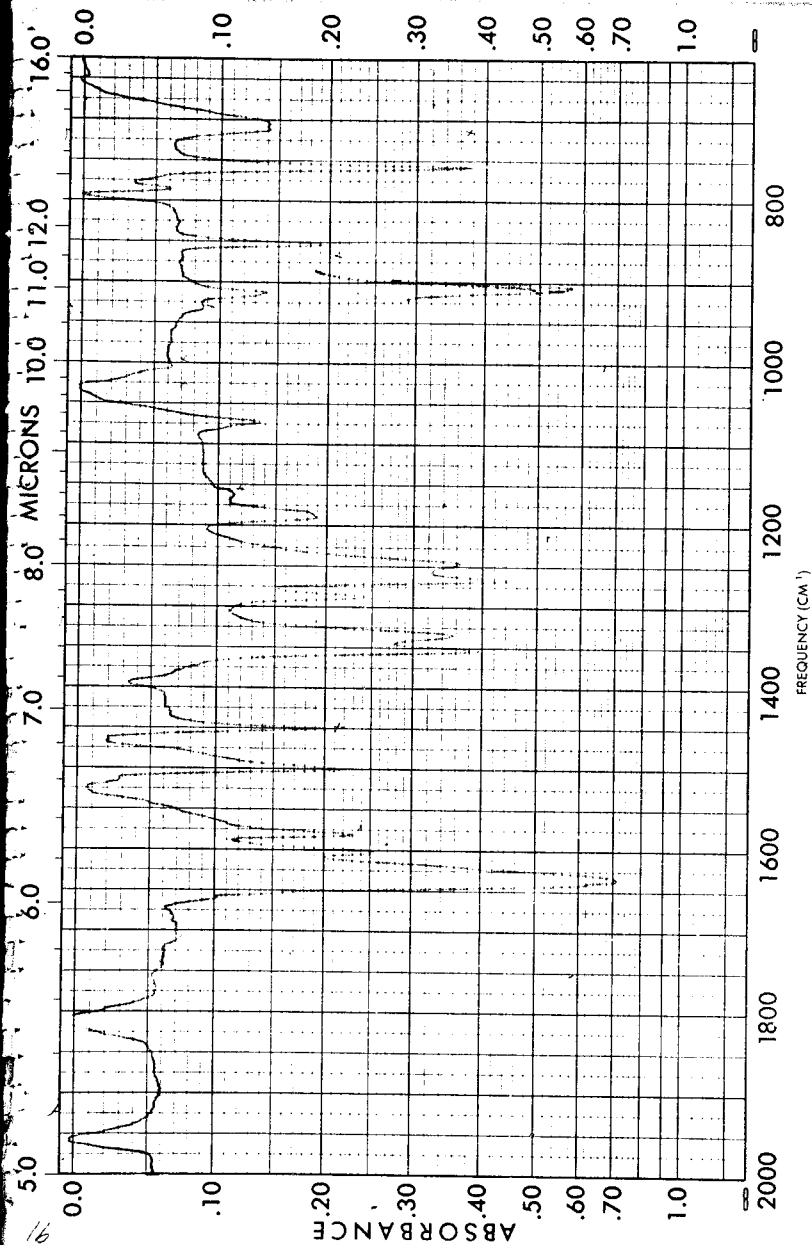


SAMPLE <i>methyl dipropylacetate</i> ORIGIN <i>JAS</i> SOLVENT <i>CCl<sub>4</sub></i>	CURVE NO. <i>12</i> CONC. <i>0.4 M</i> CELL PATH <i>0.15 cm</i> REFERENCE <i>M44</i>	SCAN SPEED <i>Fast</i> SLIT <i>8635</i> REMARKS	OPERATOR <i>JAS</i> DATE <i>12-9-76</i>
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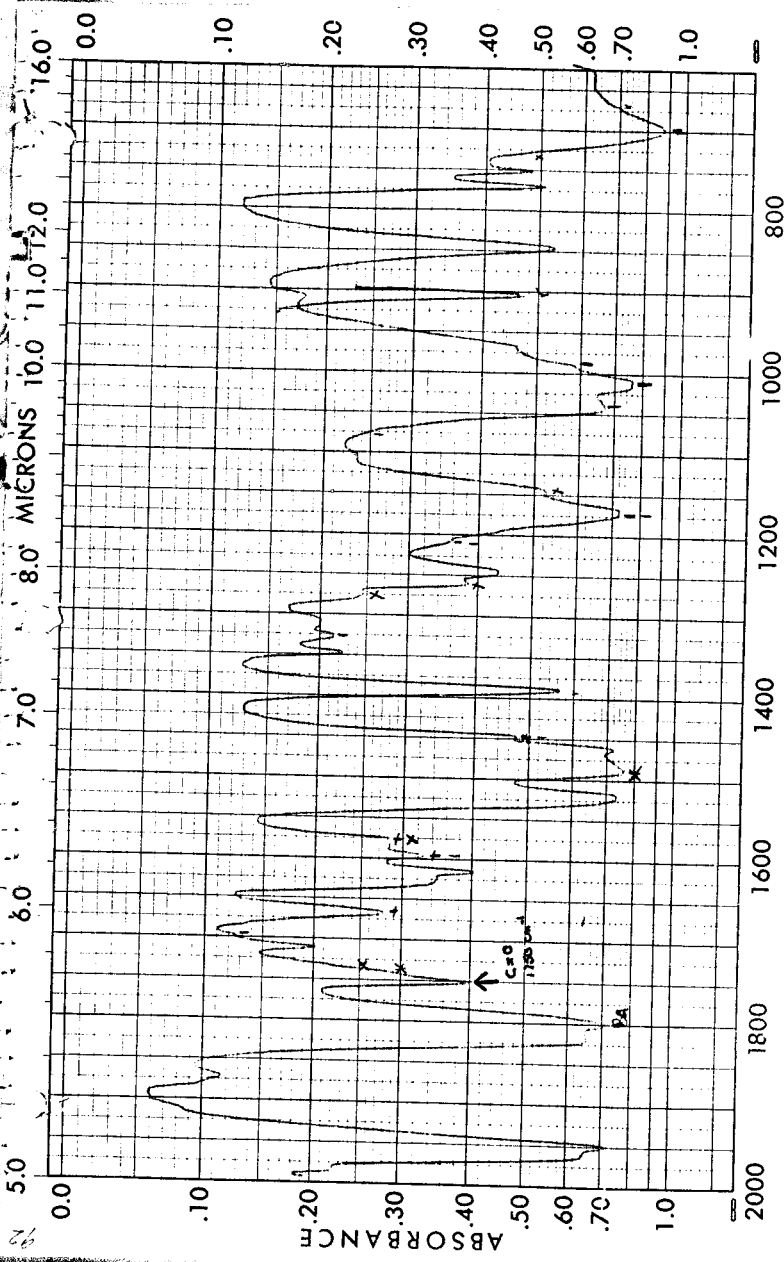




SAMPLE <i>Benzil</i>	CURVE NO. <i>14</i>	SCAN SPEED <i>500</i>	OPERATOR <i>gd</i>
	CONC. <i>0.1 M</i>	SPLIT <i>2530</i>	DATE <i>5-9-76</i>
ORIGIN	CELL PATH <i>0.1 mm</i>	REMARKS	
SOLVENT <i>CCl<sub>4</sub></i>	REFERENCE <i>906.7</i>		



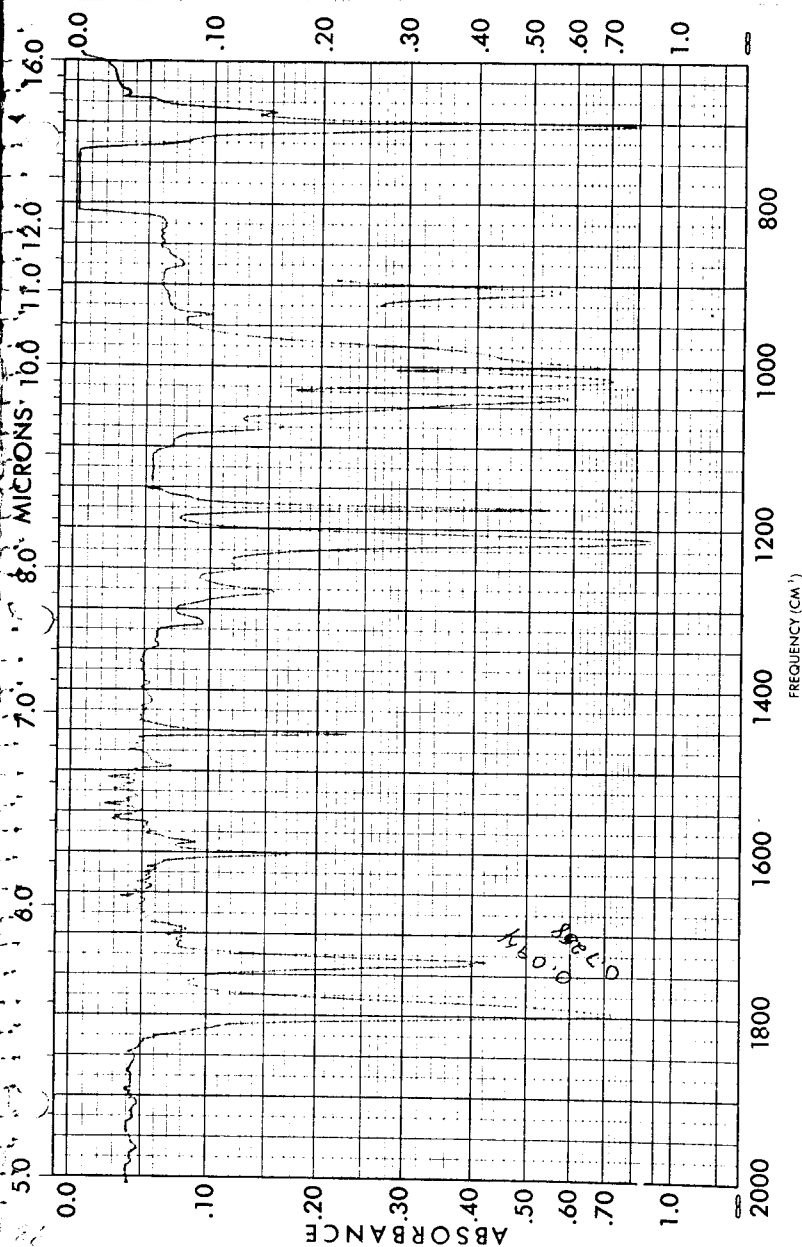
SAMPLE	2,2-benzil	CURVE NO.	15	SCAN SPEED	fast	OPERATOR	JRS
ORIGIN	JRS	CONC.		SPLIT	2535	DATE	2-22-77
SOLVENT	Benzene	CELL PATH	0.1 mm	REMARKS	no benzil present		



SAMPLE <i>2-benzil O<sub>2</sub> decamp at 1 atm</i> ORIGIN <i>JAS</i> SOLVENT <i>benzene</i>	CURVE NO. <i>16</i> CONC. CELL PATH <i>0.1 mm</i> REFERENCE <i>906.7</i>	SCAN SPEED <i>fast</i> SLIT <i>2.535"</i>		OPERATOR <i>JAS</i> DATE <i>1/18/77</i>
		REMARKS <i>both benzoic anhydride and benzil present</i>		

2000 1800 1600 1400 1200 1000 800  
 FREQUENCY (CM<sup>-1</sup>) Purple - Benzil  
 Green Benzoic anhydride





SAMPLE <i>Benzoin Anhydride</i>	CURVE NO. <i>17</i>	SCAN SPEED <i>50</i>	OPERATOR <i>JD</i>
	CONC. <i>0.11 M</i>	SUIT <i>30</i>	DATE <i>5-9-76</i>
ORIGIN	CELL PATH <i>0.11 mm</i>	REMARKS	
SOLVENT <i>CCl₄</i>	REFERENCE <i>906.7</i>		

Appendix III Original Data from Gas Chromatographic Analysis of Azibenzil Decomposition

This appendix contains a complete table of all azibenzil decomposition products reported in the experimental section. The following key is utilized:

- A = decomposition product
- B = decomposition product plus methanol
- C = decomposition product treated with base and methanol

Table 12: Raw Data

Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm <sup>2</sup> $\pm 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
51A	0	1	0.1355	0.56	trace		
		2		2.56	2.6		diphenylketene
		3		3.00	0.4		
		4		3.94	0.2		
		5		4.94	0.6	$3.25 \times 10^{-3}$	benzil
51B	0	1	0.2710	0.59	1.4		
		2		2.59	2.0		diphenylketene
		3		2.94	0.2		
		4		3.78	9.2	$4.85 \times 10^{-2}$	methyl diphenylacetate
		5		4.75	6.4	$3.8 \times 10^{-2}$	benzil
51C	0	1	0.2710	0.59	1.4		
		2		2.59	2.0		diphenylketene
		3		2.94	0.2		
		4		3.78	9.2	$4.85 \times 10^{-2}$	methyl diphenylacetate

Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm <sup>2</sup> $\pm 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
42A	0.2	5		4.75	6.4	$3.80 \times 10^{-2}$	benzil
		1	0.1354	1.47	trace		
		2		2.53	2.2		diphenylketene
		3		2.97	0.7		
		4		3.81	0.3		
42E	0.2	5		4.81	0.7		
		1	0.2703	0.59	2.4	$1.47 \times 10^{-3}$	methyl benzoate
		2		1.44	trace		
		3		2.52	0.3		
		4		2.94	1.6		
42G	0.2	5		3.81	9.2	$4.76 \times 10^{-2}$	methyl diphenylacetate
		6		4.81	6.0	$3.84 \times 10^{-2}$	benzil
		1	0.1354	0.62	0.3	$2.24 \times 10^{-3}$	methyl benzoate
		2		1.44	trace		

Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area ( $\text{cm}^2 \cdot 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
		3		2.53	0.2		
		4		2.94	0.3		
		5		3.72	1.5	$8.80 \times 10^{-3}$	methyl diphenylacetate
		6		4.75	1.7	$9.52 \times 10^{-3}$	benzil
49A	1.0	1	0.1365	0.69	trace		
		2		2.69	3.7		diphenylketene
		3		3.12	0.4		
		4		5.12	0.9	$5.38 \times 10^{-3}$	benzil
42B	1.0	1	0.1730	0.78	3.1	$1.93 \times 10^{-2}$	methyl benzoate
		2		2.69	trace		diphenylketene
		3		3.12	0.5		
		4		4.00	3.1	$1.50 \times 10^{-2}$	methyl diphenylacetate
		5		4.91	20.0	$1.23 \times 10^{-1}$	benzil

Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min:0.05)	Area ( $\text{cm}^2 \pm 1.1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
48C	1.0	1	0.2730	0.63	0.4	$2.44 \times 10^{-3}$	methyl benzoate
		2		2.69	0.2		diphenylketene
		3		3.06	0.4		
		4		4.00	1.4	$7.45 \times 10^{-3}$	methyl diphenylacetate
		5		4.88	14.2	$8.82 \times 10^{-2}$	benzil
44A	2.0	1	0.1352	0.47	trace		
		2		0.62	trace		
		3		1.44	trace		
		4		2.56	1.4		diphenylketene
		5		3.00	1.4		
		6		4.91	1.1	$6.19 \times 10^{-3}$	benzil
442	2.0	1	0.2704	0.56	4.0	$2.5 \times 10^{-2}$	methyl benzoate
		2		1.81	trace		
		3		2.56	0.7		

Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	AziBenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm <sup>2</sup> $\pm 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
44C	2.0	4		2.91	2.4		
		5		3.31	3.3	$1.69 \times 10^{-2}$	methyl diphenylacetate
		6		4.75	11.4	$7.31 \times 10^{-2}$	benzil
		1	0.1352	0.64	0.6	$5.3 \times 10^{-3}$	methyl benzoate
		2		1.54	0.6		
		3		2.91	0.3		diphenylketene
45aA	2.0	4		3.25	1.1		
		5		4.10	1.1	$5.12 \times 10^{-3}$	methyl diphenylacetate
		6		5.25	7.0	$4.02 \times 10^{-2}$	benzil
		7		6.91	0.2		dimer?
		1	0.1349	0.69	trace		
		2		0.75	trace		
		3		1.50	trace		

Run	Oxyger Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm $^2$ $\pm 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
45aB 2.0		4	0.2698	2.69	3.5		diphenylketene
		5		3.12	1.0		
		6		5.12	0.4	$2.53 \times 10^{-3}$	benzil
		1		0.66	6.1	$3.75 \times 10^{-2}$	methyl benzoate
		2		1.50	trace		
		3		2.59	0.4		diphenylketene
45aC 2.0		4	0.2698	3.00	1.7		
		5		3.88	2.5	$1.29 \times 10^{-2}$	methyl diphenylacetate
		6		4.81	13.3	$3.55 \times 10^{-2}$	benzil
		1		0.56	trace		methyl benzoate
		2		1.50	trace		
		3		2.72	1.0		diphenylketene
		4		3.12	1.8		
		5		4.06	8.6	$5.06 \times 10^{-2}$	methyl diphenylacetate



Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	benzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm $^2$ $\pm 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
52A	3.0	0		5.06	3.1	$1.73 \times 10^{-2}$	benzil
		1	0.1252	0.62	trace		
		2		0.75	trace		
		3		1.50	trace		
		4		2.50	0.9		diphenylketene
		5		3.06	1.7		
52B		6		4.94	2.8	$1.65 \times 10^{-2}$	benzil
		1	0.2765	0.47	trace		
		2		0.66	2.6	$2.16 \times 10^{-2}$	methyl benzoate
		3		1.50	trace		
		4		2.66	1.6		diphenylketene
		5		3.00	4.1		
		6		3.94	0.7	$3.37 \times 10^{-3}$	methyl diphenylacetate
		7		4.94	6.3	$3.32 \times 10^{-2}$	benzil

Pun	Oxygen Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm <sup>2</sup> $\pm 1.1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
52C	3.0	1	0.2705	0.56	trace		
		2		0.62	trace		methyl benzoate?
		3		0.75	trace		
		4		1.50	0.3		
		5		2.69	0.2		diphenylketene
		6		3.00	3.3		
		7		3.91	.4	$1.84 \times 10^{-3}$	methyl diphenylacetate
		8		4.88	5.8	$3.46 \times 10^{-2}$	benzil
47A	4.0	1	0.1353	0.62	trace		
		2		0.72	trace		
		3		1.38	trace		
		4		2.38	0.3		
		5		2.78	1.5		diphenylketene
		6		4.38	3.3	$1.8 \times 10^{-2}$	benzil

Run	Oxygen Pressure ( $\pm 0.1$ )	Peak	Azibenzil Concentration ( $\pm 0.0005$ )	Retention Time (min $\pm 0.05$ )	Area (cm $^2 \pm 1$ )	Concentration ( $\pm 0.0002$ ) (mole/liter)	Content
47B	4.0	1	0.2706	0.62	6.7	$4.10 \times 10^{-2}$	methyl benzoate
		2		1.50	trace		
		3		2.69	0.3		diphenylketene
		4		3.06	2.9		
		5		4.00	0.5	$2.47 \times 10^{-3}$	methyl diphenylacetate
		6		5.00	8.5	$5.43 \times 10^{-2}$	benzil
47C	4.0	1	0.2706	0.62	0.3	$1.80 \times 10^{-3}$	methyl benzoate
		2		1.38	trace		
		3		2.38	0.1		
		4		2.69	3.1		diphenylketene
		5		3.47	1.3	$7.30 \times 10^{-3}$	methyl diphenylacetate
		6		4.31	7.7	$4.25 \times 10^{-2}$	benzil