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The decomposition of azibenzil in the presence of oxygen

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THE DECOMPOSITION OF AZIBENZIL
IN THE PRESENCE OF OXYGEN

by

Arquette
Nancy C. Westby UC 1978
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Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE
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ABSTRACT

Name: Nancy C. Westby
Title: The Decomposition of Azibenzil in the Presence of
Oxygen
Department: Chemistry

The ozonolysis of acetylenes is thought to proceed through the formation of α -carbonyl carbonyl oxide intermediates. This reaction has been shown to parallel the effect of molecular oxygen on ketocarbenes. Azibenzil, a diazo-ketone, will decompose to a ketocarbene by the action of heat, light or a catalyst. The ketocarbene may decompose by two pathways: Wolff rearrangement and non-rearrangement. The Wolff rearrangement route will produce methyl-diphenylacetate (upon addition of methanol), benzophenone, tetraphenylglycolide and possibly other high molecular weight polymeric species. The non-rearrangement pathway will presumably produce α -carbonyl carbonyl oxides which will decompose under varying circumstances to produce benzil, benzoic anhydride, benzophenone, tetraphenylglycolide and other similar polymers. Evidence suggests that the thermal oxygenation of azibenzil proceeds principally via the rearrangement pathway; however, the production of triplet state α -carbonyl carbonyl oxides is indicated. The catalyzed reaction also

undergoes rearrangement; however, due to the ability of the catalyst to promote intersystem crossing, singlet and triplet state acyl carbonyl oxides are formed. The singlet configuration of this species appears to be responsible for the formation of the benzoic anhydride and of some benzil. The triplet state can decompose by an alternate method and generate benzophenone, tetraphenylglycolide, polymers and again some benzil.

DEDICATION

I would like to dedicate this work to Dr. L. Hull without whose confidence and patience this work would never have been completed.

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INTRODUCTION

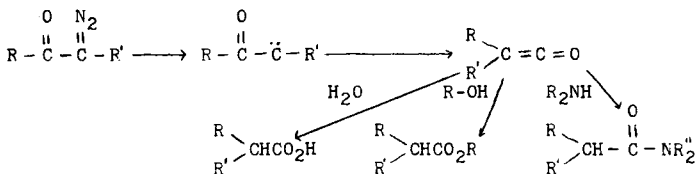
Within the last few decades, interest in the study of carbene chemistry has grown. Carbenes are the derivatives of methylene, and therefore possess two nonbonding electrons on an electron deficient carbon. These electrons may exist in two forms which differ in spin states. The singlet form is the result of the two nonbonding electrons being paired. Triplet carbenes, on the other hand, are diradicals: the unshared electrons are not paired. This difference in electron spin, gives rise to varying properties of the carbene carbon.²

For many years, it was believed that carbenes were stable and that they could be isolated. However, Staudinger and his associates in 1912 through 1916 did extensive work on determining the products of diazo and ketene decomposition.¹ Their work lent evidence to the fact that carbenes are transient species. Methylene, the parent molecule of carbene chemistry, has been shown to be formed in two ways. First, through the decomposition of diazomethane and second, through the decomposition of ketene. Both decompositions may occur photochemically or thermally. The methylene produced may then react with reactants to form ethylene. The formation

of ethylene by the interaction of the methylene with the starting material very often constitutes the major product of the photolytic decomposition.² Beyond the formation of ethylene, the fate of the methylene produced may take many forms. A few of the reactions which methylene undergoes³ are ; reaction with hydrogen to form methane, addition to carbon-carbon double bonds to form a cyclopropane unit and insertion into carbon-hydrogen bonds.

THE DECOMPOSITION OF DIAZOKETONES

The chemistry of ketocarbenes often entails the rearrangement of the carbon skeleton through the migration of aryls and alkyls bonded to the carbonyl group of the ketocarbene. The rearrangement was extensively investigated by L.Wolff who proposed the following scheme, or rationalization,⁴ for that rearrangement.

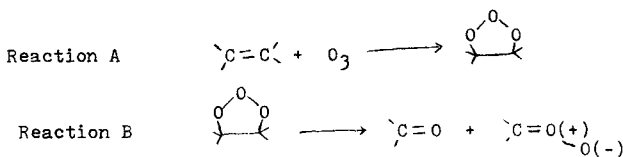


Diazoketones may be decomposed by heat, light and by various catalysts.⁵ The nature of the products produced strongly depends on the experimental conditions under which

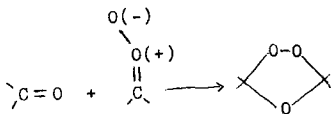
the reaction is run. Pyrolysis of a diazoketone may result in replacement of the diazo group without rearrangement as long as moderate temperatures are used. The Wolff rearrangement products are favored at higher temperatures. The photolysis of diazoketones will afford good rearrangement yields when UV irradiation is used and when there is an appropriate solvent present. The choice of catalyst to promote diazoketone decomposition must be made very carefully. Silver salts as noted by Wolff produce rearrangement products, however copper powder and most copper salts yield products resulting from intermolecular reactions. Also, rearrangement may be restricted if further functional groups are present within the diazoketone.⁶

OZONOLYSIS OF UNSATURATED COMPOUNDS

The reaction of ozone with unsaturated compounds results in the cleavage of the carbon-carbon double bond yielding aldehydes, ketones or their peroxidic derivatives as products. To explain the products of ozonolysis, Rudolf Criegee proposed the following mechanism;⁷

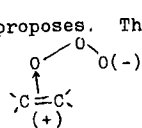
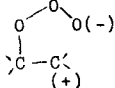
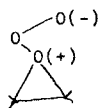


Reaction C

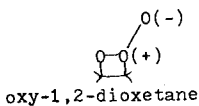


All three steps are 1,3-dipolar cycloadditions or reversions. In reaction A, ozone is added to the alkene to form 1,2,3-trioxolane which Criegee terms a primary ozonide. The 1,2,3-trioxolane does not have resonance stabilization of the ozone molecule and is thermodynamically unstable. Reaction B produces a carbonyl oxide (I) and a carbonyl compound through the decomposition of the primary ozonide. This decomposition proceeds through the cleavage of the carbon-carbon bond and the oxygen-oxygen bond, yet the carbon-oxygen bond remains intact. In reaction C, the carbonyl oxide, or zwitterion, adds to a carbonyl compound to produce a monomeric ozonide, 1,2,4-trioxolane, which contains an ether and a peroxide bridge between the two carbons.

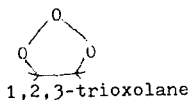
There are five possible primary ozonides which Criegee proposes. They are as follows;⁷

 π -complex σ -complex

peroxyepoxide



oxy-1,2-dioxetane



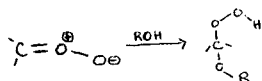
1,2,3-trioxolane

When ozone was added to trans-2,2,5,5-tetramethyl-3-hexene, a racemic 1,2 diol was produced by low temperature reduction. Of the five ozonides possible, only the oxy-1,2-dioxetane and the 1,2,3-trioxolane would yield such a product. An NMR spectrum was run on the primary ozonide of this reaction by Bailey⁸, which indicated that the environments about the two carbons were chemically equivalent. This would not be the case if the primary ozonide was oxy-1,2-dioxetane. This further lent evidence to the existence of the 1,2,3-trioxolane as the precursor of monomeric ozonide formation. However, the other suggested primary ozonides, the π -complex, σ -complex, and peroxyepoxide, may be present in the in the ozonolysis of other systems or as precursors to the 1,2,3-trioxolane. There is evidence to support the existence of the π -complex when energy rich arenes are reacted with ozone.⁹ The σ -complexes and the peroxyepoxides may exist as the result of a few ozonations in which the double bond is not completely cleaved. This is the case primarily when a reaction occurs with an olefin that is sterically hindered.¹⁰

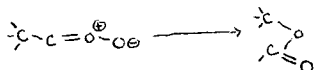
The carbonyl oxide, which is formed in reaction B of Criegee's mechanism, is an energy rich species which is a hybrid of the structures below.



Increased stabilization of this species occurs when electron-releasing substituents are present on the carbon. The carbonyl oxide produced may undergo hydrolytic solvent addition or rearrangement in the following manner;¹¹



Hydrolytic Solvent Addition
e.g. ROH



Rearrangement

In the rearrangement, the adjacent carbon-carbon single bond is ruptured oxidatively producing esters, lactones or acid anhydrides.

When the carbonyl oxide is recombined with an aldehyde or ketone, the monomeric ozonide, 1,2,4-trioxolane, or an oligomeric ozonide may be formed. Formation of the monomeric ozonide will occur under normal conditions only if

there is at least one hydrogen present at the carbon-carbon double bond. If the reaction or recombination is with a tetraalkylethylene, the oligomeric, dimeric peroxide and/or the rearrangement product will form. This is due to the fact that the ketone reacts more slowly than the aldehyde. With the ketone present, the carbonyl oxide has a longer lifetime which allows it to react in alternate ways. There are three ways though, that may be employed which will stimulate the keto group to react with the carbonyl oxide in the desired

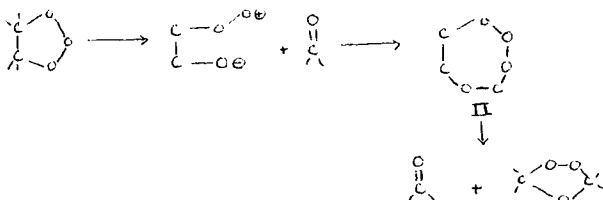
configurations. Symmetrically disubstituted trioxolanes are racemates in the trans-ozonide and meso in the cis-ozonide. The trans form, however, is the only form which affords optically active ozonides.

Olefins with keto groups may have a problem of interference by this group in the formation of the ozonide. The carbonyl oxide may react intermolecularly with the keto group of the diketone or may react intramolecularly with the keto group already present in the same molecule. In most cases, the intramolecular reaction will predominate. A cyclic olefin with a keto group present on a side chain, when treated with ozone will produce a molecule with two keto groups and one carbonyl oxide. If these two groups are symmetrically distributed about the carbonyl oxide, two ozonides will be formed as a result of the carbonyl oxide reacting separately with each of the two keto groups. This suggests that the intermediate must have a finite lifetime which allows the carbonyl oxide to choose between the two keto groups. The above reaction has also been shown to be kinetically controlled.¹³

Criegee also points out that ozonides may be formed by the photo-oxidation of diazo compounds. Murray photo-oxidized diphenyldiazomethane the result of which gave an ozonide after addition of a carbonyl compound.¹⁴ The intermediate or precursor of this reaction was presumably a carbene complex which resulted from the removal of nitrogen

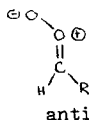
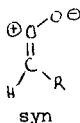
from the diazo compound and the subsequent addition of oxygen.

Criegee's mechanism predicts that both cis and trans ozonides when decomposed should afford the same fragments. These fragments when added to a carbonyl compound should then give cis/trans isomeric forms. It was found that this was not the case. To account for this inconsistency, Story¹⁵ proposed the following Aldehyde-Interchange mechanism:



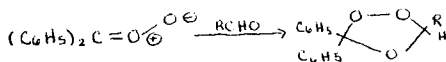
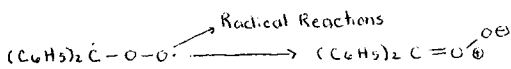
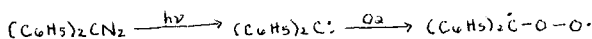
This mechanism would explain the reason for different monomeric ozonides being formed when cis and trans primary ozonides are used, however precursor II has an extremely improbable structure. In terms of bonding and thermodynamics the structure of II is very unstable. Further work done by others to determine and isolate precursor II has been unsuccessful. For this reason, the above mechanism is thought not to be valid.

Bailey, in attempting to work out the problem, suggests that syn and anti forms of the carbonyl oxide are possible.¹⁶ The two forms are shown below.



Cis and trans ozonides would probably yield differing amounts of the syn and anti carbonyl oxides which would then go on to give different recombination products when added to the aldehyde.

Murray and Suzui¹⁷ sought to improve upon Criegee's mechanism of ozonolysis since they felt that the mechanism did not take into account concentration, solvent, geometry or olefin steric requirements. They photolysed diazo compounds in the presence of oxygen and aldehyde. Limitation to this reaction would lie in the ability of the carbenes to form the triplet state. The triplet state reacts easier and faster with oxygen than the singlet form does. The reaction of the diazo compound with oxygen would form the triplet carbene, which when reacted with oxygen would produce the diradical carbonyl oxide.

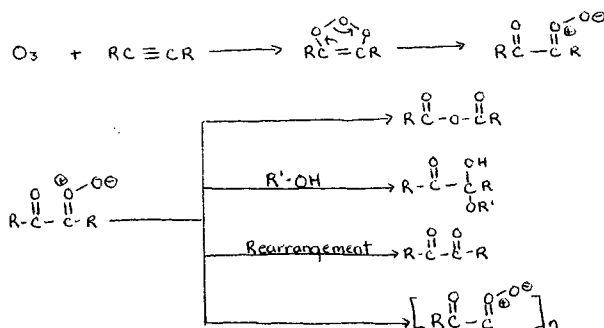


Murray and Suzui photolyzed 1-naphthyl-1-phenyldiazomethane in acetaldehyde which produced 1-(1-naphthyl)-1-propene ozonide as a cis/trans pair. Through the use of column chromatography, glpc, distillation and recrystallization, the isomers were separated. When either geometric isomer of the propene was ozonized, the same product mixture was obtained. The products included 2-butene ozonide formed from cross-ozonation, among other things. They found that the photooxidation of 1-(1-naphthyl)-1-phenyldiazomethane led to a cis/trans ratio which was not the same as the ratio obtained when cis olefin was used but which was most nearly the same as the ratio the trans olefin gives. Their work lent increasing evidence to the speculation that the trans olefin utilizes the carbonyl oxide pathway to a greater extent than the cis olefin.

Further work done by Murray and Higley¹⁸ showed that diazo compounds may be converted to ozonides through the reaction with singlet oxygen and aldehyde. They photooxidized diphenyldiazomethane with singlet oxygen. Their evidence for the reactions occurrence is as follows; the presence of a singlet oxygen quencher showed no diazo concentration change, the use of nitrogen instead of oxygen showed little or no diazo decomposition, and decomposition is twenty-five times more complete in sensitized photooxidations than in an unsensitized one.

THE OZONOLYSIS OF ACETYLENES

The ozonolysis of alkynes is believed to proceed through an α -carbonyl carbonyl oxide. The following mechanism for that ozonolysis was presented by Criegee and Lederer,¹⁹



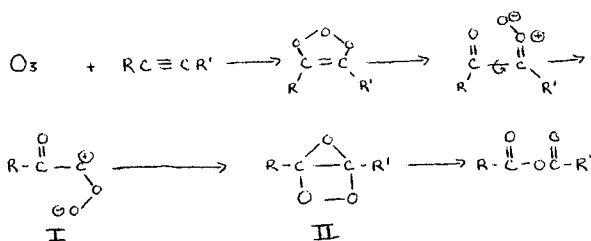
Keay and Hamilton²⁰ investigated the ozonolysis of alkynes and have shown that many intermediates and products are produced, at least three of which are capable of converting alkenes to epoxides. Using a 2-butyne-ozone-cyclohexene system, they discovered that cyclohexene oxide was the only major product. Also it was shown that alkene epoxidation is dependent upon the prior reaction of the alkyne with ozone and that no epoxide is formed if the alkene is ozonized in the presence or absence of alkyne. Keay and Hamilton propose that there are three epoxidizing species present: X, Y,

and Z. X is a "low temperature" species which is formed at -70°C and which reacts immediately with alkynes. Y is the "intermediate temperature" species which accounts for about one sixth of the epoxidation. It is formed at 70°C but only reacts between -25°C and -15°C at which point it decomposes. Z, the "room temperature" species is apparently peroxyacetic acid. It is also formed at -70°C but is very stable at room temperature. Its reaction with alkenes takes about two hours at room temperature though. Addition of methanol to the 2-butyne system during ozonolysis resulted in the reduction of the cyclohexene epoxide yield to twenty-five percent. If the methanol was added after ozonolysis had occurred, little or no reduction in the epoxide yield was obtained. These two results point to the conclusion that X, Y, and Z are stable in methanol, however some intermediate in their production is not. Keay and Hamilton are drawn to the conclusion that the "low temperature" species, X, is 1,2,3-trioxolene which has ring stabilization at low temperatures but which decomposes at higher temperatures. The mechanism for attack is not concerted since epoxidation by X does not occur with stereochemical retention.

Hull and coworkers²¹ further provided evidence for the existence of 1,2,3-trioxolene as the precursor for the acyl carbonyl oxide in the Criegee-Lederer mechanism. They determined that for propargyl compounds, reaction proceeds almost exclusively through the formation of the anhydride.

It was shown that the intermediate formed in the rate determining step is unlikely to be polar or capable of accepting hydrogen bonds from the solvent. This insensitivity to the polarity of the substituents, is characteristic of 1,3-dipolar cycloadditions. Of the possible precursors to the acyl carbonyl oxide, only the 1,2,3-trioxolene structure will have the above mentioned properties.

Another possible mechanism in the ozonolysis of alkynes was presented by Hull and coworkers²². The proposed mechanism is as follows;

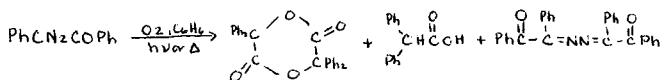


In the mechanism, species I is formed through the rotation about the carbon-carbon single bond in the α -carbonyl carbonyl oxide. The possibility of structure II is quite feasible since its formation is extremely similar to the addition of carbonyl oxide to ketones and aldehydes to form the monomeric ozonide, 1,2,4-trioxolane. Hull showed that the precursor in anhydride formation is insensitive to polar and solvent effects. Beyond this the structure of II is very stable. It is for these reasons that the above mech-

anism must be further investigated and must be considered a feasible explanation regarding the fate of the ozonolysis of alkynes.

THE DECOMPOSITION OF AZIBENZIL

In the photooxygenation of azibenzil at 77K, Trozzolo et. al.²³ reported that the products obtained were benzil, ketene and a high yield of solvent-substituted deoxybenzoins. The photochemical or thermal decomposition of the azibenzil with molecular oxygen afforded tetraphenylglycolide and no peroxides or ketones as reported by Tanaka and coworkers.²⁴ Tanaka's scheme for this decomposition is as follows;



The structure of the tetraphenylglycolide was confirmed by Tanaka through molecular weight determination, IR, ¹H NMR, ¹³C NMR and the reaction.

Recent work has been done by J.Sawyer²⁵ on the copper catalysed decomposition of azibenzil (phenylbenzoyldiazomethane) by oxygen. A work up was done on the untreated products of the decomposition and those treated with methanol. For the untreated products, analysis showed that benzil,

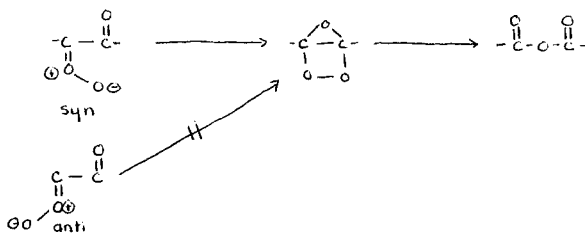
diphenylketene and benzoic anhydride were present. The products treated with methanol were determined to be benzil, diphenylketene, methyl benzoate and methyl diphenylacetate. The presence of the methyl benzoate in the treated analysis gave further proof to the existence of the benzoic anhydride in the untreated mixture. Similarly, the presence of the methyl diphenylacetate confirms the fact that the ketene was present. The different products obtained, point to the fact that rearrangement and non-rearrangement occurred in the above reaction.

Tanaka did not identify benzil or benzoic anhydride but specifically did identify the presence of tetraphenylglycolide. Sawyer suspected that the glycolide was present but was unable to confirm its existence. To explain the difference in products obtained between Tanaka's and her work, Sawyer points out that the conservation of spin multiplicity may be important. The ketocarbene produced during azibenzil decomposition is probably in the singlet state.²⁶ Upon reaction with triplet molecular oxygen, an acyl carbonyl oxide is produced which must be in the triplet state to conserve spin multiplicity. This triplet acyl carbonyl oxide may then dimerize to form the tetraphenylglycolide reported by Tanaka. However, the presence of the heavy metal, copper, in the reaction affords both triplet and singlet α -carbonyl carbonyl oxides. The singlet, due to its paired electrons, then goes on to react intramolecularly producing benzil and

benzoic anhydride. The copper allows intersystem crossing to take place.

Beyond this, Sawyer found that benzoic anhydride production increases with oxygen pressure increase while the concentration of methyl diphenylacetate decreases. This suggests that non-rearrangement products are favored by high oxygen pressures while the opposite is true of the Wolff rearrangement products.

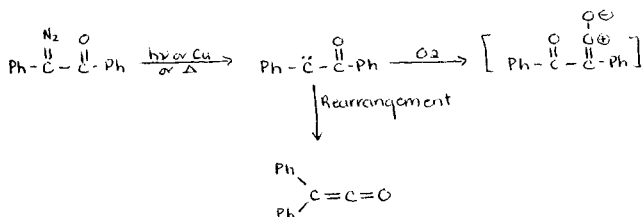
The following reaction to form the anhydride has been suggested by Sawyer;



The syn configuration due to geometry, may, as hypothesized by Hull and coworkers, go on to produce the stable dioxetane which may then go on to produce the anhydride. The anti form will not proceed by this route since it is unlikely for it's structure to cyclize. However, it may be entirely possible for the longer lived anti configuration to lose an oxygen to form benzil

PROPOSED RESEARCH IN THE DECOMPOSITION OF AZIBENZIL

As has been shown, the decomposition of azibenzil may proceed in two ways; Wolff rearrangement or formation of the α -carbonyl carbonyl oxide in the presence of oxygen. The following reaction outlines these two pathways;



The products produced from the acyl carbonyl oxide have been shown by Sawyer to be benzil, benzoic anhydride and perhaps tetraphenylglycolide. Upon addition of methanol, the methyl benzoate is formed. The rearrangement product when treated with methanol produces methyl diphenylacetate.

The purpose of this study is to use thermal and photolytic methods to monitor the azibenzil decomposition in oxygen. In looking at the products produced under these two conditions, it may be possible to confirm the existence of the α -carbonyl carbonyl oxide. It may also be possible to elucidate the syn and anti configurations of that intermediate through the presence or absence of specific products. Once the syn and anti forms are confirmed, evidence may be built up for the presence of the dioxetane as precursor to the anhydride.

EXPERIMENTAL

Instruments Used in Analyses

1. All Gas Chromatograph results were obtained by using a Perkin Elmer 900 Gas Chromatograph employing the flame ionization mode. The column was four feet by one quarter inch consisting of 15% DC-200 on Chrom. P, 80/100 mesh, with a maximum temperature of 250°C. The conditions used were as follows; 1 microliter injection, injector 150°C, manifold 150°C, program 150°C-200°C, 3 minutes initial, 24°C per minute, hold final, 60 mm/min, solvent chloroform.

2. All the IR work was carried out on a Perkin Elmer 237.

3. All the NMR work was done on a Hitachi-Perkin Elmer R24A.

Production of Benzil Monohydrazone²⁷

0.75 moles (45 grams) of 85% hydrazine hydrate are slowly dropped with stirring into a hot solution of 0.75 moles (158 grams) benzil and 300 milliliters of ethanol. The product begins to separate after three quarters of the hydrazine hydrate has been added. The mixture is refluxed for five minutes and then cooled to 0°C. The benzil monohydrazone is filtered and washed twice with 100 milliliter portions of cold ethanol. (IR spectrum No.1)

Synthesis of Azibenzil (phenylbenzoyldiazomethane)²⁸

30 grams (0.134 moles) of benzil monohydrazone, 60 grams (0.28 moles) of yellow mercuric oxide and 15 grams (0.110 moles) of anhydrous calcium sulfate are mixed thoroughly in a mortar and pestle. The mixture is introduced into a 500 milliliter stoppered bottle and covered with 200 milliliters of absolute ethyl ether. 18 milliliters of saturated ethanol solution of potassium hydroxide is added to catalyze the reaction. The mixture is shaken vigorously for one hour.²⁹ The solution is filtered and the residue is washed several times with absolute ether until the filtrate is only slightly colored. The ethereal extracts are evaporated to dryness on a rotoevaporator with heating at a temperature not exceeding 40°C. Caution- The material may explode at temperatures above 40°C. The yellow-orange crystalline material is recrystallized from anhydrous ether, dried and stored in the refrigerator in an amber bottle to prevent decomposition.

Confirmation of the azibenzil structure (IR No. 3) was done by comparing its spectrum with the spectra of benzil monohydrazone (IR No.1) and benzil (IR No.2). Also azibenzil has been shown to have a strong characteristic peak at 2100 cm⁻¹. Thin Layer Chromatography was also used in the determination of the purity of the azibenzil. A one to three diethyl ether-hexane solution was used which allowed good separation of azibenzil, benzil monohydrazone, and benzil.

Azibenzil Decompositions

A. Thermal Oxygenation

1 gram of azibenzil in 10 milliliters of benzene was refluxed with stirring for three hours with oxygen being passed through the solution. After reaction had occurred, the benzene was removed on the rotoevaporator and 10 milliliters of methanol was added to the residue. The methanol solution was allowed to reflux for one hour at which time the methanol was removed and 10 milliliters of chloroform was added to the solution. 1 milliliter of the chloroform solution was extracted and 0.0134 grams of dodecane was added to it.

B. Copper Catalyzed Oxygenation

1 gram of azibenzil and 0.1 grams of copper powder in 10 milliliters of benzene were allowed to react, with stirring, under oxygen for three hours at a temperature between 50°C and 55°C. After three hours, the copper was filtered off carefully and the benzene was evaporated off. To this mixture, 10 milliliters of methanol was added and the solution was refluxed for one hour. The methanol was subsequently removed and 10 milliliters of chloroform was added to the residue. 1 milliliter of the chloroform solution was extracted and to this 0.0114 grams of dodecane was added.

C. Production of Tetraphenylglycolide³⁰

8.5 grams of azibenzil in 85 milliliters of benzene were refluxed for four and a half hours under oxygen. 40 milliliters of water and 40 milliliters of ether were then added to the reaction mixture. From the organic layer, benzene and ether were removed under reduced pressure. 100 milliliters of methanol was added to the residue. The methanol solution was cooled and white powders precipitated. Elution with benzene gave tetraphenylglycolide which was recrystallized from ethyl acetate.

Confirmation of tetraphenylglycolide was done by the presence of a 1750 cm^{-1} absorption band in the spectrum of the above crystals (IR No.4).

D. Photooxidation of Azibenzil

1. Unsensitized

1 gram of azibenzil was dissolved in 450 milliliters of ethyl ether. The light source used was a high intensity mercury lamp which was placed inside a pyrex water jacket. The mixture of azibenzil in ether was placed around this water jacket and oxygen was allowed to bubble through the solution. The reaction mixture was stirred thoroughly during photolysis to insure even mixing of the oxygen with the azibenzil in the ether. The photooxidation was allowed to go until there was no more evidence of azibenzil being present. After one hour of photooxidation, IR (spectrum No. 5) showed the absence of any starting material at 2100 cm^{-1} ,

and the color of the reaction solution had bleached from orange to nearly white. The 450 milliliters of ether were removed and 10 milliliters of methanol was added to the residue. This mixture was allowed to reflux and after one hour the methanol was removed and 10 milliliters of chloroform was added. 1 milliliter of the solution was taken and 0.0179 grams of dodecane was added.

2. Sensitized

The set up for the sensitized photooxidation is the same as the set up described above with the exception of 2.3 grams of 2-Acetonaphthone, as photosensitizer, being added to the azibenzil and ether solution. 2-Acetonaphthone has a molar extinction coefficient of 1600 at 330 centimeters while azibenzil has an extinction coefficient of 487 at 320 centimeters. Therefore 2.3 grams of 2-Acetonaphthone in 1 gram of azibenzil corresponds to a situation where the sensitizer will absorb ninety percent of the light emitted by the mercury lamp. To the 1 milliliter chloroform, 0.0164 grams of dodecane was added.

3. Blank Number One

This reaction was run exactly as the unsensitized photooxidation; however, no oxygen was allowed to pass through the reaction mixture. 0.0094 grams of dodecane was added to 1 milliliter of the chloroform solution.

4. Blank Number Two

The conditions for reaction here again were the same as those described in the unsensitized photooxidation with the exception that no oxygen was allowed to react with the photolysis solution until one hour had passed. After one hour, oxygen was added and the system was allowed to photooxidize for another hour. 0.0153 grams of dodecane was then added to a 1 milliliter extraction of the final chloroform solution.

E. Decomposition to form Diphenylketene

1. Reaction with Nitrogen

1 gram of azibenzil in 25 milliliters of benzene was refluxed for nineteen and a half hours under a nitrogen atmosphere. At this time an IR was taken (IR No.6) which indicated the presence of diphenylketene (2100 cm^{-1}). 10 milliliters of this benzene solution was then reacted with oxygen for an additional four hours (IR No.7) while the remaining 15 milliliters of the solution was continued to reflux under nitrogen for the four hours (IR No.8).

2. Blank Number Three

1 gram of azibenzil in 10 milliliters of benzene was allowed to reflux without oxygen present for three hours in order to produce the diphenylketene (IR No.9). Oxygen was then added to the reaction mixture and the solution was refluxed under these conditions for an additional three hours. At that time, the benzene was evaporated off and 10 milliliters of methanol was added to the residue and

was allowed to reflux for one hour. The methanol was removed and 10 milliliters of chloroform was added and a 1 milliliter sample was extracted and 0.0238 grams of dodecane was added to this mixture.

Alternate Method of Generating Tetraphenylglycolide

11.4 grams of benzoic acid, 0.9511 grams of p-toluene sulfonic acid monohydrate and 500 milliliters of benzene was refluxed for four hours. After refluxing, the mixture was washed twice with 50 milliliter portions of ten percent sodium carbonate and then washed once with 50 milliliters of water. The remaining mixture was dried by removing the solvent on the rotoevaporator which produced white crystals. 100 milliliters of carbon tetrachloride was added to the crystals to remove any impurities, and this solution was subsequently filtered. The remaining crystals were recrystallized from ethylacetate. 4.32 grams of product was obtained with a melting point of 198°C-201°C and an Infrared spectrum (IP No.10) showed the characteristic absorption of tetraphenylglycolide at 1750 cm⁻¹.

Synthesis of 3-methyl-2,4-pentanedione³¹

65.2 grams (0.65 moles) of 2,4-pentanedione, 113 grams (0.80 moles) of iodomethane, 84 grams of anhydrous potassium carbonate and 250 milliliters of acetone are placed in a 1000 milliliter round bottom flask with a condenser and

a calcium chloride guard tube. The mixture is heated under reflux for twenty hours with constant stirring, and then cooled. The insoluble matter is removed by filtration and washed thoroughly with acetone. The filtrate is concentrated on the rotoevaporator (During the removal of the acetone, potassium iodide is deposited and it is advisable to decant the crude methylpentane-2,4-dione from this material before distillation) and the residual oil is distilled. An NMR (spectrum No.14) was taken on the distillate collected between 170°C and 171°C which indicates that the product is relatively pure.

Ozonolysis of Diphenylacetylene

All the ozonolysis work done was done on a Welsbach Model T-408 Ozonator. The standardization of this particular model was done by Sawyer²⁵ who determined that a flow rate of 0.3 corresponds to 1.4×10^{-4} moles of ozone produced per minute. 1 gram of diphenylacetylene in 10 milliliters of carbontetrachloride under went ozonolysis for forty minutes with refluxing. At this time, the color of the solution had considerably darkened and the carbon tetrachloride was removed and 10 milliliters of methanol was added to the residue which was then refluxed for one hour. The methanol was subsequently removed and 10 milliliters of chloroform was added. From this resulting mixture, 1 milliliter was extracted and 0.0247 grams of dodecane was added to the

milliliter of solution.

The Ozonolysis of 3-methyl-2,4-pentanedione

A. 1.18 milliliters (1 Molar) of 3-methyl-2,4-pentanedione in 10 milliliters of carbon tetrachloride underwent ozonolysis for two hours, twenty-two minutes and forty-eight seconds at 0°C. The flow rate was maintained at 0.3. 1 milliliter of the ozonolysis mixture was taken and to it 0.0341 grams of o-dichlorobenzene was added.

B. 0.594 milliliters (0.5 Molar) of 3-methyl-2,4-pentanedione in 10 milliliters of carbon tetrachloride underwent ozonolysis for one hour, eleven minutes and twenty-four seconds at 0°C. To one milliliter of this mixture, 0.0221 grams of o-dichlorobenzene was added.

C. 0.237 milliliters (0.2 Molar) of 3-methyl-2,4-pentanedione in 10 milliliters of carbon tetrachloride was ozonized at 0°C for twenty-eight minutes and thirty-six seconds. 0.0327 grams of o-dichlorobenzene was added to one milliliter of the resulting solution.

D. 0.118 milliliters (0.1 Molar) of 3-methyl-2,4-pentanedione in 10 milliliters of carbon tetrachloride was ozonized for fourteen minutes and twelve seconds at 0°C.

0.0271 grams of o-dichlorobenzene was subsequently added to

one milliliter of this carbon tetrachloride solution.

RESULTS

The analysis of the products obtained from the various methods employed in the decomposition of azibenzil, was principally due to the work up of the reaction mixtures on the Gas Chromatograph. As noted in the experimental section, a known amount of dodecane was added to the product solutions. The dodecane was used as an internal standard for these mixtures to facilitate and quantify the Gas Chromatographic analysis. With this internal standard present, it was possible to determine relatively accurately the concentrations of the components in the decompositions. Aside from this important function of the internal standard, the presence of the dodecane allowed the analyses to be independent of any fluctuations in injection sizes. Dodecane was chosen specifically as the standard because its retention time did not overlap with or affect the true retention times of the products obtained from the reactions.

In the experimental work up, all of the decomposition mixtures were eventually placed in chloroform. It was found that the addition of methanol to the reaction mixtures often caused a precipitate and/or an oil to form. Staudinger^{32,33} noted that tetraphenylglycolide and other high molecular weight polymeric species in decompositions of this type, are relatively insoluble in methanol. The mixtures

had to be treated with methanol though so that all of the products would be stable and be able to withstand the analysis techniques. The addition of chloroform to the residue of the reactions caused any oils or precipitates to immediately go into solution insuring accurate Gas Chromatographic results.

A standard solution containing known quantities of the products of the decompositions was analyzed to obtain information regarding each components response relative to the internal standard; dodecane. By analyzing each constituent in this way, the concentrations of each of them in the product mixtures was able to be determined. Table 1 indicates the results obtained from the Gas Chromatography of the standards.

The thermal oxygenation of azibenzil yielded the results outlined in Table 2. The analysis was only able to account for 17.17 percent of the products. Apparently, the principle products of this type of reaction are high molecular weight polymers such as tetraphenylglycolide. Analysis of these polymers by gas chromatographic techniques, using the columns available, proved futile. An Infrared spectrum of the product mixture was taken (IR No.11) which does indicate the presence of tetraphenylglycolide by it's characteristic absorption at 1750 cm^{-1} .

The copper catalyzed oxygenation of azibenzil was found to be very influenced by the temperature at which the

Table 1: Standardization of the Decomposition of Azibenzil

Peak	Component	Area ($\text{cm}^2 \pm 5\%$)	Concentration ($\text{M} \pm 5\%$)	Correction Factor ($\pm 5\%$)
1	Methyl Benzoate	49632.0	0.088	1.43
2	Dodecane	442368.0	0.547	1.0
3	Methyldiphenylacetate	51456.0	0.153	2.40
4	Benzil	82432.0	0.263	2.58
1	Dodecane	393856.0	0.418	1.0
2	Benzophenone	138000.0	0.418	2.85

Table 2: Thermal Oxygenation of Azibenzil

<u>Peak</u>	<u>Content</u>	<u>Area (cm² \pm 5%)</u>	<u>Concentration (M \pm 5%)</u>	<u>Mole % of Azibenzil (\pm 5%)</u>
1	Methyl Benzoate	-----	-----	-----
2	Dodecane	91136.0	0.079	-----
3	Benzophenone	19392.0	0.048	-----
4	Methyldiphenylacetate	11232.0	0.023	10.70%
5	Benzil	2496.0	0.006	5.13%
				1.34%

reaction was run. To avoid any competition in this reaction due to thermal influences, the reaction mixture was kept between 40°C and 45°C . However, it was found that after even four hours, no reaction had occurred. When this mixture was brought up to 50°C , it was still evident that the azibenzil was not decomposing. Another copper solution of this type was run; however, this time the mixture was allowed to stay at 50°C to 55°C . Within one hour, reaction was complete and no azibenzil was present as shown by IR. Apparently, reaction occurs too slowly at the lower temperature and that at this temperature, the copper may eventually be rendered inactive. The analysis of the catalyzed oxygenation is shown in Table 3. Again, only 18.74 percent of the products of the decomposition were characterized. The remaining products are then the polymeric species discussed previously, as indicated by the Infrared spectrum (IR No.12) obtained on the product mixtures.

In the photolytic decompositions of azibenzil, it was found that it is extremely important for the reaction mixtures to have good contact with the light with which they are exposed. Previous to using the light source and the set up described in the experimental section, photooxidation was attempted by just placing one side of the reaction flask next to the lamp. Photolysis occurred only after fifteen hours and even then there was great doubt as to the validity of the results. Using the technique described in the exper-

Table 3: Copper Catalyzed Oxygenation of Azibenzil

<u>Peak</u>	<u>Content</u>	<u>Area (cm² \pm 5%)</u>	<u>Concentration (M \pm 5%)</u>	<u>Mole % of Azibenzil (\pm 5%)</u>
1	Methyl Benzoate	16128.0	0.016	3.57%
2	Dodecane	99328.0	0.067	-----
3	Benzophenone	10500.0	0.020	4.46%
4	Methyldiphenylacetate	25632.0	0.041	9.15%
5	Benzil	4224.0	0.007	1.56%

imental section, reaction occurred quickly and most probably most accurately. The results of the photooxidations are given in Table 4.

Blank 3 described in the experimental section involves the decomposition of azibenzil to the diphenylketene which is then allowed to undergo reaction with oxygen. The results of this type of experiment will aid in determining the fate of the diphenylketene produced upon the decomposition of azibenzil by the techniques described above. The Infrared spectrum (IR No.9) taken after three hours of refluxing without oxygen shows the presence of the diphenylketene at about 2100 cm^{-1} . The spectrum taken after this mixture was subsequently exposed to oxygen (IR No.13) indicates that benzophenone (1660 cm^{-1}) and tetraphenylglycolide (1750 cm^{-1}) are both present. The gas chromatograph analysis of this blank is given in Table 5.

Table 6 is a summary of the mole percent of azibenzil which has been consumed in the decompositions already outlined. Of the five decompositions listed, it should be noted that the high molecular weight polymeric species, which could not be characterized, are the major products in all of the reactions done. In the thermal, catalytic and photolysis decompositions, these species represent approximately eighty percent of the total products produced, while Blank 3 only has sixty percent of the products unaccounted for. This table will be further referred to in the following discussion

Table 4: Photooxidation of Azibenzil

Run 1- Unsensitized Photolysis
 Run 2- Sensitized Photolysis
 Run 3- Photolysis Blank 1
 Run 4- Photolysis Blank 2

Run Peak Content		Area(cm ² ±5%)	Concentration(M±5%)	Mole % of Azibenzil(±5%)
1	1 Methyl Benzoate	-----	-----	-----
2	Dodecane	227136.0	0.105	-----
3	Benzophenone	6912.0	0.009	2.01%
4	Methyldiphenylacetate	2496.0	0.003	0.67%
5	Benzil	66816.0	0.080	17.9%
2	1 Methyl Benzoate	-----	-----	-----
2	Dodecane	162560.0	0.096	-----
3	Benzophenone	-----	---	-----

Run	Peak	Content	Area(cm ² ±5%)	Concentration(M±5%)	Mole % of Azibenzil(±5%)
2	4	Methyldiphenylacetate	1536.0	0.002	0.45%
	5	Benzil	58752.0	0.089	19.9%
3	1	Methyl Benzoate	2240.0	0.002	0.45%
	2	Dodecane	72960.0	0.055	-----
	3	Benzophenone	1088.0	0.002	0.45%
	4	Methyldiphenylacetate	3904.0	0.007	1.56%
	5	Benzil	55808.0	0.109	24.33%
4	1	Methyl Benzoate	2560.0	0.003	0.67%
	2	Dodecane	127360.0	0.090	-----
	3	Benzophenone	3312.0	0.007	1.56%
	4	Methyldiphenylacetate	2184.0	0.004	0.89%
	5	Benzil	25344.0	0.046	10.23%

Table 5: Blank 3 of the Decomposition of Azibenzil

Peak	Content	Area(cm ² ±5%)	Concentration(M±5%)	Mole % of Azibenzil(±5%)
1	Methyl Benzoate	-----	-----	-----
2	Dodecane	174080.0	0.140	-----
3	Benzophenone	3096.0	0.007	-----
4	Methyldiphenylacetate	86912.0	0.168	1.56%
5	Benzil	2048.0	0.004	37.5%
				0.89%

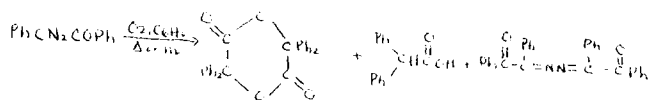
Table 6: Mole Percent of Azibenzil (±5%):
A Summary of the Decompositions

Content	Thermal Oxygenation	Catalytic Oxygenation	Unsensitized Photooxidation	Sensitized Photooxidation	Blank 3
Methyl Benzoate	-----	3.57%	-----	-----	-----
Benzophenone	10.7%	4.46%	2.01%	-----	1.56%
Methyldiphenylacetate	5.13%	9.15%	0.671%	0.447%	37.5%
Benzil	1.34%	1.56%	17.9%	19.9%	0.89%

section.

The decomposition of azibenzil to form the diphenylketene in the absence of any oxygen was run as a blank to determine if the diphenylketene dimer would form. After nineteen and a half hours of reaction under nitrogen, an infrared spectrum (IR No.6) was taken which proved that the diphenylketene was present in the reaction mixture. One portion of this reaction was subsequently allowed to react with oxygen while the remaining amount of the reaction mixture was allowed to continue refluxing under nitrogen. Infrared spectrum taken on these new solutions (IR No.7 and IR No.8 respectively) did not indicate the presence of any diphenylketene dimer at 1748 cm^{-1} .

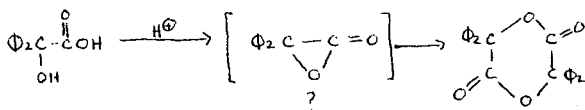
Tetraphenylglycolide has been shown to be an important product in any of the decompositions done on azibenzil. As outlined in the experimental section, two methods of producing this species were attempted. The first procedure followed the reaction conditions specified by Tanaka.³⁰ The reaction which occurred in this process is as follows;



Tanaka reported that the mole percent of the tetraphenylgly-

colide was forty percent. Using the same conditions for the thermal oxygenation of the azibenzil outlined by Tanaka, we were unable to obtain neither pure nor large amounts of the tetraphenylglycolide. An Infrared spectrum (IR No.4) was taken on the tetraphenylglycolide which does not indicate a very strong absorption at 1750 cm^{-1} .

The alternate method of generating the tetraphenylglycolide did result in visibly purer crystals and the yield in this case was about five times as great as the yield obtained from the procedure indicated above. The reaction which took place is as follows;



Several methods were employed to try and characterize the amount of tetraphenylglycolide present in the decomposition mixtures. Unfortunately though, none of the following analyses attempted shed any light on the role the tetraphenylglycolide played in the reactions. All of the gas chromatographic analyses on this species proved futile. Injection of tetraphenylglycolide in chloroform didn't afford any clear indication of the tetraphenylglycolide's presence. In one instance, perhaps four peaks would form on the gas chromat-

ograph however injection of a second comparable solution would not yield any peaks. In other words, it was found that if there was any response by the tetraphenylglycolide, it was very inconsistent and was subsequently too inaccurate to be used as a quantitative determination of this species presence. Using a solution of tetraphenylglycolide to spike the decomposition solutions did not cause any increase in the height of the peaks present in the decomposition mixtures. All of the analyses have been reported as being carried out on a DC-200 column. However beyond this column an SE 30 and a Carbowax column were used. Again, these columns were unable to elucidate any tetraphenylglycolide. The above problems in using the gas chromatograph as a technique to determine the amount of tetraphenylglycolide present in the reaction mixtures is most probably due to the fact that it is too high of a molecular weight species to be analyzed by conventional gas chromatograph techniques.

Solubility differences between the tetraphenylglycolide and the other known products of decomposition was employed. It was found that tetraphenylglycolide was insoluble in carbon tetrachloride whereas the other components were found to be soluble in this solvent. Two milliliters of the chloroform solutions of the decompositions was used in this analysis. The chloroform was removed on the rotoevaporator and two milliliters of carbon tetrachloride was subsequently added to the residue. The resulting solution was

filtered and the material remaining after filtration was weighed. It was found that this material only weighed about 0.009 grams. A weight of this size is much too small to make the analysis quantitative.

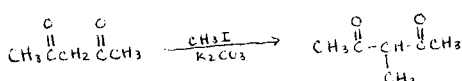
One final attempt was made at elucidating the tetraphenylglycolide which was through the use of Infrared spectroscopy. Both tetraphenylglycolide and methyldiphenylacetate were found to have characteristic absorption bands at approximately 1750 cm^{-1} . It was therefore necessary to remove the methyldiphenylacetate so that a true measure of the amount of tetraphenylglycolide present could be determined. It was found that the tetraphenylglycolide was not soluble in methanol, as noted in previous observations, whereas the methyldiphenylacetate was very soluble in this solvent. Methanol was added to the dried residue from the reaction mixtures and the solution was filtered. The material which remained behind was dissolved in chloroform and an Infrared spectrum was taken. Unfortunately the peak remaining at 1750 cm^{-1} was broad and unsymmetrical. For this reason, it was again not possible to make a good quantitative conclusion about the tetraphenylglycolide since it appeared that there was too much interference by other components of the product mixtures. The interference which resulted perhaps may be due to the presence of even higher molecular weight polymeric species.

The ozonolysis of diphenylacetylene was run as a form

of blank to determine the fate of the proposed α -carbonyl carbonyl oxide intermediate in this system. Again not all of the products could be accounted for in this reaction. Table 7 lists the results obtained through analysis of the product solutions by gas chromatography.

The ozonolysis was obviously not run to completion due to the presence of the starting material in the product mixture; however, it was feared that if too much ozone was used that peroxides would form. If this occurred, any results obtained in the analysis would be inaccurate and incomplete.

The ozonolysis of 3-methyl-2,4-pentanedione was carried out to determine if there were intermediates in its reaction with ozone which parallel the intermediates suspected in the decompositions of azibenzil and in the ozonolysis of diphenylacetylene. The formation of 3-methyl-2,4-pentanedione from 2,4-pentanedione is as follows;



The production of the 3-methyl-2,4-pentanedione was relatively complex since it was found that simple distillation of the crude mixture was not enough to produce pure sample. Instead three distillations had to be run. The first of these was a simple distillation, the second involved redis-

Standardization of Diphenylacetylene			
Peak	Content	Area (cm ² ±5%)	Concentration (M±5%)
1	Dodecane	17459.2	5.0
2	Diphenylacetylene	7104.0	5.0
Ozonolysis Product Mixture			
Peak	Content	Area (cm ² ±5%)	Concentration (M±5%)
1	Methyl Benzoate	10448.0	0.124
2	Dodecane	174720.0	0.145
3	Benzophenone	4256.0	0.010
4	Diphenylacetylene	56736.0	0.116
5	Benzil	16992.0	0.036
			Correction Factor(±5%)
1			1.0
2			2.46
			Mole % of Diphenylacetylene
1			22.1%
2			-----
3			1.78%
4			20.67%
5			6.42%

tillation of the higher fractions taken from the previous distillation, and the last was a hemple distillation run on the highest fractions obtained from the second work up. It was found that dodecane was not a suitable standard for this system since its peak interfered with a peak later identified as biacetyl. Instead, o-dichlorobenzene was used and a set of standard solutions were made up in the same manner previously discussed. The gas chromatographic analysis was also different since it was determined that the DC-200 column used in all the other analyses up until now was inappropriate for this system. The column used was a four foot carbowax column and the detector was in the flame ionization mode. The program was as follows; temperature ranged from 80°C to 150°C with an initial time of two minutes and a temperature rise of 24°C per minute. The injection size remained at one microliter and the chart speed was set at 60 millimeters per minute. Table 8 gives the results of the standardization using o-dichlorobenzene.

Tables 9 and 10 give the results obtained from the ozonolysis done on the 3-methyl-2,4-pentanedione.

There are two very important things which must be noted regarding the gas chromatograph analyses outlined in these tables. The first and most obvious is that apparently there must be some other product of these reactions which has the same retention time as the 3-methyl-2,4-pentanedione. In all four runs, analysis would otherwise indicate that

Table 8: Standardization of the Ozonolysis of 3-Methyl-2,4-pentanedione

Peak	Content	Area($\text{cm}^2 \pm 5\%$)	Concentration($\text{M} \pm 5\%$)	Correction Factor($\pm 5\%$)
1	Biacetyl	207360.0	1.33	2.8
2	Acetic Anhydride	146432.0	1.33	3.97
3	Acetic Acid	95744.0	1.33	6.06
4	O-Dichlorobenzene	580608.0	1.33	1.0
1	3-Methyl-2,4-pentanedione	215680.0	1.0	2.04
2	O-Dichlorobenzene	18304.0	0.0415	1.0

Table 9: Ozonolysis of 3-Methyl-2,4-pentanedione

Run 1: 1M ozonolysis
 Run 2: 0.5M ozonolysis
 Run 3: 0.2M ozonolysis
 Run 4: 0.1M ozonolysis

Run	Peak	Content	Area (cm ² ± 5%)	Concentration (N ± 5%)
1	1	Eiacetyl	11520.0	0.090
	2	Acetic Anhydride	30720.0	0.376
	3	3-Methyl-2,4-pentanedione	384896.0	2.42
	4	Acetic Acid	8064.0	0.15
	5	O-Dichlorobenzene	75264.0	0.232
2	1	Eiacetyl	15232.0	0.083
	2	Acetic Anhydride	7040.0	0.054
	3	3-Methyl-2,4-pentanedione	181952.0	0.719

<u>Run</u>	<u>Peak</u>	<u>Content</u>	<u>Area (cm²-%)</u>	<u>Concentration (M±%)</u>
2	4	Acetic Acid	1920.0	0.023
5		O-Dichlorobenzene	77440.0	0.150
3	1	Biacetyl	9728.0	0.052
2		Acetic Anhydride	880.0	0.007
3		3-Methyl-2,4-pentanedione	52192.0	0.203
4		Acetic Acid	512.0	0.005
5		O-Dichlorobenzene	116160.0	0.222
4	1	Biacetyl	4992.0	0.029
2		Acetic Anhydride	192.0	0.0015
3		3-Methyl-2,4-pentanedione	25760.0	0.110
4		Acetic Acid	128.0	0.0011
5		O-Dichlorobenzene	38320.0	0.184

Table 10: Summary of the Concentrations($M \pm 5\%$) of the
Products Obtained in the Ozonolysis Runs

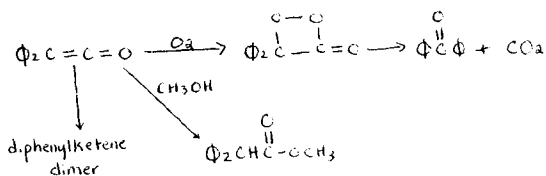
Peak	Content	Run 1	Run 2	Run 3	Run 4
1	Biacetyl	0.09	0.083	0.052	0.029
2	Acetic Anhydride	0.376	0.054	0.007	0.0015
3	3-Methyl-2,4-pentanedione	2.42	0.719	0.203	0.110
4	Acetic Acid	0.15	0.023	0.005	0.0011

almost twice as much starting material is present in the product mixture than material used before reaction. Also, the 3-methyl-2,4-pentanedione had two peaks associated with itself. Spiking the reaction mixtures with a known sample of the 3-methyl-2,4-pentanedione resulted in a change in two of the peaks of each gas chromatograph. The conclusion is that the two peaks represent the keto and the enol forms of the 3-methyl-2,4-pentanedione. It was not possible to discern which peak corresponded to which form since the two forms are in equilibrium when vaporized by the flame in the gas chromatograph.

DISCUSSION

The decomposition of azibenzil to form the ketocarbene has been shown to be easily accomplished by the methods employed in the experimental section. However, the fate of that ketocarbene can be both complex and highly diverse. Before any discussion of the results obtained for these decompositions, it appears necessary to outline and discuss the possible products associated with various intermediates of reactions of this type.

One possible intermediate in the decompositions is diphenylketene which would result from a Wolff rearrangement of the ketocarbene. There are three possible ways in which the ketene may react to form products. A scheme for the principle products is outlined below.

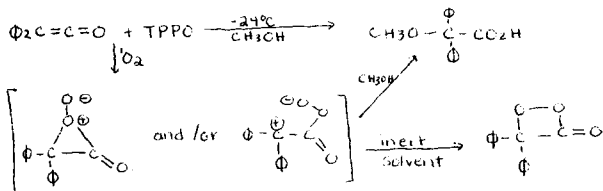


Blank 3 of the decomposition of azibenzil was done in such a way as to produce the diphenylketene. The reaction of the ketene produced with oxygen resulted in the formation of principally methyl diphenylacetate, species II, as

indicated in table 6. The reaction which took place in this experiment was solely between diphenylketene and oxygen. The use of the azibenzil only afforded a facile way in producing this ketene. The above figure would indicate that the final product of Blank 3 would most probably be benzophenone, species III, and carbon dioxide. However, this was not the case. It must then be true that the reaction of oxygen with the diphenylketene to produce the benzophenone is a slow process and that instead addition of methanol after a long period of oxygenation to the reaction mixture produces the methyldiphenylacetate. There was some benzophenone produced, however it's concentration is almost insignificant compared to the concentration of methyldiphenylacetate. From these results, it appears that if the diphenylketene is produced, then it will react in such a way as to form either methyldiphenylacetate or the diphenylketene dimer as the preferred products.

Species I is diphenyl- α -peroxylactone, and the precursor to the formation of benzophenone. Staudinger and coworkers³² reacted diphenylketene with benzene in the presence of molecular oxygen and determined that benzophenone was produced. The work done by Staudinger lends evidence to the formation of the α -peroxylactone upon reaction of triplet oxygen with diphenylketene. Further work done by Bollyky³⁴ also suggests that diphenyl- α -peroxylactone is the precursor of benzophenone. Recently, work done by Turro and

coworkers³⁵ produced the α -peroxylactone in another fashion. Turro reacted the ketene with triphenyl phosphite ozonide (TPPO) at low temperatures and was able to produce the α -peroxylactone. Bartlett and Mendenhall³⁶ determined that the triphenyl phosphite ozonide donates oxygen at the temperature Turro ran his reaction and that the oxygen produced was most probably singlet oxygen. From this evidence, Turro concluded that the production of the α -peroxylactone is due to the reaction of ketene with singlet oxygen acting as the oxidizing species. He further points out that there is an intermediate in the formation of the α -peroxylactone which is most probably a perepoxyde and/or zwitterion. Turro reacted diphenylketene with triphenyl phosphite ozonide in the presence of methanol and found that an α -methoxy peracetic acid was formed and that the production of the α -peroxylactone was totally suppressed. However, it was determined that the diphenyl- α -peroxylactone was very stable in methanol. The above evidence then suggests that the methanol must intercept some intermediate in the formation of the diphenyl- α -peroxylactone. The scheme below has been proposed by Turro as a result of the studies he performed.



The above description of Turro's work and the work done by Staudinger and Bollky reacting diphenylketene with molecular oxygen all lend strong evidence to the existence of the diphenyl- α -peroxylactone in the reaction of diphenylketene. The intermediates proposed by Turro in the formation of the α -peroxylactone may well be present in the reaction of triplet oxygen with diphenylketene, however there is no evidence at this time to draw such a conclusion.

In attempting to determine if it was feasible for the diphenylketene dimer to be present in the decomposition mixtures, the reaction of the ketene under nitrogen and under oxygen was tested. Both experiments had to be characterized so that it would be possible to evaluate the products obtained in the azibenzil decomposition mixtures. Under both sets of conditions, no diphenylketene dimer was produced as indicated in the results section. The absence of this species under all the possible reaction conditions that the decompositions took place, suggests that the diphenylketene dimer could not be present in the azibenzil reactions. Furthermore, these results along with the results obtained from Blank 3, point to the conclusion that the principle product of the reaction of diphenylketene will be methyl diphenylacetate. The absence of the dimer in these determinations, also rules it out as being one of the unaccounted products of the decomposition reactions. Therefore it is quite possible that the eighty percent of unknown

products in the azibenzil reactions is due primarily to tetraphenylglycolide and other similar polymeric species.

Work done by Tanaka and coworkers³⁷ resulted in the following proposal for the formation of tetraphenylglycolide.

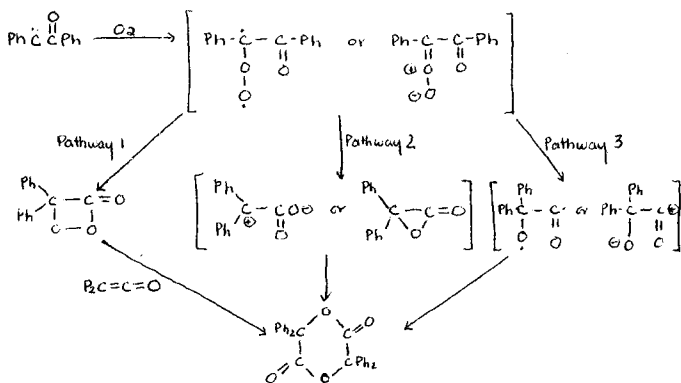


Figure 1: Production of Tetraphenylglycolide

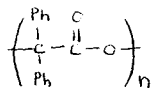
The intermediate produced by pathway one is the diphenyl- α -peroxylactone which was just discussed. For this species to proceed to the tetraphenylglycolide, the single bond between the two oxygens must first break. This newly generated species then adds across the carbon-carbon double bond on the ketene to form the tetraphenylglycolide. The presence of the diphenyl- α -peroxylactone has already been suggested to occur in the reaction of oxygen with the diphenylketene. Tanaka's proposal for the fate of this species

as being responsible for the tetraphenylglycolide would suggest that perhaps the production of benzophenone and carbon dioxide is not the chief purpose of the α -peroxylactone. An explanation of this type would account for not observing much benzophenone in Blank 3. The proposal made by Tanaka that the α -carbonyl carbonyl oxide produced the α -peroxylactone is also quite feasible energetically. From the two schemes presented, it would seem that more tetraphenylglycolide would be produced by the decomposition of the diphenylketene since the ketene and the diphenyl- α -peroxylactone are part of the same reaction system. This pathway then gives an explanation for the production of tetraphenylglycolide from the α -carbonyl carbonyl oxide and also suggests a possibly important function of the α -peroxylactone produced by the addition of molecular oxygen to the diphenylketene formed from the Wolff rearrangement. This last conclusion is strengthened by the work done by Staudinger³². In an early paper, Staudinger reported that the reaction of diphenylketene in benzene under oxygen produced a sixteen percent yield of tetraphenylglycolide. Also an Infrared spectrum (IR No.13) of Blank 3 indicates the presence of tetraphenylglycolide by its characteristic absorption at 1750 cm^{-1} .

Pathway two of Tanaka's scheme involves a 1,2 aryl shift and a deoxygenation to form the precursor for the tetraphenylglycolide. These intermediates produced are both

possible on energetic grounds. The formation of the tetraphenylglycolide from these species would only entail dimerization. The intermediates produced in pathway three are less favorable intermediates to the production of the tetraphenylglycolide. In this pathway, a carbocation is being produced which is not very stable. The intermediate of pathway two would be preferred precursor between these two pathways. Therefore, Tanaka's proposal of pathway three existing seems infeasible in light of the fact that it is not energetically as stable a mechanism as the other two alternative pathways provided.

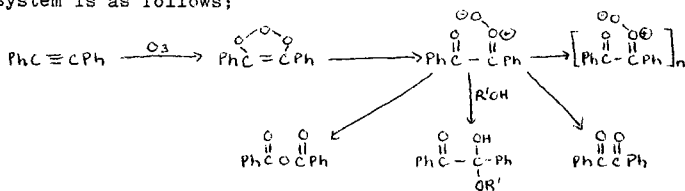
The intermediates provided by Tanaka's work may also be present in the formation of other high molecular weight species. Staudinger et.al.³² reported that reaction of molecular oxygen with diphenylketene produced high molecular weight ketene-oxide polymers. The intermediates given by Tanaka may produce the following polymeric form;



The structure of this is simply the monomer of pathway two which dimerizes to form the tetraphenylglycolide. Staudinger³³ also suggests that a polymer of this type could be present in the reaction of diphenylketene with oxygen. Unfortunately, Staudinger did not report any quantitative

details regarding the polymers produced in the diphenylketene reaction. If this polymer is produced, it's presence, along with the presence of the tetraphenylglycolide, could account for a large portion of the products produced in the decompositions which could not be characterized.

The ozonolysis of diphenylacetylene parallels the reaction of oxygen with ketocarbenes as shown by Murray et. al.¹⁴ The reaction which is thought to take place in this system is as follows;



In the above scheme, the α -carbonyl carbonyl oxide intermediate which is formed is suspected to have the syn configuration. This species then goes onto the products shown by rearrangements and solvent additions. The major characterized product in the ozonolysis of diphenylacetylene was methyl benzoate. The methyl benzoate arises from the addition of methanol to benzoic anhydride. Another product of this reaction was benzil, however it's concentration was much less than the concentration of the methyl benzoate produced. The results obtained leads one to the conclusion

that the syn form of the α -carbonyl carbonyl oxide produced in a reaction of this kind is responsible for the formation of primarily methyl benzoate. Again, much of the products of the ozonolysis could not be quantitatively determined. However, if Tanaka's proposed scheme for the formation of tetraphenylglycolide is valid, it is quite possible for the tetraphenylglycolide and other polymeric species to be present in this reaction because in Tanaka's work and in this ozonolysis, the intermediates are the same. The polymers produced, would most probably be formed by pathway two of Tanaka's proposal since it is a more favorable pathway than three and since pathway one in this ozonolysis does not exist; no diphenylketene is present in the reaction system.

In summary, the reaction of azibenzil with oxygen, may take place to form two possible precursors to the products detected; diphenylketene and α -carbonyl carbonyl oxide. The diphenylketene may react to form methyldiphenylacetate, benzophenone and carbon dioxide, tetraphenylglycolide and other high molecular weight polymeric species. It does not react to form the diphenylketene dimer under the reaction conditions employed for the decompositions of azibenzil. The α -carbonyl carbonyl oxide may be present in two forms; anti and syn. Evidence suggests that the syn form may be responsible for the formation of methyl benzoate while both forms may react to form tetraphenylglycolide and other associated polymers. The following figure details the fate of

the azibenzil.

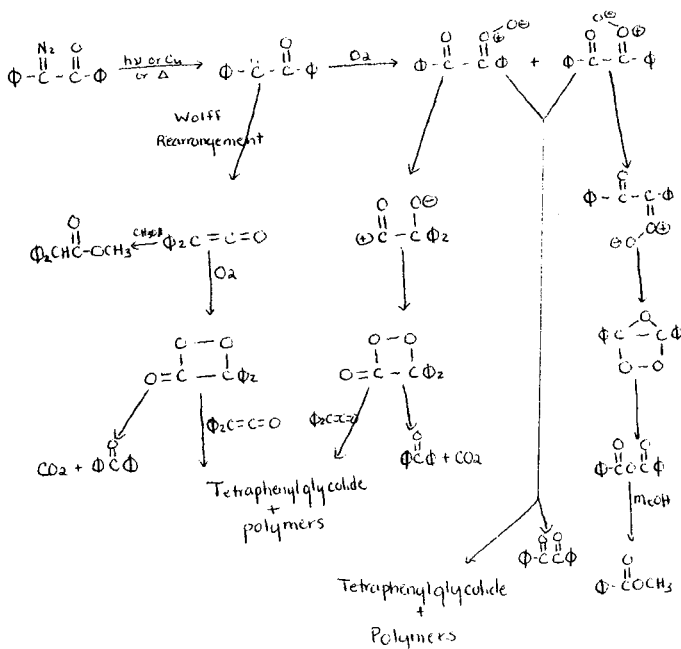


Figure 2: Decomposition of Azibenzil

The results obtained for the thermal oxygenation of azibenzil show that benzophenone and methyldiphenylacetate are the major low molecular weight products formed. Both of these products indicate that a Wolff rearrangement is occurring in this reaction to form the diphenylketene. This route in the thermal decomposition is to be expected since

a rearrangement of the ketocarbene to form the ketene is promoted by elevated temperatures. It has been previously shown that the production of benzophenone from the decomposition of the diphenyl- α -peroxylactone does not take place as readily as the formation of the methyl diphenylacetate. It also appears that the formation of polymeric species from the reaction of the α -peroxylactone with its precursor, diphenylketene, is preferred over the formation of benzophenone. Therefore, the relatively large amount of benzophenone produced in this process may be due to the decomposition of the α -peroxylactone formed from the α -carbonyl carbonyl oxide and from a similar decomposition incurred in the reaction of the diphenylketene. The α -carbonyl carbonyl oxide intermediate must be forming because benzil is being produced by the thermal oxygenation of the azibenzil.

The α -carbonyl carbonyl oxide which is produced may assume four different forms. The anti and syn configurations of this acyl carbonyl oxide may be present, however beyond this, each of these two configurations may be in a singlet or a triplet state. The spin states of these α -carbonyl carbonyl oxides must be carefully taken into consideration since their precursor is a ketocarbene which itself may involve two different spin states.

The ketocarbene formed during the thermal, catalytic or photochemical decompositions of azibenzil has been suggested to be in the singlet state in which the two electrons

on the electron deficient carbon are paired.²⁶ All of the oxygenations carried out on these decompositions involved molecular oxygen which is present in the triplet state. The reaction of two species with opposing spin states must take place to form products that possess a spin state that does not violate the principle of spin multiplicity. According to this principle, the products produced from the reaction of a singlet species with a triplet one must be present in the triplet spin state. Therefore the intermediates formed (presumably the α -carbonyl carbonyl oxides) in this type of reaction are in the triplet state.

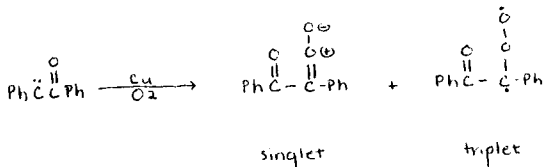
The reaction of ozone, singlet state, with a singlet state acetylene will result in a singlet state intermediate again due to the conservation of spin multiplicity. The diphenylacetylene used in the ozonolysis is this type of acetylene. As was previously discussed, the mechanism of this type of ozonolysis most probably involves the syn form of the α -carbonyl carbonyl oxide being present as the intermediate in product formation. By the above reasoning then, this syn carbonyl carbonyl oxide would have a singlet spin state. The major characterized product in the ozonolysis of diphenylacetylene was benzoic anhydride (reported as methyl benzoate). It may then be possible to conclude that the singlet state syn form of the acyl carbonyl oxide is a facile route to obtaining this product. Furthermore, any α -carbonyl carbonyl oxide which has the anti configuration

would also have to be present in the singlet state due to similar spin multiplicity considerations.

The thermal oxygenation of the azibenzil did not produce any methyl benzoate which can be seen by the results obtained in table 6. The arguments given above would then suggest that no syn α -carbonyl carbonyl oxide possessing a singlet spin state is being formed in this reaction. If no singlet state syn form of this species is being produced, then it is not possible for an anti form to be present in the singlet state under the reaction conditions employed here. Further investigation of the products obtained for this thermal decomposition show that benzil is present. The Wolff rearrangement pathway is unable to produce such a species so it must be that some form of the α -carbonyl carbonyl oxide is present in this reaction. By the above reasoning, these α -carbonyl carbonyl oxides are most probably in the triplet state.

Triplets tend to act like diradicals. Therefore internal bond formation in a triplet state is not favored and instead dimerization is preferred. This dimerization was suggested by Sawyer²⁵ to be responsible for some of the formation of the tetraphenylglycolide. This characteristic of the triplet state also supports pathway two of Tanaka's proposed scheme for the formation of tetraphenylglycolide. The presence of benzil and benzophenone in the thermal decomposition also indicates that the triplet states are

feasible precursors to these products. A scheme of the singlet and triplet precursors formed is as follows;



Intersystem crossing is a process by which a singlet state may be transformed into a triplet state or vice versa. For example, in the ozonolysis of diphenylacetylene it has been shown that singlet state products would result since the reaction occurring is between two singlet systems. If intersystem crossing were to take place, the products obtained would be in the singlet state as well as in the triplet state. This does not violate the principle of conservation of spin multiplicity as long as the conditions under which reaction is occurring promotes this intersystem crossing. Heavy metals have been shown to promote this intersystem crossing.³⁹ Thus the oxygenation of azibenzil with copper present will result in the formation of singlet and triplet state intermediates; the α -carbonyl carbonyl oxides.

The catalyzed decomposition was carried out in such a way to try and avoid any thermal decomposition of the starting material. By running the reaction in this fashion, the results obtained for this copper catalyzed process will

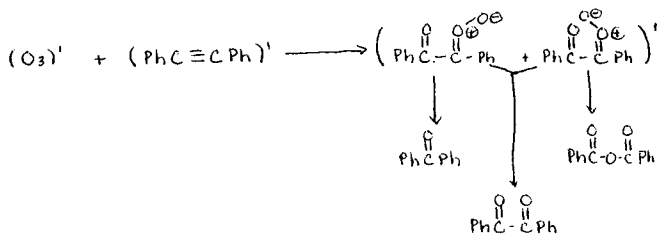
be independent of the results found for the thermal decomposition of the starting material. As indicated in table 6 of the results section, methyl diphenylacetate and benzophenone are present in the copper decomposition. Again, these products indicate that a Wolff rearrangement of the ketocarbene is occurring. Work done by Yates⁴⁰ suggests that the action of copper on the decomposition of a diazoketene will yield Wolff rearrangement products in very low yields and that a catalyzed reaction of this type will proceed primarily through a non-rearrangement pathway. Yates's findings are also supported by the original work done on diazoketones by Wolff.⁶ Unlike the thermal decomposition, the copper catalyzed reaction did afford methyl benzoate which is the result of the non-rearrangement of the ketocarbene. The intermediate in the formation of this product has been shown to probably be the α -carbonyl carbonyl oxide. Beyond this, the arguments for the formation of the methyl benzoate given in a prior section of this discussion would indicate that a singlet state syn α -carbonyl carbonyl oxide is present in the reaction. The thermal decomposition was shown to involve triplet state intermediates so it may be concluded that in this catalyzed reaction intersystem crossing to form the singlet state in fact has occurred.

Benzil is still present in this catalyzed decomposition. This product may be formed by either or both of the two configurations of the α -carbonyl carbonyl oxides. Also

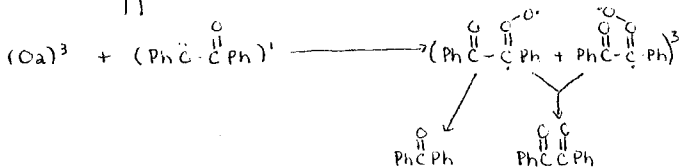
it is not clear that any distinction between the singlet and triplet spin states of these intermediates can be made due to the presence of the benzil. In comparing the results of the thermal decomposition with the copper catalyzed reaction, it can be seen that a slight increase in benzil concentration has occurred in the catalyzed decomposition. If in fact the thermal decomposition proceeds through the formation of the triplet α -carbonyl carbonyl oxide, then the additional benzil may be due to the presence of the singlet state form of this intermediate. It has been concluded that the singlet form of the syn α -carbonyl carbonyl oxide produces primarily the methyl benzoate. Therefore, the additional benzil formed in the catalyzed reaction may be due to the decomposition of the singlet state anti configuration of the acyl carbonyl oxide. The formation of benzophenone may partially be due to the limited reaction of the diphenylketene with oxygen and/or due to the 1,2 aryl shift on the anti α -carbonyl carbonyl oxide. Both reactions lead to the formation of the diphenyl- α -peroxylactone which in turn will cleave to produce carbon dioxide and benzophenone.

In comparing the results obtained for the thermal oxygenation with the copper catalyzed oxygenation, the most significant difference between the two lies in the formation of methyl benzoate in the catalyzed reaction. The thermal decomposition appears to proceed via the production of triplet intermediates, while the copper catalyzed decomposition

seems to produce intersystem crossing resulting in singlet and triplet state species. The main products in both reactions though, involve the uncharacterized tetraphenylglycolide and other high molecular weight species. The presence of these products in these reactions would tend to indicate that both triplet and singlet forms of the intermediates primarily decompose in such a way as to promote polymerization. The following scheme of the various forms that the α -carbonyl carbonyl oxide may assume may be helpful in understanding the fates of these species. The formation of tetraphenylglycolide and the other polymers is not indicated but it must be kept in mind that these products are the principle ones associated with the azibenzil decompositions.



Thermal Oxygenation



Copper Catalyzed Oxygenation

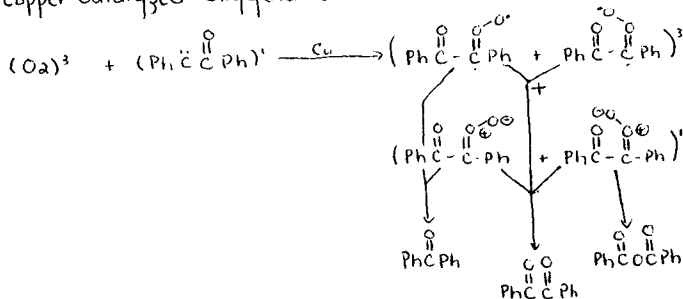


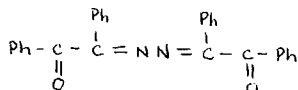
Figure 3: Formation of Singlet and Triplet α -carbonyl carbonyl oxides

Two photooxidation decompositions of azibenzil were done; sensitized and unsensitized. The analysis of the products produced in these reactions, given in table 6, indicates that the principle characterized product in both photolytic reactions is benzil. Benzil has been shown to arise solely from the decomposition of the ketocarbene by non-rearrangement methods. Therefore, the production of the α -carbonyl carbonyl oxides in these reactions is of primary importance. There is a small concentration of methylphenylacetate present in both photolytic techniques, so there must be a Wolff rearrangement occurring here to a limited

extent also. The amount of the rearrangement product is so small that it may be concluded that the sensitized and the unsensitized photooxidations primarily proceed to form the acyl carbonyl oxide intermediates. The most important result to note in both of these decompositions is that neither of them produce methyl benzoate. The methyl benzoate has already been hypothesized to arise from the decomposition of the singlet state syn form of the α -carbonyl carbonyl oxide so it would appear that the photooxidations involve the production of triplet state intermediates. Therefore these reactions more closely parallel the thermal decomposition of azibenzil rather than the catalytic decomposition. Again it can be seen that the tetraphenylglycolide and other polymeric species constitute approximately eighty percent of the products produced in the photolytic decompositions. However, this large amount of uncharacterized material most probably arises from the decomposition of the α -carbonyl carbonyl oxides since the Wolff rearrangement does not seem to play an important role in decompositions of this nature. In all the decompositions done on the azibenzil (thermal, catalytic and photochemical) roughly the same amount of uncharacterized products were obtained. The thermal and catalytic oxygenations have been shown to proceed via the Wolff rearrangement to a large extent while the photooxidations appear to take place by the non-rearrangement pathway. It may be then, that the formation of tetraphenylglycolide and other related

polymers is equally probable regardless of the decomposition pathway the ketocarbene undergoes. Further analysis of these processes must be done though in order for any quantitative conclusions to be drawn on this subject.

The work done by Tanaka³⁷ on the decomposition of azibenzil is closely related to the work done here. Unfortunately, Tanaka used only thermal and photolytic methods to promote reaction and did not investigate the effect of a copper catalyst on the oxygenation decompositions. Tanaka reports that the products obtained from the reaction of oxygen with azibenzil are tetraphenylglycolide, bis-benzilketazine and diphenylacetic acid. The second product listed by Tanaka has the following structure:



bis-benzilketazine

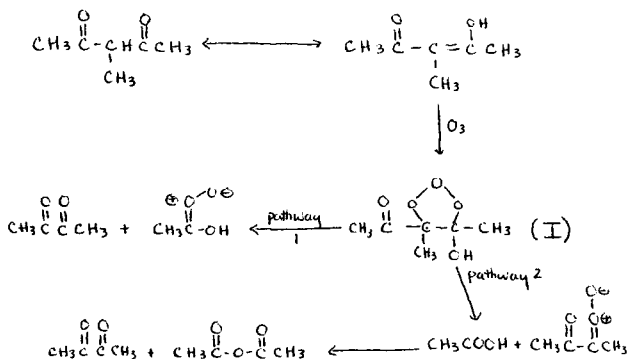
No spectral data is available on this compound, however it has been determined that it does in fact exist.⁴¹ It could be entirely possible that this species may then be present in the decompositions we have run and may be responsible for a percentage of the uncharacterized products obtained. On the other hand, Tanaka does not report the presence of any benzil, benzophenone or benzoic anhydride which have been

found to be significant products of the decompositions. The fact that these products do appear in this analysis, seems vital to the understanding of the different fates a decomposition of a ketocarbene may take. As previously discussed, the elucidation of species such as tetraphenylglycolide, bis-benzilketazine and other high molecular weight polymers was not accomplished, yet the products that were able to be determined have given an idea as to the proposed outcome of the decompositions of ketocarbenes. Tanaka also proposes that the photochemical reaction of azibenzil with molecular oxygen proceeds directly to the formation of tetraphenylglycolide and will not yield any benzil as a product. In both the sensitized and the unsensitized photooxidations done here, benzil accounts for approximately twenty percent of the products of the decompositions.

The mechanism for the formation of tetraphenylglycolide proposed by Tanaka has given a strong idea of how this species is formed in reactions which involve the decomposition of a ketocarbene. The discrepancy between Tanaka's results and those obtained here, most probably arise from the different product analysis techniques used. It was found that confirmation of the high molecular weight compounds reported by Tanaka was impossible by the methods that were employed here. On the other hand, determination of benzil, benzophenone and methyl benzoate in Tanaka's work was not accomplished probably because elucidation of the major pro-

ducts produced was probably more important than the confirmation of other low molecular weight species.

As an addendum to the proposed research outlined in the introduction, the ozonolysis of 3-methyl-2,4-pentanedione was looked at. The reaction which occurs in this process is as follows;



In the above scheme, the enol form of the 3-methyl-2,4-pentanedione is the configuration which undergoes ozonolysis due to the presence of the double carbon-carbon bond in its structure. The ozone adds to this double bond and structure I is formed. The decomposition of structure I may occur in two ways as indicated by pathways one and two. Pathway two is of primary importance to this discussion since an α -carbonyl carbonyl oxide should be formed. In accordance with the results obtained for the ozonolysis of diphenylacetylene

and with the oxygenations of azibenzil, biacetyl and acetic anhydride are the proposed products of this α -carbonyl carbonyl oxides decomposition. From the above scheme, it is not clear which of the two pathways will be preferred in the reaction of structure I, however analysis of the products may aid in drawing conclusions regarding structure I's fate. The results obtained, as indicated in table 10 are relatively inconclusive since there is some product which has the same retention time on the gas chromatograph as the starting material. The ozonolyses were run at four different concentrations to observe whether or not the concentration of the 3-methyl-2,4-pentanedione has an effect on the amount of the various products produced. If there is a dependence on the relative concentration of the starting material then it may be that pathway one is preferred since reaction via pathway two should yield equal amounts of biacetyl and acetic anhydride. The results obtained are inconclusive since the gas chromatographic analysis does not seem to be very accurate. Further work must be done on this system before any sound conclusions can be drawn regarding the fate of a structure similar to I. However, once this type of analysis is perfected, it's results may be applied to the decomposition of a ketocarbene since both entail the formation of the α -carbonyl carbonyl oxide.

FUTURE WORK

Further work must be done to characterize the presence of tetraphenylglycolide and other high molecular weight polymeric species. With the analysis techniques available, it appears that the best course of action in determining the polymer's presence will be an analysis of the monomeric unit comprising the polymers. Once this is accomplished, the fates of the α -carbonyl carbonyl oxides may be better understood.

The ozonolysis of 3-methyl-2,4-pentanedione should also be continued as an alternate method of generating the acyl carbonyl oxide. Careful analysis of the products of this decomposition will allow one to determine the importance of this intermediates presence in systems of this type. The investigation of the acyl carbonyl oxide carried out in this ozonolysis will directly determine the fate of this species in both the decomposition of azibenzil and in the ozonolysis of acetylenes.

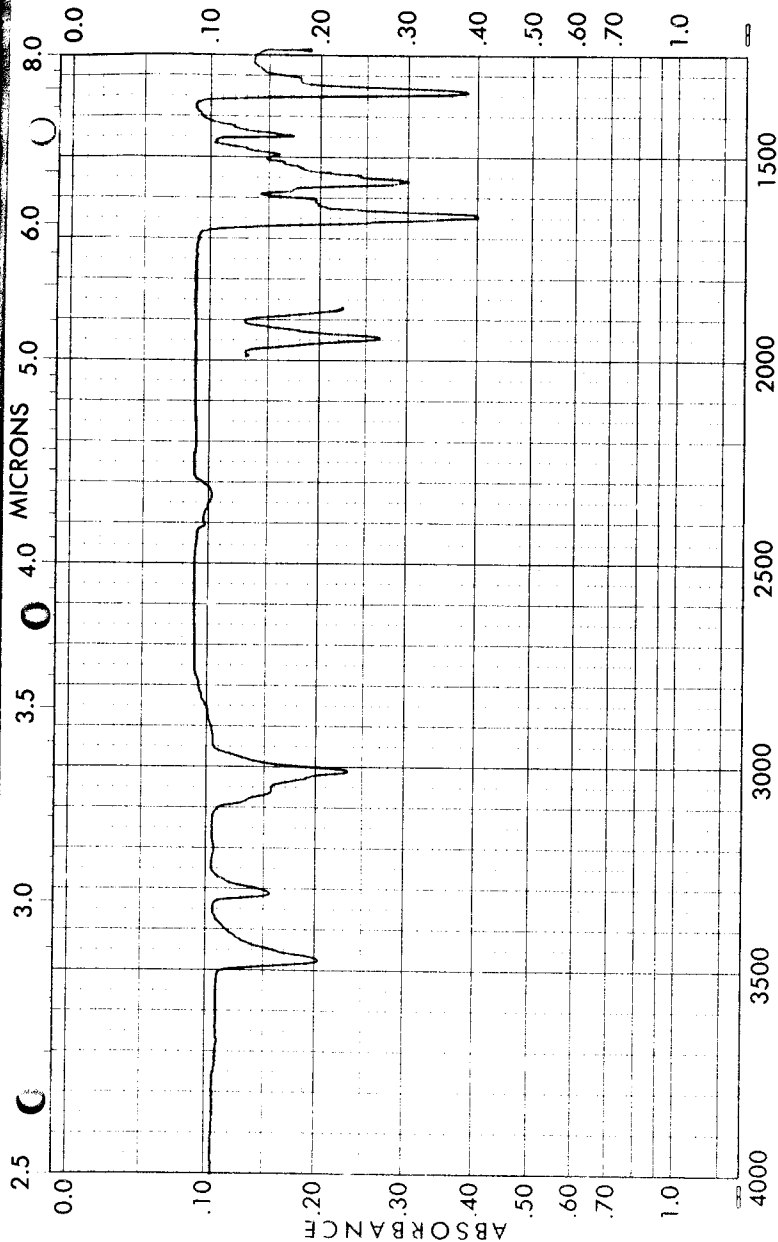
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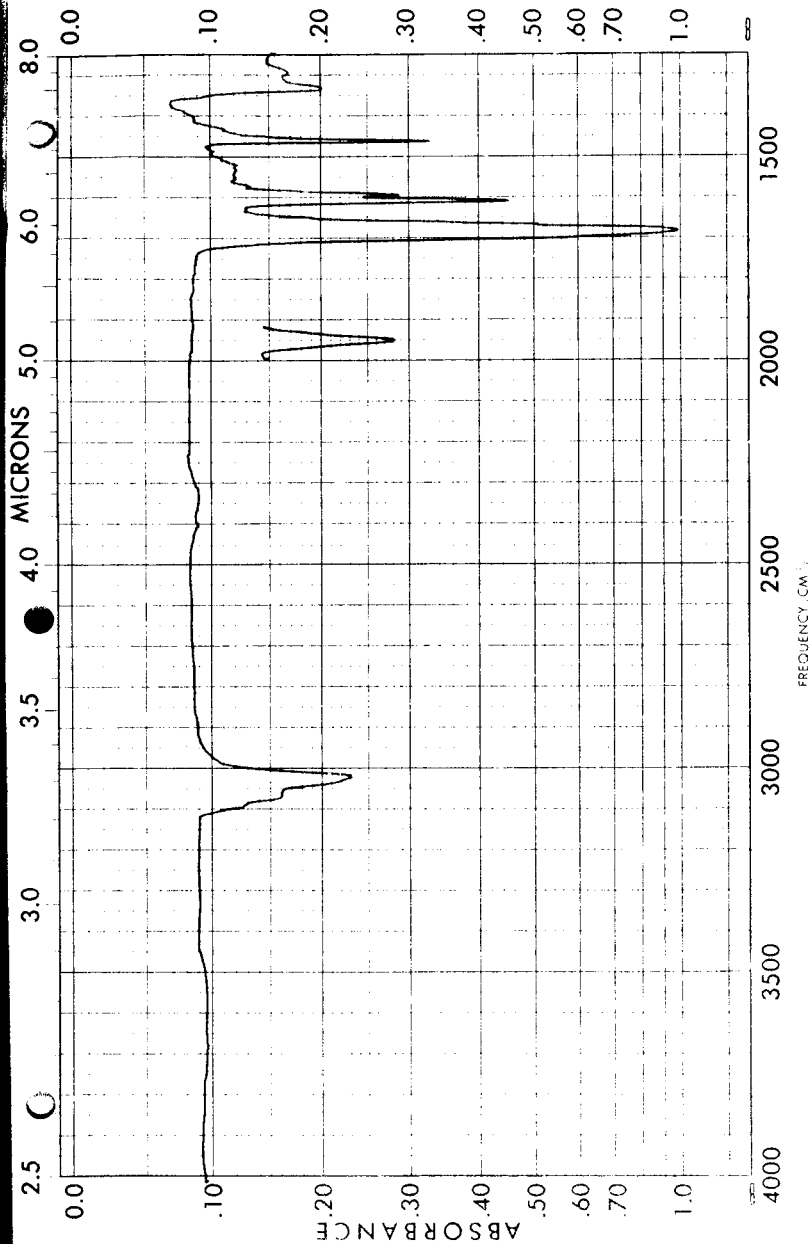
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APPENDIX

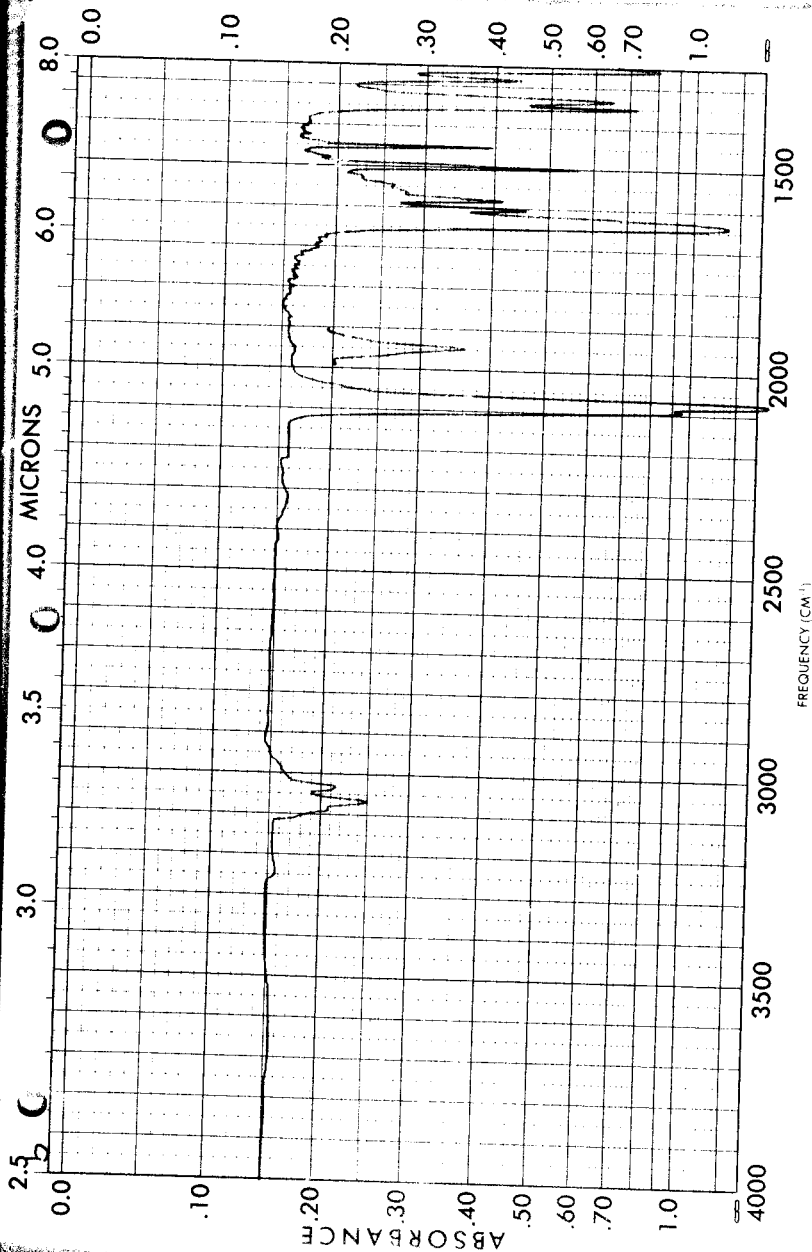


SAMPLE Benzal monohydrate made 4/13/77 ORIGIN Oxy. Syn. vol. 3 pg. 356 SOLVENT CCl ₄	CURVE NO. 1 CONC. CELL PATH REFERENCE 1744 Polyethylene	SCAN SPEED Fast SUI 30	OPERATOR N.W. DATE 4/23/77 REMARKS 3000-3500 cm⁻¹ - Benz. 1 monohyd. (4.26) C.
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23



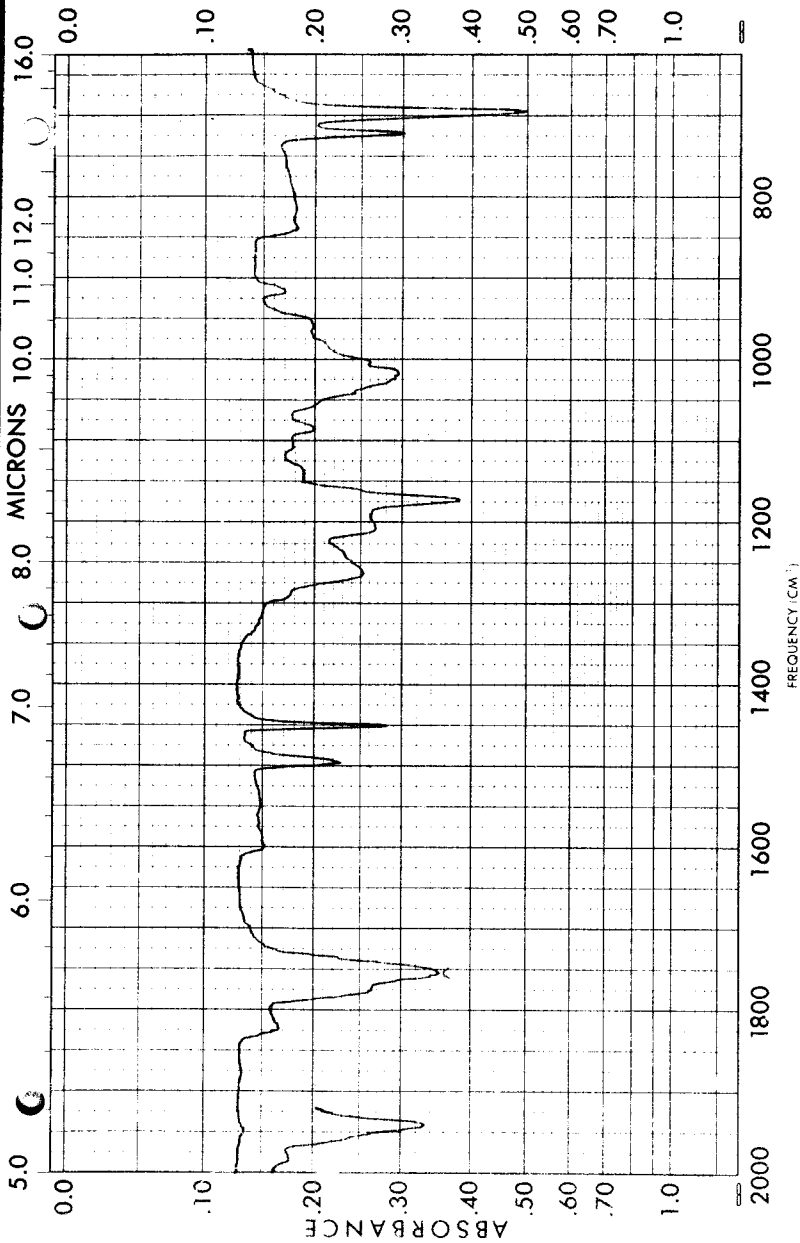
SAMPLE Benzil	CURVE NO 2	SCAN SPEED Fast	OPERATOR N.W.
SOLVENT CHCl ₃	CONC	SLIT 36	DATE 4/23/72
CELL PATH		REMARKS Used to determine purity of Benzil in benzene	
REFERENCE 1944 Polyscience			



SAMPLE <i>n</i> -butyl male <i>6</i> 124177 1 st copy ORIGIN <i>Org</i> Syn-Vol 89, 476 SOLVENT <i>CCl</i> ₄ REFERENCE 1944 Polystyrene	CURVE NO. <i>3</i> CONC. CELL PATH REFERENCE 1944 Polystyrene	SCAN SPEED <i>Fast</i> SLIT <i>25</i> REMARKS <i>Absence of butyl methoxybenz- (3500)</i> <i>and no butyl</i>	OPERATOR <i>NCW</i> DATE <i>6/27/77</i>
		80	

INSTRUMENT 7237-10321

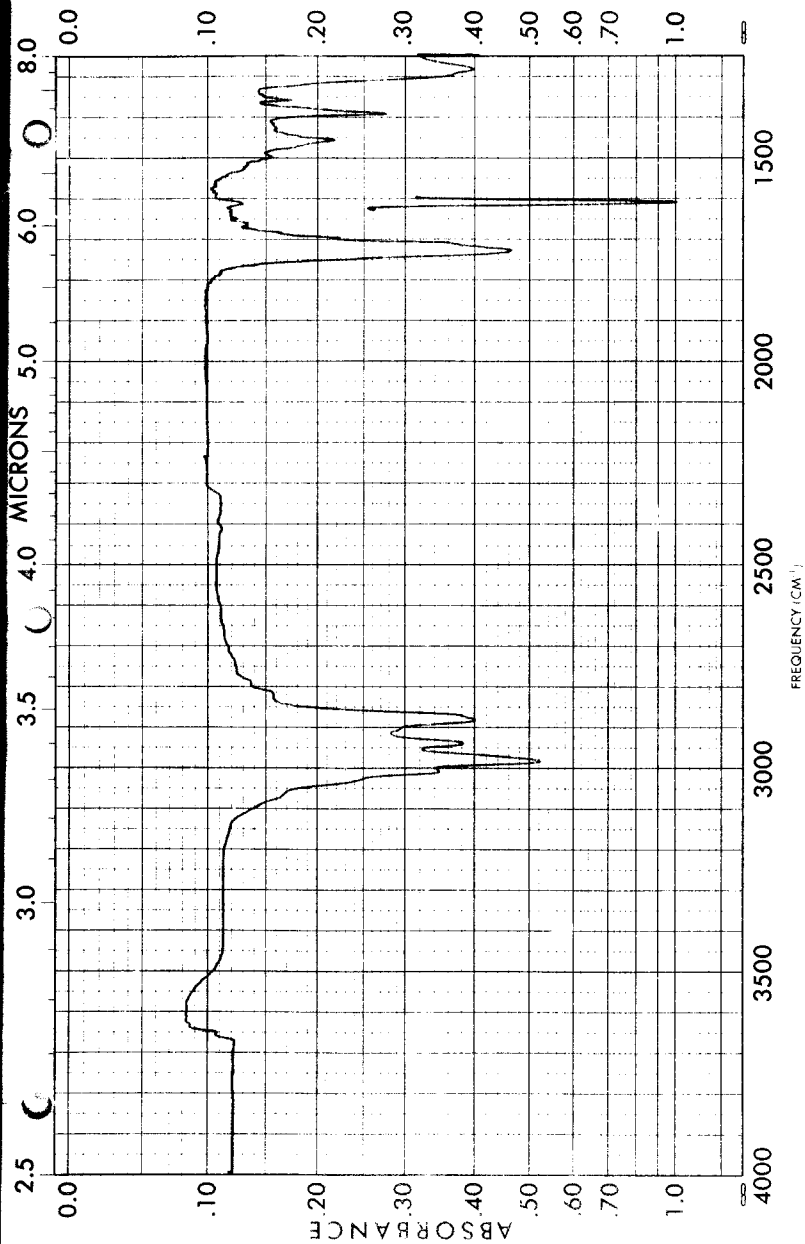
REC'D IN CHARTS



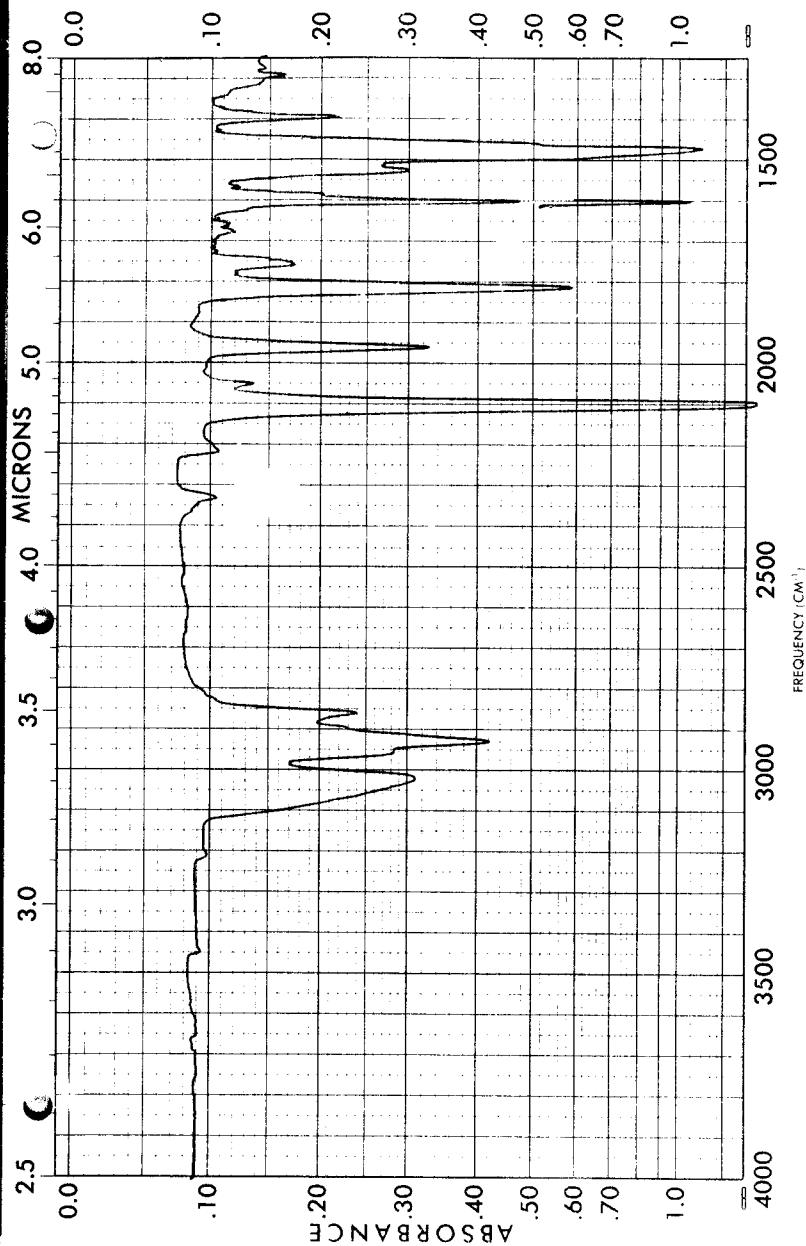
SAMPLE <i>Tetraphenylglycidide</i> ORIGIN <i>Tanaka</i> SOLVENT <i>CCl₄</i>	CURVE NO. <i>244</i> CONC. CELL PATH <i>.1 mm</i> REFERENCE <i>1944 Polystyrene</i>	SCAN SPEED <i>Fast</i> SLIT <i>25</i>	OPERATOR <i>NCW</i> DATE <i>7/5/77</i> REMARKS <i>After recrystallization in Ethyl Acetate and methanol. presence of 1750 cm⁻¹</i>
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PR 18R (237-1035)

RECORDING CHARTS



SAMPLE Photocopying by Agfa, Inc. in 450 ml ether after 1 hr. in 1 ml CCl ₄ + ether exp. 15 ml CCl ₄ + ether ORIGIN 8/11/77 SOLVENT ether CCl ₄	CURVE NO. 4 5 CONC. CELL PATH 1 mm REFERENCE 1601.4 polystyrene	SCAN SPEED Fast SLIT 25 OPERATOR NCJ DATE 8/11/77
REMARKS No aglycosyl present (2000 cm ⁻¹) TPG present		

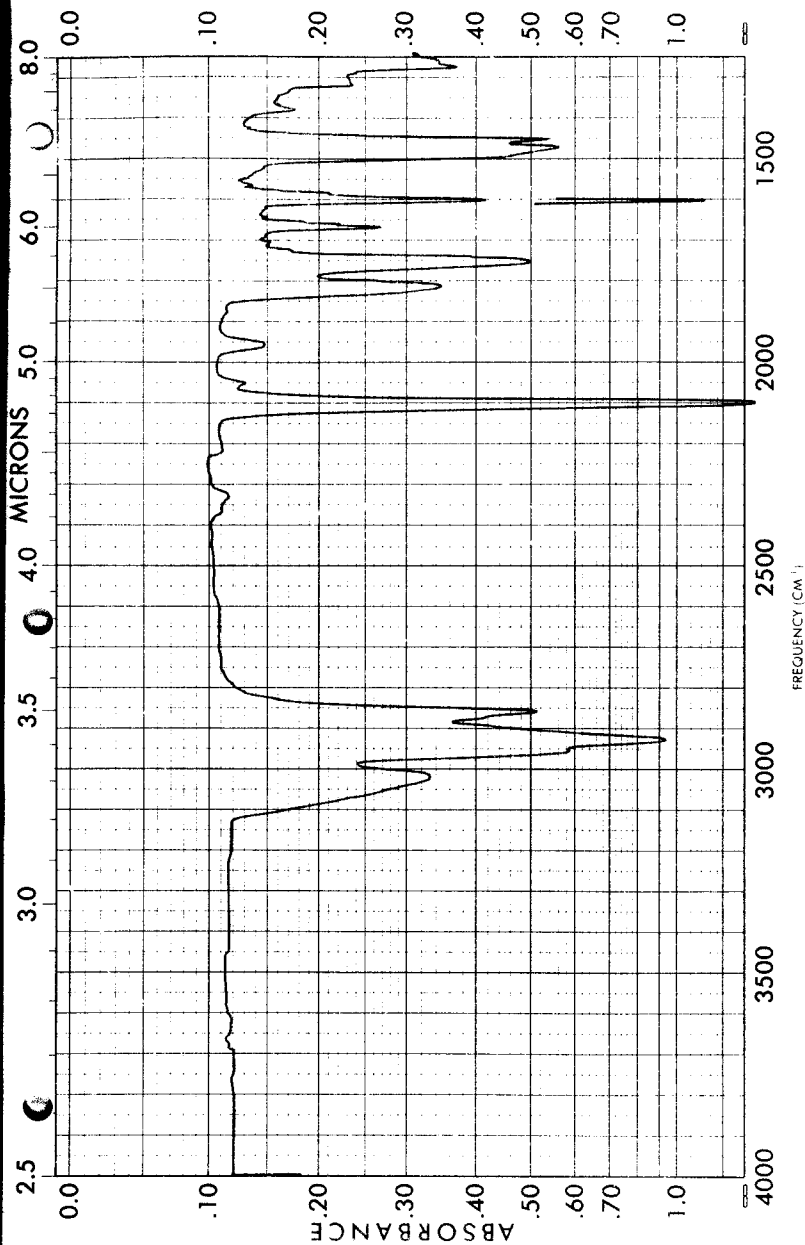


SAMPLE: Polythene in 25ml cells after refluxing for 9 1/2 hrs in a NaCNrespirometer ORIGIN: Hail SOLVENT: CCl ₄	CURVE NO. 4 CONC. CELL PATH 1 mm REFERENCE 16014 polythene	SCAN SPEED Fast SUII 25	OPERATOR NJW DATE 7/26/77
		REMARKS: Sample taken pieces to 10ml extract in from red flask which will undergo analysis	

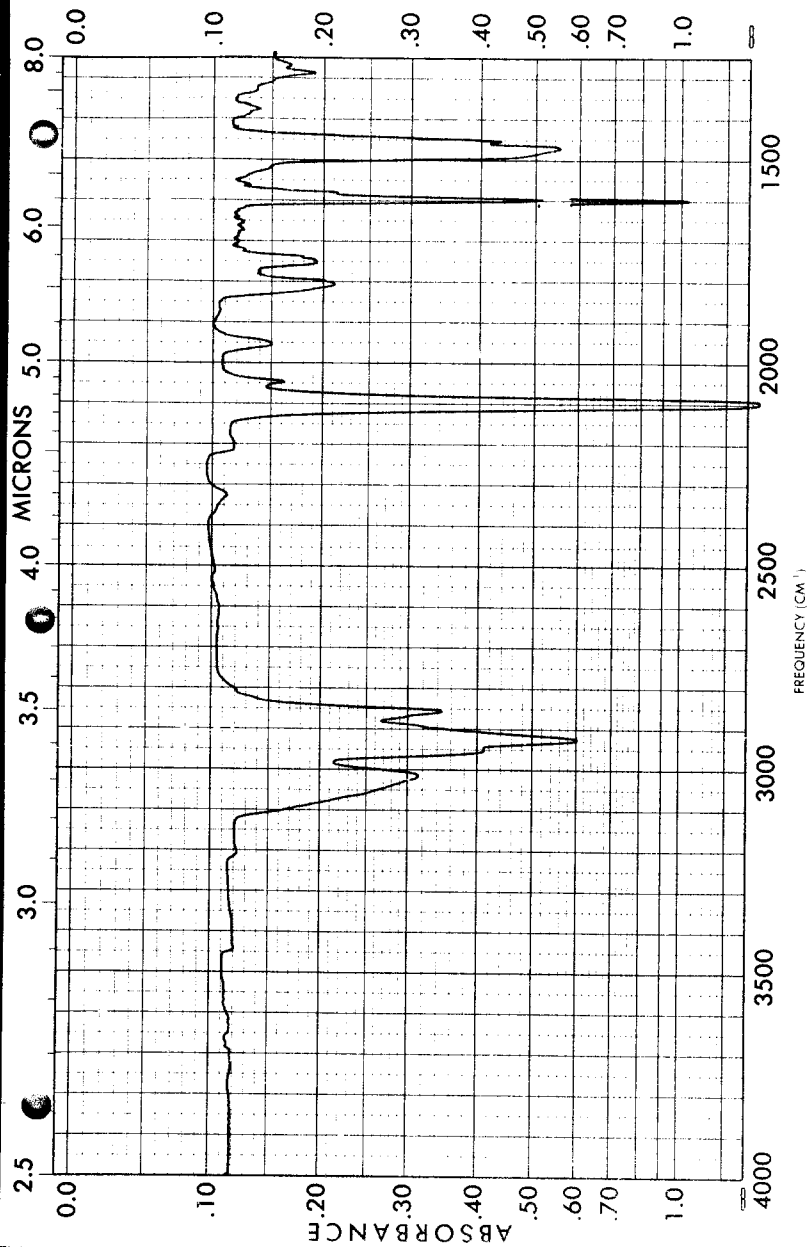
NO. PR19R 7237-10321

RECORDING CHARTS

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SAMPLE: P-3001 in 25-ml. CCl ₄ - 10 ml. extract in 1% methanol with 0.2 for 4 hrs. ORIGIN: Hull SOLVENT: CCl ₄	CURVE NO. 7 CONC.	SCAN SPEED: Fast SLIT: 35 REMARKS: before with conc. of 1% and 1% of 1% added conc. ref. used	OPERATOR: ALW DATE: 7/26/77
	CELL PATH: 1 mm REFERENCE: 100% polypropylene		

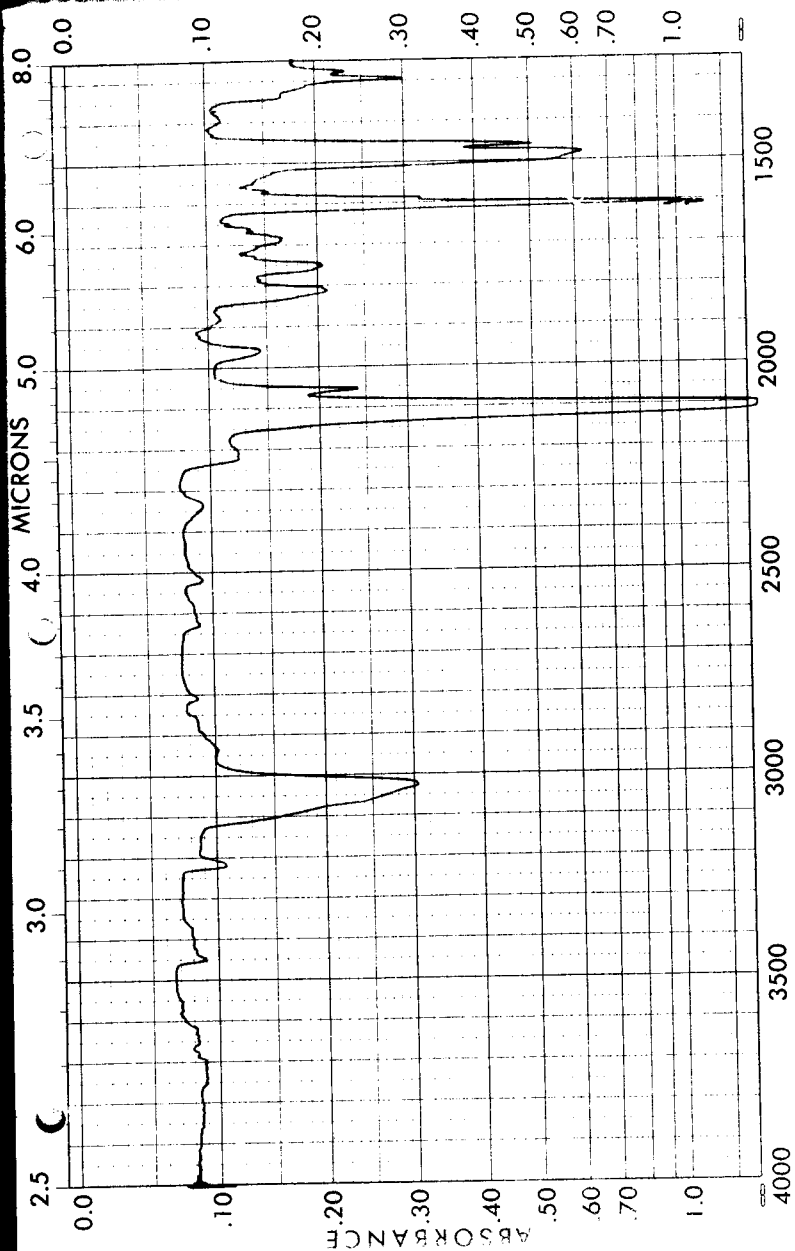


SAMPLE Polyethylene film after refluxing for 2 1/2 hours in 50% $\text{C}_2\text{H}_5\text{OH}$ atmosphere ORIGIN H_2O SOLVENT $\text{C}_2\text{H}_5\text{OH}$	CURVE NO. 8 CONC. CELL PATH 1mm REFERENCE 16014 polyethylene	SCAN SPEED Fast SLIT 25 REMARKS Taken before the temp off and 10 mi MeOH added and refluxed for 2 hrs	OPERATOR NCU DATE 7/26/77
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NO PRIOR 1237-10321

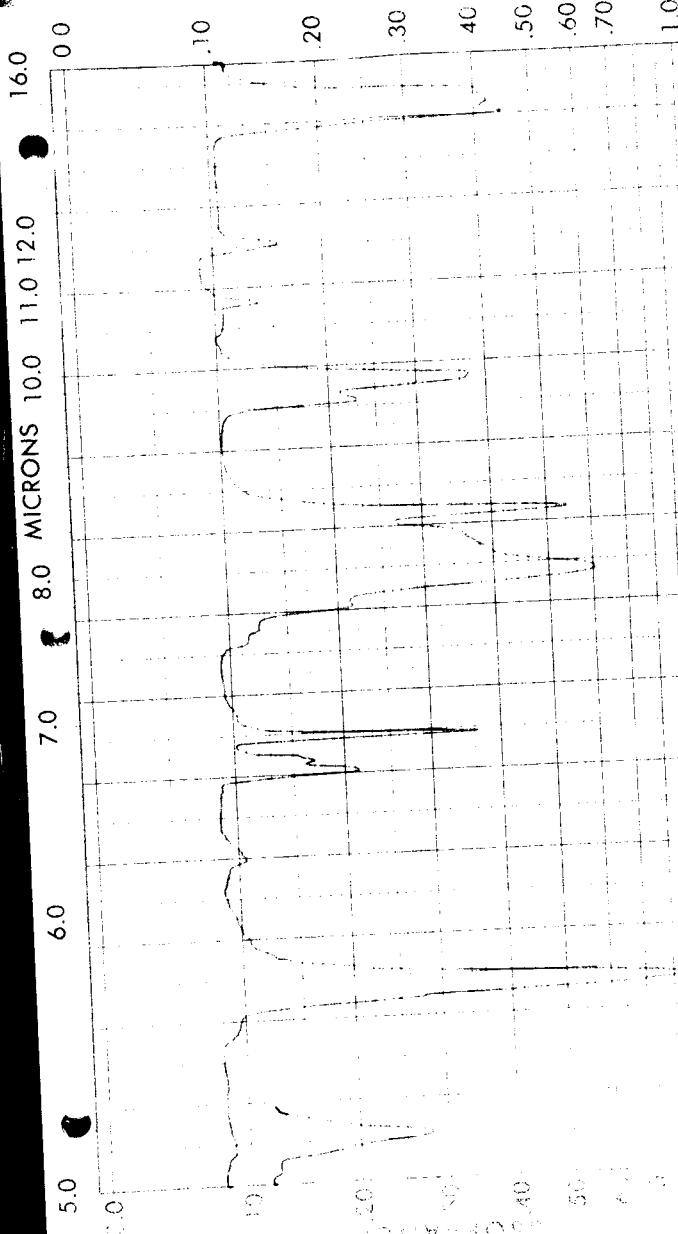
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RECORD NO. CHARTS



RECORDING CHARTS

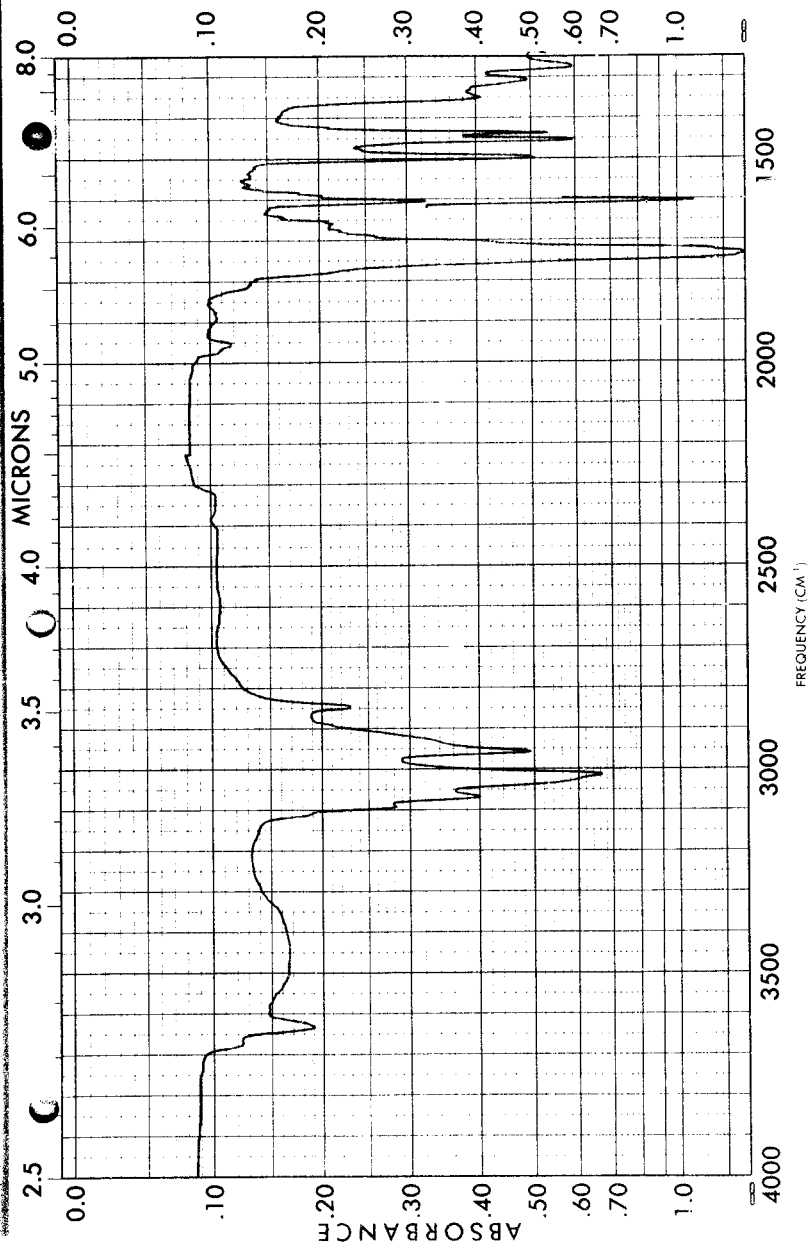
SAMPLE: 10 ml. Cu ²⁺ after 30 min. exposure Cu ²⁺ ORIGIN: 3/17/77 SOLVENT: Cu ²⁺	CURVE NO. 9 CONC. CELL PATH: 1mm REFERENCE: 100% polyethylene	SCAN SPEED: Fast SLIT: 35 REMARKS: Krypton present	OPERATOR: New DATE: 3/17/77
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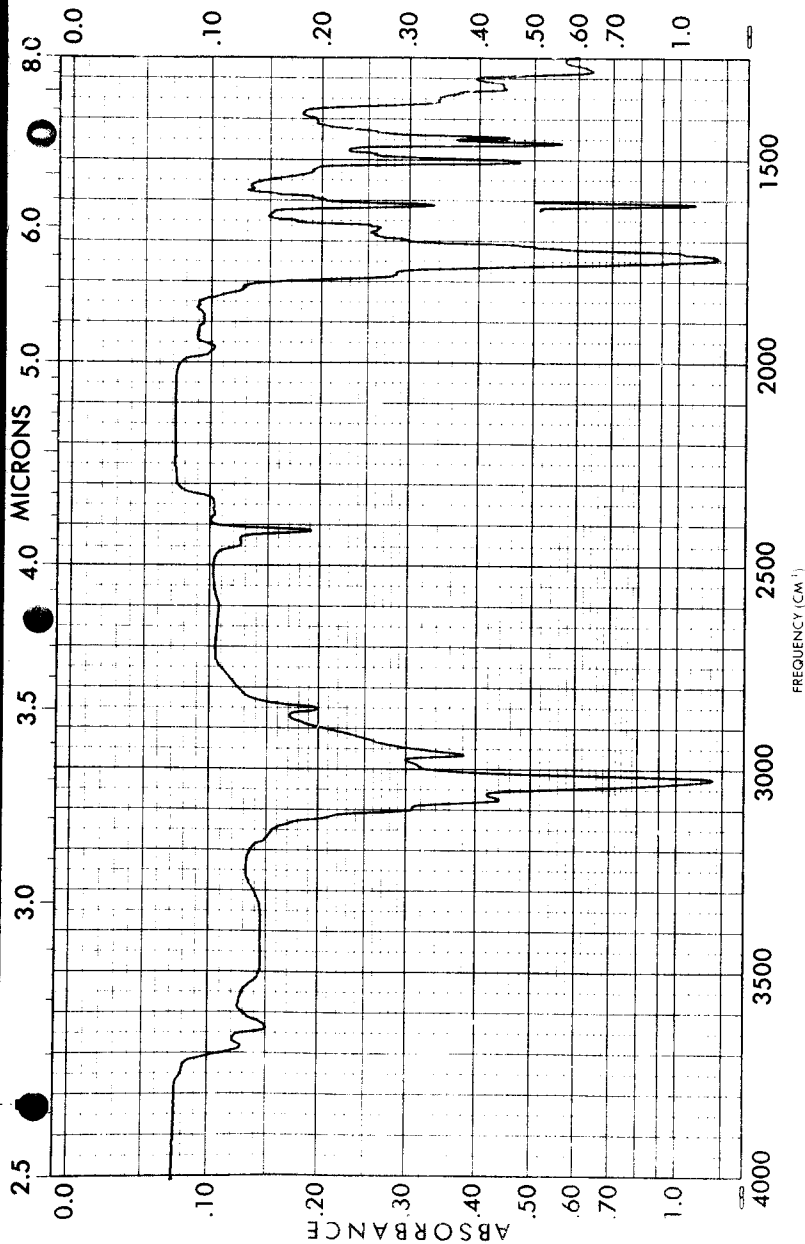
CURVE NO. 10 CONC. CELL PATH. 1 mm. REFERENCE 3-PHASE Polyethylene		SCAN SPEED Feet SLIT 25 REMARKS strong 1750 cm⁻¹ ⇒ pg	OPERATOR NW DATE 11/17/77
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RECORDING CHARTS

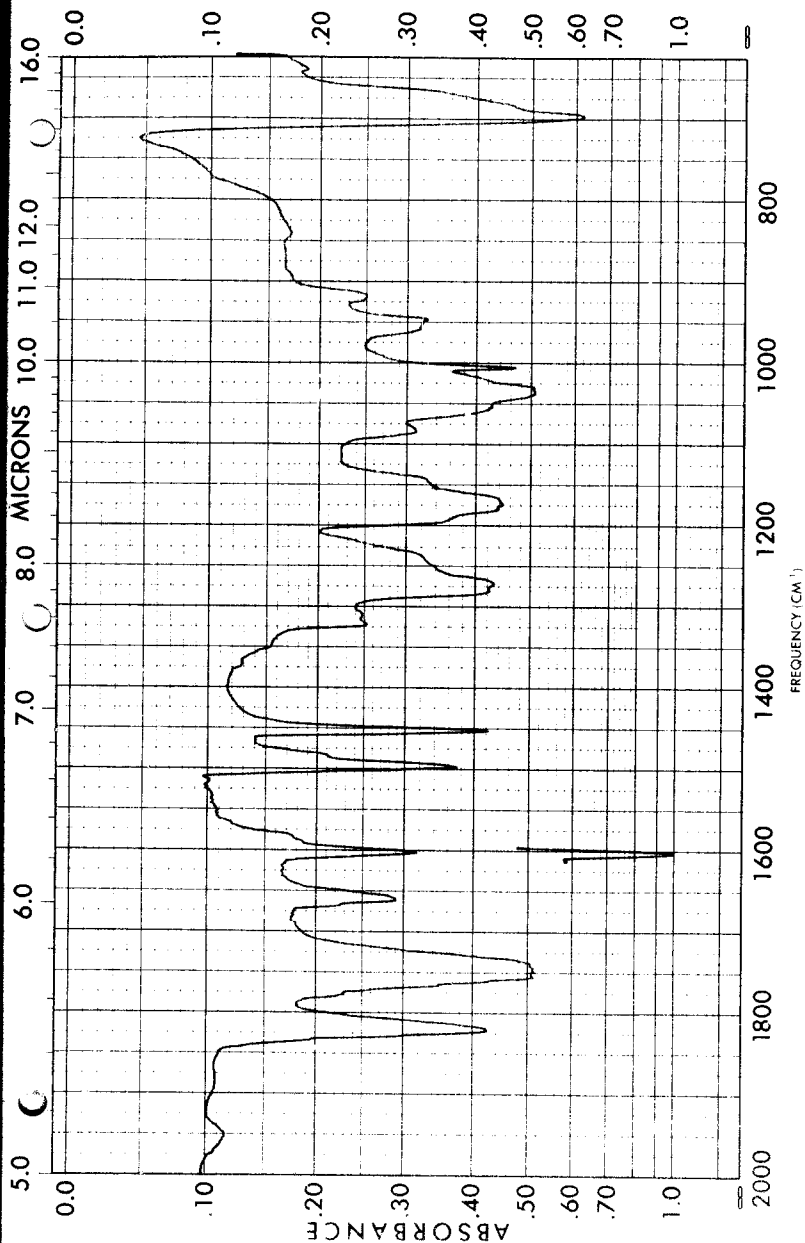
11/17/77 12:31 (1033)



SAMPLE Hydrolyzed resin after treatment w/ HCl (sample after 10 min. HCl) ORIGIN H-14 SOLVENT CHCl ₃	CURVE NO. 11 CONC. CELL PATH .1 mm REFERENCE 16 (1:1) polyethylene	SCAN SPEED Fast SUT 25	OPERATOR R.W. DATE 1/25/67 REMARKS 1950 cm⁻¹ - TPO - 1040 - 1000 - 1000 - 1000 TPO 1000

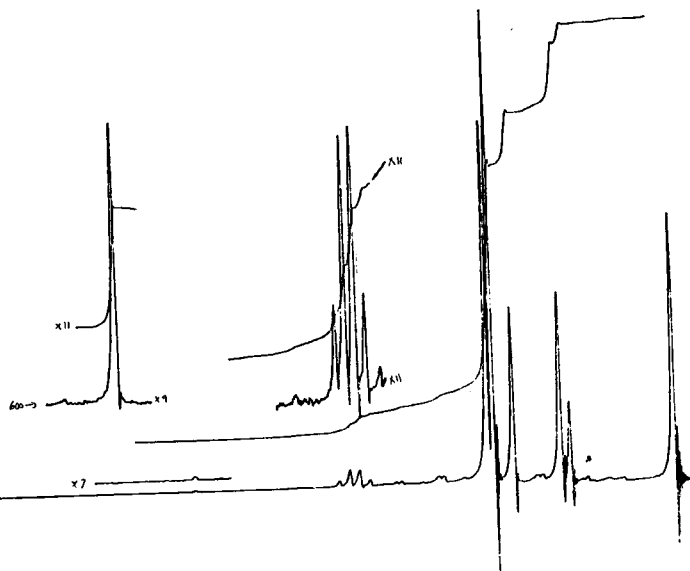


SAMPLE: benzyl isocyanate w/ Cu after treatment with TiCl_4 (conc off) and 10% CHCl_3 added ORIGIN: H ₂ O SOLVENT: CHCl_3	CURVE NO. 12 CONC. CELL PATH 1mm REFERENCE 100% polyethylene	SCAN SPEED Fast SLIT 25 REMARKS 1350 cm^{-1} -TPG	OPERATOR NCU DATE 4-15-77
			39



SAMPLE: <i>Aspirin</i> 5% in <i>CHCl₃</i> + 5% <i>refractive index</i> in <i>CHCl₃</i> + 5% <i>refractive index</i> in <i>CHCl₃</i> - <i>Calc. 1000</i> ORIGIN: 9/17/77 SOLVENT: <i>CHCl₃</i>	CURVE NO. 13 CONC. CELL PATH: 1 mm REFERENCE: 100% <i>CHCl₃</i>	SCAN SPEED: Fast SUI: 25	OPERATOR: N.W. DATE: 8-8	90
		REMARKS: <i>Aspirin</i> up but sm. cont. of 1600 <i>cm⁻¹</i> 5 <i>Ketone</i> 103 → sm. cont. of <i>benzophenone</i>		

170-180 °C. 10 min. fraction
 done 11/15/77
 3-methyl-2-pentanol



TMS
 0.1
 ~75%

45
 X5

11/17
 NEW

Rotating pure 2-pentanol