OZONOLYSIS OF CERTAIN α,β-UNSATURATED CARBONYL COMPOUNDS

by

Alan Howard Wynn UC 1979

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ABSTRACT

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One of the intermediates in the ozonolysis of alkynes is the αcarbonyl carbonyl oxide. The Hull rearrangement mechanism suggests that the α carbonyl carbonyl oxide can then rearrange via a rotation and cyclization to an anhydride. Ozonolysis of α,β-unsaturated carbonyl compounds provided an alternative synthesis of the α carbonyl carbonyl oxide. Mesityl oxide, phorone, trans-cinnamaldehyde, trans-4-phenyl-3-buten-2-one, trans-chalcone and trans-dibenzoylethylene were the α,β-unsaturated carbonyl compounds ozonized. In general the products were ozonides, glyoxals, aldehydes and anhydrides. Trans-chalcone and trans-dibenzoylethylene were the only olefins to produce the anhydride. The products were consistent with the Bauld-Bailey syn-anti carbonyl oxides. By the implications of the Hull mechanism, the anti carbonyl oxides formed the ozonides and the syn carbonyl oxides produced the anhydride. Because of steric hinderance trans-chalcone and trans-dibenzoylethylene were the only reactants which produced the syn carbonyl oxide and therefore an anhydride. The Hull mechanism was consistent with the experimental evidence. There was also experimental evidence to support the suggestion by Hull that two carbonyl oxides can react to form two aldehydes and O_2.

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INTRODUCTION

When the scientist Van Marum passed oxygen through a stream of electric sparks, he found that the resulting gas had a peculiar smell and tarnished mercury. In 1840, Christian F. Schönbein showed ozone was produced during the electrolysis of acidified water and he gave it the name ozone, which, in Greek means to smell. Later ozone was found to have the formula O_3. Ozone has a bond length of 1.278 A, a bond angle of 117° and is a hybrid of four resonance structures[1].

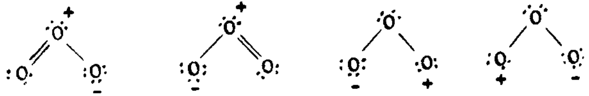


Figure 1 Resonance structures of ozone

It has a boiling point of -111.9°C, melting point of -192.5°C, as a gas it is colorless while in the liquid phase it is indigo blue and very explosive. Commercially ozone is prepared by passing O_2 through an electrical discharge.

"The oxidative cleavage of unsaturated compounds with ozone in solution (ozonolysis), which was first studied in detail by Harries[3] at the turn of the century is in many respects an unusual reaction."[2] After a thorough study of the products of ozonolysis of alkenes, Criegee and coworkers[4] proposed the following mechanism:

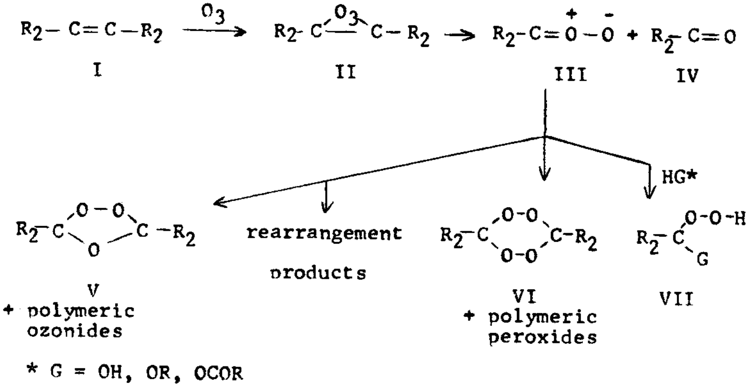


Figure 2 Criegee Mechanism of Alkene Ozonolysis

At present the Criegee mechanism is widely accepted. The Criegee mechanism, as shown, involves at least three descrete steps, I→ II, II→III and IV, and III and IV → V. All of the steps shown are 1,3-dipolar cycloreactions ([2+3] additions or reversions)[5].

It is proposed that the unsaturated compound reacts with the ozone to form a primary ozonide (II). There are five conceivable ways in which we can formulate an olefin-ozone adduct[2,6].

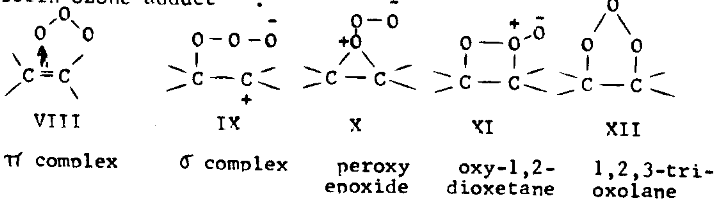
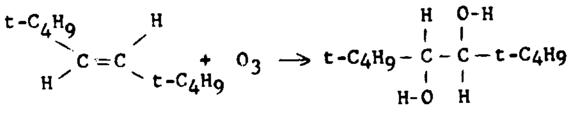


Figure 3 Possible olefin-ozone adducts

Prior to 1957, XI and XII were the proposed major modes of attack[7]. XI was favored because it can split in only one way, favoring the formation of the zwitterion (III) from one particular side of an unsymmetrical molecule and it explains the easy cleavage of the double bond under the mild conditions of ozonolysis[8]. It was suggested XII was formed by the initial formation of a π complex (VIII). The π complex should quickly collapse by a concerted process to form XII and it is not unreasonable to assume that the inductive effects rather than the resonance effects of the neighboring groups should determine the direction of cleavage[7]. In 1957, Bailey[9] showed by NMR that for the primary ozonide of trans-2,2,5,-tetramethyl-3-hexene (XIII) the carbons were equivalent.



XIII XIV

Scheme 1 Ozonolysis of trans-2,2,5,5-tetramethyl-3-hexene

The product of the above reaction after reduction was the meso 1,2-diol (XIV). Only XII could support this data. Bailey[10] has detected the presence of the π complex in the reaction of electron-rich arenes with ozone at -150°C. Thus it is most likely that a loose π complex forms initially which then collapses to the trioxolane.

Structure II is a primary ozonide and when the mechanism was proposed, its existence and structure was in doubt. But in 1958, Schroder[11] detected crystals at -78°C which disappeared on warming but did not form again on cooling. The primary ozonide is very unstable and cleaves to a carbonyl oxide (a zwitterion, III) and a ketone or aldehyde (IV).

The carbonyl oxide is an energy rich species but it is resonance stabilized[2].

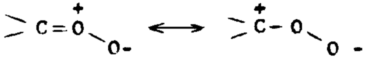
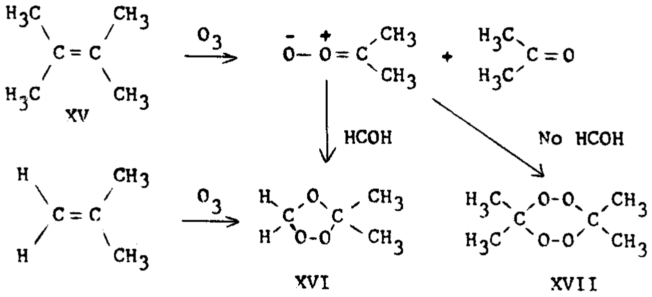


Figure 4 Resonance Stabilization of the Carbonyl Oxide

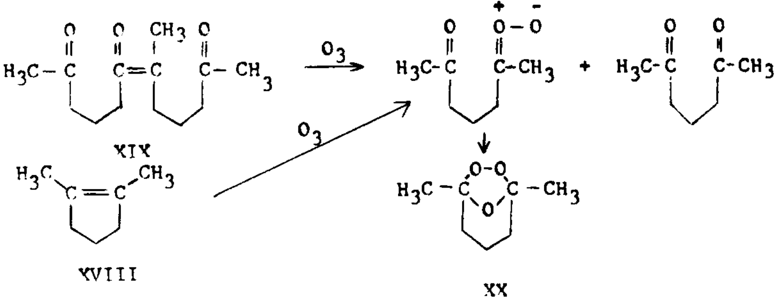
The existence of the zwitterion has been shown in four ways. First when tetramethylethylene (XV) is ozonized in an inert solvent containing formaldehyde, the product was isobutene ozonide (XVI) instead of dimeric peroxides (XVII).[12]



Scheme 2 Ozonolysis of tetramethylethylene in formaldehyde

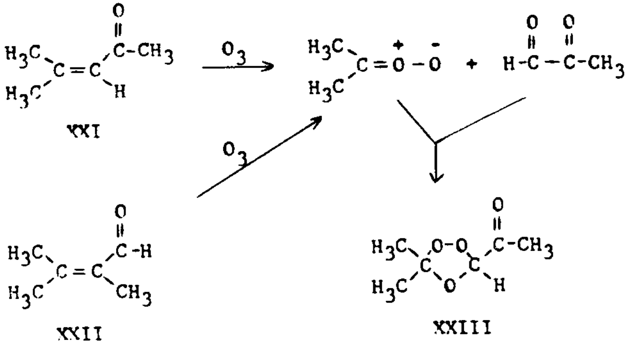
Thus ozone must cleave the C-C bond and produce a zwitterion which then reacted with the most reactive species (formaldehyde).

The second example is that the ozonolysis of 1,2-dimethylcyclopentene (XVIII) and 6,7-dimethyl-6-dodecene-2,11-dione (XIX) produce the same ozonide (XX), thus showing that the same carbonyl oxide was formed[13].



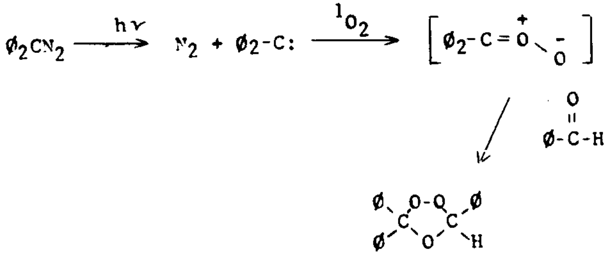
Scheme 3 Ozonolysis of 1,2-dimethylcyclopentene and 6,7-dimethyl-6-dodecene-2,11-dione

Ozonolysis of mesityl oxide (XXI and 2,3-dimethylcrotonaldehyde (XXII) in inert solvents give the same ozonide (XXIII)[4]. This could only happen if the intermediates were the same.



Scheme 4 Ozonolysis of mesityl oxide and 2,3-dimethylcroton-aldehyde

The fourth example is the photo-oxidation of diphenyldiazomethane. Murray[14] found that when diphenyldiazomethane was photo-oxidized in the presence of benzaldehyde, he detected a short lived product which then reacted to yield the ozonide of triphenylethylene.

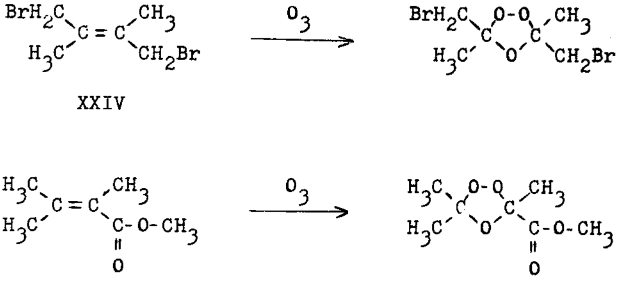


Scheme 5 Photo-oxidation of diphenyldiazomethane

Murray's work is independent of ozonolysis and shows that ozonides can be formed from the addition of a carbonyl oxide and a carbonyl compound[2].

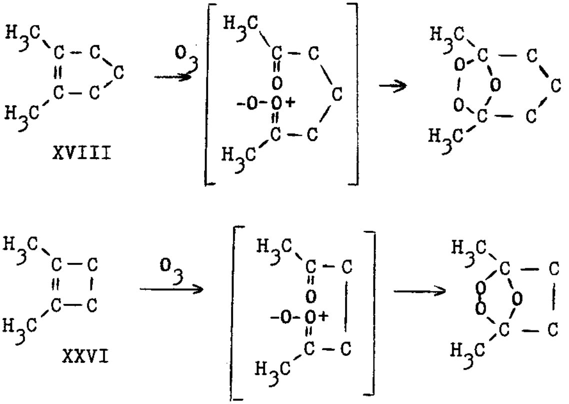
As shown in Figure 2 (page 2), the carbonyl oxide can react in at least four ways: (a) polymerize, (b) rearrangement, (c) react with aldehydes and ketones and (d) react with the solvent[4]. All four reactions are competitive and it is unlikely that the zwitterion will react in only one way.

As has been mentioned, the carbonyl oxide can react with ketones and aldehydes to produce the ozonide. The ketones or aldehydes are produced along with the zwitterion, so it is likely that they will react together. In general, ketones are less reactive than aldehydes in cycloaddition reactions. The ketones can be made more reactive if the neighboring substituents are electron withdrawing groups such as halogens (XXIV) or ester groups (XXV)[15].



Scheme 6 Effect of electron withdrawing groups on ozonolysis

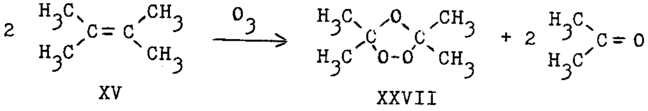
The carbonyl oxide also adds to a keto group when they are in the same molecule[2]. 1,2-dimethylcyclopentene (XVIII)[16] and 1,2-dimethylcyclobutene (XXVI)[17] yield cycloozonides.



Scheme 7 Production of cycloozonides

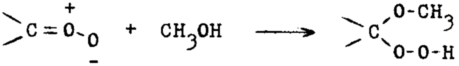
When the double bond is present in rings with six or more members, no monomeric but only oligermeric ozonides are produced[18]. Carbonyl oxides can also react with aldehydes or ketones other than the one produced during ozonolysis[12] (see scheme 2 page 4).

As was mentioned, ketones are not very reactive in dipolar cycloaddition reactions. Often when a ketone is produced along with the zwitterion, the zwitterion instead of reacting with the ketone dimerizes to form "dimeric keto- (or aldehydes) peroxides (XXVII) (1,2,4,5-tetraoxanes)"[2,18]



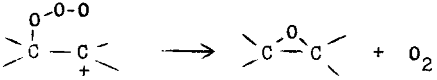
Scheme 8 Formation of 1,2,4,5-tetraoxanes

Carbonyl oxides also react with hydroxylic solvents to form geminal alkoxyhydroperoxides. The way which, for example methanol, adds to the carbonyl oxide gives further evidence for the existence of the carbonyl oxide[2].

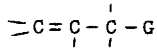
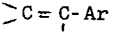


Scheme 9 Addition of hydroxylic solvent to the carbonyl oxide

The sigma complex and peroxyepoxide were suggested as a means by which ozone can attack the olefin. It has been suggested that these structures took no part in ozonolysis, but they can be assumed to be the primary product in ozonations of sterically hindered olefins[7]. In this case the double bond is only partially cleaved and the products are the epoxide and O_2.



Scheme 10 Epoxide formation

There are cases of ozonolysis from which abnormal products are obtained. In general, the products will be abnormal if the olefin possesses either the system  $>C=\underset{|}{C}-\underset{|}{\overset{|}{C}}-G$ (G=N,O or S) or the system  $>C=\underset{|}{C}-Ar$ (Ar is an aryl group with N,O, or S)[19,20]. Young and coworkers[21] found that it was unlikely the abnormal products were due to allylic rearrangement or the oxidative workup procedure. They concluded that the production of abnormal products was related to the basicity of the unshared electron pairs on the atom joining the radical G to the allylic system. Young also ozonized α,β-unsaturated compounds and suggested the following mechanism for the rearrangement:

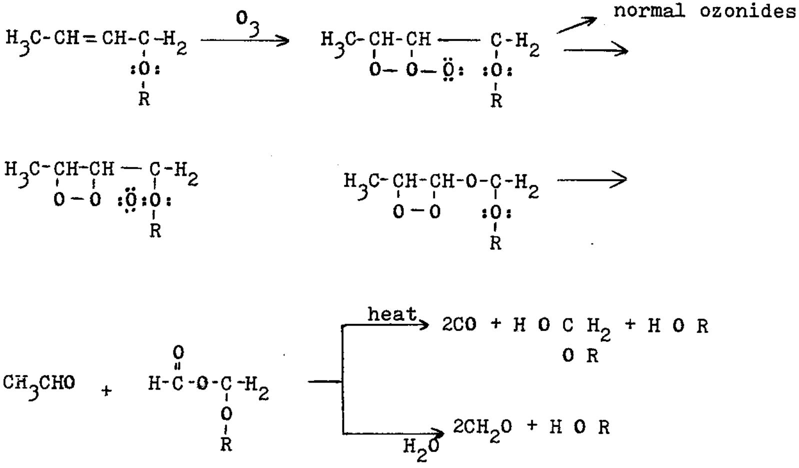


Figure 5 Young rearrangement mechanism

The rearrangement is based on the Staudinger mechanism[22] which has been replaced by the Criegee mechanism. Thus it seems unlikely this is the mechanism.

Barton and Seoane proposed that the reaction proceeds by the following mechanism:

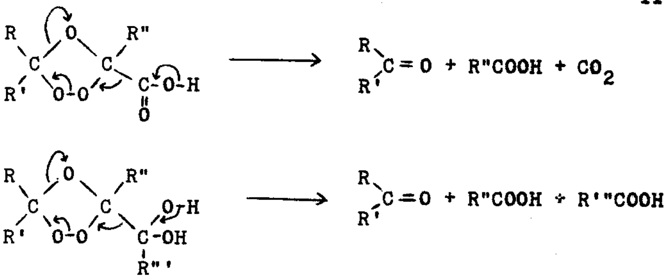


Figure 6 Barton and Seoane rearrangement mechanism

The problem with the above mechanism is that it does not account for the formation of carbon monoxide (as reported by Young[21]) and it also requires the formation of an ozonide[7].

A third mechanism was suggested by Karrer and Haab[24]:

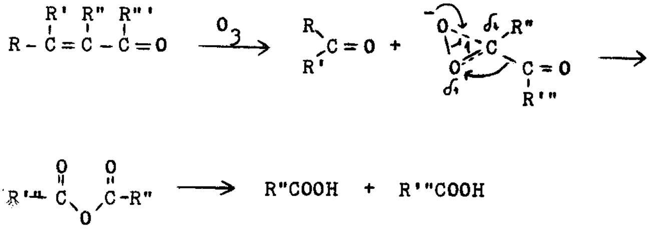


Figure 7 Karrer and Haab rearrangement mechanism

This mechanism does not involve an ozonide and if R" or R'" is a hydrogen it could account for the CO.

Yang and Pelletier[25] while ozonizing a 3-hydroxymethylene derivative of camphor(XXVIII) detected the presence of the 3-keto camphor (XXIX) and the anhydride(XXX). From this result, they suggested that the anhydride formation is the result of a Baeyer-Villiger oxidation of the α diketone generated during ozonolysis:

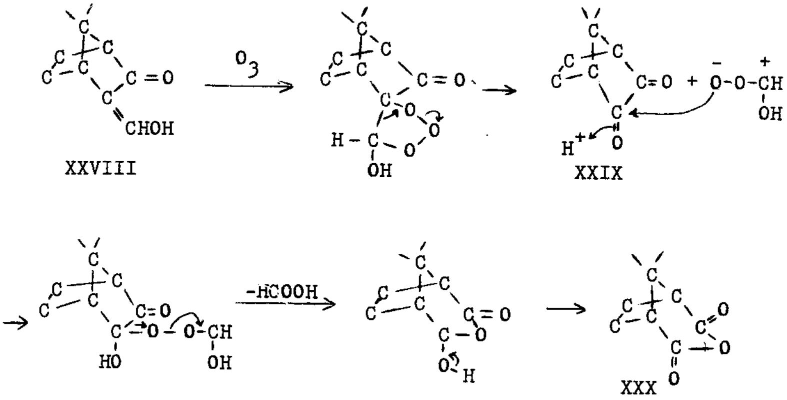


Figure 8 Yang and Pelletier rearrangement mechanism scheme 1

Yang has suggested a second scheme which differs in that it involves a peracid:

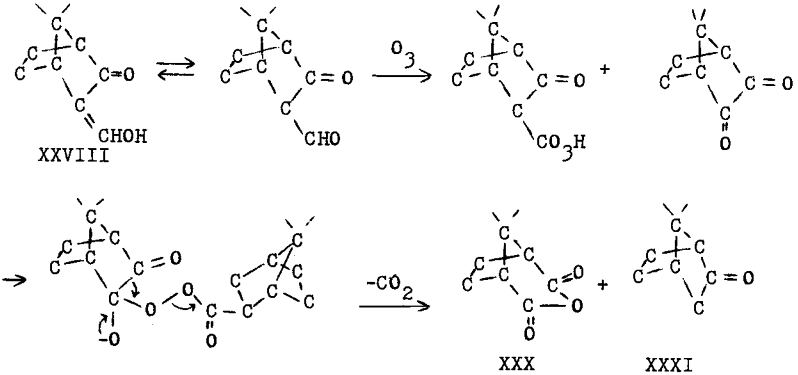


Figure 9 Yang and Pelletier rearrangement mechanism scheme 2

Yang supports scheme 2 by the isolation of small amounts of camphor (XXXI), and the detection by Bernatek[26] and Story[27] that peracids are produced during the reaction of ozonides with carboxylic acids and in ozonolysis by oxidation of aldeyhdes.

Hull and coworkers[28] in their mechanism for alkyne ozonolysis (see later) imply another mechanism. This mechanism is a modification of the Criegee mechanism:

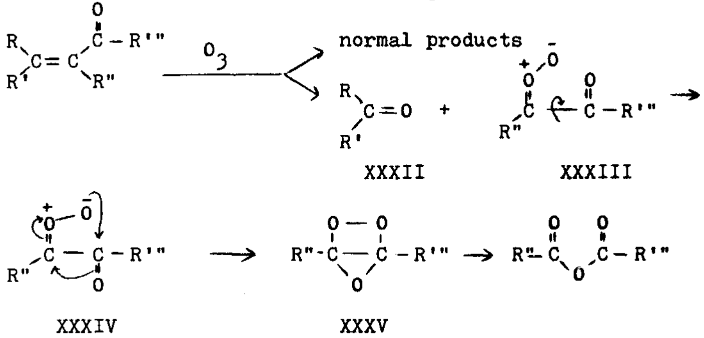


Figure 10 Hull rearrangement mechanism

The step from XXXIII to XXXIV is the rotation about the C-C single bond. As long as there is no steric hinderance, this step should not be energetically unfavorable. Hull supports the existence of species XXXV by the fact that the rate constant for XXXV to form products would be insensitive to polar substituents and solvent effects. This is typical of the reaction of alkynes with ozone[29]. XXXV is also supported by the detection of chemiluminescence upon decomposition of the precursor to the anhydride. If R and R' are not hydrogens, ozonolysis would produce a ketone (XXXII) which would be less reactive than the α carbonyl. Since formic acid anhydrides are unstable, carbon monoxide and a carboxylic acid would be the products if R" or R'" were hydrogens.

The Criegee mechanism does not account for the finding that cis and trans olefins give different cis-trans ozonide ratios[30]. In order to explain this, Bauld and Bailey[31] proposed that the cis and trans primary ozonide decompose stereoselectively to give syn and anti carbonyl oxides. The carbonyl oxides then react stereoselectively. The stereoselectivity follows three rules. All of the rules can be explained by cycloaddition reactions. First, in the disrotatory cleavage of primary ozonides equatorial substituents are converted into anti and axial substituents into syn carbonyl oxides. Second, an equatorial substituent is incorporated into a zwitterion in preference to an axial substituent. And third, aldehydes preferentially interact with anti carbonyl oxides to orient bulky substituents on the 1,2,4-trioxolane ring into an axial-equatorial (cis) conformation while aldehydes interact with syn carbonyl oxides to orient bulky substituents diaxially (trans)[32]. The third rule is a modification of the original Bauld-Bailey rules. This is because it was found that the 1,2,4-trioxolanes have a oxygen-oxygen half chair configuration rather than the carbon-oxygen half chair[33,34]. These rules are shown below:

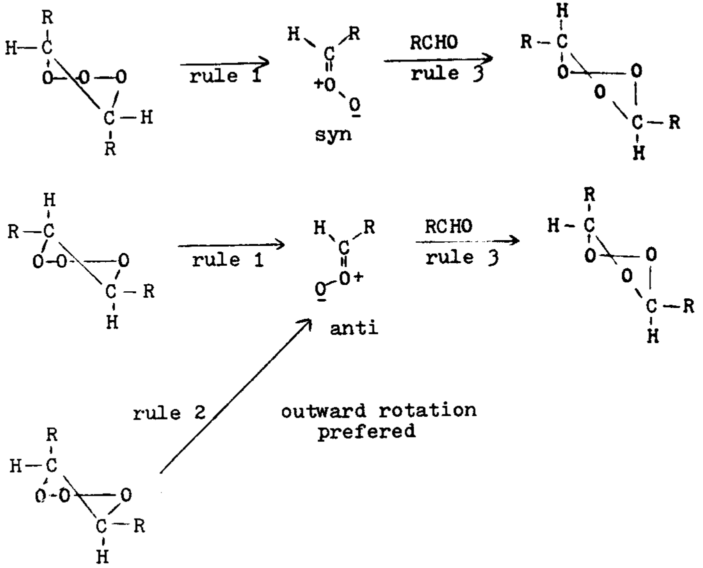


Figure 11 Bauld-Bailey rules for the stereoselective formation of ozonides

The Criegee mechanism of alkene ozonlysis as modified by syn and anti carbonyl oxides is a satisfactory explanation for the experimental evidence.

Compared to the ozonolysis of alkenes, very little work has been done on the mechanism of alkyne ozonolysis. Criegee and Lederer[35] modified the Criegee mechanism to account for the products of alkyne ozonolysis:

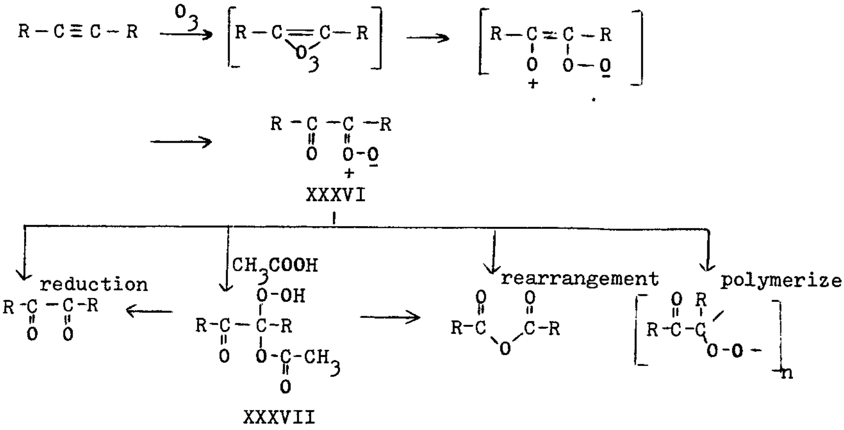
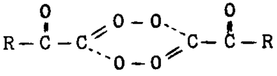


Figure 12 Criegee-Lederer mechanism for alkyne ozonolysis

The mechanism proposes the existence of the α carbonyl carbonyl oxide (XXXVI). Lederer gives evidence for this intermediate by carrying out the reaction in the presence of acetic acid and trapping the α carbonyl carbonyl oxide (XXXVII). Like the carbonyl oxide, the carbonyl carbonyl oxide can undergo any of four reactions: (a) reduction, (b) react with a hydroxylic solvent, (c) polymerize or (d) rearrangement. The last, rearrangement is of the most interest to this work.

DeMore[36] has performed kinetic studies on the gas phase ozonolysis of acetylene and found that the preexponential factor was 10^3 times higher than for ethylene and that the activation energy was 10.8 Kcal/mole. These results were explained by proposing a radical mechanism[37]. The radical mechanism and not an ionic intermediate was necessary to account for the high preexponential factor. The mechanism involves an anhydride intermediate. The anhydride, because of the energy which it possesses, is unstable and decomposes to an acid and carbon monoxide (or a ketone).

When DeMore and Lin[38] studied the ozonolysis in the liquid phase,they were able to detect the anhydride (by IR spectroscopy) and found that the anhydride was stable. They proposed that the anhydride was produced by some precursor and that the reaction was temperature dependent. From the IR spectra they suggested that the precursor was the carbonyl carbonyl oxide dimer (XXXVIII).



XXXVIII

Scheme 11 Carbonyl carbonyl oxide dimer

Keay and Hamilton[39] while studying the alkene epoxidation by the intermediates of alkyne ozonolysis found that there were three different intermediates which could donate an oxygen for the epoxidation. All three intermediates were present only over certain temperature ranges. To account for this the following mechanism was proposed:

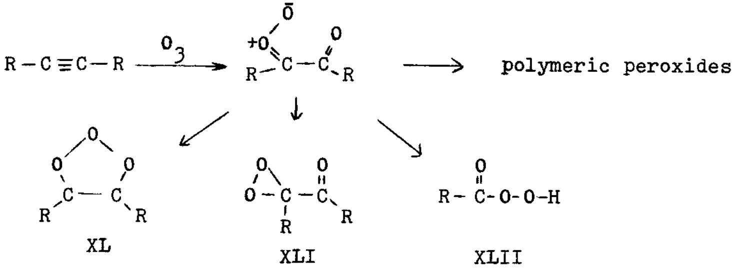


Figure 13 Keay and Hamilton Alkyne rearrangement mechanism

The structure of XL is supported by the formation of biacetyl when reduced with diethyl sulfide. It is stable between -70 and -50°C. It has been estimated[40] that ring closure is slightly exothermic and at -70°C the trioxolene could be stable. At higher temperatures the trioxolene would decompose, probably through the carbonyl carbonyl oxide (XXXIX).

XLI is a three membered peroxide ring and recent calculations[41] suggest that this form of the carbonyl oxide is more stable than XXXIX. XLI was stable below -15°C. As mentioned, DeMore and Lin suggested the peroxide dimer as the structure of a species (which would correspond to XLI), which is thermally unstable during the -45°C ozonolysis of alkynes. But the dimer being the structure is unlikely because the diperoxides should not be unstable at the subambient temperatures[39].

Reduction with NaI was used to identify XLII, but no mechanism was given to explain its formation.

The Criegee Lederer alkyne mechanism does not suggest a mode of rearrangement to the anhydride. Hull and coworkers[29] give the following extension of the mechanism to account for the anhydride:

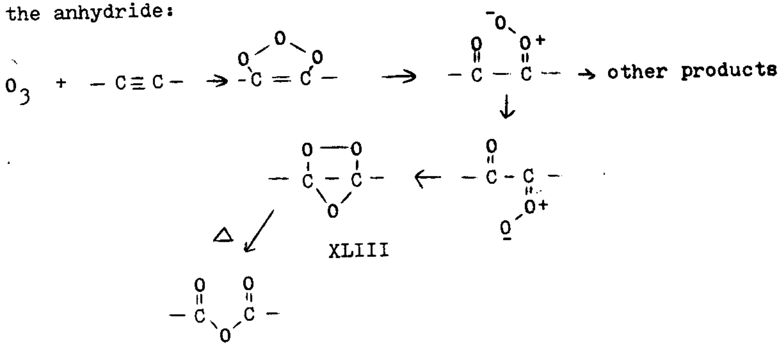


Figure 14 Hull alkyne rearrangement mechanism

The above mechanism is analogous to the alkene mechanism already discussed (see page 13), and it does not assume any new intermediates. Species XLIII is similar to the 1,2,4-trioxolanes and Hull suggests that this is the relatively stable anhydride precursor.

It is the goal of this work to find evidence for the mechanism of rearrangement involving ozonolysis of α,β -unsaturated carbonyl compounds. We propose to do this by an alternative synthes [illegible] the α carbonyl carbonyl oxide. We hope to generate the carbonyl carbonyl oxide by the ozonolysis of α,β -unsaturated compounds. If analysis shows that abnormal products are being formed, we will then go to lower temperatures and attempt to trap and identify the intermediate(s).

EXPERIMENTAL PROCEDURES

The IR analyses were performed on a Perkin Elmer 237. The NMR used was a Hitachi-Perkin Elmer R24A. Ozone was produced by a Welsbach T-408 Ozonator (see appendix A).

Ozonolysis of 2,3-dimethyl-2-butene

0.23 M (1.0 ml) of 2,3-dimethyl-2-butene in 35 ml of CCl_4 was ozonized for 12 minutes at 0°C (spectrum 6).

Ozonolysis of 4-methyl-3-penten-2-one (mesityl oxide)

0.47 M (2.0 ml) of 4-methyl-3-penten-2-one with 0.20 ml chlorobenzene (as an internal standard) in 35 ml of CCl_4 or CH_3CN was ozonized for 30 minutes at 0°C (spectra 1-4,37-38). Samples were removed at five minute intervals for NMR analysis. NMR spectra were taken at various times after removal.

Ozonolysis of 2,6-dimethyl-2,5-heptadien-4-one (phorone)

0.35 M (2.0 ml) of 2,6-dimethyl-2,5-heptadien-4-one with 0.30 ml chlorobenzene and/or 0.20 ml 1,4-dioxane (as an internal standard) in 35 ml of CCl_4 or CH_3CN was ozonized for 17 minutes (ozonize first double bond) or 38 minutes at 0°C. (spectra 7-8). For the 38 minute ozonolysis, samples were removed after 0,15,30 and 38 minutes. 30 ml of the product in CCl_4 was refluxed for 15 minutes in order to decompose the anhydride (spectrum 39). Note that there was no anhydride present, see results.

Ozonolysis of trans-cinnamaldehyde

0.43 $\underline{M}$ (2.0 ml) of trans-cinnamaldehyde with 0.1 ml of 1,4-dioxane in 35 ml of CCl_4 or CH_3CN was ozonized for 22 minutes at 0°C (spectra 9-12). A sample was removed after 15 minutes.

Ozonolysis of trans-1,3-diphenyl-2-propen-1-one (chalcone)

0.43 $\underline{M}$ (3.1g) of trans-1,3-diphenyl-2-propen-1-one and 0.20 ml of 1,4-dioxane in 35 ml of CCl_4 or CH_3CN was ozonized for 20 minutes at 0°C(spectra 17-20). A sample was removed after 12 minutes.

Ozonolysis of trans-4-phenyl-3-buten-2-one

0.47 $\underline{M}$ (2.3-2.4 g) of trans-4-phenyl-3-buten-2-one with 0.10 ml of 1,4-dioxane in 35 ml of CCl_4 or CH_3CN was ozonized for 25 minutes at 0°C (spectra 13-14,16-17). Samples were removed after 10,15,20 and 25 minutes. 0.37 $\underline{M}$ (1.08g) with 0.06 ml 1,4-dioxane in 20 ml of $CHCl_3$ was ozonized for 10 minutes at 0°C. 0.44 $\underline{M}$ (.32g) in 5 ml of deuterochloroform was ozonized for 3 minutes at 0°C (spectrum 15).

In order to study the effects of initial reactant concentration on the product ratio, the ozonolysis at ¼,½,2 and 4 times the above concentration were run. 0.090 $\underline{M}$ (0.46g), 0.29 $\underline{M}$ (1.51g), 0.819 $\underline{M}$ (4.19g) and 1.66 $\underline{M}$ (8.51g) of trans-4-phenyl-3-buten-2-one with 1,4-dioxane in 35 ml of CCl_4 were ozonized for 4.5,10,44 and 90 minutes respectively at 0°C. 0.13 $\underline{M}$ (0.67 g), 0.19 $\underline{M}$ (0.98g) and 0.21 $\underline{M}$ (1.05g) samples in 35 ml of CCl_4 were also ozonized for 2,3 and 5 minutes respectively.

Ozonolysis of trans-1,4-diphenyl-2-buten-1,4-dione
(dibenzoylethylene)

Because of the insolubility of trans-1,4-diphenyl-2-buten-1,4-dione in solvents which are suitable for ozonolysis, some of the solutions were heterogeneous. 3.8 to 4.0 g were added to 35 or 40 ml of CCl_4 and ozonized from 15 to 76 minutes at 0°C. These samples were heterogeneous (spectra 26,32-34). 0.056 M (1.0g) in 75 ml of CCl_4 was ozonized for 5 minutes at 0°C. This solution was homogeneous (spectrum 27). All of the following ozonolyses were homogeneous. 0.13 M (0.30g) in 10 ml of 3-pentanone was ozonized for 1.5 minutes at 0°C. 0.27 M (2.92g) with 0.08 ml 1,4-dioxane in 45 ml of CH_3CN was ozonized for 16 minutes at 35°C (spectra 30,35-36). 0.23 M (4.0g) in 65 ml of ethyl acetate was ozonized for 15 minutes at 0° (spectrum 31).

The following conditions were used for the experiments on the effect of added benzaldehyde: 0.49 M (4.01g), 0.49 M (4.06g), 0.48 M (4.04g), 0.47 M (4.00g), 0.48 M (4.11g), 0.45 M (4.01g), 0.43 M (4.03g), 0.51 M (5.37g), 0.47 M (6.11), and 0.47 M (6.12g) with 0.00,0.30,0.60, 1.20, 1.20, 2.40, 4.80, 9.80, 20.00 or 20.00 ml of benzaldehyde respectively, were ozonized for 23 to 33 minutes (80% calculated ozonolysis) at 35°C (spectra 28, 35). 0.45 M (3.77g), 0.45 M (3.78g), 0.45 M (3.78g) and 0.44 M (3.80g) with 0.00, 0.30, 0.60 or 1.20 ml of benzaldehyde in 35 ml of acetone were ozonized for 20 minutes at 35°C.

Addition of triphenylphosphine, diphenylsulfide and D_2O to the ozonolysis products

Triphenylphosphine and diphenylsulfide were added in order to determine which products were reducible. D_2O was added to detect the exchangable protons. Approximately 0.1g of triphenylphosphine or 0.2g of diphenylsulfide was added to 0.7 ml of ozonolysis products in an NMR tube. The tube was shaken to dissolve the reducing agent and allowed to react for 10 minutes. An NMR spectrum was then taken.

0.5 ml of D_2O was added to 0.7 ml of ozonolysis products in an NMR tube. The tube was shaken and an NMR spectrum taken 15 minutes later.

The above quantities of triphenylphosphine, diphenylsulfide and D_2O were in excess of the stoichiometric quantities necessary.

Synthesis of mesityl oxide epoxide[42]

To 5.0 ml of mesityl oxide in 50 ml of tetrahydrofuran, 80 ml of 0.51 M $Ca(ClO)_2$ (Pittchlor) was added. The reaction vessel was stirred for 10 minutes. Three aliquots of dimethyl ether were added to extract the organic phase. The ether was dried over magnesium sulfate and removed by vacuum distillation. The NMR and IR spectra (40-43) indicate that the product was mesityl oxide.

Synthesis of methyl glyoxal (pyruvic aldehyde)

Aldrich Chemical Company supplies methyl glyoxal in a 40% aqueous solution. But since during the ozonolysis no water was present, it was necessary to remove the water. Extraction with CCl_4 was unsuccessful. When distilled using a Konte short path distillation apparatus, the product distilled from 102-114°C. The NMR (spectrum 44) does not show the expected aldehyde peak near 9.0 ppm.

In a third attempt to remove the water, 60 ml of benzene was added to 50 ml of methyl glyoxal and refluxed. Upon distillation the water was removed. The benzene was removed by distillation and the methyl glyoxal was distilled at reduced pressure. The NMR, (spectrum 45), shows a very small amount of methyl glyoxal may be isolated by this method.

Since the water could not be removed and the glyoxal produced in good yield, methyl glyoxal was synthesized by the method of Riley et al[43]. 62 ml of propanal and 27.4g SeO_2 were refluxed for 4½ hours and the product was extracted with 50 ml of ether. After standing overnight with magnesium sulfate as a drying agent and to coagulate the selenium, the solution was filtered and washed with an additional 20 ml of ether. The ether was removed by vacuum distillation. The product was then distilled under reduced pressure and a fraction was collected from 55-65°C. The NMR (spectrum 46), indicates that the aldehyde proton absorbs at 9.35 ppm.

Isolation of Phenyl Glyoxal

Aldrich also supplies phenyl glyoxal monohydrate. The phenyl glyoxal could be extracted with CCl_4 and the aldehyde proton absorbs at 9.46 ppm (spectra 21-22).

Synthesis of Benzoic Formic Anhydride[44]

Two drops of saturated sodium formate solution was added to 0.7 ml of benzoyl chloride in CCl_4 in an NMR tube. The reaction was followed by NMR (spectrum 23). The presence of the anhydride was confirmed by running the reaction in D_2O and CCl_4 instead of H_2O. Since the NMR still showed a peak at 535 hz, the peak was due to the anhydride and not benzoic acid. When excess water was added, the anhydride peak disappears (spectrum 25).

In order to confirm the ozonolysis observation that the peak at 9.1 ppm did not disappear upon addition of triphenylphosphine, the anhydride was reduced. Spectrum 24 indicated that the anhydride was not reduced by triphenylphosphine.

Synthesis of Formic Acetic Anhydride

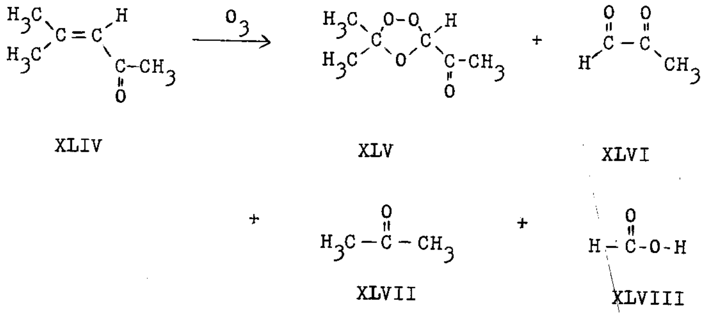
To 0.7 ml of CCl_4 in an NMR tube, 4 drops of acetyl chloride and 4 drops of saturates sodium formate were added. The presence of the anhydride was confirmed by the NMR (spectrum 47).

RESULTS

Analysis of the ozonolysis products was done primarily by NMR. Unless otherwise noted, all spectra of the products were taken within 20 minutes after completion of the ozonolysis. The products were identified by comparison with NMR of known samples, reduction with triphenylphosphine and D_2O exchange.

Among the products was an anhydride. Bailey[32] points out that the anomolous products are often due to overozonation. In this study only 80% of the calculated ozone was bubbled into the reaction vessel. The NMR spectra also showed that some reactant remained after ozonolysis.

Ozonolysis of mesityl oxide (XLIV) yielded four products;3-aceto-5,5-dimethyl-1,2,4-trioxolane (XLV), methyl glyoxal (XLVI), acetone (XLVII) and formic acid (XLVIII) (spectra 1-4).



XLIV

XLV

XLVI

XLVII

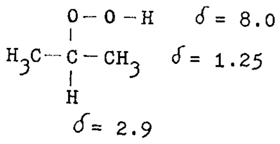
XLVIII

Bailey[32] has compiled NMR studies of ozonides and reports that the protons on the trioxolane ring from alkenes with nonterminal double bonds absorb in the range of 4.87 to 5.38 ppm. The NMR of the ozonolysis products gave a peak at 5.15 ppm. This peak was assigned to the ozonide (XLIV). From the integration and the ratio of methyl protons to the trioxolane proton, it can be seen that the doublet at 1.50 was from the methyl groups attached to the ozonide. The protons on the methyl groups adjacent to the carbonyl absorb at 2.2 ppm but were indistinquishable from the other protons in that region. These peak assignments are supported by the reduction with triphenylphosphine. Spectrum 1 shows the products before reduction and spectrum 4 was after. The peaks at 5.15 and 1.50 ppm were both missing after the addition of triphenylphosphine. The ozonide decomposed upon standing (see later discussion) and both peaks disappeared.

Horn and Schuster[45] synthesized methyl glyoxal and report that the pure sample gave an NMR spectrum in CCl_4 with the aldehyde proton absorbing at 9.07 ppm and the methyl protons at 2.25 ppm. The peak at 9.0 was assigned to methyl glyoxal. The broad peak in the IR (spectrum 3) at 1725 cm^{-1} also supports the presence of methyl glyoxal[46].

The acetone was identified by comparison to the NMR of an actual sample (spectrum 5).

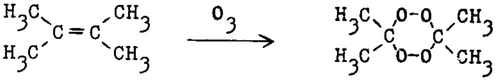
The assignment of the peak at 7.95 ppm to formic acid was more difficult to confirm. It is possible that the peak could also be due to formic acetic anhydride or a hydroperoxy proton. Comparison of the NMR and IR of the ozonolysis products to formic acid in CCl_4 show that the spectral data are in agreement. Stevens and Van Es[47] synthesized formic acetic anhydride from ketene and formic acid. They reported the following spectral data: NMR: $\delta=9.0$ (1H), $\delta=2.3$ (3H), IR: strong peaks at 1800,1780,1830,1180 and 1050 cm^{-1}. Neither the IR nor the NMR of the ozonolysis products support the presence of the anhydride. Swern, Clements and Luong[48] synthesized and purified some alkyl hydroperoxides. They found that in a 1 M CCl_4 solution the hydroperoxy proton absorbs at about 8 ppm. The peak was concentration dependent and at 0.5 M shifts upfield to 7.8 ppm. Methyl protons β to the hydroxyperoxy proton were unaffected by it and gave a singlet in the same region as the alcohol. Fujiwara and coworkers[49] report that the protons α to the hydroperoxy protons absorb slightly upfield than the alcohol at 2.9 ppm. So for instance, propyl-2-hydroperoxide should absorb in the following regions;



$$H_3C-\overset{O-O-H}{\underset{H}{C}}-CH_3$$

A hydroperoxide is reducible by triphenylphosphine. Comparison of spectra 1 and 4 show that the peak at 8.0 was not reducible. The peaks α and β to the hydroperoxide were not present. Therefore it was concluded that the peak was due to formic acid and not a hydroperoxide.

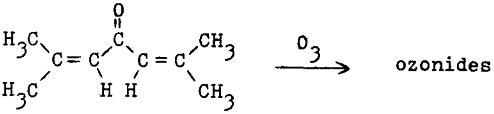
Another possible product was the dimer of the carbonyl oxide (IL). IL was produced by the ozonolysis of 2,3-dimethyl-2-butene. The NMR (spectrum 6) showed that the protons of



IL

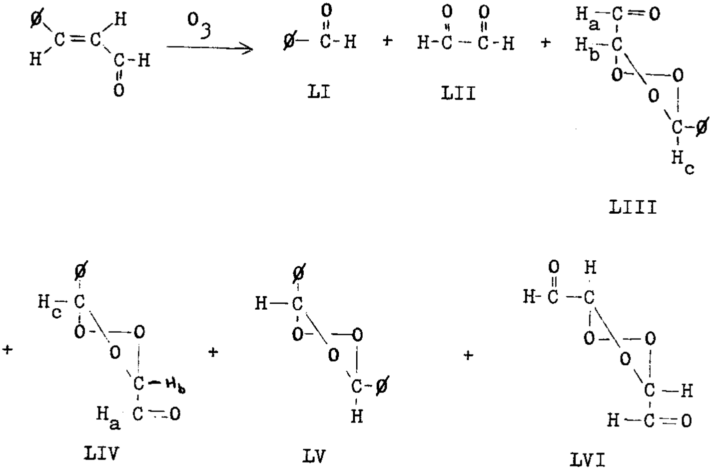
the peroxide dimer gave a multiplet centered at 1.3 ppm. Since the ozonolysis of mesityl oxide did not give this set of peaks, IL was not a product.

Ozonolysis of phorone (L) was more difficult to analyse (spectra 7-8). The possibility of ozonizing two bonds greatly complicates the assignment of NMR peaks to structures. It is unknown what effect ozonolysis of the first double bond has on ozonolysis of the second. Among the products were ozonides, but exactly which ozonides is uncertain. No anhydride was present. Because the products could not be identified, the results of phorone will not be discussed further.



L

Ozonolysis of trans-cinnamaldehyde gave benzaldehyde (LI), glyoxal (LII), the cis (LIII) and trans (LIV) ozonide, cross ozonides (LV and LVI) and a hydroperoxide (spectra 9-11).



Benzaldehyde was an expected product of the ozonolysis and is known to absorb at 10.0 ppm. This assignment is also supported by the observation that it was not reduced by triphenylphosphine (spectrum 12).

The peak at 7.95 has been assigned to glyoxal. Glyoxal is one of the products predicted by the Criegee mechanism. The peak disappeared on reaction with triphenylphosphine. Note, that since the peak disappeared it could not be due to formic acid.

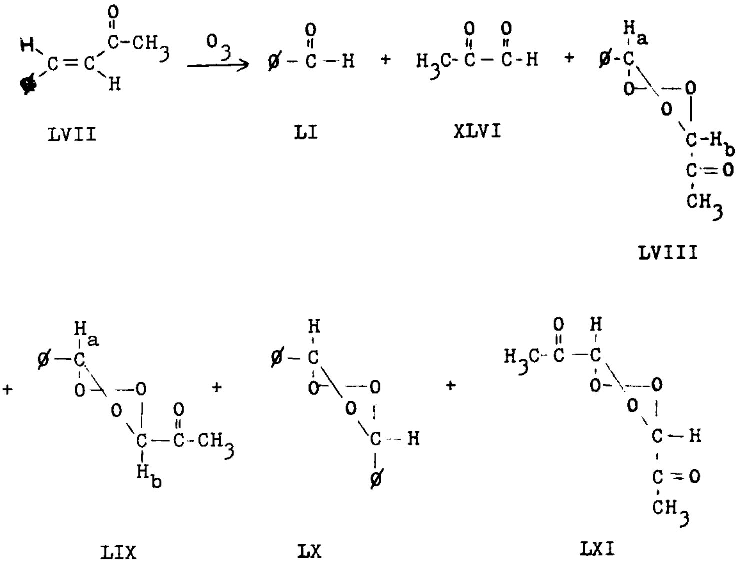
The Bauld-Bailey syn and anti zwitterion mechanism[31] accounts for the formation of the cis and trans ozonides. The syn zwitterion yields the trans (a,a) ozonide while the anti zwitterion leads to the cis (a,e) ozonide[32]. Murray et al[50] were able to partially separate the cis and trans ozonides of 2-butene by gpc. The NMR spectrum showed that the methine protons of the cis and trans ozonides absorbed at slightly different fields. The protons on the cis ozonide absorbed 0.06 ppm downfield relative to the trans isomer. Experimentally it was found that the ozonide of trans-cinnamaldehyde gave a pair of doublets at 5.35 and 5.30 ppm. The cis ozonide (LIII) was assigned to the downfield peak at 5.35 and the trans ozonide (LIV) to the peak at 5.30. The Bauld-Bailey mechanism predicts that for a trans olefin the diequatorial primary ozonide preferentially forms the anti zwitterion while the diaxial primary ozonide preferentially forms the syn zwitterion. The initial ozonide of trans-cinnamaldehyde is more stable in the diequatorial configuration so more anti carbonyl oxide and therefore more cis ozonide should be produced (see the discussion for a more thorough treatment). This was supported by the results. The NMR shows that more cis rather than trans ozonide was formed.

The aldehyde proton, H_a, and the ozonide proton, H_b, are spin spin coupled. Therefore H_a and H_b appear as doublets. The aldehyde protons for the cis and trans isomers of the ozonides were at 9.32 and 9.28 ppm respectively. The ozonide proton H_c, β to the phenyl ring absorbed at 5.92 ppm. Carles and Fliszar[51] ozonized styrene and report that the proton β to the phenyl ring absorbs at 5.81 ppm. As further evidence for these peak assignments, all of the above peaks were reducible with triphenylphosphine (spectrum 12).

The integration of the ozonide peaks shows that the ratio of the ozonide peaks, H_b to H_c was 3.0 to 2.0 If only normal ozonide (LIII or LIV) were being produced, it would be expected that this ratio would be one to one. The peak at H_b was due to the proton adjacent to the carbonyl group. Since H_b peak area was greater than H_c, it is possible that the diformyl trioxolane (LVI) was being formed. If one cross ozonide was produced the other cross ozonide, diphenyl trioxolane (LV) should also be produced. This result can not be detected by the NMR spectrum because the protons on the diphenyl trioxolane absorb at the same magnetic field as H_c on the normal ozonide. So no conclusion can be reached about the ratio of the ozonides, only that if x is the amount of normal ozonide formed, $\frac{1}{2}(2.0-x)$ is the diphenyl ozonide and $\frac{1}{2}(3-(2.0-x))$ is the peak area due to the diformyl ozonide. The three ozonides may be able to be detected and separated by GC analysis[31].

Upon standing the ozonide rearranged. The peaks at 5.35 and 5.92 became singlets and shifted downfield to 5.44 and 5.98 respectively. The aldehyde peaks at 9.3 disappeared but two new peaks appeared at 9.22 and 8.64 ppm. All of the new peaks were reducible. When cinnamaldehyde was ozonized in acetonitrile, there was no ozonide found, only the rearranged ozonide (spectrum 11).

Ozonolysis of trans-4-phenyl-3-buten-2-one (LVII) yielded benzaldehyde (LI), methylglyoxal (XLVI), cis (LVIII) and trans (LIX) ozonides, cross ozonides (LX and LXI) and an unknown hydroperoxide (spectra 13-15). The benzaldehyde and methyl glyoxal were identified in the same manner as was explained in the cinnamaldehyde and mesityl oxide ozonolysis respectively.



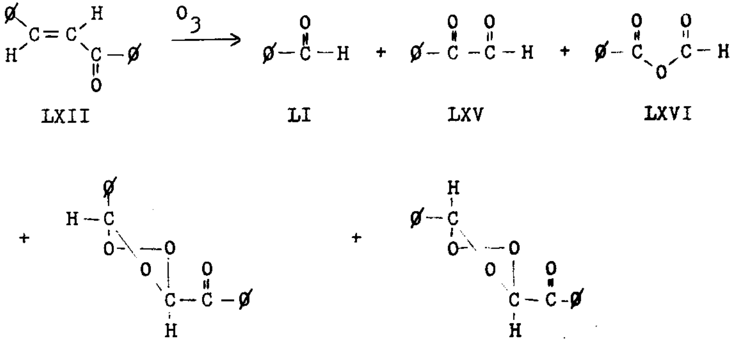
The normal ozonide (LVIII and LIX) ahould have an NMR absorption similar to the cinnamaldehyde ozonide (LII and LIV). On this basis, the peaks at 6.02 (H_a) and 5.47 (H_b) were assigned to the ozonide. The different absorption between the cis and trans ozonides as found in cinnamaldehyde was not present. So it is not known whether the ozonide peaks were due to the cis or trans ozonide,or possibly both.

From the peak integration the ratio of H_a to H_b was 2.5 to 0.5. Since the ratio was not one to one, it was assumed that some cross ozonide (LX) was being produced. By similar arguments used for trans-cinnamaldehyde it is believed that the other cross ozonide (LXI) was also produced. Again, nothing can be said about the amount of each ozonide formed.

The NMR also showed peaks at 9.47, 2.58 and 1.55 ppm. All three peaks were reducible and decomposed upon standing (spectrum 16). The peak at 2.58 was not present in all spectra while the other peaks were present in all spectra. Swern et al[48] report the β protons to peroxy acids absorb at about 2.40. Fujiwara et al[49] found that the α protons on hydroperoxides absorb at 2.9 ppm. So it is possible that the peak at 2.58 was due to either type of proton. Swern[48] also reports that β protons on hydroperoxides absorb in the range 1.20 to 1.55 ppm. It was also found in this work that the methyl protons on mesityl oxide ozonide absorb at 1.50 ppm. All these explanations would be consistent with the peak at 1.55. The hydroperoxide protons absorb in the range 7.6 to 9.2 ppm with the upfield shift occuring upon dilution or in polar solvents. Peroxy acid protons are in the range 11.0 to 13.5 ppm[48]. From the chemical and spectral properties given above, it was thought that the unidentified protons were due to a peroxy acid or hydroperoxide. No structure is suggested that is consistent with all the NMR peaks.

The effect of concentration of trans-4-phenyl-3-buten-2-one on products was also studied (Table I page 36). The peak area for each product was very small (i.e. 2.0 ± 0.2). Thus when the percentages of each product was calculated a large error limit arose. Because of the large error limits no conclusion could be reached about the effect of reactant concentration on products formed.

Ozonolysis of chalcone (LXII) gave benzaldehyde (LI), cis (LXIII) and trans (LXIV) ozonides, phenyl glyoxal (LXV) and formic benzoic anhydride (LXVI) (spectra 17,18).


LXII LI LXV LXVI

LXIII LXIV

Table I

Effect of concentration of trans-4-phenyl-3-buten-2-one on products

concentration of reactant	% ozonized ± 15%	% ozonized calc* ± 15%	% benzaldehyde ± 40%	% glyoxal ± 40%	% ozonides ±40 %
0.0891 <u>M</u>	63.2	88.0	38.8	27.2	36.9
0.225 <u>M</u>	69.2	77.4	31.4	31.4	23.6
0.819 <u>M</u>	63.0	63.8	35.3	29.4	20.6
1.66 <u>M</u>	50.2	62.9	62.3	62.3	36.7

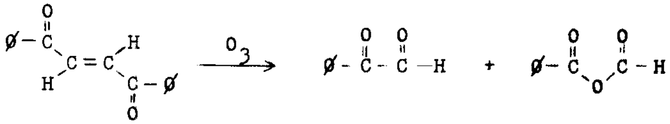
* Ozone was produced at a rate of 0.61 mmoles/min (see appendix A).

Benzaldehyde was identified by its peak at 10.0 ppm. The ozonide peaks were at 6.02 and 5.70 ppm. Very little ozonide was present (less than 20% of the total products).

There was an NMR peak at 9.52 ppm. The peak was eliminated by triphenylphosphine (spectrum 19) and exchangable with D_2O (spectrum 20). A sample of phenyl glyoxal extracted into CCl_4 absorbed at 9.46 ppm (spectrum 21). The phenyl glyoxal was exchangable and eliminated by treatment with triphenylphosphine (spectrum 22).

The presence of formic benzoic anhydride was indicated by the peak at 9.18 ppm. The peak was not reducible but two hours after addition of D_2O, the peak disappeared. An anhydride should not be reducible but would hydrolyse. When formic benzoic acid was prepared, it was found to absorb at 8.97 ppm (spectrum 23). The peak was not reducible (spectrum 24) but did hydrolyse (spectrum 25). Note that since the peak was not reducible it could not be due to a peroxy acid or hydroperoxide.

Ozonolysis of trans-dibenzoylethylene (LXVII) produced only phenyl glyoxal (LXV), formic benzoic anhydride (LXVI) and a peroxyacid or hydroperoxide (spectra 26-32). The NMR spectra indicated that no ozonide was formed.



LXVII LXV LXVI

The phenyl glyoxal and formic benzoic anhydride absorbed at 9.55 and 9.20 ppm respectively. The presence of formic benzoic anhydride was further supported by the IR. The ozonized sample had bands at 1780, 1745, 1035 and 1015 cm^{-1} (spectrum 32). Fanta[44] reports that formic benzoic anhydride has strong bands at 1785, 1755, 1045 and 1020 cm^{-1}.

The NMR spectra also gave a peak at 8.65 ppm. It was both eliminated by triphenylphosphine (spectrum 33) and exchanged with D_2O (spectrum 34). By the arguments used for trans-4-phenyl-3-buten-2-one, this peak was assigned to a peroxy acid or hydroperoxide.

Carbon tetrachloride, acetonitrile, deuterochloroform, 1,4-dioxane, acetone and ethyl acetate were used as solvents for the reactions. The effect of solvent on product ratios are shown in Table II (pages 39-40). In general, more polar solvents favored the production of aldehydes and reduced the amount of ozonide present.

Trans-dibenzoylethylene was ozonized with benzaldehyde as a trapping agent (spectra 35-36 are representative). The benzaldehyde could have reacted with the carbonyl oxide to form LVIII or LIX, the ozonide of trans-4-phenyl-3-buten-2-one. The ozonide protons absorbed at 6.02 and 5.47 ppm. The yield of phenyl glyoxal, formic benzoic anhydride and hydroperoxide are given in Table II (page 42 and shown in figure 15 page 43). Two trials were run, first with 1,4-dioxane as the solvent, then with acetone as the solvent.

Table II

Effect of solvent on products

Peak areas* and ratios** of products***

Mesityl Oxide

	Ozonide (XLIV)		Methyl Glyoxal (XLV)		Formic Acid (XLVII)	
CCl_4	16.2	81.	1.5	7.5	0.3	1.0
CH_3CN	7.5	6.3	8.7	7.3	1.2	1.0

Trans-cinnamaldehyde

	Benzaldehyde (LI)		Glyoxal (LII)		Normal Ozonides (LIII & LIV)		Cross Ozonides (LV & LVI)		Rearranged Ozonide	
CCl_4	0.3	1.0	1.0	3.3	2.0	6.7	0.5	1.7	0.0	
CH_3CN	1.5	1.0	1.5	1.0	0.0		0.0		2.0	1.5

Trans-4-phenyl-3-buten-2-one

	Benzaldehyde (LI)		Methyl glyoxal (XLV)		Normal Ozonides (LVIII & LIX)		Cross Ozonides (LX & LXI)	
CCl_4	2.2	3.7	2.0	3.3	0.6	1.0	0.7	1.2
$CDCl_3$	2.5	8.7	2.2	7.3	0.5	2.5	0.3	1.0
CH_3CN	3.5	17.5	3.2	16.0	0.5	1.7	0.2	1.0

Table II con't

<u>Chalcone</u>

	Benzaldehyde (LI)		Phenyl Glyoxal (LXV)		Formic Benzoic Anhydride (LXVI)		Normal Ozonides (LXIII & LXIV)	
CCl_4	2.0	6.7	0.3	1.0	2.0	6.7	0.8	2.7
CH_3CN	2.5	8.3	0.3	1.0	2.0	6.7	0.7	2.3

<u>Trans-dibenzoylethylene</u>

	Phenyl Glyoxal (LXV)		Formic Benzoic Anhydride (LXVI)		Hydroperoxide (or peroxy acid)	
CCl_4****	0.4	1.0	2.0	5.0	1.0	2.5
1,4-dioxane	3.5	1.4	5.5	2.2	2.5	1.0
Acetone	3.0	1.0	5.0	1.7	3.5	1.2
CH_3CN	3.0	1.5	2.0	2.0	1.0	1.0
Ethyl Acetate	0.5	1.0	5.0	10.0	3.0	6.0

* All peak areas were corrected so that they are due to only one proton.

** The ratios were calculated relative to the species present in the lowest concentration.

*** Peak areas are on the left, ratios are on the right.

**** The solution was heterogeneous.

In all cases little or no ozonide was formed. At high benzaldehyde concentrations (greater than 1.0 M) the phenyl glyoxal peak areas could not be determined because the benzaldehyde spinning sidebands interfered with the integration. No internal standard was used to calibrate the integration. This accounts for some of the variation of the peak areas for different benzaldehyde concentrations.

As was stated, the ozonide from mesityl oxide decomposed on standing. The decomposition of the ozonide was studied in CCl_4, CH_3CN and in an overozonized mesityl oxide sample (spectra 1,37,38 are representative). All the samples showed approximately first order kinetics (figures 2-4). The half-lives and rate constant are shown in table IV (page 47).

Table III

Ozonolysis of trans-dibenzoylethylene in the presence of benzaldehyde

Conc. Dibenzoyl Ethylene (M)	Conc. benzaldehyde (M)	Peak area (± 0.5) benzaldehyde	phenyl glyoxal	formic benzoic anhydride	hydroperoxide (or peroxy acid)
Solvent:1,4-dioxane					
0.485	0.00	-	3.5	5.5	2.5
0.487	0.083	2.5	2.0	8.0	2.7
0.480	0.16	5.0	3.2	7.0	2.7
0.468	0.32	8.5	2.2	6.0	2.2
0.453	0.63	17.2	3.0	6.0	3.2
0.427	1.18	35.5		6.7	1.7
0.506	2.11	30.0*		7.0	2.0
0.471	3.57	47.0*		2.0	2.0
Solvent:Acetone					
0.456	0.00	-	3.0	5.0	3.5
0.454	0.083	0.0	0.7	10.0	2.7
0.449	0.16	2.0	2.0	6.0	2.0
0.445	0.32	7.0	0.2	13.5	2.0

* These integrations were at attenuation = 13 while all other integrations were at attenuation = 15.

Figure 15

Effect of benzaldehyde on the ozonolysis products of dibenzoyl ethylene

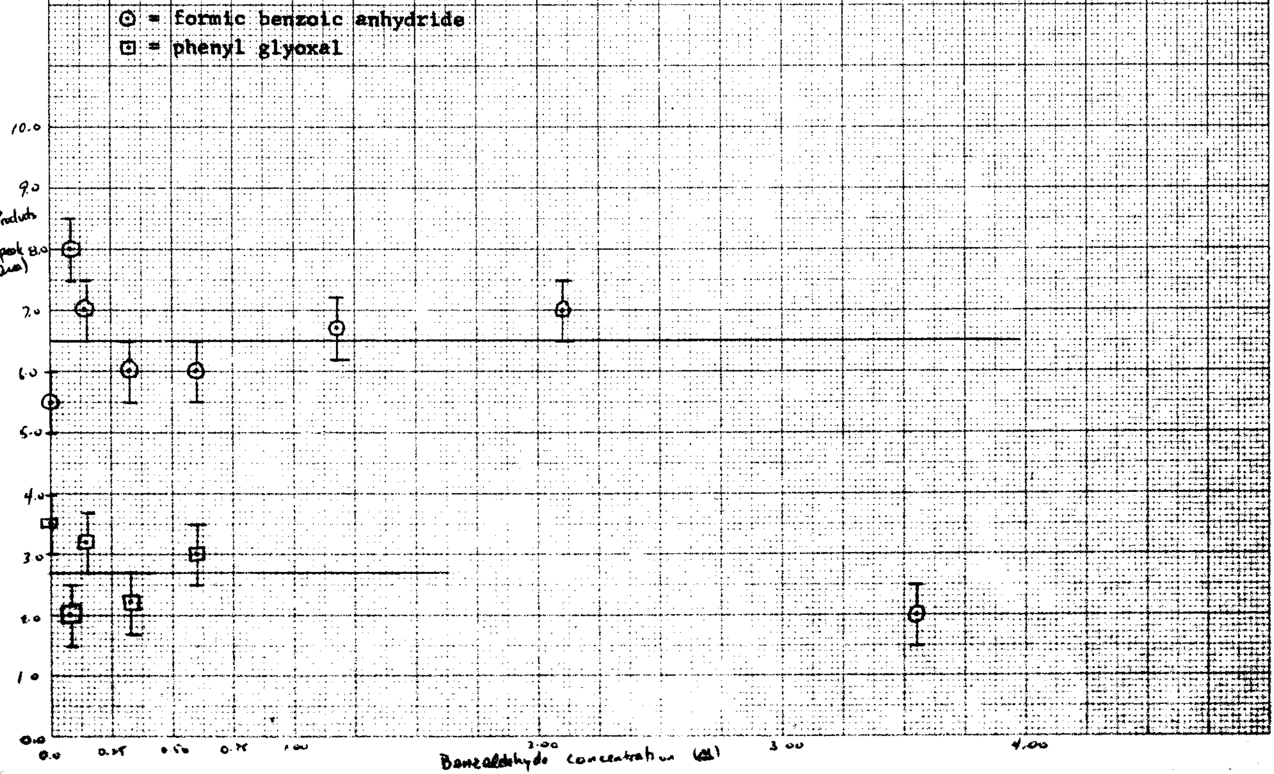


Figure 16

Decomposition of mesityl oxide ozonide: CCl_4 sample

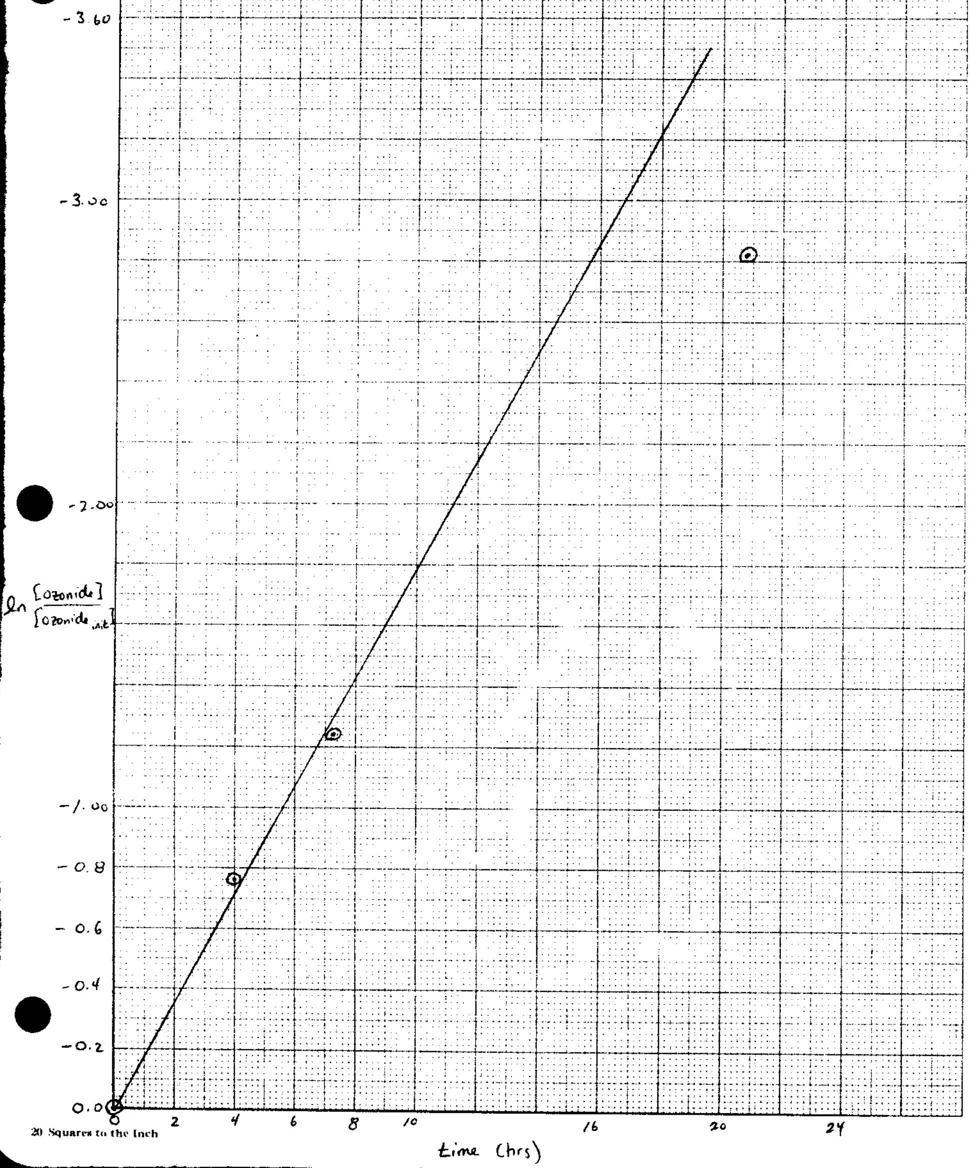


Figure 17

Decomposition of mesityl oxide ozonide: CH_3CN sample

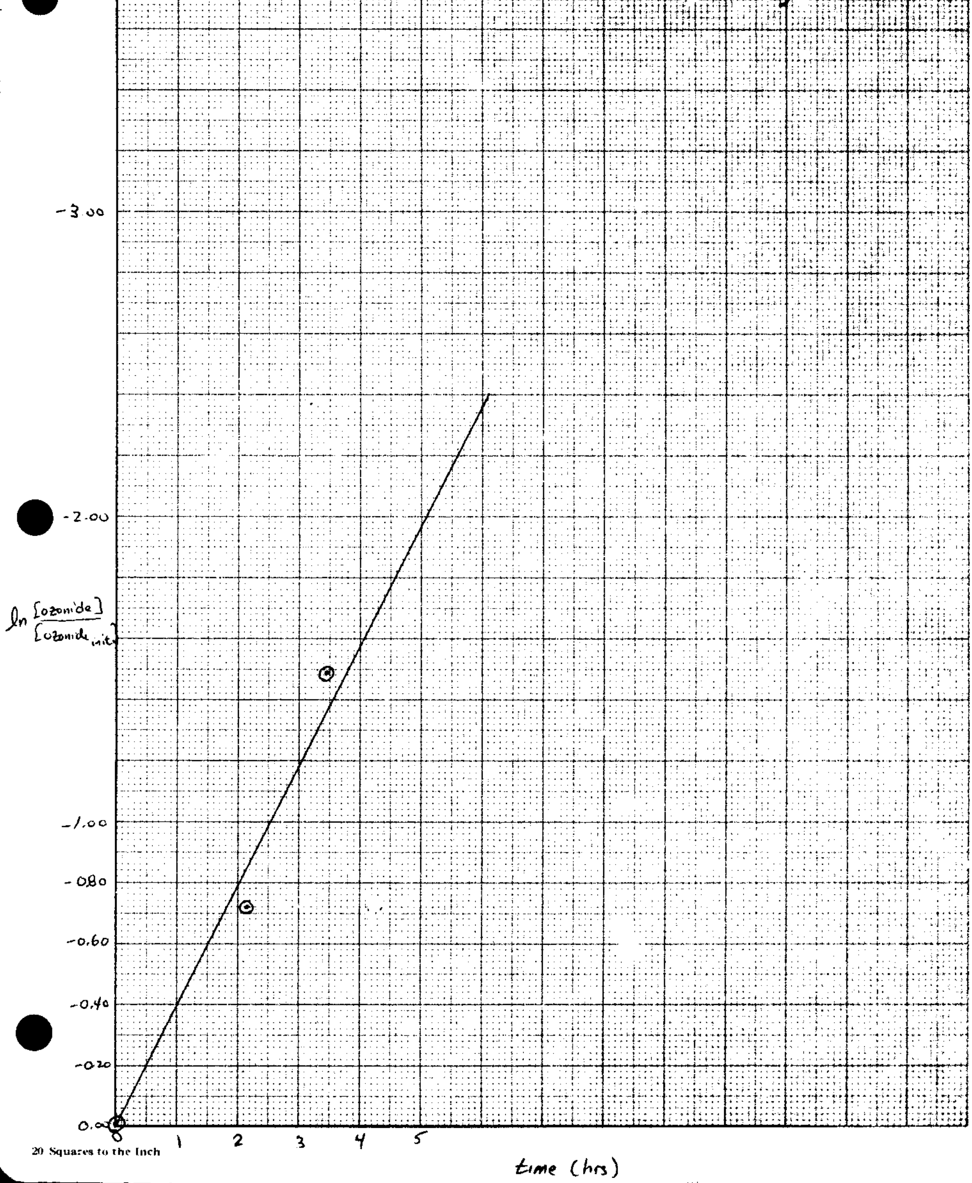


Figure 18

Decomposition of mesityl oxide ozonide: overozonized sample

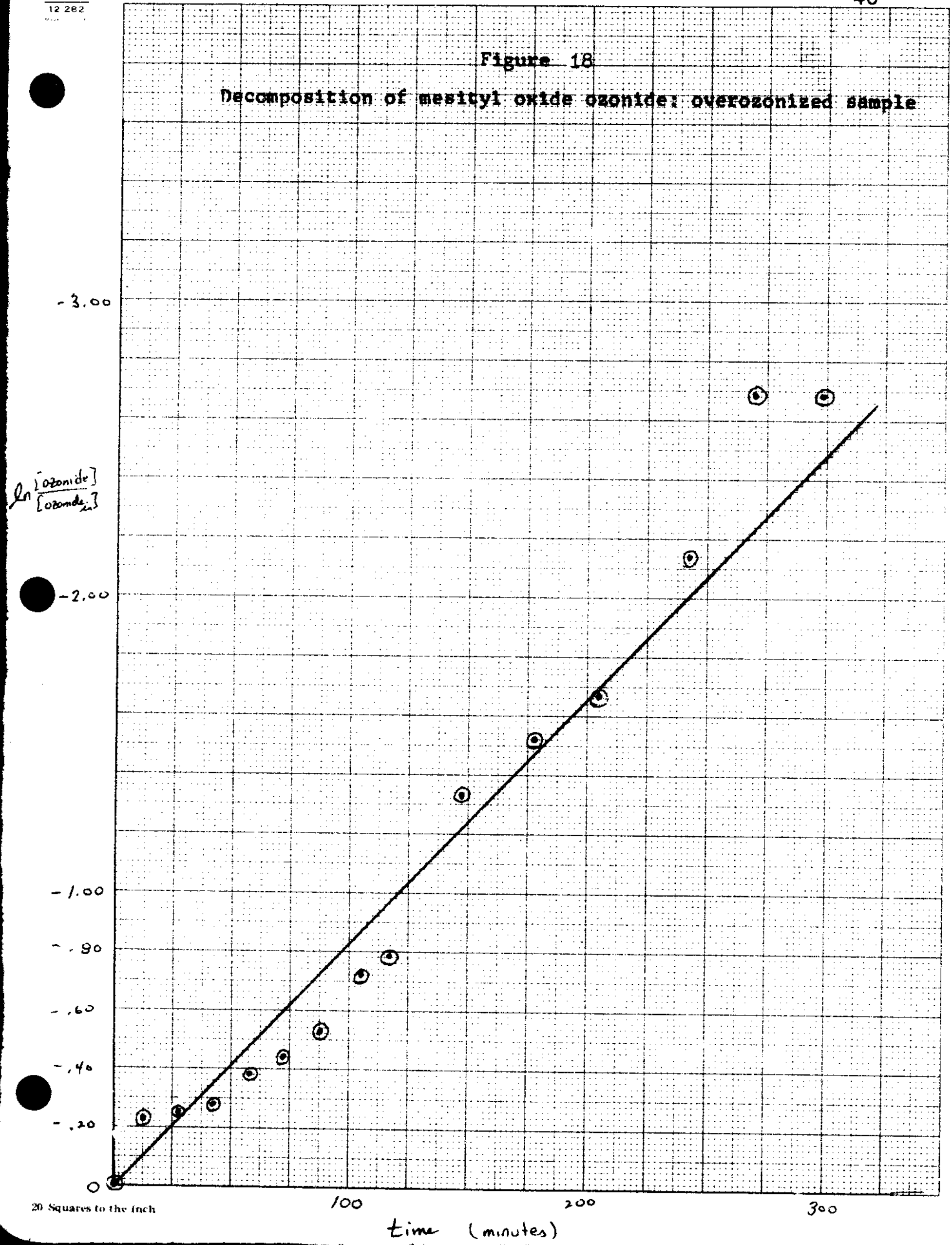


Table IV

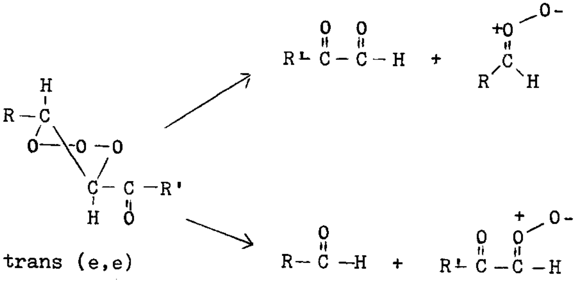
Decomposition of mesityl oxide ozonide

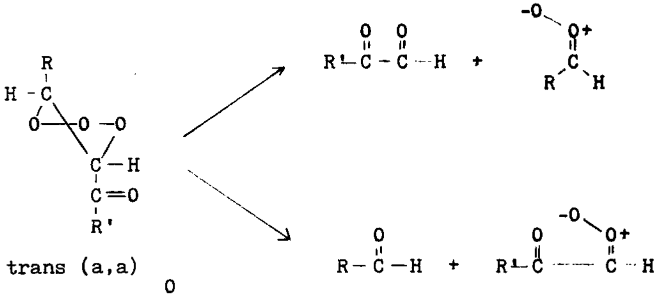
Sample	Half-life	Rate constant
CCl_4	3.8 ± .2 hrs.	0.003 ±.003 min^{-1}
CH_3CN	1.7 ± .2 hrs.	0.007 ±.003 min^{-1}
overozonized	1.4 ± .2 hrs.	0.008 ±.003 min^{-1}

DISCUSSION

As was explained in the introduction, the carbonyl oxide can react to form an ozonide, polymeric peroxides, peroxides when a hydroxylic solvent is used and "anomolous" products. The results of this work show that the ozonolysis products of α,β-unsaturated carbonyl compounds are in general, ozonides, glyoxals, aldehydes and anhydrides. But how can their formation be accounted for?

The Bauld-Bailey[31] mechanism assumes that the 1,2,3-trioxolane is a nonplanar ring. In a disubstituted five membered ring, the substituents can be diaxial, diequatorial or axial-equatorial. In this work all the reactants were trans olefins (except mesityl oxide). Therefore the configuration of the primary ozonide can be diaxial or diequatorial. According to Bailey, the trans (e,e) and trans (a,a) ozonides then form the anti and syn carbonyl oxides respectively.





trans (a,a)

$R = CH_3$, Ø, $\overset{O}{C}$ Ø

$R' = H, CH_3$, Ø

Figure 19 Formation of the Bauld-Bailey syn and anti carbonyl oxides

From studies of substituted cyclohexanes it is known that the conformation with the largest substituents in the equatorial positions is more stable by a few kilocalories/mole[52]. Thus it is likely that the trans (e,e) configuration for the ozonide was more populated than the trans (a,a) configuration. This was supported when space-filling models constructed for the trans (e,e) and trans (a,a) forms of the trans-cinnamaldehyde and trans-4-phenyl-3-buten-2-one primary ozonide were examined. But when models of chalcone and dibenzoylethylene primary ozonide were examined it was apparent that they had two very large groups attached to the trioxolane ring. If it is assumed that in order to maximize conjugation, the benzoyl group was planar, both the diaxial and diequatorial configurations had unfavorable interactions with the trioxalane ring and other substituents. This repulsion occurs to a greater extent in dibenzoylethylene than in chalcone ozonide. So it is possible that for chalcone and dibenzoylethylene ozonides the trans (a,a) isomer is significantly populated. As stated before, the trans (a,a) ozonide primarily forms the syn carbonyl oxide. Therefore chalcone and dibenzoylethylene should produce more of the syn zwitterion than the other alkenes.

The syn and anti carbonyl oxides are isomers of each other. Therefore there is a thermodynamically controlled equilibrium concentration of each species. But because of the low temperatures of the ozonolysis experiments and the high reactivity of the carbonyl oxide, the equilibration should not occur[31]. Hull[41] used MINDO/3 to study the syn-anti isomerization. An activation energy of 25.3 Kcal/mole was needed for the isomerization. Using this figure, Hull calculated a first order rate constant of $3. \times 10^{-8}$ sec^{-1}. The rate constant for the syn-anti isomerization is too slow to compete with the other reactions of the carbonyl oxide[41]. Since the syn and anti zwitterions were produced in preferential proportions depending on the configuration of the initial ozonide and equilibration of the syn and anti isomers does not occur, the products can be an indication of the proportion of the two species.

With the above discussion in mind, the products detected in these experiments are consistent with the Bauld-

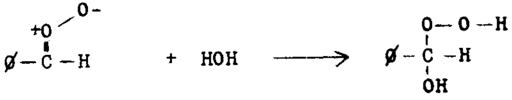
Bailey modification of the Criegee mechanism.

The most stable conformation of the primary ozonide formed by trans-cinnamaldehyde and trans-4-phenyl-3-buten-2-one is trans diequatorial. This then cleaves to the anti zwitterion. The zwitterion then reacts with an aldehyde to form an ozonide. Chalcone and dibenzoylethylene primary ozonides should also form some anti carbonyl oxide. Chalcone trans (e,e) ozonide is slightly less sterically hindered than that of dibenzoylethylene, so it is possible that chalcone produces more anti carbonyl oxide. The anti zwitterion can then react with an aldehyde to form an ozonide. Experimentally, ozonolysis of chalcone yields a small amount of ozonide but dibenzoylethylene yields none. This can be justified by one of two explanations. First the diaxial configuration is much more stable than the diequatorial isomer and thus only syn carbonyl oxides are formed, or the anti carbonyl oxide undergoes some other reaction (i.e. peroxide formation, oxygen loss). Because reactions other than ozonide formation are possible for the carbonyl oxide, the latter explanation cannot be ruled out. But in light of the results with trans-cinnamaldehyde and trans-4-phenyl-3-buten-2-one where secondary ozonides were formed from the anti carbonyl oxide, one would expect the secondary ozonide from any anti carbonyl oxides produced from the chalcone and dibenzoylethylene ozonolyses.

The NMR integration shows that some cross ozonides were being produced. Trans-cinnamaldehyde gave the diformyl trioxolane while trans-4-phenyl-3-buten-2-one gave the diphenyl trioxolane. As stated in the results, no definite conclusion could be reached about the ratio of the cross ozonides and normal ozonides.

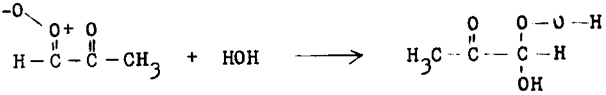
From the stoichiometry of ozonolysis, one aldehyde should be produced for each carbonyl oxide formed. So in order to produce a cross ozonide, first two carbonyl oxides and aldehydes must be formed. Then one carbonyl oxide and aldehyde from each olefin can combine to form the symmetric cross ozonide. But this still leaves a carbonyl oxide and an aldehyde in solution. If they were to react with each other, the second symmetric cross ozonide would be formed. Therefore it would be expected that an equal amount of each cross ozonide is formed. But as stated above, this was not found experimentally. Thus the carbonyl oxide must have some other fate.

The Criegee mechanism suggests the formation of a peroxide as a competing reaction. The carbonyl oxide can react with any hydroxylic group. A reaction of a carbonyl oxide from trans-4-phenyl-3-buten-2-one with HOH is shown below:



$$\phi-\overset{\overset{O^-}{\diagup}}{\overset{+O}{\overset{\|}{C}}}-H + HOH \longrightarrow \phi-\underset{OH}{\overset{O-O-H}{C}}-H$$

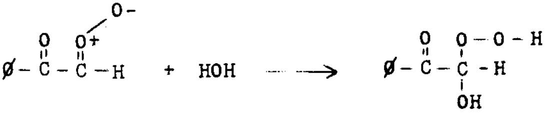
LXVIII



$$H-\overset{\overset{-O\diagdown}{O+}}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 + HOH \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-\underset{OH}{\overset{O-O-H}{C}}-H$$

LXIX

The peroxide protons on both LXVIII and LXIX should absorb at about 8.0 ± .5 ppm[48] and the α protons at about 2.9 ppm[49]. Because of hydrogen bonding, the alcoholic proton can absorb in the range of 2 to 4 ppm depending on the concentration, solvent and temperature[53]. Dilution or higher temperature cause the absorption to occur further upfield. The unidentified peaks of trans-4-phenyl-3-buten-2-one were at 9.47, 2.58 and 1.55 ppm. The peak at 2.58 could be due to the α proton or the hydroxyl proton. But it is doubtful that the peak at 9.47 is due to the hydroxy proton or the peak at 1.55 is from the methyl group adjacent to the carbonyl. Dibenzoylethylene gave a reducible peak at 8.65 ppm. Addition of water to the carbonyl oxide would yield:



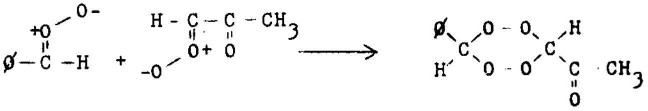
$$\phi-\overset{O}{\overset{\|}{C}}-\overset{\overset{O^-}{\diagup}}{\overset{O+}{\overset{\|}{C}}}-H + HOH \longrightarrow \phi-\overset{O}{\overset{\|}{C}}-\underset{OH}{\overset{O-O-H}{C}}-H$$

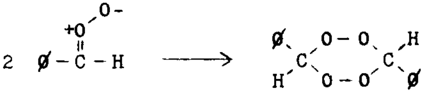
The peak at 8.65 is consistent with a hydroperoxide but there were no upfield peaks to support the α protons or the hydroxyl proton. Therefore it seems unlikely that the hydroperoxide was due to the addition of water This should be expected since the reactions were performed under anhydrous conditions.

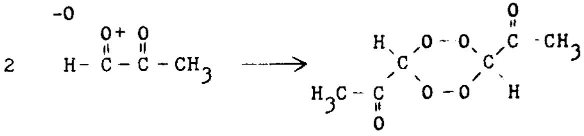
In general carbonyl oxide could react with a species such as ROH. The product would have an ether oxygen rather than a hydroxylic proton. The change to ROH would not change the absorption of the hydroperoxide proton or the α proton. Therefore by the same reasoning used for the addition of water, it is unlikely that this reaction was taking place.

From the stoichiometry of the ozonolysis reaction, one aldehyde molecule should be produced for each anhydride formed. The amount of benzaldehyde and formic benzoic anhydride in the chalcone trial was in agreement with the stoichiometry. In the dibenzoylethylene ozonolysis, more anhydride was always produced than phenyl glyoxal. But the sum of the peak areas of the phenyl glyoxal plus the unknown peroxide approximately equals the area of formic benzoic anhydride. Possibly the phenyl glyoxal was being ozonized to peroxy phenyl glyoxalic acid. The acid proton on phenyl glyoxalic acid absorbs at about 10.0 ppm (spectrum 50). The acidic protons on peroxy acids always appear upfield relative to the carboxylic acid proton[48]. The peak at 8.65 could be peroxy phenyl glyoxalic acid. The chemical propeties were consistent with this assignment. The problem with this identification is that it involves the ozonolysis of phenyl glyoxal. Ozonolysis of aldehydes is slower than alkenes and it is unlikely that any aldehyde will be ozonized when an alkene is present[32]. The identity of the peak at 8.65 is still an open question.

The Criegee mechanism also suggests the formation of peroxide dimers. The possible reactions of the trans-4-phenyl-3-buten-2-one carbonyl oxides are shown below:







Ozonolysis of tetramethylethylene yields the peroxide dimer. The methyl groups on the peroxide dimer absorbed at 1.3 ppm. So the dimer does not have a drastically different NMR spectrum than the ozonide. Therefore it is unlikely that this can account for the peaks found at 9.47, 2.58 and 1.55

in the ozonolysis of trans-4-phenyl-3-buten-2-one or the peak at 8.65 found in the ozonolysis of dibenzoylethylene.

A final possibility for the structure of the unknown product is an epoxide. As discussed in the introduction, Keay and Hamilton[39] suggest that any of three products of the ozonolysis can donate an oxygen to an alkene, resulting in the epoxidation of the alkene. One of the species which they suggest donates the oxygen is the cyclic planar carbonyl oxide, XLI. Because of steric hinderance, XLI could only be formed from the anti carbonyl oxide. Thus it seems reasonable that the anti carbonyl oxide of trans-4-phenyl-3-buten-2-one could form XLI. Calculations by Hull[41] indicate that the activation energy for the cyclization of the carbonyl oxide is large enough to prohibit the conversion. Experimental evidence suggests that the unidentified peaks were not due to an epoxide. An epoxide is not reducible by diphenylsulfide[39] but the unidentified peaks were reduced by triphenylphosphine.

In the ozonolysis of trans-cinnamaldehyde and trans-4-phenyl-3-buten-2-one excess aldehyde was produced. For example, the trans-4-phenyl-3-buten-2-one yields methyl glyoxal and benzaldehyde. The yields of the aldehydes show approximately a one to one ratio (see Table II pages 39-40). This could indicate that the carbonyl oxide can stabilize itself by the loss of an oxygen atom. One possible means is suggested by Hull[41]. Combination of two formaldehyde carbonyl oxides to produce tha aldehydes and molecular oxygen is thermodynamically favorable. The stoichiometry of this type of reaction is supported by the data. Production of O_2 could not be detected experimentally because the ozone was in an O_2/O_3 mixture.

α,β-unsaturated compounds were used as a reactant because it was hoped that they would provide an alternative way to generate the α carbonyl carbonyl oxide produced in alkyne ozonolysis. Hull[28] reports that in the ozonolysis of diphenylacetylene, benzoic acid, benzoic anhydride and benzil were produced. Benzoic anhydride/Benzoic acid was produced in a 70 to 80% yield. Formic benzoic anhydride was the major product in the ozonolysis of trans chalcone and trans dibenzoylethylene. Chalcone and dibenzoylethylene give results similar to alkyne ozonolysis; consistent with the postulated α carbonyl carbonyl oxide in the alkene and alkyne cases.

In the introduction several mechanism were suggested to account for the presence of an anhydride. The scheme proposed by Barton and Seoane[23] (figure 6 page 11) requires the formation of the ozonide. Ozonolysis of mesityl oxide yields an ozonide. As predicted by Barton and Seoane, it decomposes. But none of the decomposition products were an anhydride. Ozonolysis of dibenzoylethylene yields the anhydride but no ozonide. Therefore it is unlikely that their mechanism correctly explains the anhydride. There is no direct evidence supporting or refuting the suggestions of Yang and Pelletier[25] that the anhydride is a result of a Baeyer-Villiger reaction (figures 8-9 page 12). As Yang points out, acids catalyze the reaction. But in the ozonolysis of mesityl oxide, formic acid was present but no anhydride was produced. Yet in the ozonolysis of dibenzoylethylene or chalcone an anhydride was produced but no acid.

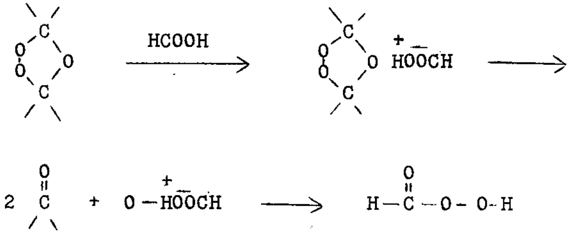
Karrer and Haab[24] suggest another mechanism (figure 7 page 11). The mechanism does not invole an ozonide or an acid but it does require an anti carbonyl oxide. Hull and coworkers[28] imply that the anhydride is a result of rotation of the carbonyl oxide about the C-C bond and then the rearrangement via a cyclization to an anhydride (figure 10 page 13). The Hull mechanism requires a syn configuration for the zwitterion.

As was already discussed, trans-cinnamaldehyde and trans-4-phenyl-3-buten-2-one should form almost exclusively the trans (e,e) primary ozonide. This then decomposes to the anti carbonyl oxide. Thus by Karrer and Habb, the carbonyl oxide can then rearrange to form the anhydride. But no anhydride was detected. Since there is very little syn carbonyl oxide, the Hull mechanism predicts that there would be at most a small amount of anhydride. Chalcone and dibenzoylethylene can form both the trans (e,e) and (a,a) ozonides (for steric reasons) and therefore both the syn and anti carbonyl oxides. The Hull mechanism predicts that the syn carbonyl oxide could then form an anhydride. This was supported experimentally.

The experiments with added aldehyde also support the syn-anti carbonyl oxides and the Hull mechanism. The amount of products was virtually uneffected by the added aldehyde (see Table III and figure 15 pages 42-43). The formation of the anhydride is an intramolecular reaction and if it is assumed that it occurs at least as fast as the reaction of a syn carbonyl oxide with an aldehyde, it is not surprising that no ozonide was produced. The assumption of reaction rates is supported by the third rule of the Bauld-Bailey scheme. The cylcoaddition of the syn carbonyl oxide and the aldehyde is hindered because the zwitterion must place its substituents axially in the transition state leading to the ozonide[31]. If dibenzoylethylene formed the anti zwitterion, the reaction with benzaldehyde would not be hindered and the ozonide would probably be produced. So the results of the addition of benzaldehyde support the statement that dibenzoylethylene and chalcone produced the syn carbonyl oxide which in turn rearranged by the Hull mechanism to the anhydride.

In the discussion up to this point mesityl oxide has not been mentioned. This is due to the fact that mesityl oxide does not have a cis or trans configuration. For this reason the syn and anti carbonyl oxides must be applied slightly differently. The most stable configuration of the initial ozonide is with the acetyl group equatorial. Cleavage of the primary ozonide will lead to the anti carbonyl carbonyl oxide or the propanone carbonyl oxide. Obviously the propanone carbonyl oxide is neither syn nor anti with respect to a separate methyl group. The anti carbonyl carbonyl oxide or the propanone carbonyl oxide can then react to form the ozonide and not the anhydride. This was found experimentally, ozonide but not anhydride was detected. The origin of the formic acid is unknown. It could be speculated that the ozonolysis produced formic acetic anhydride. The anhydride then hydrolyzed to form formic acid and acetic acid. But the NMR shows that no acetic acid was present. So it was concluded that no anhydride was produced and therefore this does not account for the formic acid.

The decomposition of mesityl oxide ozonide showed first order kinetics. Bernatek and Ledaal[54] studied the acidolysis of ozonides. They proposed the following mechanism:



The performic acid was detected after distillation. Ozonolysis of mesityl oxide was the only reaction to produce formic acid or any other acid. The ozonide of mesityl oxide was the least stable of all the ozonides formed and this would be consistent with Bernatek acidolysis. The decomposition in the overozonized sample gave the shortest half-life. Overozonolysis in O_2/O_3 mixtures ozonizes aldehydes to acids and peracids[55]. In overozonolysis the concentration of acid is increased, so as observed, the ozonide should decompose faster.

The choice of solvent can have a large effect on the products formed. When the primary ozonide cleaves it yields the polar zwitterion and aldehyde. Decomposition of the initial ozonide is enhanced by polar solvents. An increase in solvent polarity encourages the separation of the carbonyl oxide and aldehyde, thus increasing the chance for side reactions[31]. This is supported by the observation that in the ozonolysis of unsymmetrical olefins, as the solvent polarity is increased the ratio of cross to normal ozonides increases[31,56].

The results of this work were in agreement with the above predictions for the effect of solvent polarity (see Table II pages 39-40). In general the ozonide yield decreased when the solvent was changed from CCl_4 to CH_3CN. The change to CH_3CN also increased the amount of aldehyde formed. This would support the speculation by Hull that two carbonyl oxides can stabilize themselves by reacting together to lose an O_2 molecule[41]. In a more polar solvent a carbonyl oxide would have the chance to diffuse away from the aldehyde and towards some other species it can react with such as another carbonyl oxide. The yields of formic benzoic anhydride were unaffected by solvent. This is expected since the anhydride formation is an intramolecular rearrangement.

In conclusion, all of the results can be explained by a combination of the Bauld-Bailey syn-anti carbonyl oxides and the implications of the Hull alkyne ozonolysis rearrangement mechanism. It was also shown that the Karrer and Haab rearrangement does not adequately explain the results. In reaching these conclusions it should be recalled that it was assumed that in order to generate the syn carbonyl oxide the primary ozonide must be in the more stable diaxial configuration. The discussion also used the assumption that chalcone and dibenzoylethylene were considered to have large steric interactions with the primary ozonide and trans-cinnamaldehyde and trans-4-phenyl-3-buten-2-one did not have these interactions. Both cinnamaldehyde and 4-phenyl-3-buten-2-one have large groups attached to the double bond and could also have steric interactions. The justification of the configuration of the primary ozonide must be supported by further work.

FUTURE WORK

All of the evidence supporting the discussion of ozonide versus anhydride formation was based on the diaxial versus diequatorial configuration of the primary ozonide. The stability of the configuration was determined by examining space-filling models. More quantitative work using quantum mechanical calculations should be done to determine the stability of the conformations of the initial ozonide with large substituents attached to the ring.

If available, ozonolysis of the cis olefins could also be used to support the results of this work. The cis olefin preferentially yields the anti carbonyl oxide. So by the discussion presented, cis and trans cinnamaldehyde and cis and trans-4-phenyl-3-buten-2-one should yield the same products. Cis-chalcone and cis-dibenzoylethylene should yield little or no anhydride.

Ozonolysis of trans-4-phenyl-3-buten-2-one and dibenzoylethylene yielded products which were thought to be peroxides. They should be identified. The source of the unidentified product of dibenzoylethylene could be found by ozonizing phenylacetylene. If it is from a rearrangement or reaction of the carbonyl oxide, the ozonolysis should give peaks at 9.2 from the anhydride and another at 8.6 from the peroxide. If the peak at 8.6 was due to ozonolysis of phenyl glyoxal, only the peak at 9.2 should be present in the ozonolysis of phenylacetylene.

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55. P.S. Bailey and H.M. White, J. Org. Chem., 30, 3037 (1965).

56. F. L Greenwood, J. Am. Chem. Soc., 88, 3146 (1966).

57. J. Sawyer, The Decomposition of Phenyl-Benzoyl-Diazomethane and its relavance to Alkyne Ozonolysis, Honors Thesis, Department of Chemistry, Union College (1977).

APPENDIX A

Ozonolysis Procedure

O_2 was passed into a drying tube and then into the Welsbach ozonator. The settings on the Welsbach were as follows:

Pressure 8.0 ± 0.2 psi
Power . 90 volts
Rate : 0.60 ± 0.05

In order to produce a constant ozone flow, the ozonator was conditioned by making ozone for at least twenty minutes prior to any ozonolysis.

The rate of ozone production was determined by the amount of mesityl oxide that remained after 25 minutes of ozonolysis.

Table V

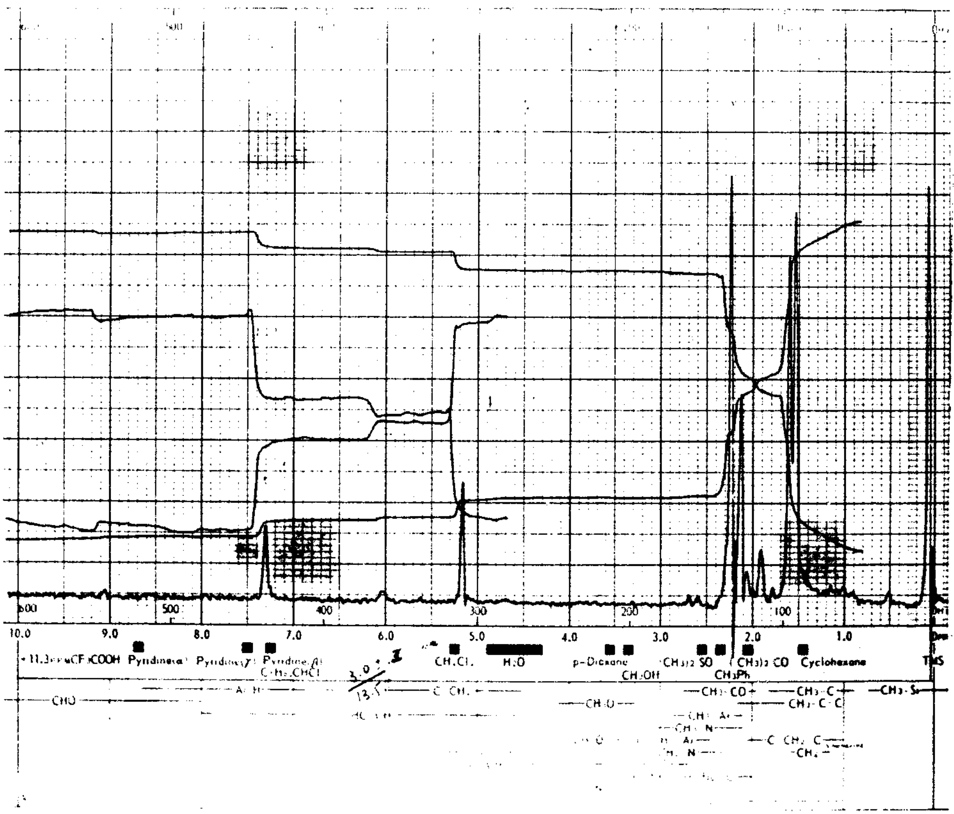
Rate of ozone production at 0°C.

Trial	mmoles mesityl oxide	initial peak area mesityl oxide vs. chlorobenzene	peak area mesityl oxide after 25 min. vs. chlorobenzene	ozone production (mmoles/min)
1	17.6	1.56 ± 8.4% (spectrum 48)	0.22 ± 12% (spectrum 1)	0.60 ± 20%
2	17.6	1.83 ± 8.6% (spectrum 49)	0.24 ± 11% (spectrum 2)	0.61 ± 20%

The rate of ozone production has been previously determined by J. Sawyer[57]. Using 1-decene vs. dodecane, Sawyer found that 5.9×10^{-4}, 3.9×10^{-4} and 5.1×10^{-4} moles/min ± 10% at -27, -42 and -62°C respectively were produced. Within experimental errors, the production reported in this paper agree with the previously reported figures.

APPENDIX B

Spectral Data



Spectrum No: 1

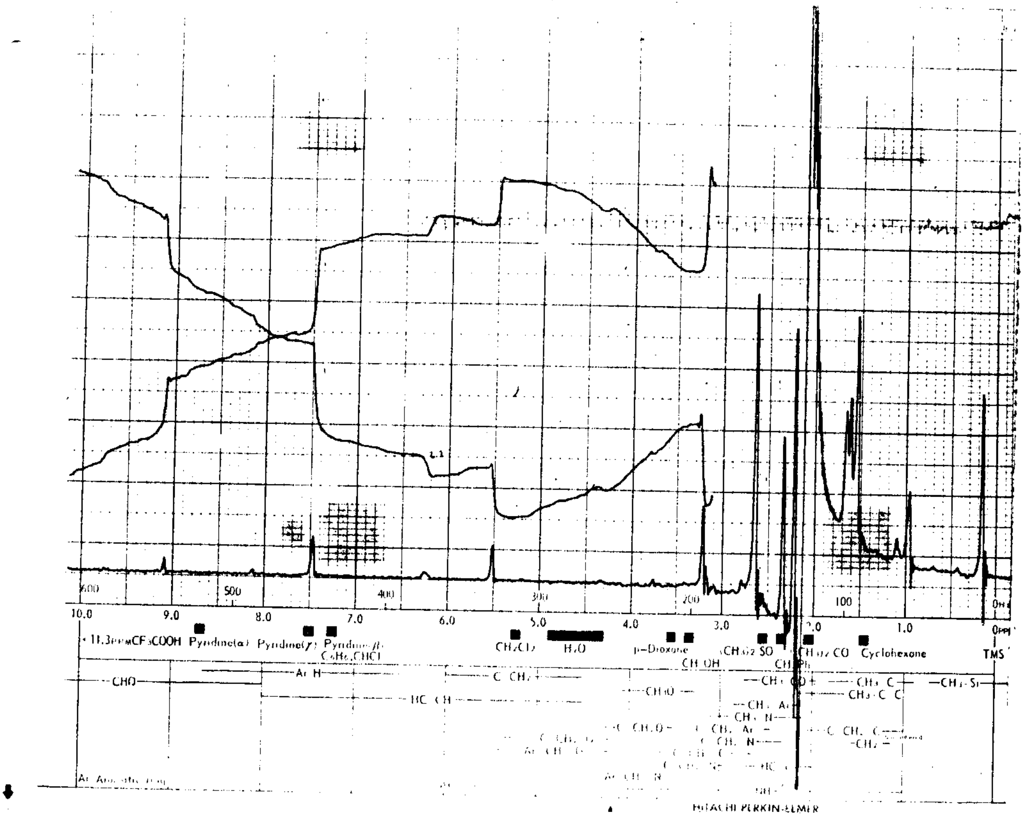
Sample:
Ozonized
Mesityl Oxide

Solvent: CCl_4

Amplitude

Spectrum: 10

Integration: 10



Spectrum No: 2

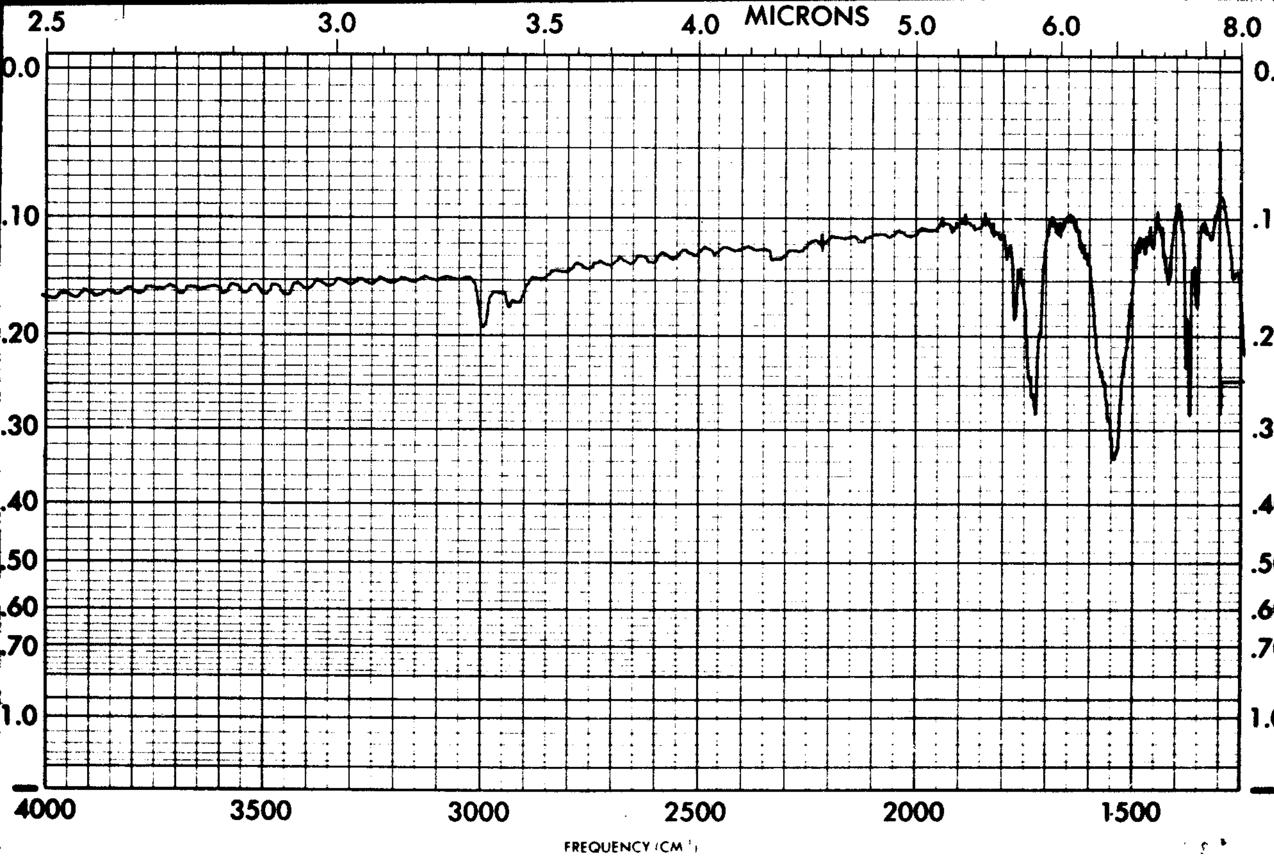
Sample:
Ozonized
Mesityl Oxide

Solvent: CH_3CN

Amplitude

Spectrum: 8

Integration: 15



SAMPLE Ozonized Mesityl Oxide

ORIGIN See page 31

SOLVENT CCl_4

CURVE NO. 3

CONC. ·

CELL PATH .0573 mm

REFERENCE CCl_4 .100 mm

SCAN SPEED Fast

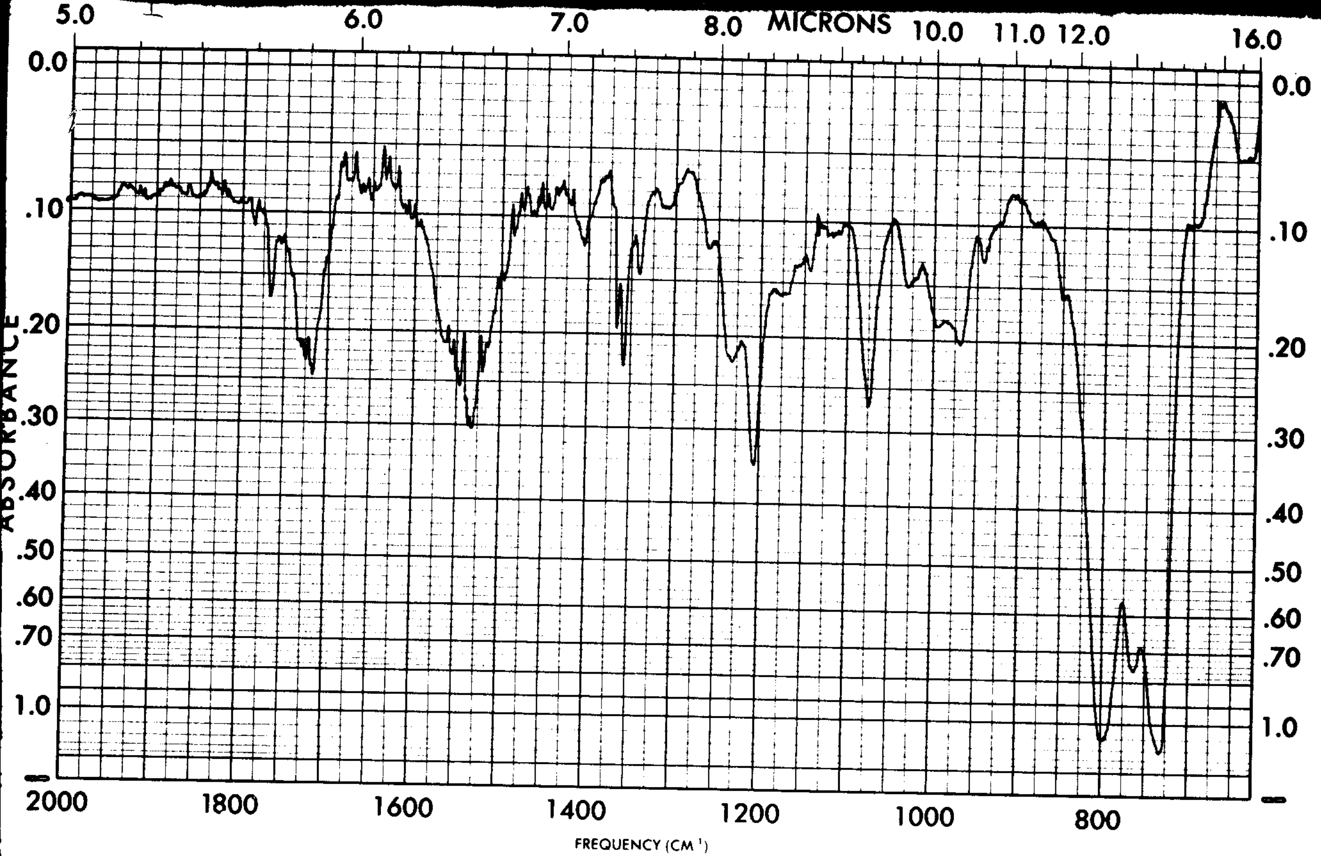
SLIT 75

OPERATOR A.W

DATE 5/18/78

REMARKS see page 53

PR 19R (237-1032)



SAMPLE Ozonized Mesityl Oxide

ORIGIN See page 31

SOLVENT CCl4

CURVE NO. 3

CONC. -

CELL PATH .0972 mm

REFERENCE CCl4 (.100mm)

SCAN SPEED Fast

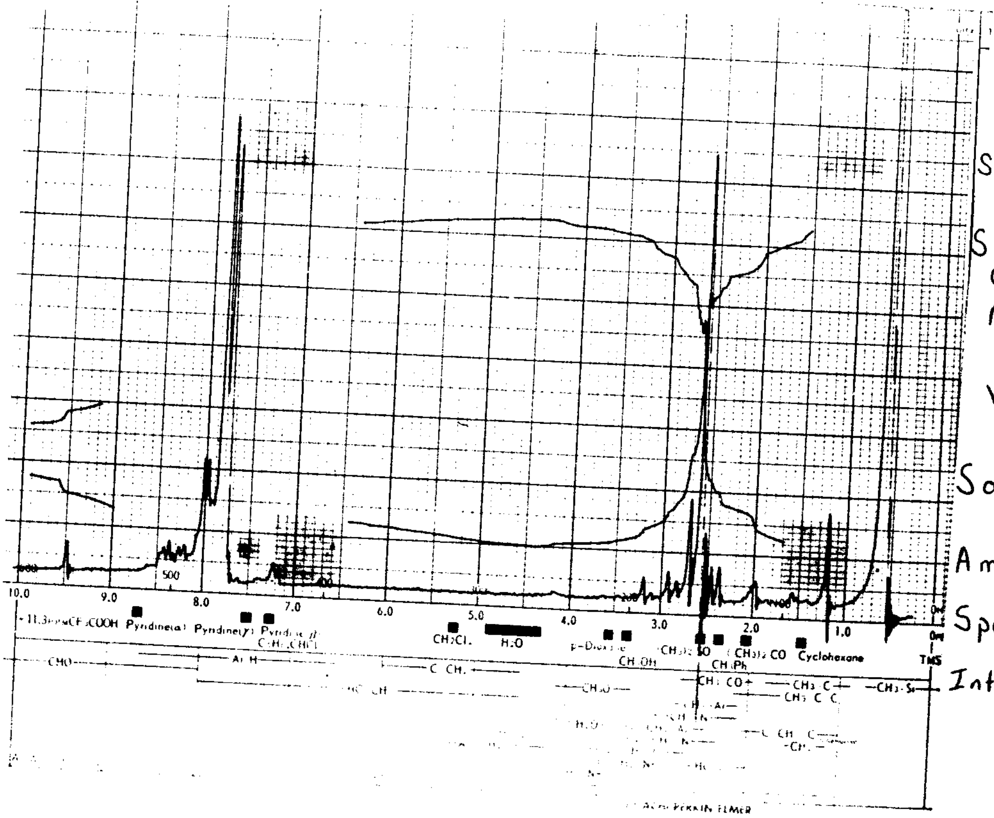
SLIT 25

OPERATOR A.W

DATE 5/18/78

REMARKS see page 32

No PR 18R (237-1023)



Spectrum No: 4

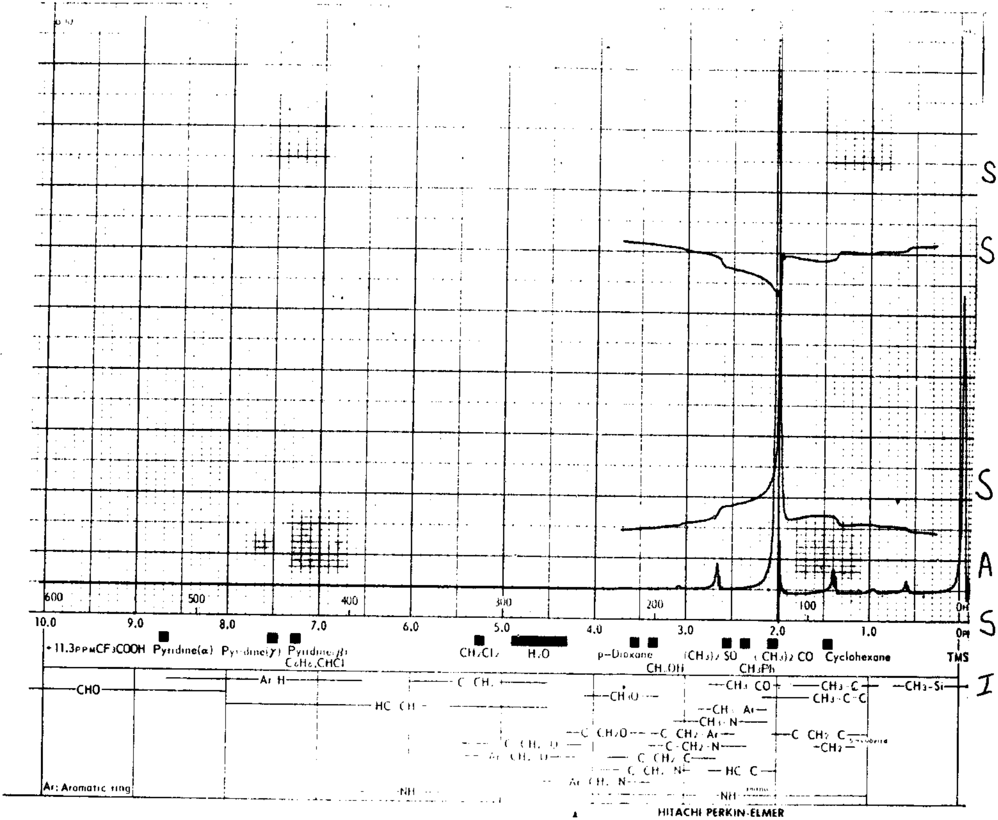
Sample:
Ozonized
Mesityl Oxide
Reduced
With $\Phi_3 P$

Solvent: CCl_4

Amplitude

Spectrum: 8

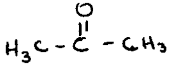
Integration: 11



Spectrum No: 5

Sample:

Acetone



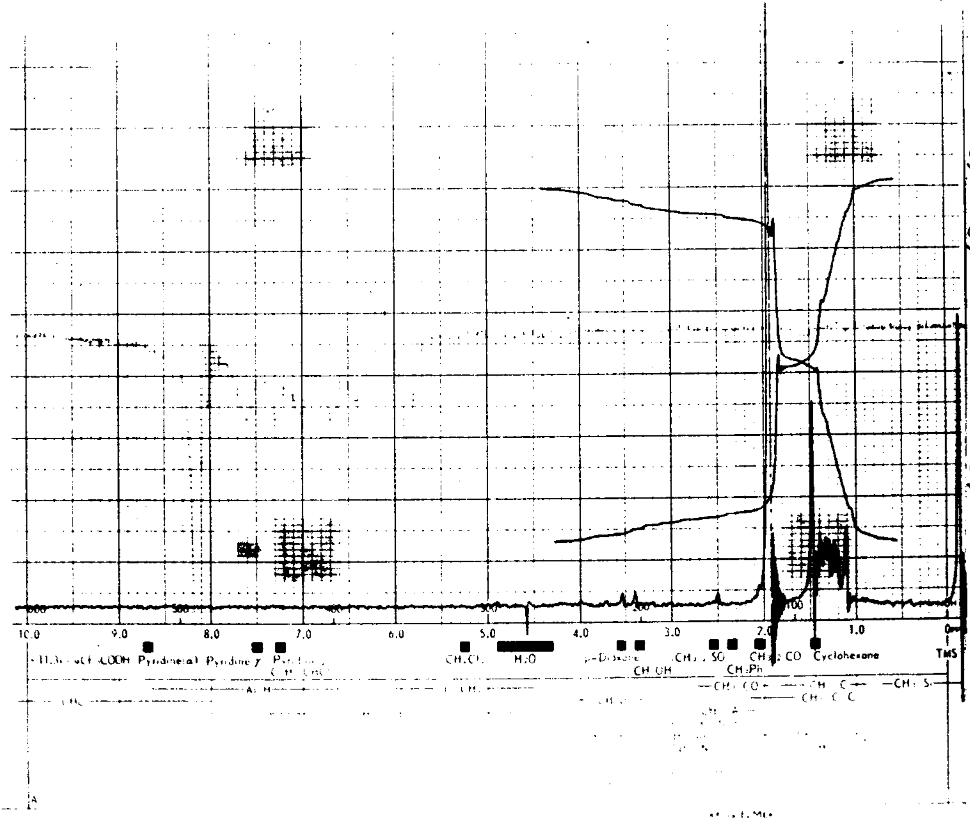
$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$

Solvent: CCl₄

Amplitude

Spectrum: 3

Integration: 4



Spectrum No. 6

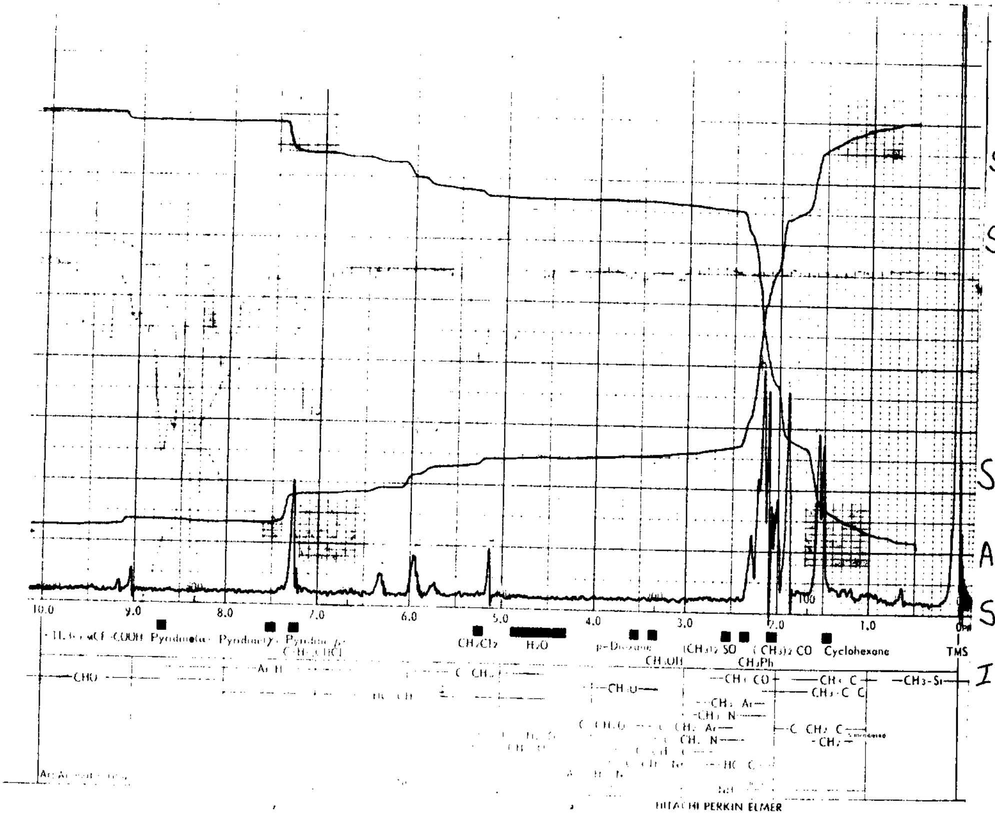
Sample:
Ozonized
tetramethyl-
ethylene.

Solvent: CCl₄

Amplitude

Spectrum: 9

Integration: 11



Spectrum No: 7

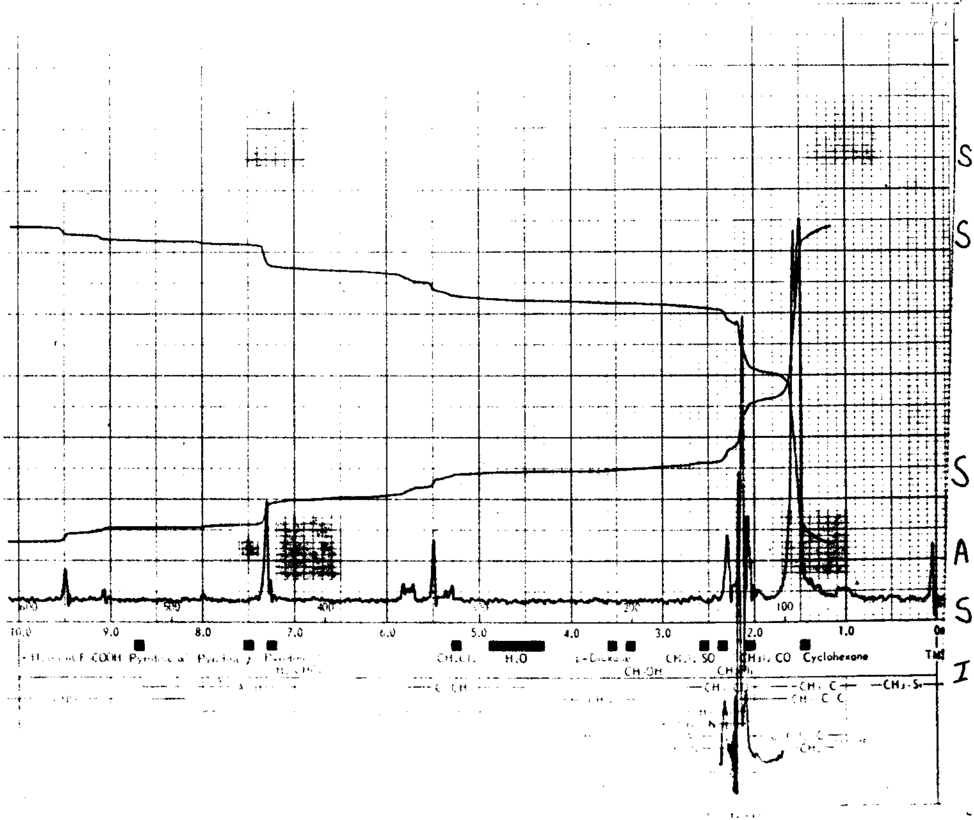
Sample:
Ozonized
Phorone

Solvent: CCl4

Amplitude

Spectrum: 10

Integration: 11

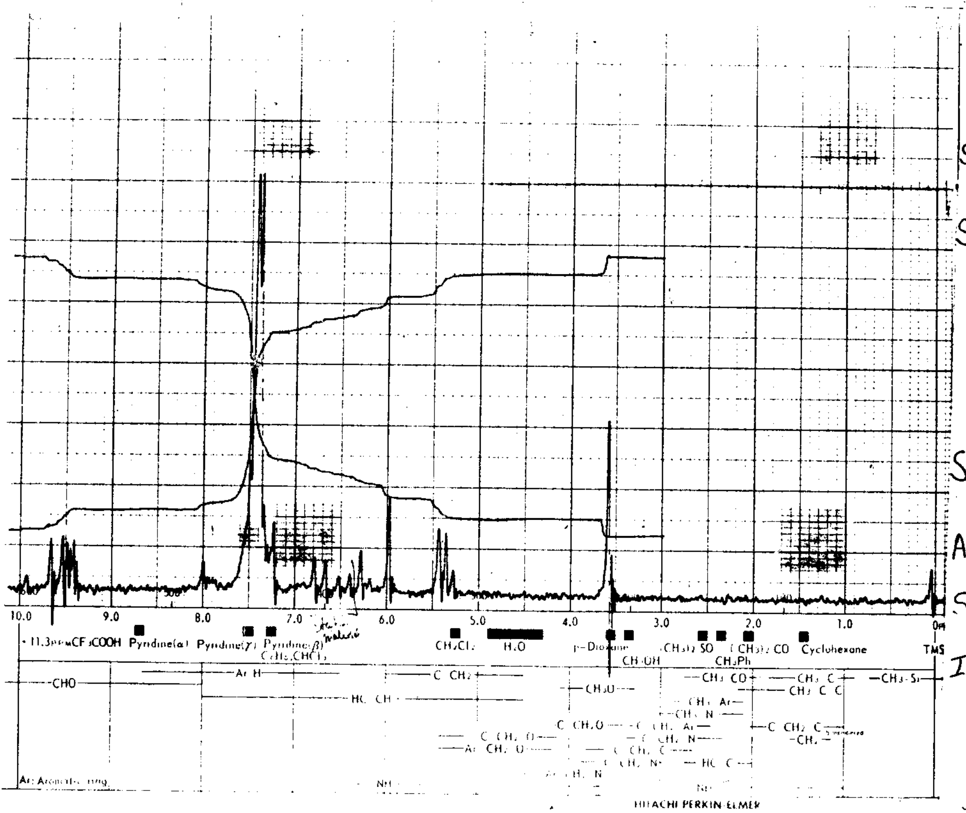


Spectrum No: 8

Sample:
Ozonized
Phorone

Solvent: CCl_4

Amplitude
Spectrum: 10
Integration: 10



Spectrum No: 9

Sample:

Ozonized

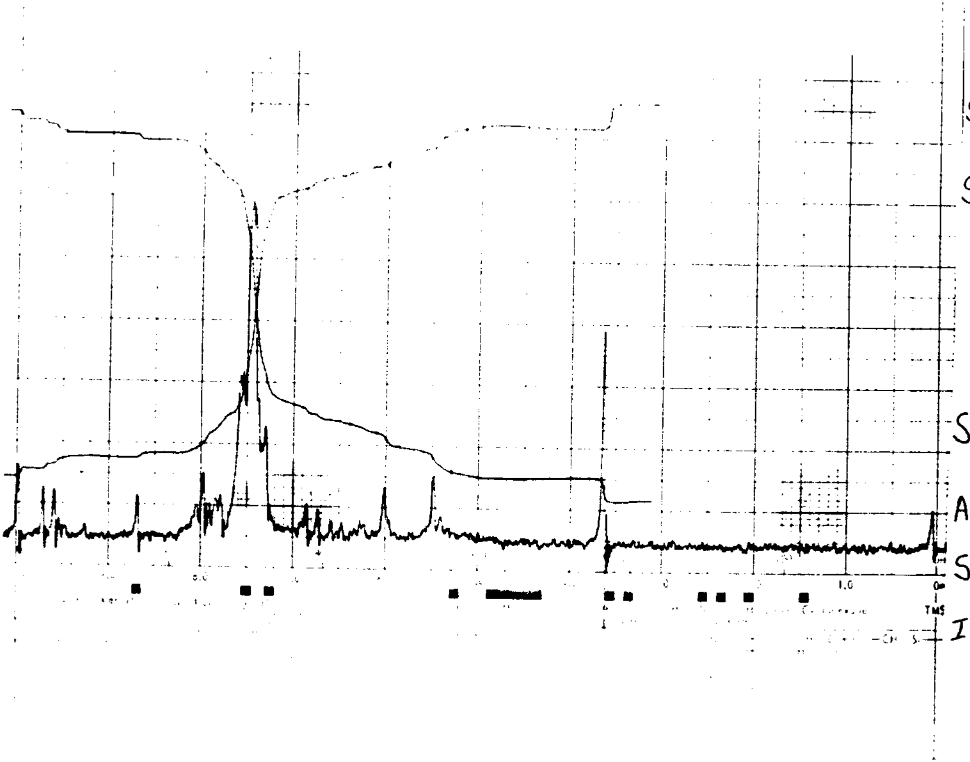
Cinnamaldehyde

Solvent: CCl_4

Amplitude

Spectrum: 11

Integration: 11

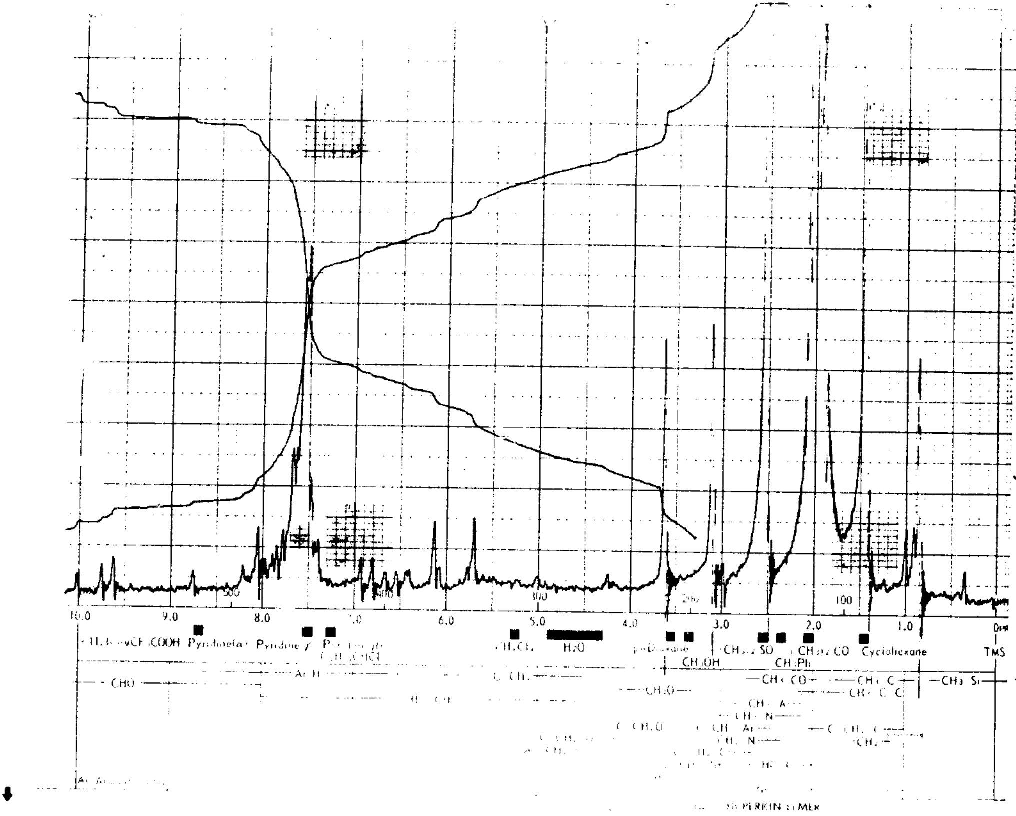


Spectrum No: 10

Sample:
Ozonized
Cinnamaldehyde

Solvent: CCl_4

Amplitude
Spectrum: 12
Integration: 12



Spectrum No: 11

Sample:

Ozonized

Cinnamaldehyde

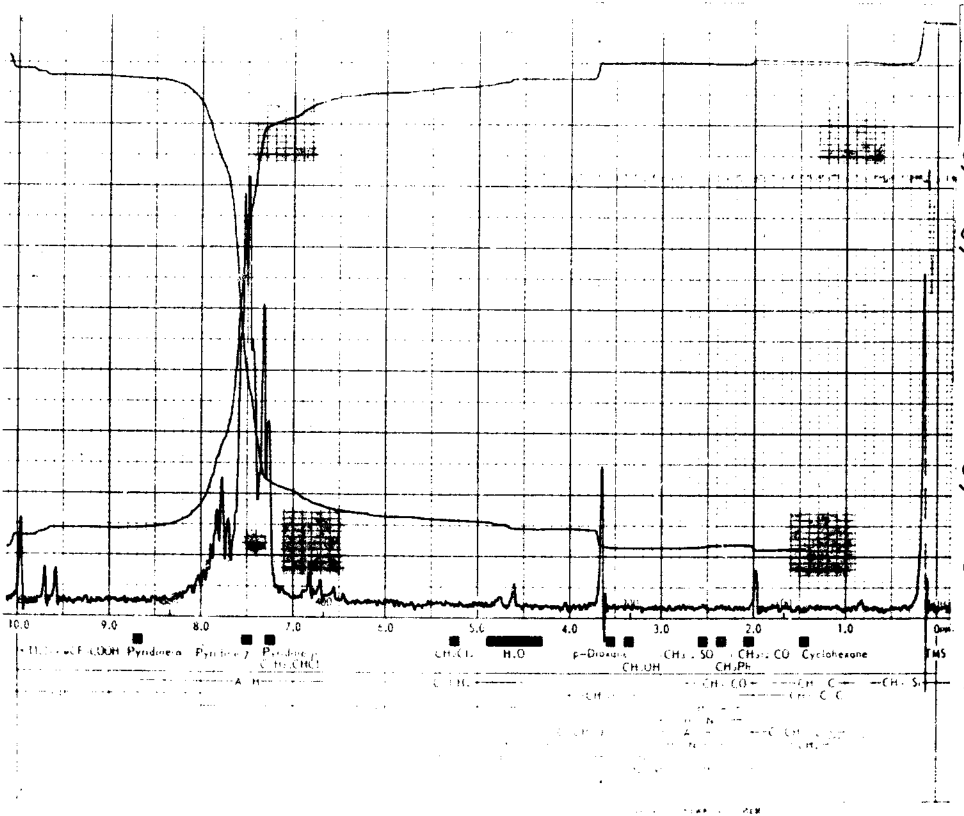
Solvent: CH_3CN

Amplitude

Spectrum: 11

Integration: 11

CHART NO. 435-7204 PRINTED IN U.S.A.



Spectrum No: 12

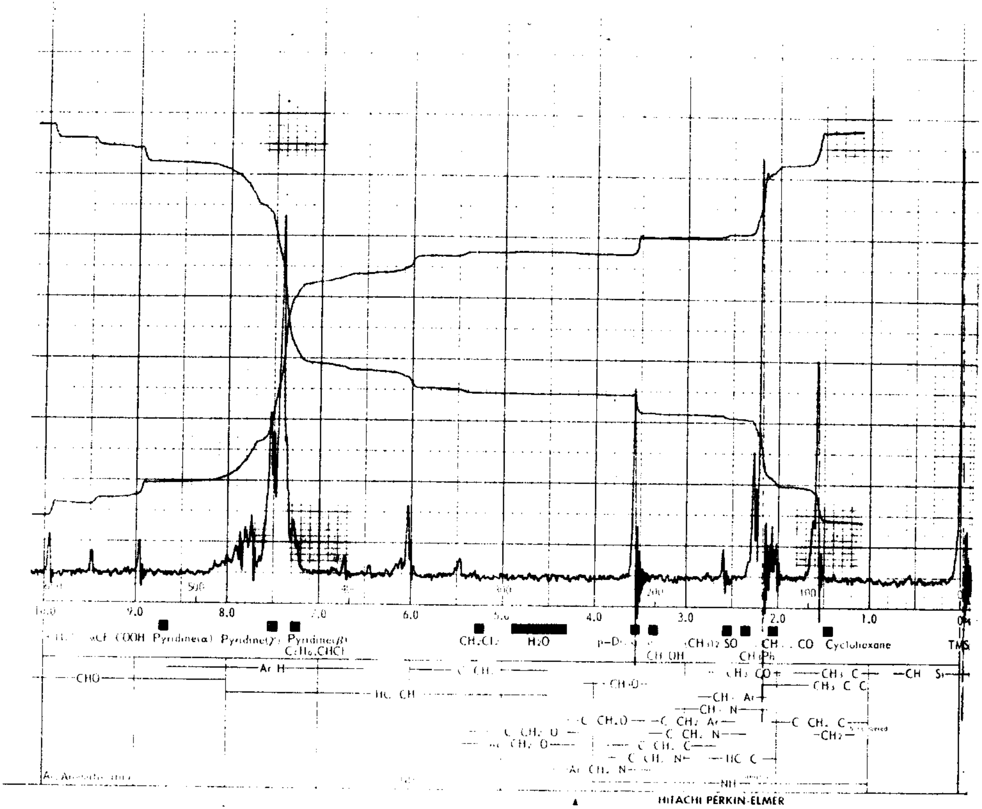
Sample:
Ozonized
Cinnamaldehyde
Reduced with
Φ_3P

Solvent: CCl_4

Amplitude

Spectrum: 1'

Integration: 1'



Spectrum No: 13

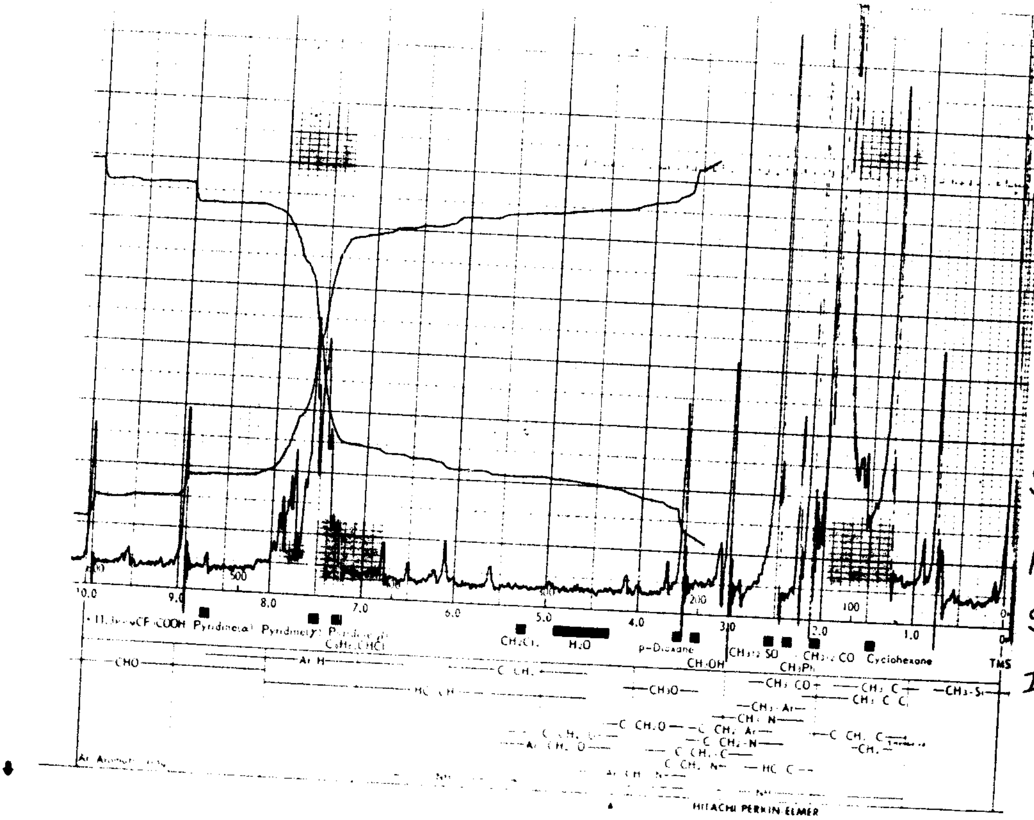
Sample:
Ozonized
trans-4-phenyl-
3-buten-2-one

Solvent: CCl_4

Amplitude

Spectrum: 11

Integration: 11



Spectrum No: 14

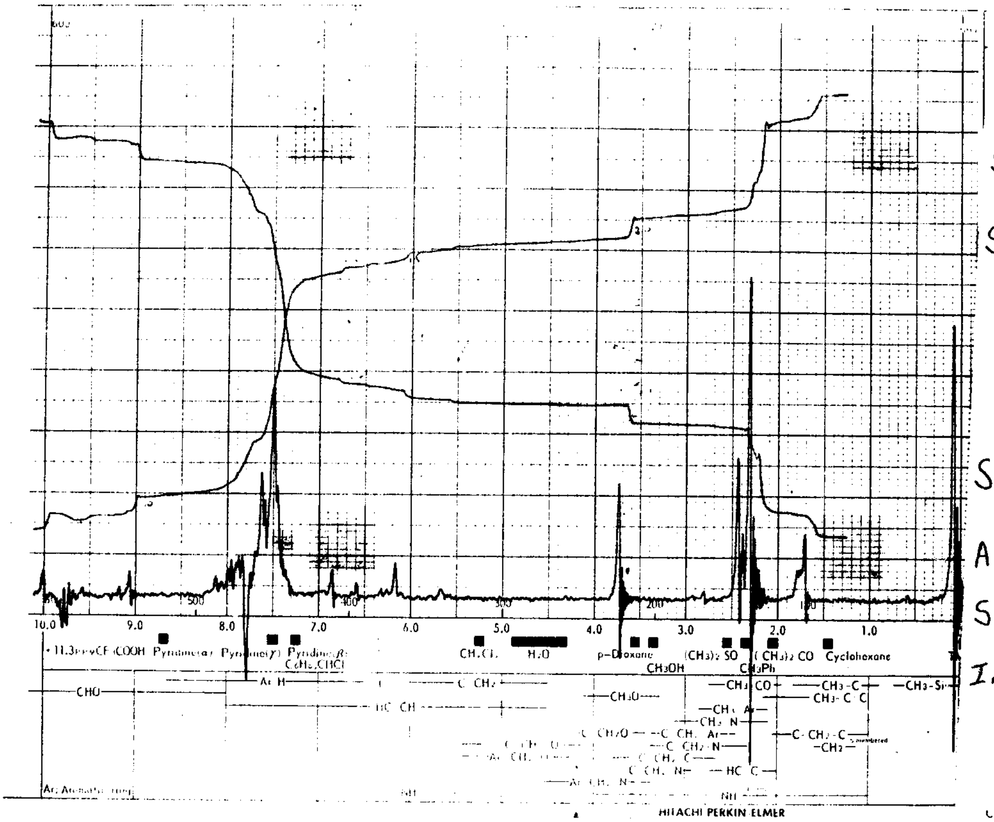
Sample:
Ozonized
trans- 4- phenyl-
3-buten- 2-one

Solvent: CH_3CN

Amplitude

Spectrum: 11

Integration: 11



Spectrum No: 15

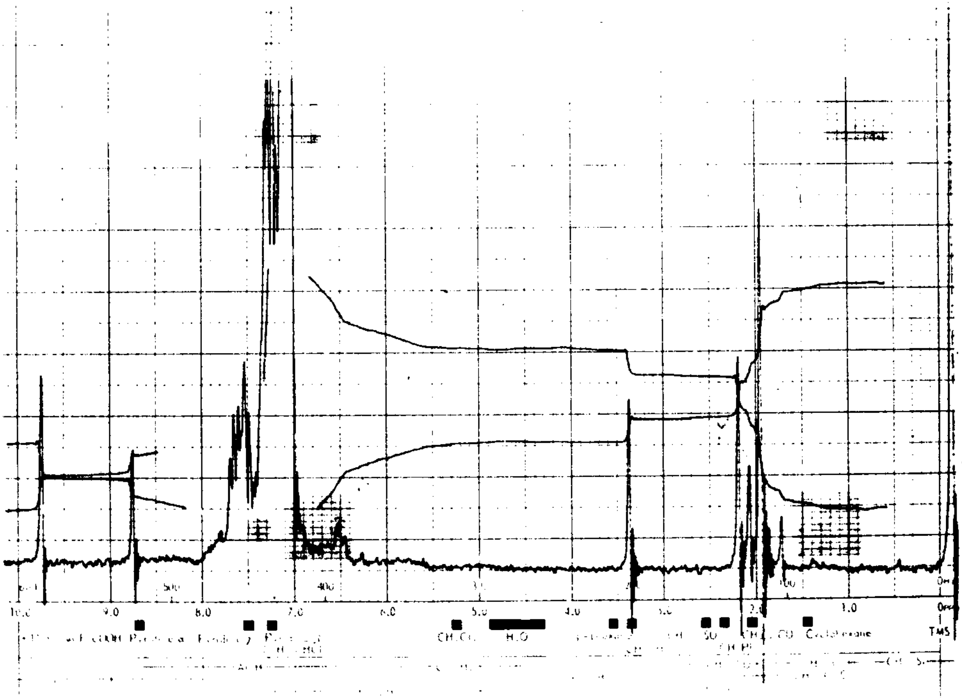
Sample:
Ozonized
4-phenyl-3-buten-
2-one

Solvent: $CDCl_3$

Amplitude

Spectrum: 10

Integration: 11



Spectrum No: 16

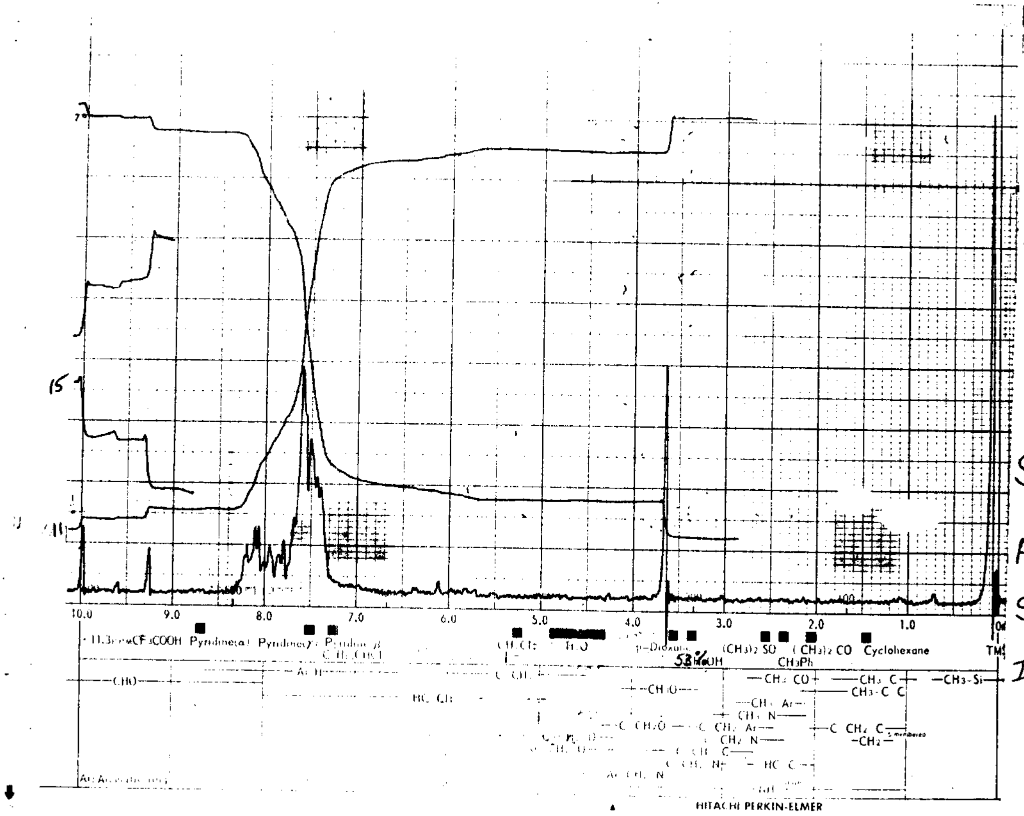
Sample:
Ozonized
4-phenyl-3-buten-2-one
Reduced with $\Phi_3 P$

Solvent: CCl_4

Amplitude

Spectrum: 11

Integration: 12

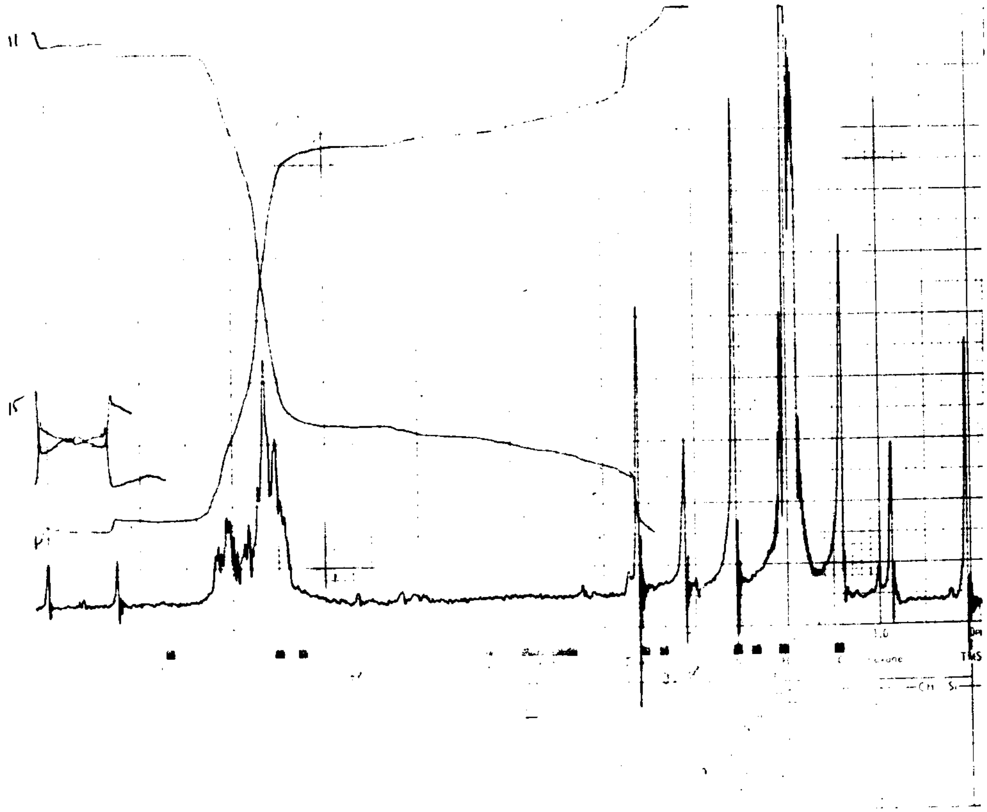


Spectrum No: 17

Sample:
Ozonized
Chalcone

Solvent: CCl_4

Amplitude
Spectrum: 10
Integration: 11.15



Spectrum No: 18

Sample:

Ozonized

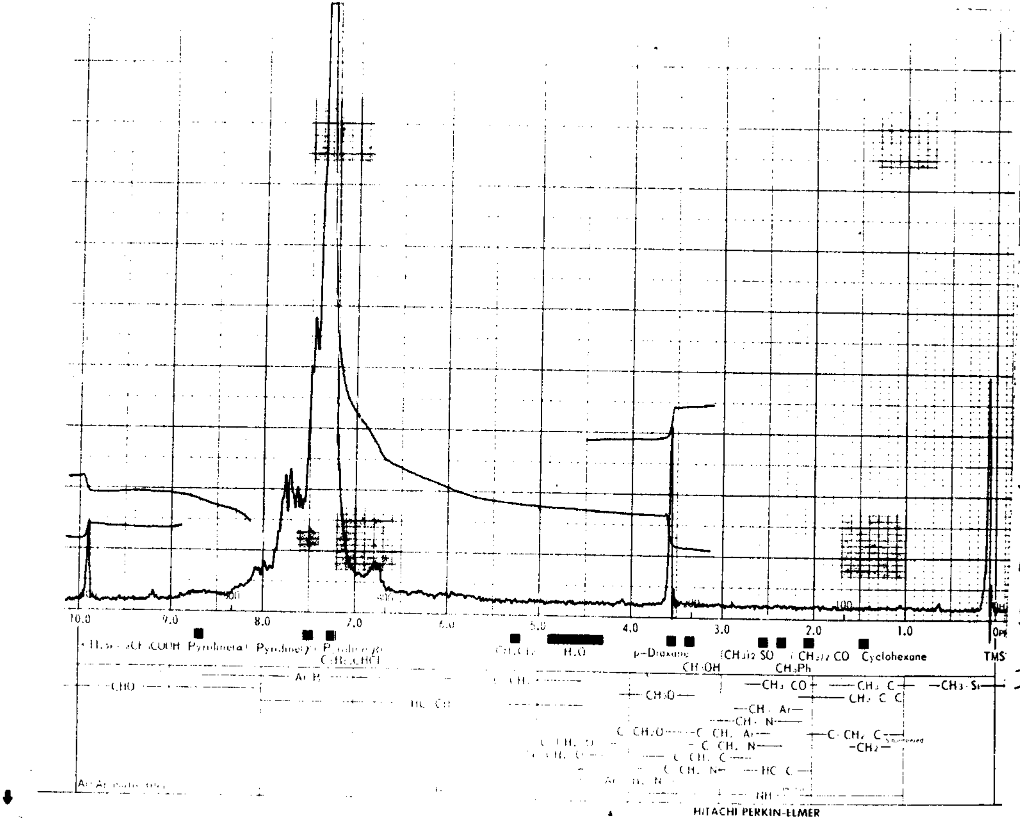
Chalcone

Solvent: CH_3CN

Amplitude

Spectrum: 10

Integration: 11,15



Spectrum No: 19

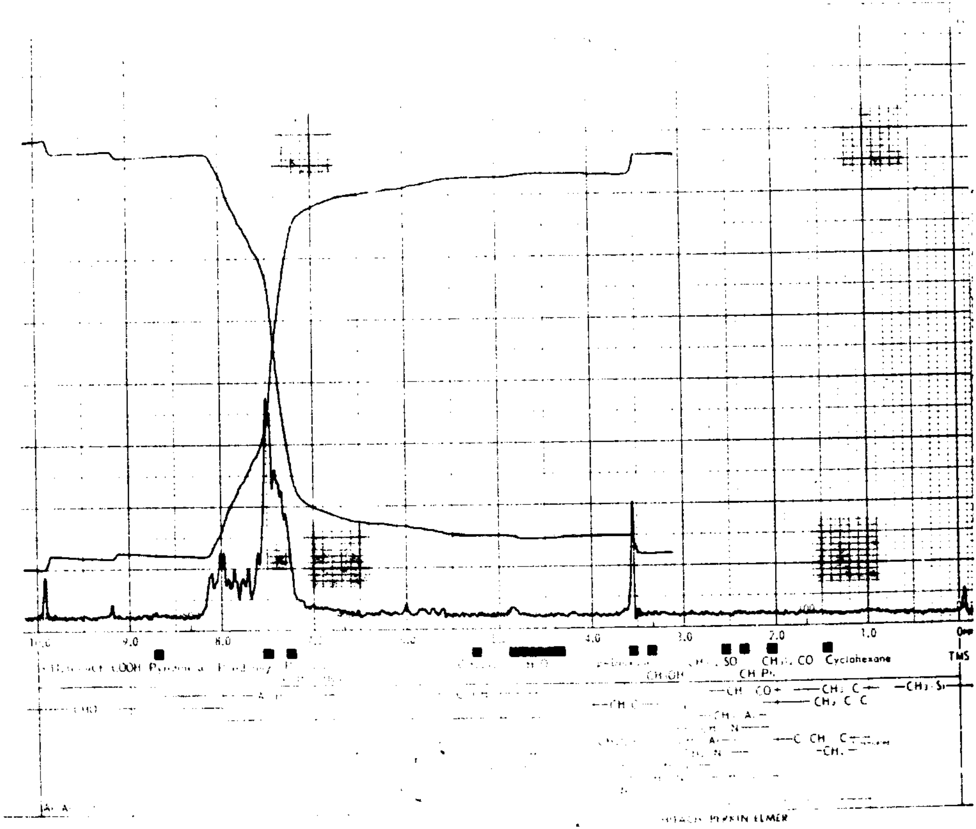
Sample:
Ozonized
Chalcone
Reduced with
$\phi_3 P$

Solvent: CCl_4

Amplitude

Spectrum: 10

Integration: 11

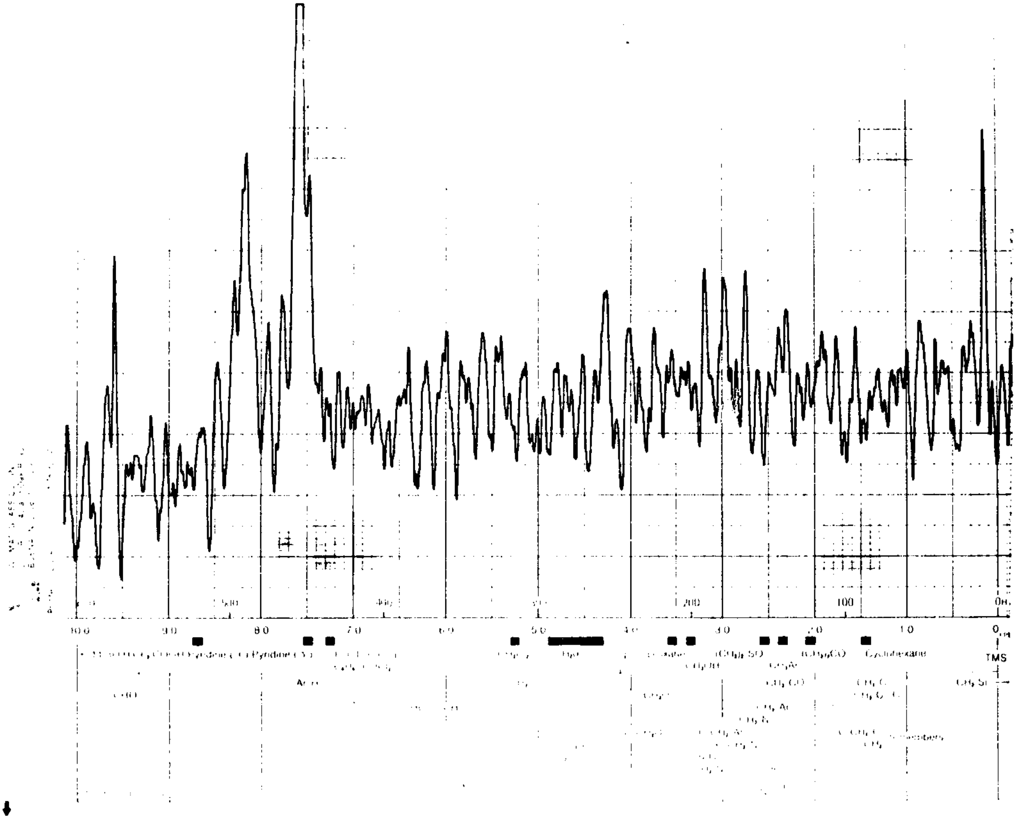


Spectrum No: 20

Sample:
Ozonized
Chalcone with
D_2O exchange

Solvent: CCl_4

Amplitude
Spectrum: 10
Integration: 11



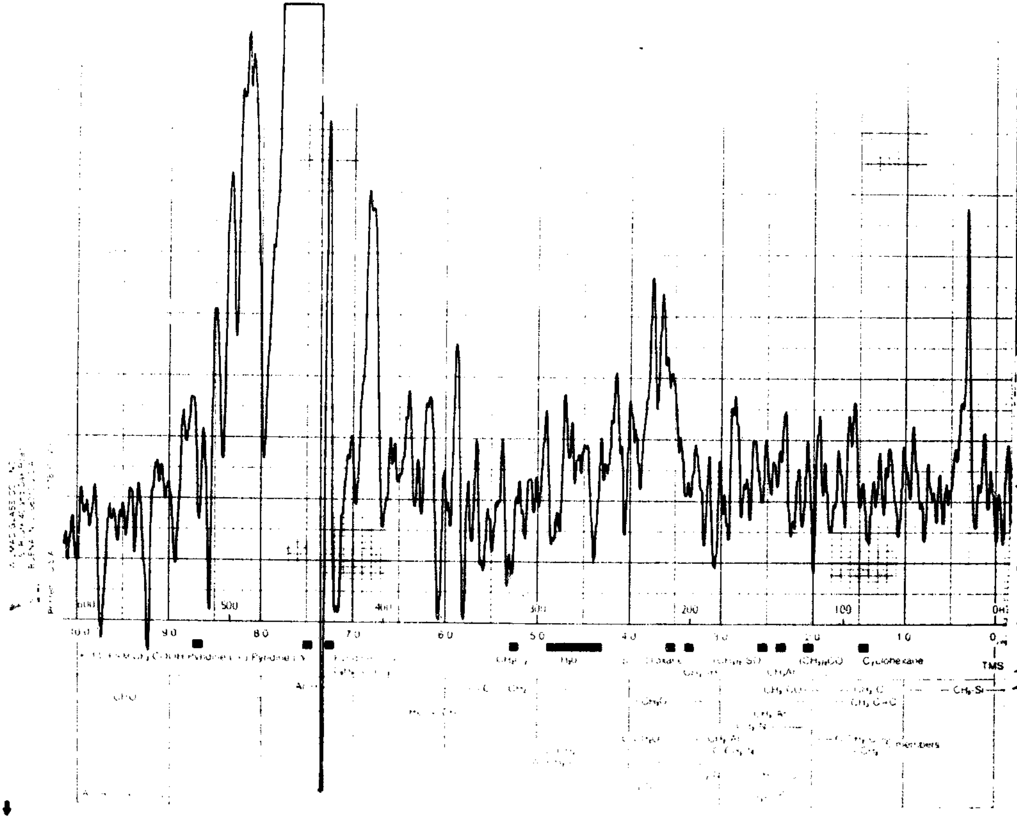
Spectrum No: 21

Sample:
Phenyl Glyoxal

Solvent: CCl4

Amplitude
Gain x10
Spectrum: 15

Integration: ____



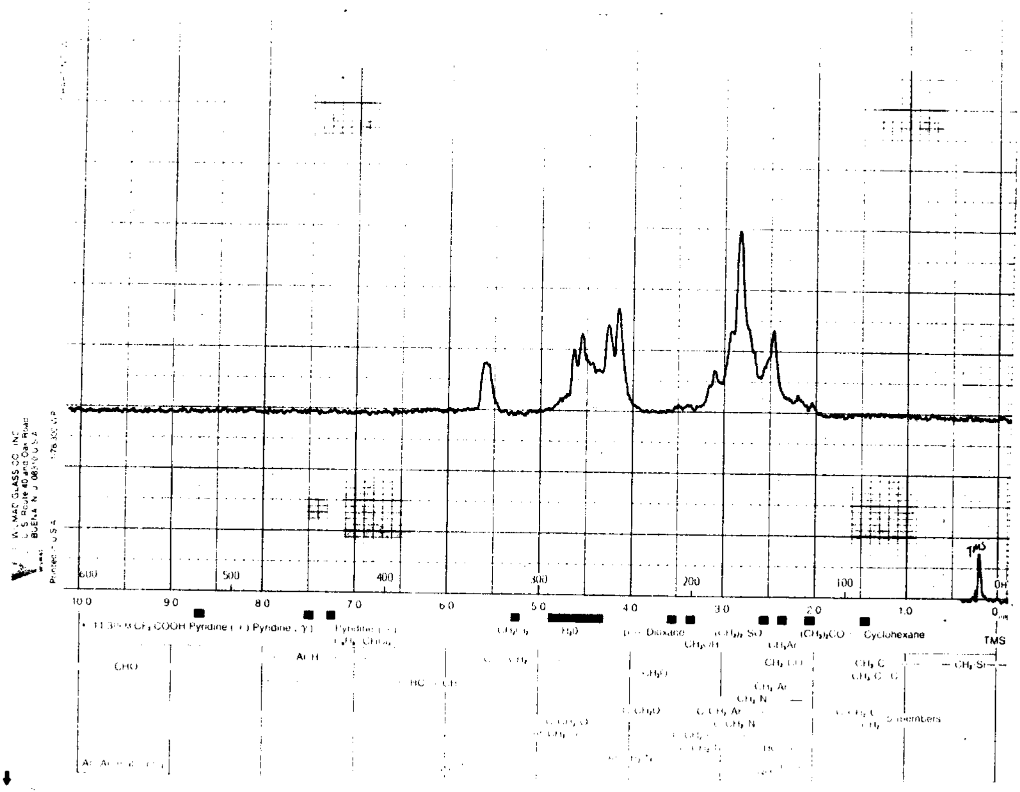
Spectrum No: 22

Sample:
Phenyl Glyoxal
Reduced With
Φ_3P

Solvent: CCl_4

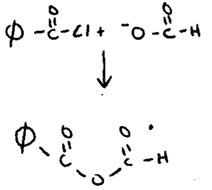
Amplitude
Gain x10
Spectrum: 15

Integration: ___



Spectrum No: 23

Sample:



$\phi-\overset{O}{\overset{\|}{C}}-Cl + {}^{-}O-\overset{O}{\overset{\|}{C}}-H \rightarrow \phi-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-H$

Solvent: CCl₄

Amplitude

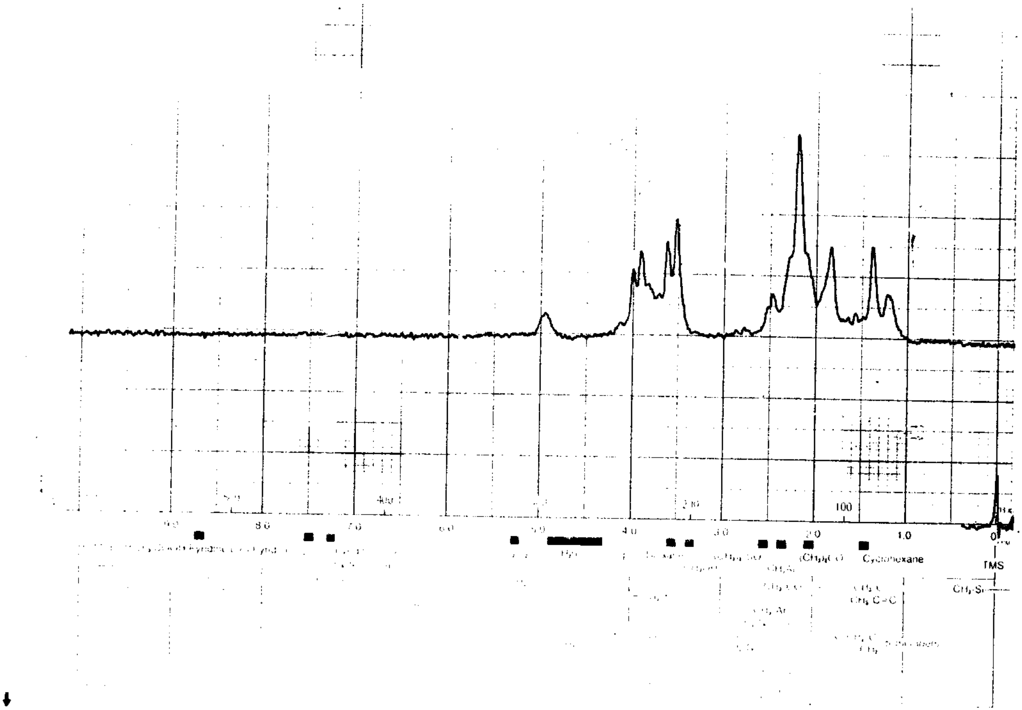
Spectrum: 10

Integration: ___

400 - 600 hz

UN82 WYNN, A.H. OZONOLYSIS OF CERTAIN B-UNSATURATED, ETC.
W988o/1979 CHEMISTRY HRS. 3/79 SHT. 2 OF 2

END



Spectrum No: 24

Sample:

Formic Benzoic
Anhydride
Reduced with
$\phi_3 P$

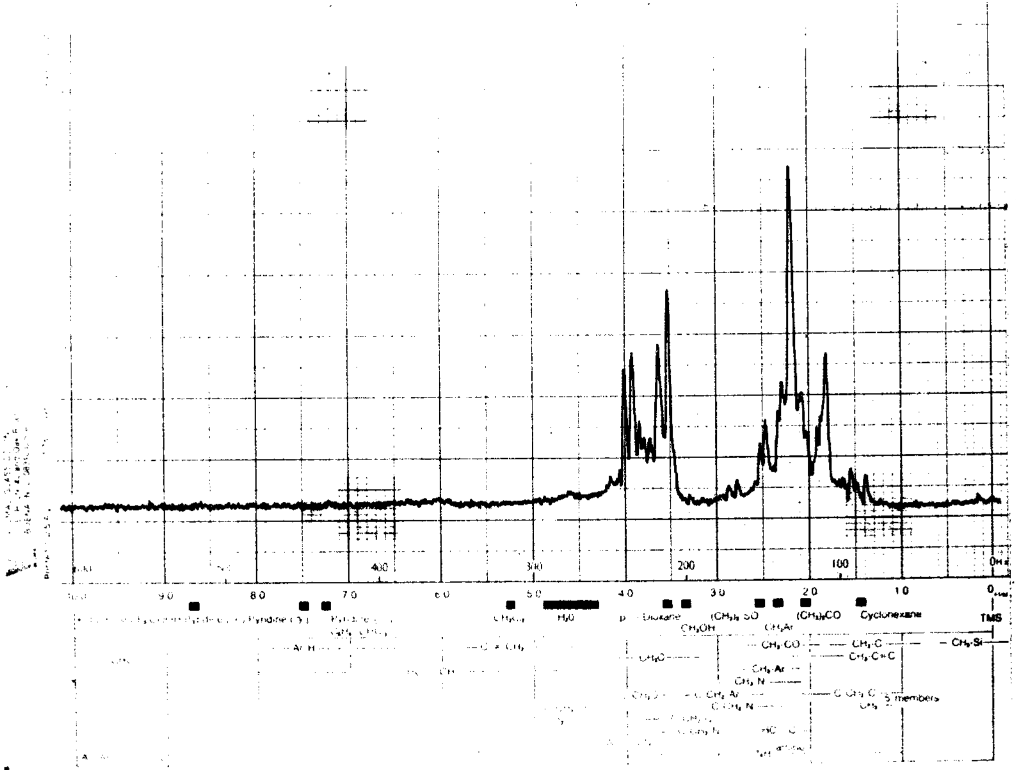
Solvent: CCl4

Amplitude

Spectrum: 10

Integration: ___

400 - 600 hz



Spectrum No: 25

Sample:
Formic Benzoic
Anhydride
plus
H_2O

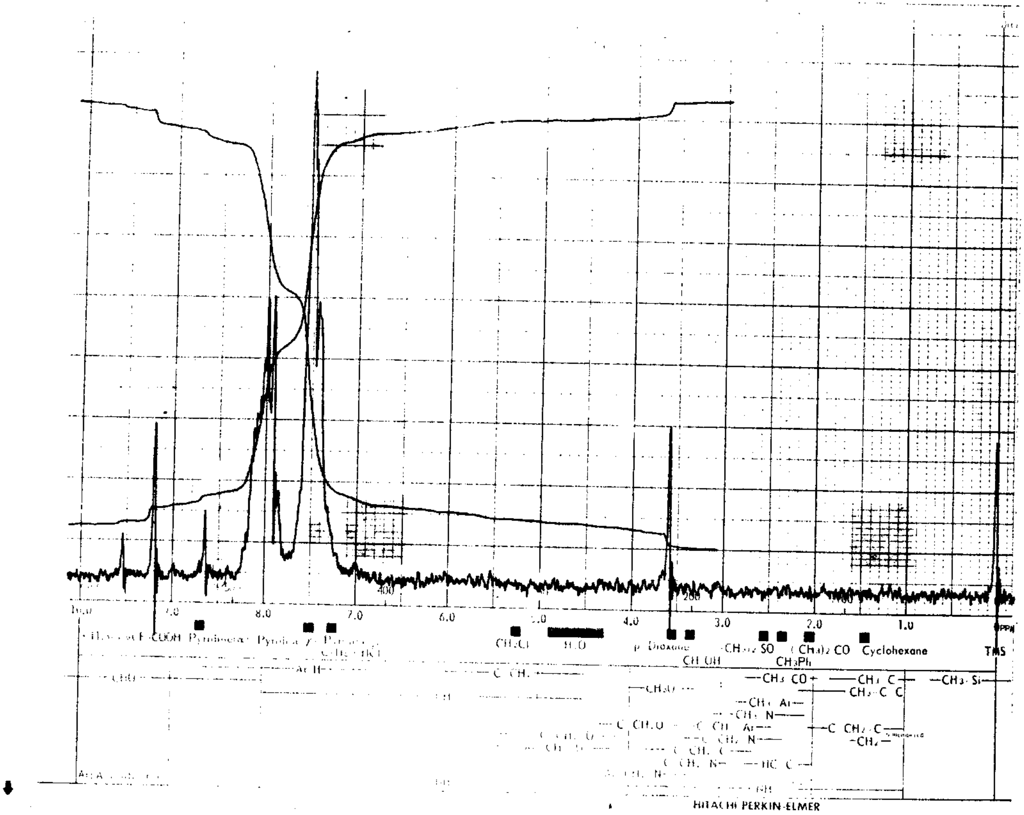
Solvent: CCl_4

Amplitude

Spectrum: 11

Integration: ___

400 - 500 hz



Spectrum No: 26

Sample:
Ozonized
Dibenzoyl
Ethylene

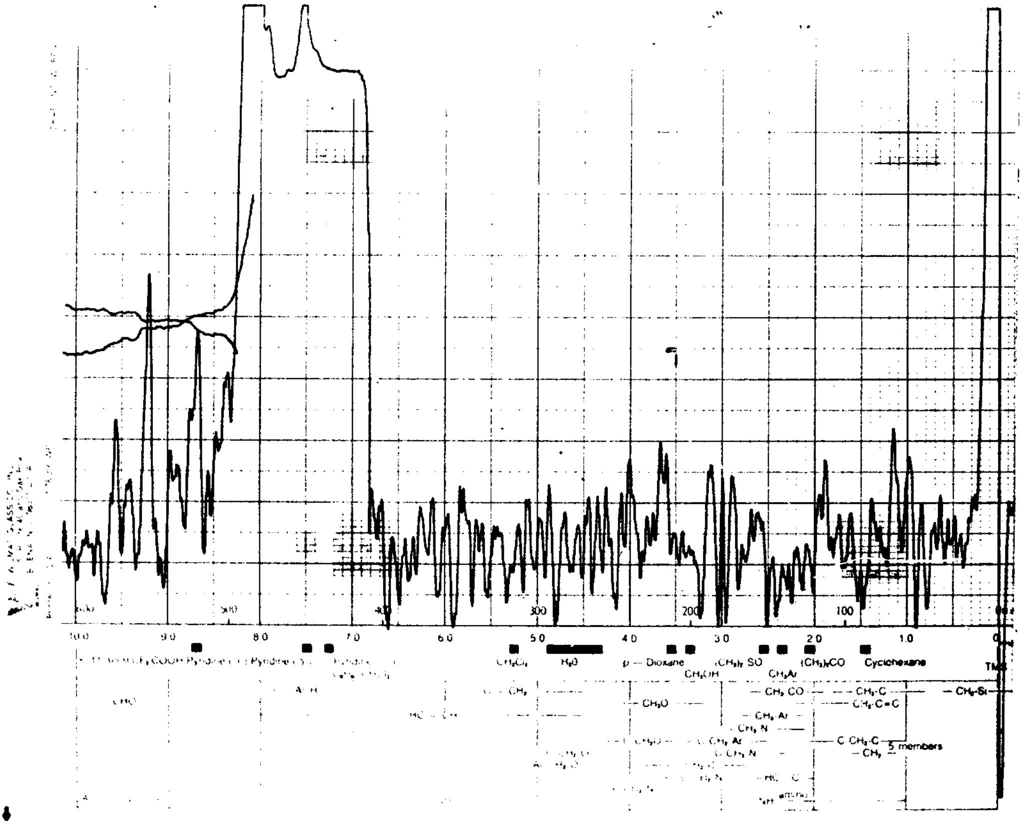
(Heterogeneous)

Solvent: CCl_4

Amplitude

Spectrum: 13

Integration: 12



Spectrum No: 27

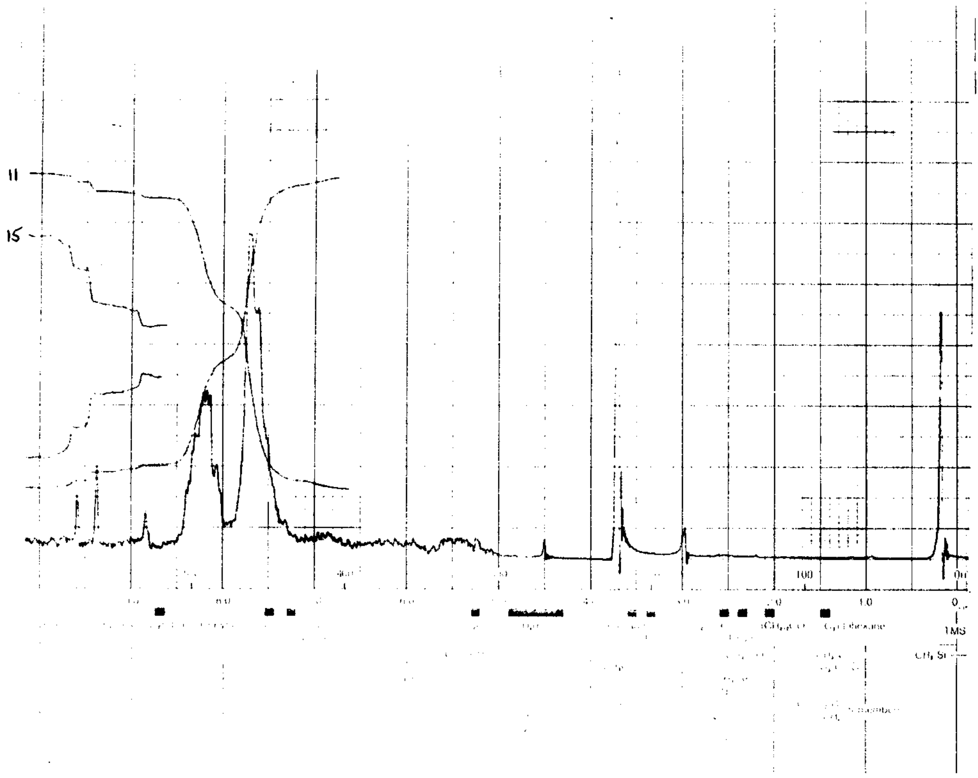
Sample:
Ozonized
Dibenzoyl
Ethylene

(Homogeneous)

Solvent: CCl4

Amplitude
Gain x10
Spectrum: 15

Integration: ___



Spectrum No: 28

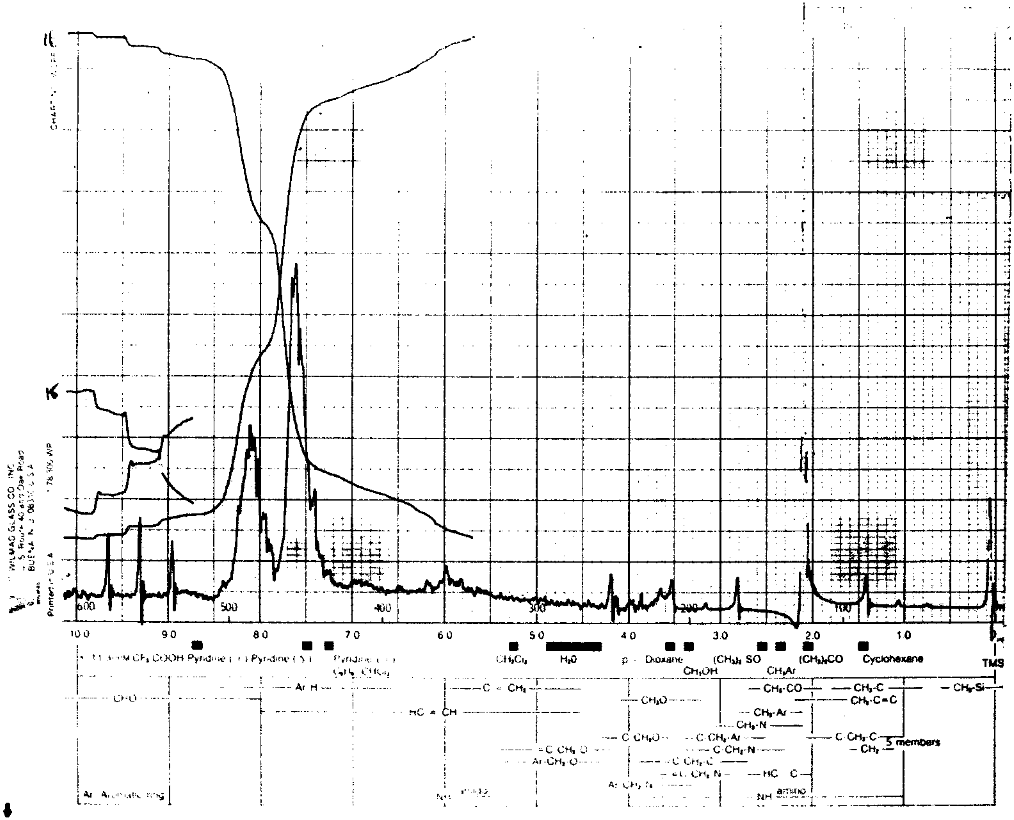
Sample:
Ozonized
Dibenzoyl
Ethylene

Solvent: p-Dioxane

Amplitude

Spectrum: 12

Integration: 11,15



Spectrum No: 29

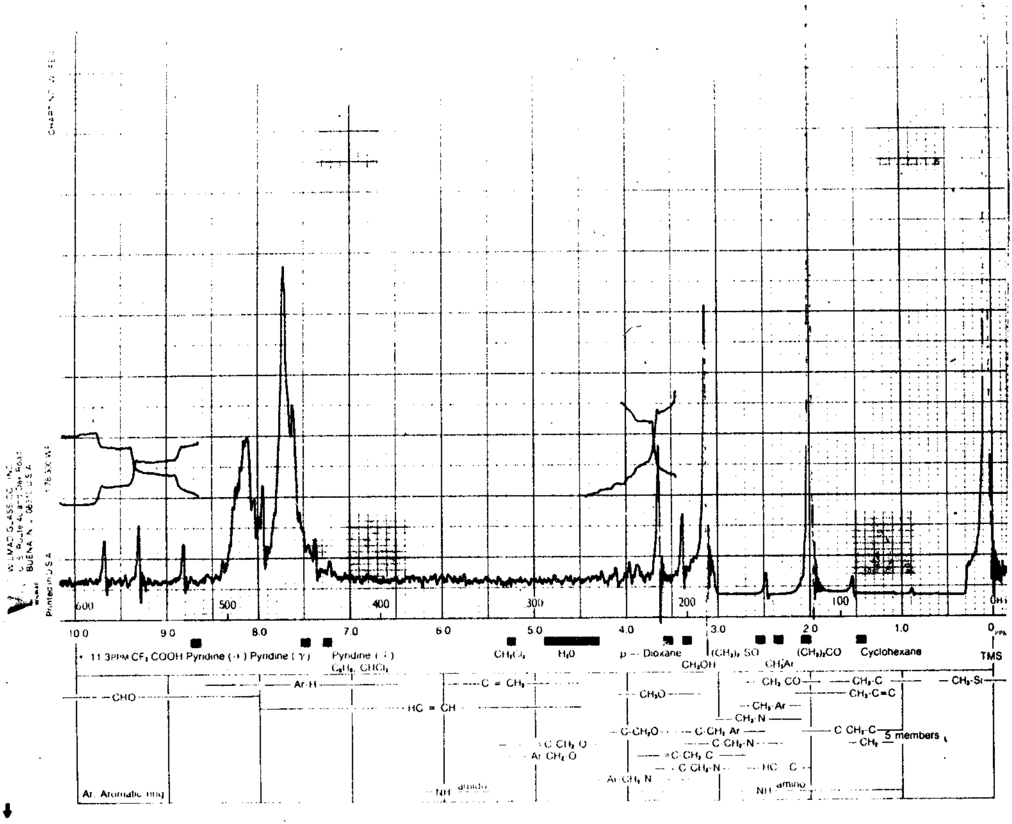
Sample:
Ozonized
Dibenzoyl
Ethylene

Solvent: Acetone

Amplitude

Spectrum: 11

Integration: 11, 15



Spectrum No: 30

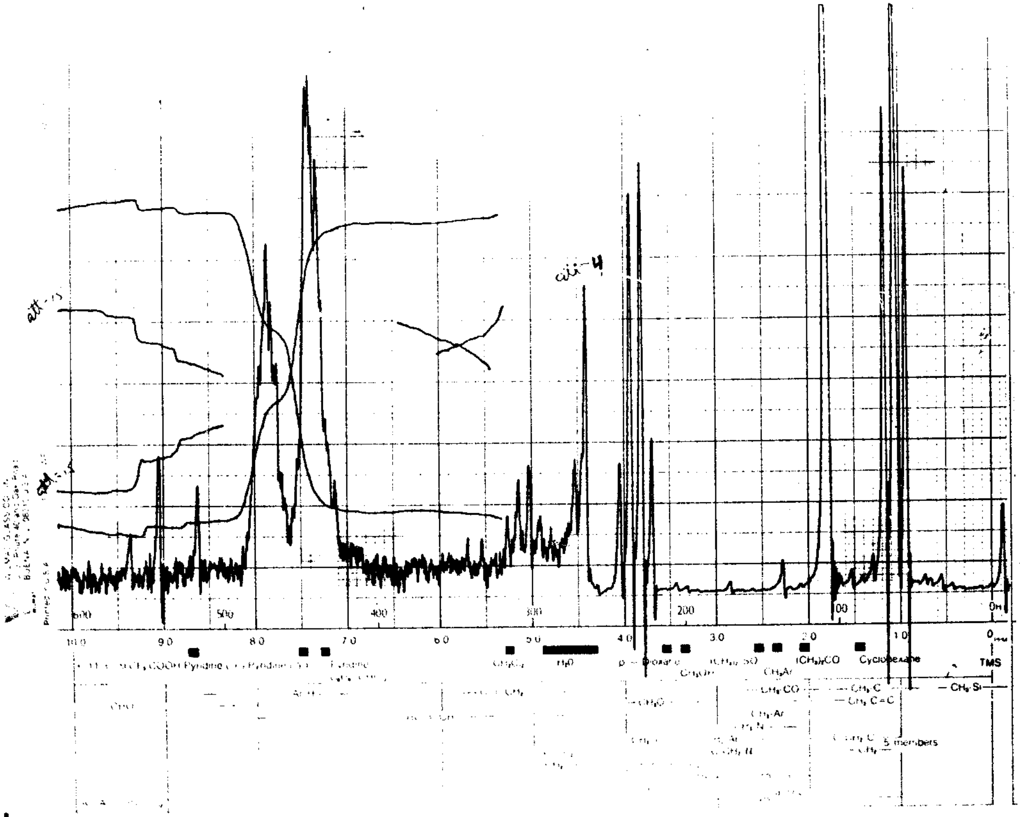
Sample:
Ozonized
Dibenzoyl
Ethylene

Solvent: CH₃CN

Amplitude

Spectrum: 12

Integration: 15



Spectrum No: 31

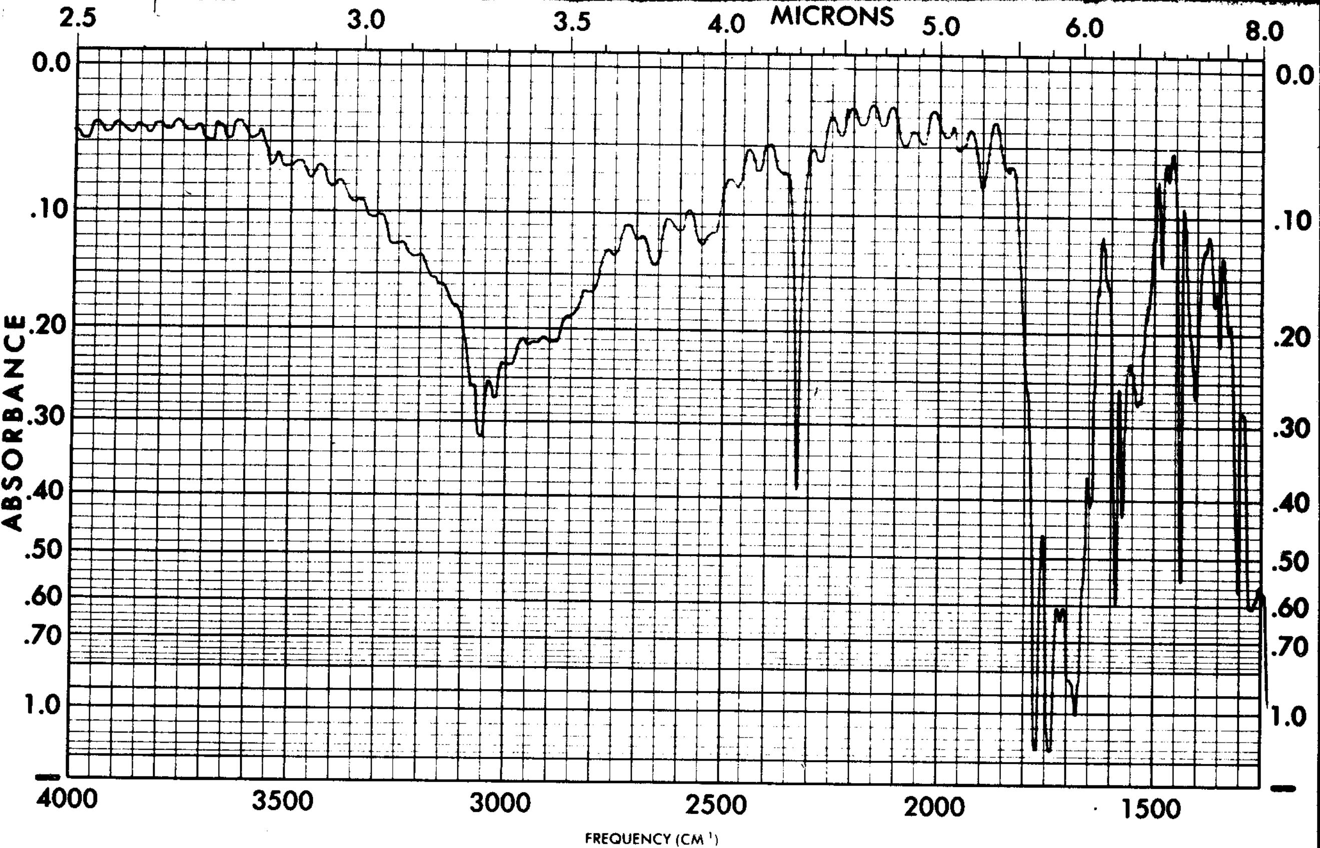
Sample:
Ozonized
Dibenzoyl
Ethylene

Solvent: Ethyl Acetate

Amplitude

Spectrum: 15

Integration: 13



SAMPLE ozonized dibenzoyl ethylene

ORIGIN

SOLVENT CCl4

CURVE NO. 32

CONC.

CELL PATH

REFERENCE

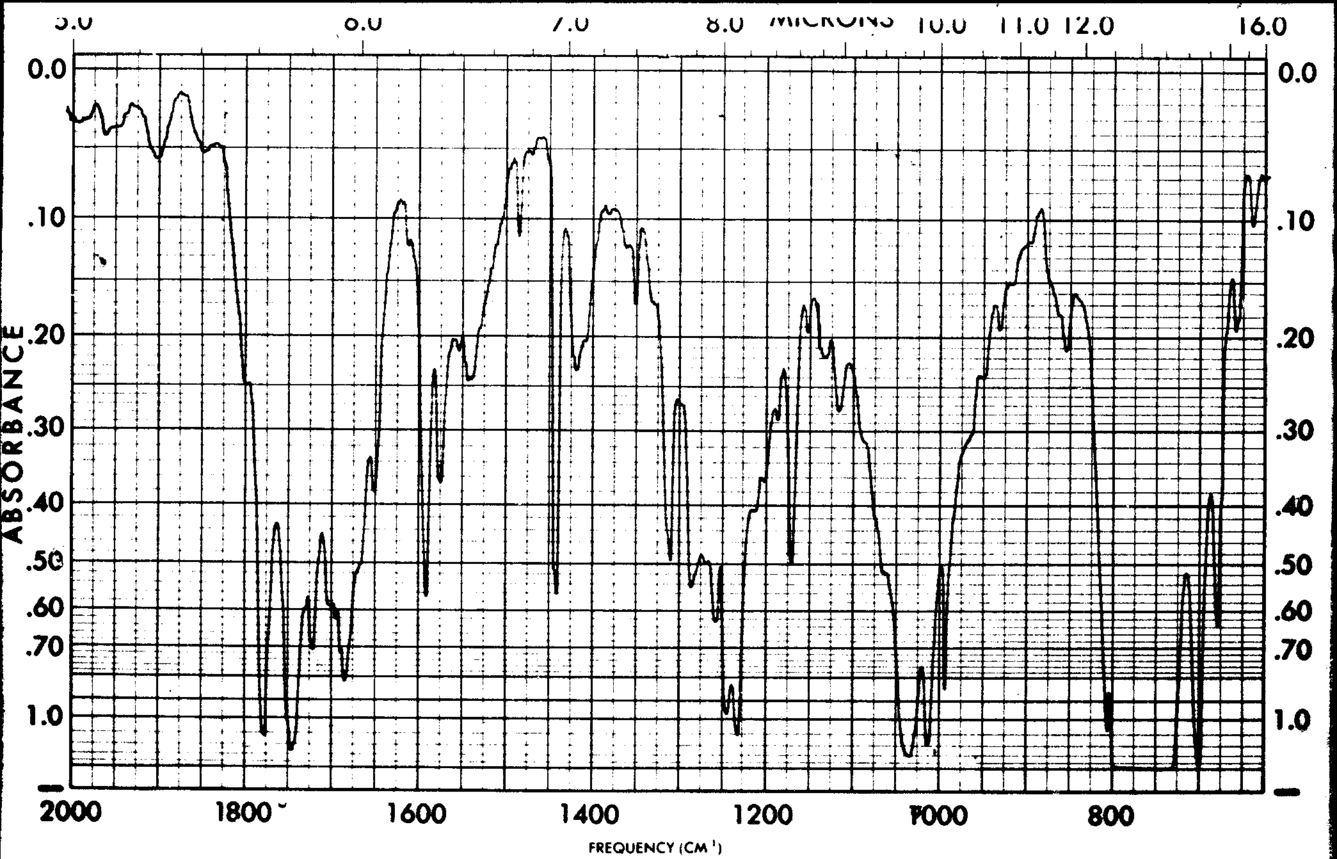
SCAN SPEED 3 per

SLIT 25

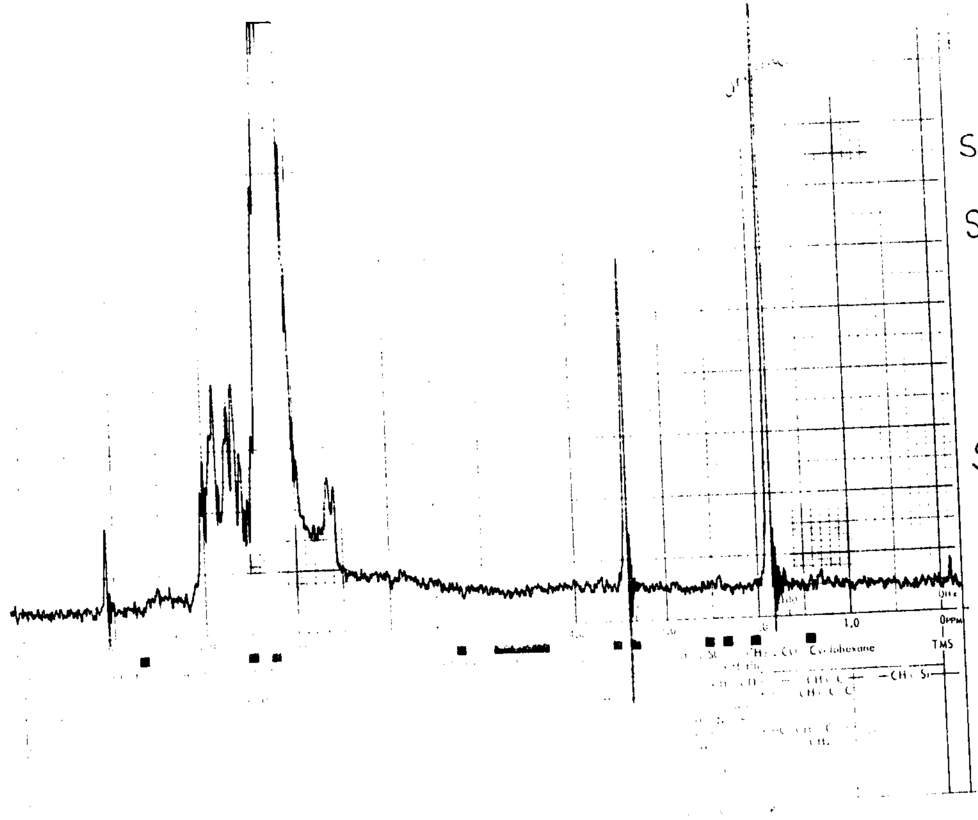
OPERATOR

DATE 1/12

REMARKS See Page 29



SAMPLE ozonized dibenzoyl ethylene	CURVE NO. 32	SCAN SPEED fast	OPERATOR
	CONC.	SLIT	DATE 10/17
ORIGIN	CELL PATH	REMARKS See Page 79	
SOLVENT CCl_4	REFERENCE CCl_4		



Spectrum No: 33

Sample:

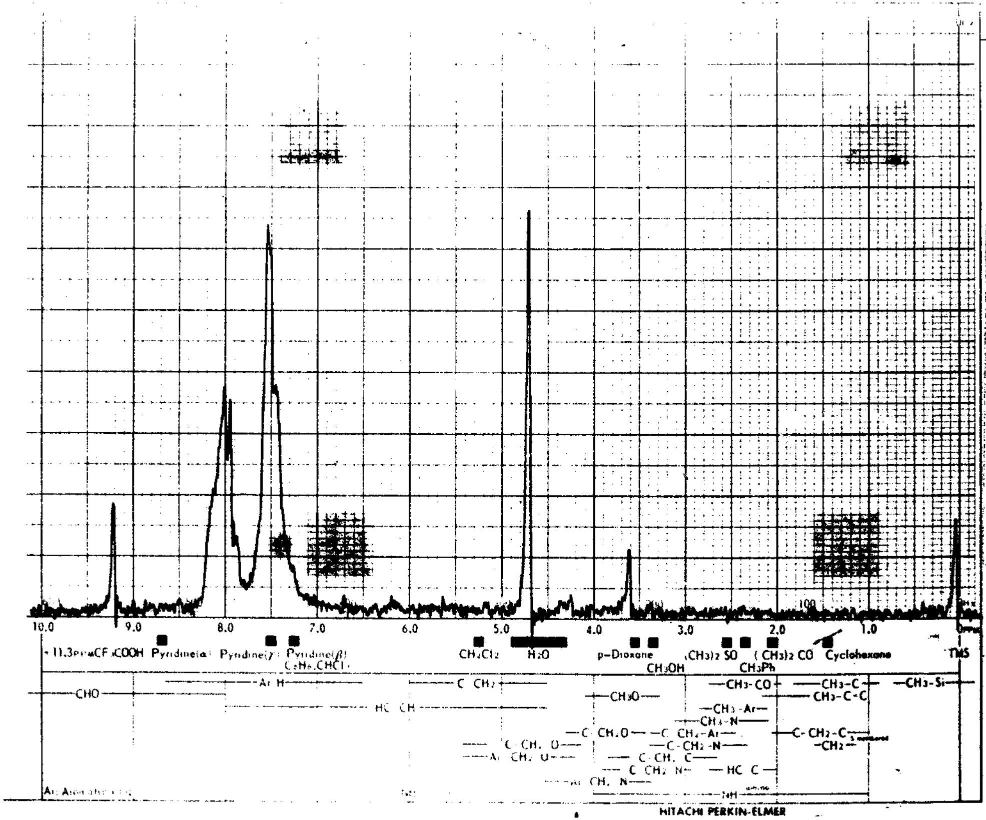
Ozonized
Dibenzoyl
Ethylene
Reduced with
$\phi_3 P$

Solvent: CCl_4

Amplitude

Spectrum: 13

Integration: ____



Spectrum No: 31

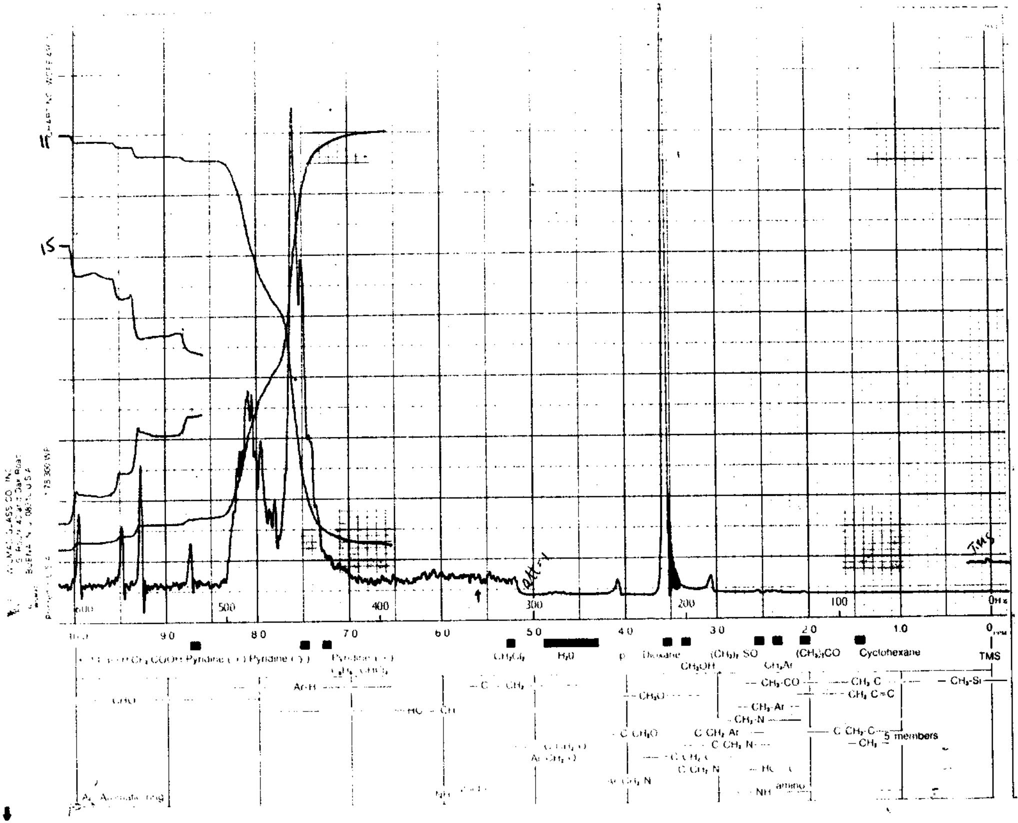
Sample:
Ozonized
Dibenzoyl
Ethylene with
D₂O Exchange

Solvent: CCl_4

Amplitude

Spectrum: 13

Integration: ____



Spectrum No: 35

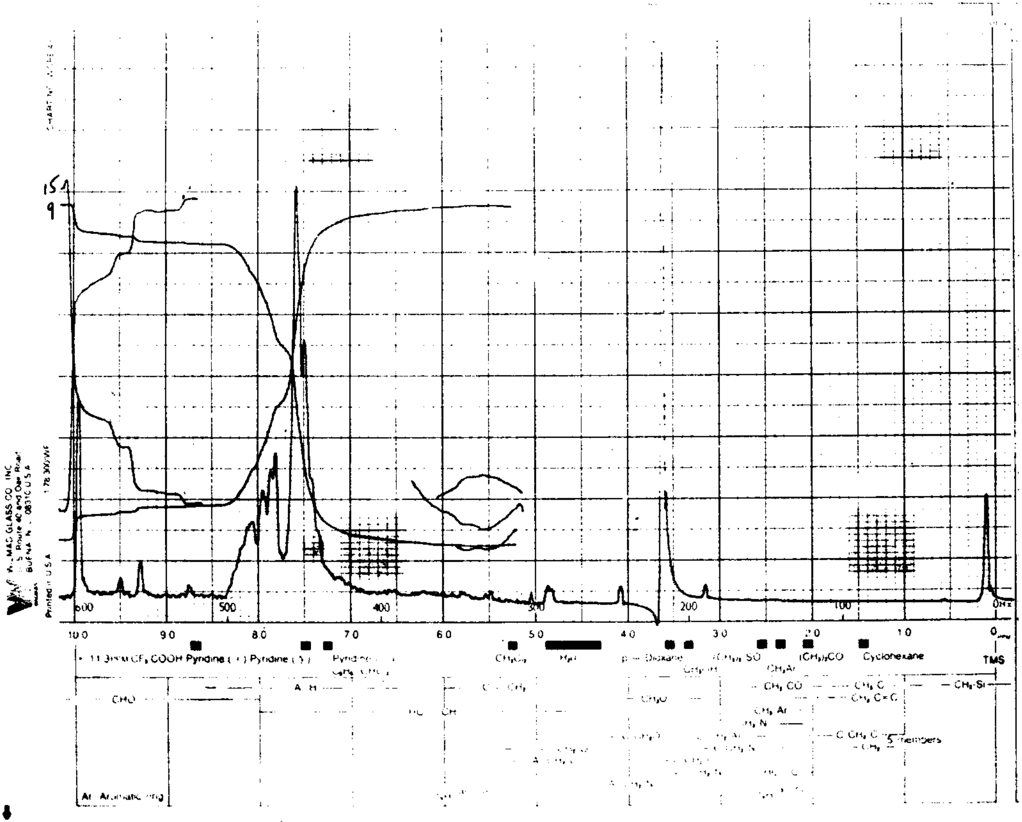
Sample :
Ozonized
Dibenzoyl
Ethylene and
Benzaldehyde

Solvent: p-dioxane

Amplitude

Spectrum: 12

Integration: 11,15



Spectrum No: 36

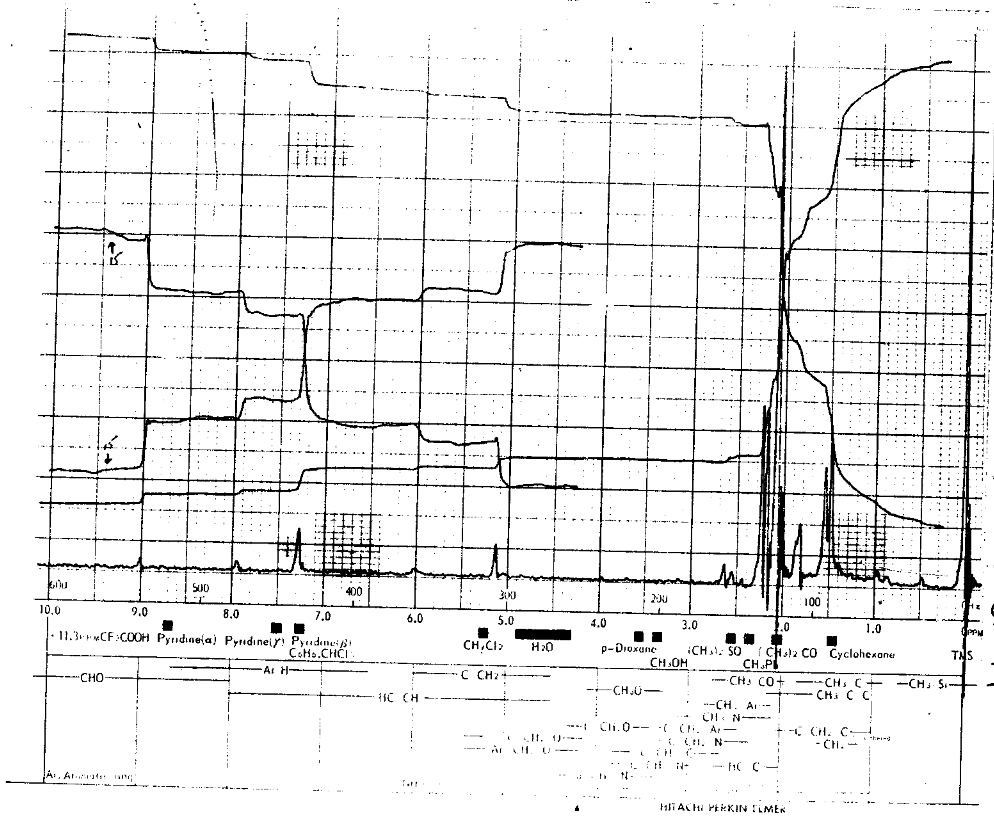
Sample:
Ozonized
Dibenzoyl
Ethylene and
Benzaldehyde

Solvent: p-dioxane

Amplitude

Spectrum: 10

Integration: 9.15



Spectrum No: 37

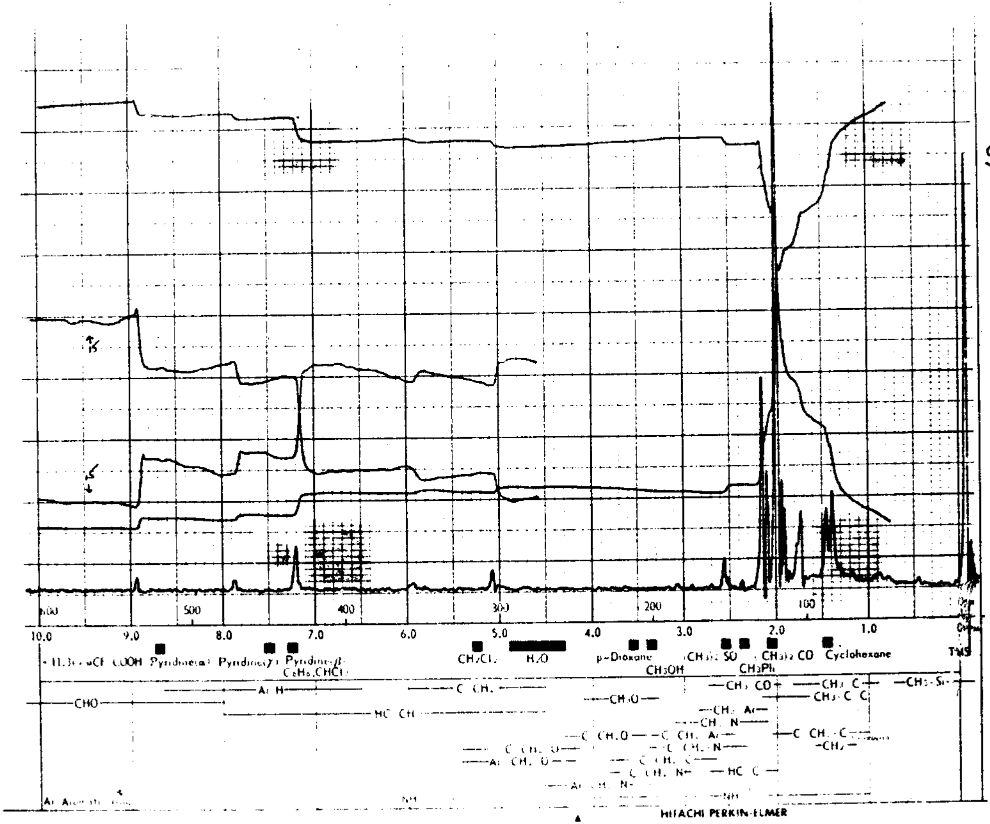
Sample :
Ozonized
Mesityl Oxide

Solvent: CCl4

Amplitude

Spectrum: 9

Integration: 11

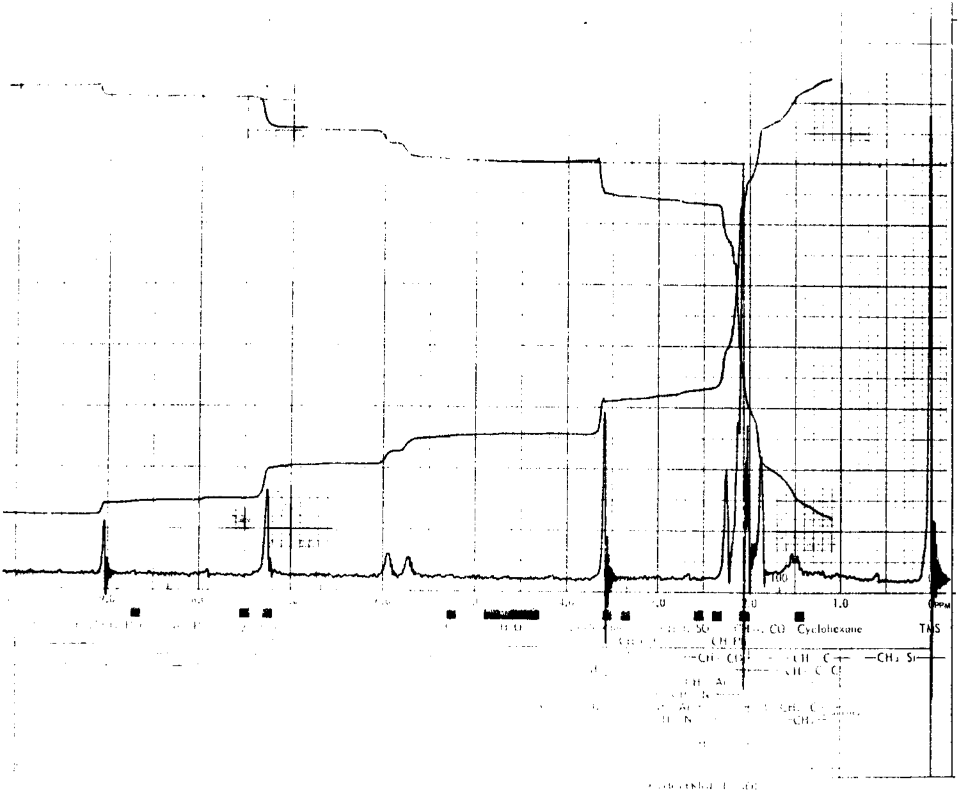


Spectrum No: 38

Sample:
Ozonized
Mesityl Oxide

Solvent: CCl4

Amplitude
Spectrum: 9
Integration: 11



Spectrum No: 39

Sample:

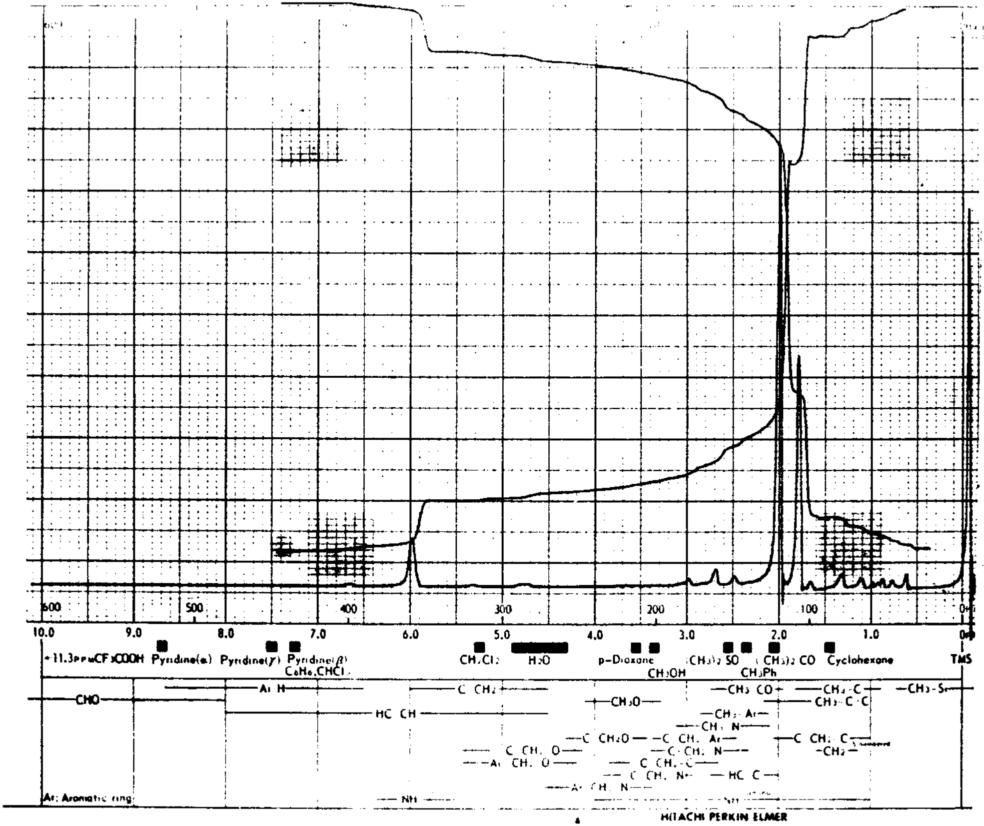
Ozonized
Phorone after
Reflux

Solvent: CCl4

Amplitude

Spectrum: 9

Integration: 11



Spectrum No: 40

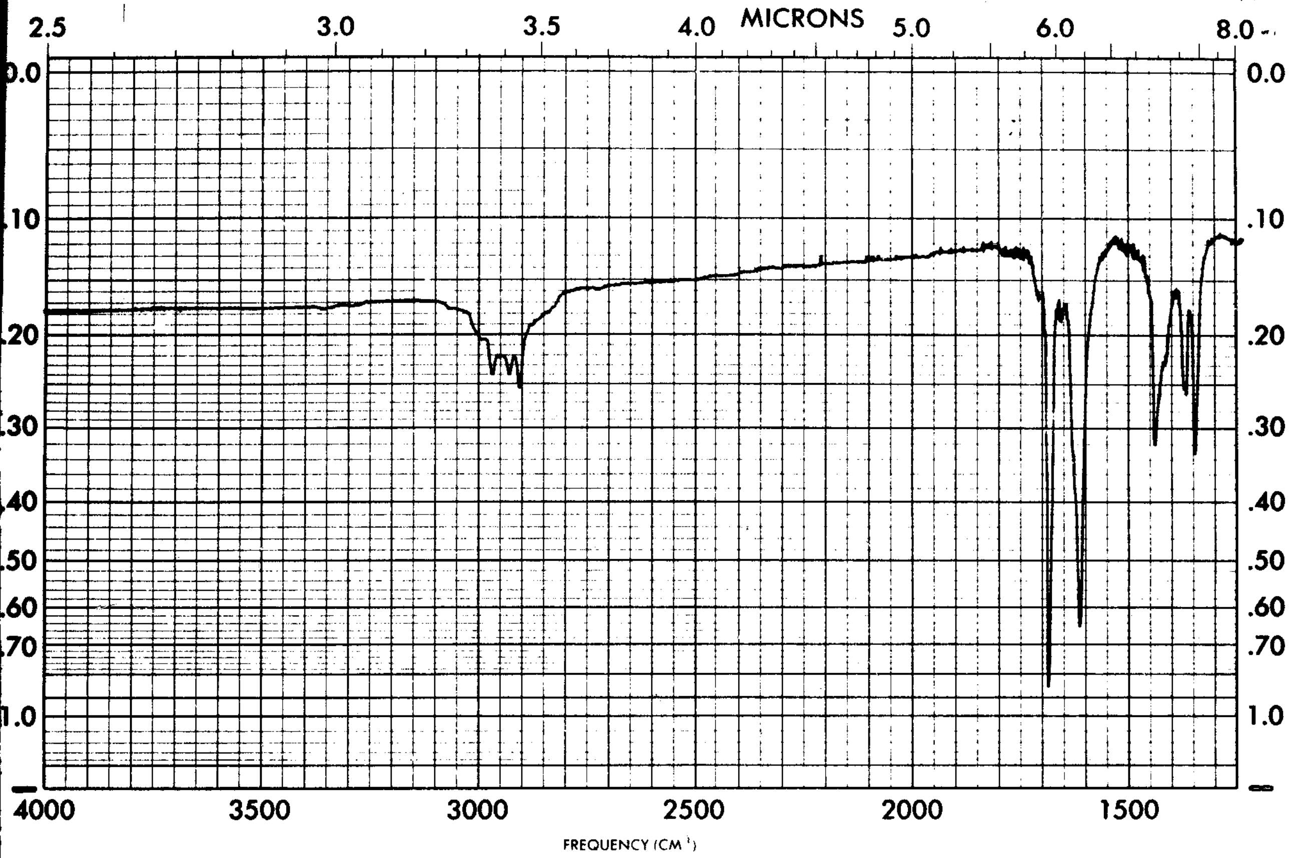
Sample :
Mesityl Oxide

Solvent: CCl4

Amplitude

Spectrum: 4

Integration: 5



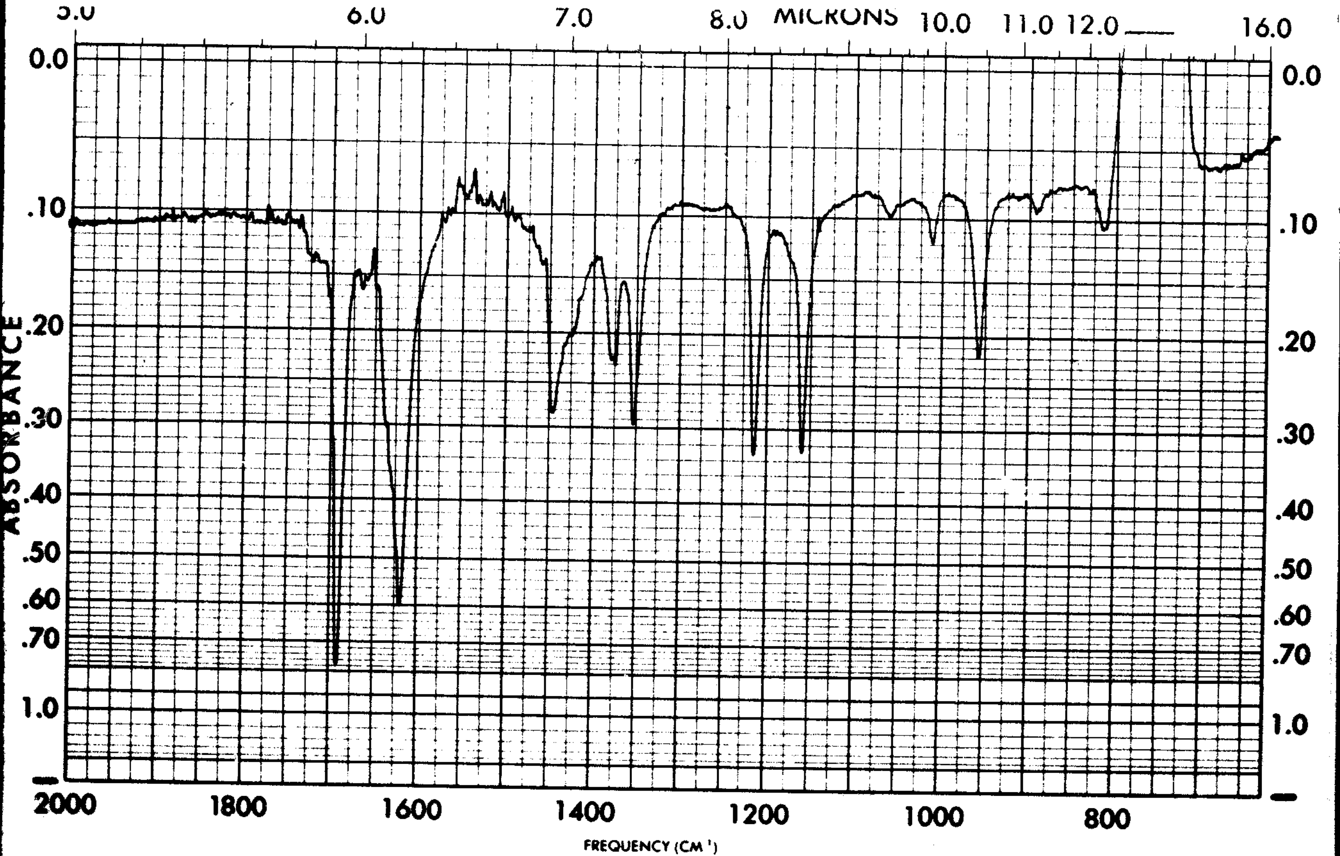
SAMPLE Mesityl Oxide
distilled 2nd Fraction
ORIGIN stock bottle
SOLVENT CCl_4

CURVE NO. 41
CONC.
CELL PATH .0972 mm
REFERENCE CCl_4 .100 mm

SCAN SPEED Fast
SLIT 25

OPERATOR A.W.
DATE 5/9/78

REMARKS see page 26



SAMPLE Mesityl Oxide distilled 2nd fraction

ORIGIN stock bottle

SOLVENT CCl_4

CURVE NO. 41

CONC.

CELL PATH .0972 mm

REFERENCE CCl_4 .100 mm

SCAN SPEED Fast

SLIT X

OPERATOR A-W

DATE 5/8/78

REMARKS See page 26

PR 18R (287-1033)

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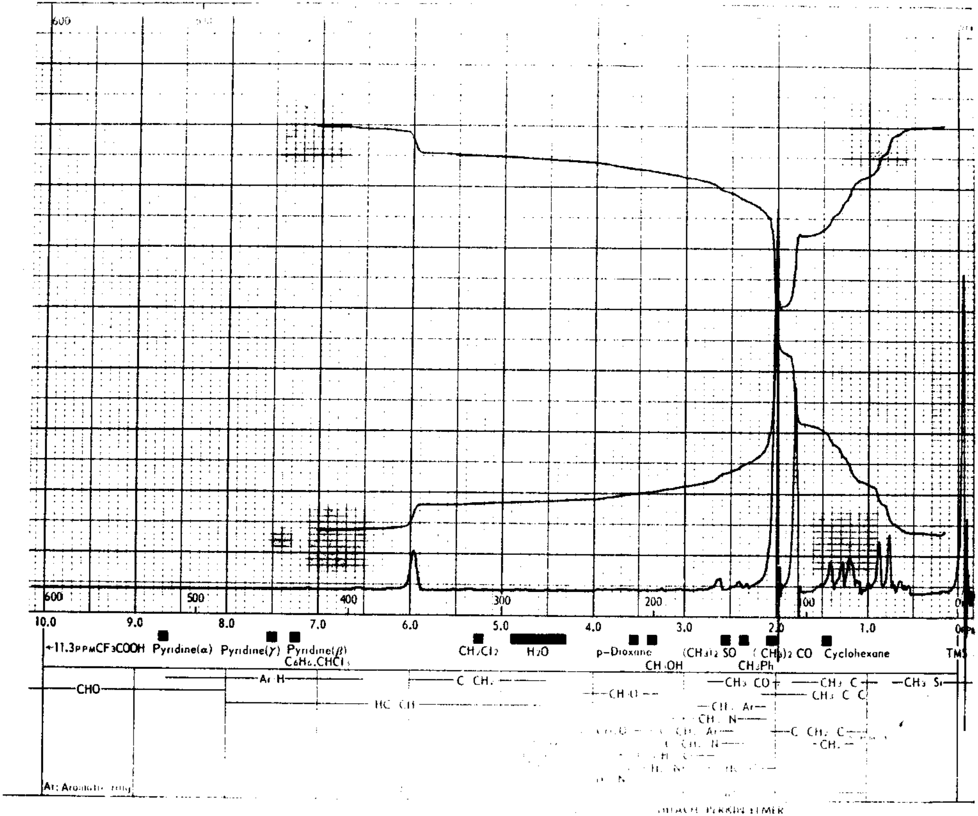
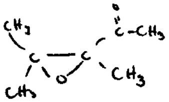


Spectrum No: 42

Sample:
Mesityl Oxide
Oxirane

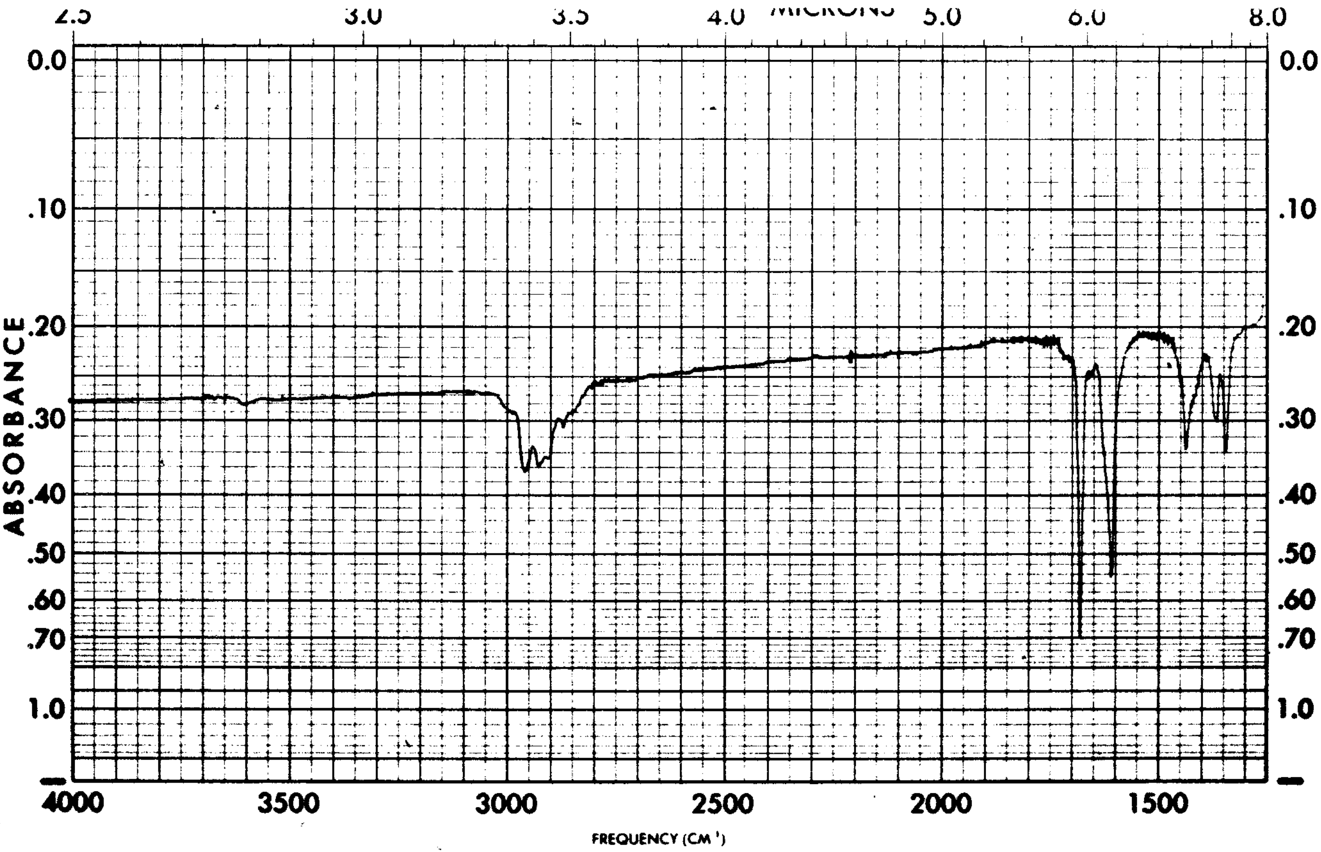


Solvent: CCl₄

Amplitude

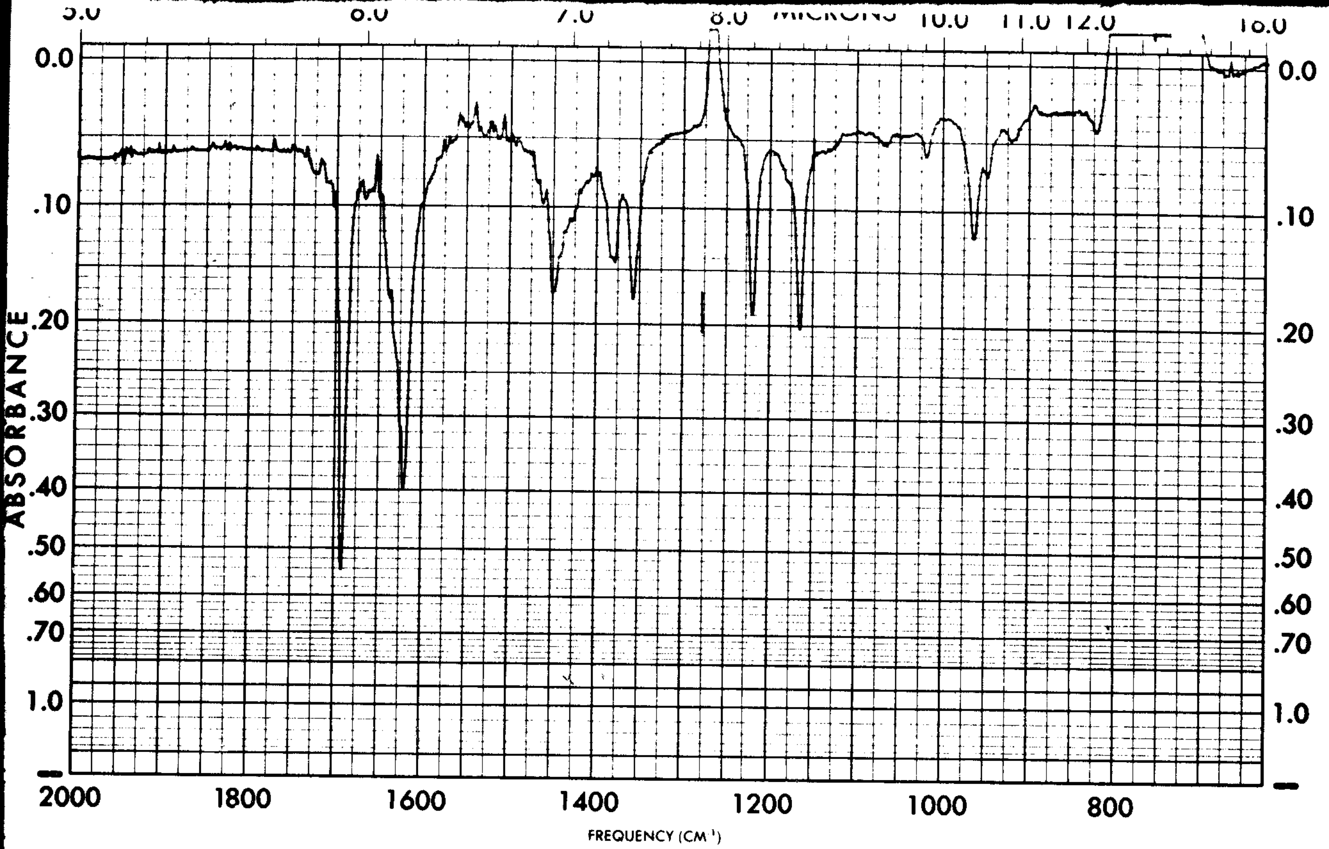
Spectrum: 4

Integration: 6



SAMPLE Mesityl Oxide Epoxide	CURVE NO. 43	SCAN SPEED Fast	OPERATOR AJS
	CONC.	SLIT X	DATE 5/8/78
ORIGIN Epoxide Synthesis	CELL PATH .097mm	REMARKS see page 26	
SOLVENT CCl4	REFERENCE CCl4 .100mm		

PR 10R (237-1032) PRINTED IN U.S.A. RECORDING CHARTS GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK



SAMPLE Mesityl oxide 'epoxide

ORIGIN epoxide synthesis

SOLVENT CCl_4

CURVE NO. 43

CONC.

CELL PATH .0972 mm

REFERENCE CCl_4 (.100 mm)

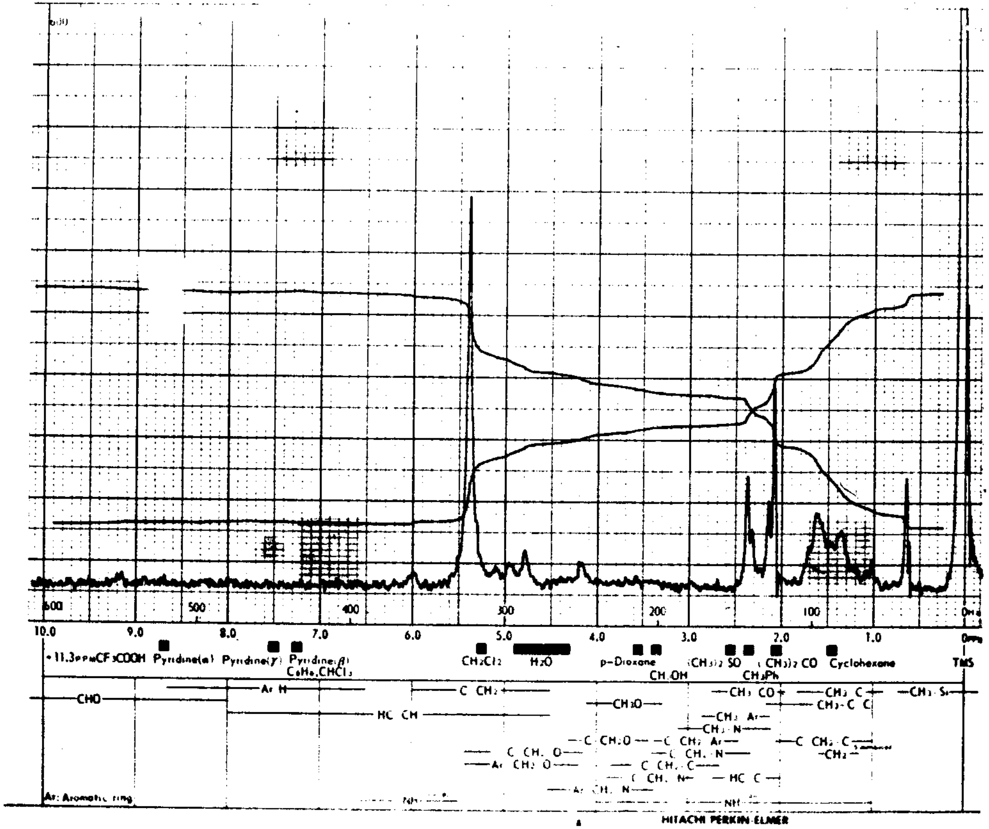
SCAN SPEED Fast

SLIT 2.5

OPERATOR A.W.

DATE 5/8/78

REMARKS See pgs. 26 + 25



Spectrum No: 44

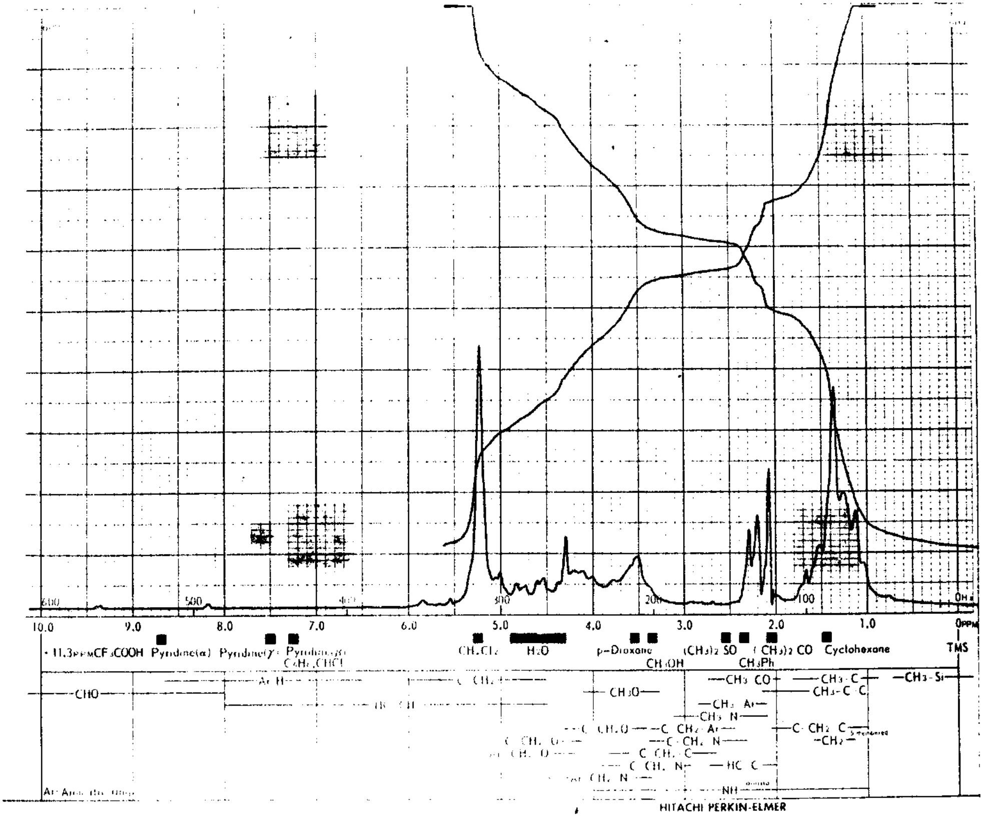
Sample :
Methyl Glyoxal

Solvent: Neat

Amplitude

Spectrum: 12

Integration: 11



Spectrum No:.45

Sample :

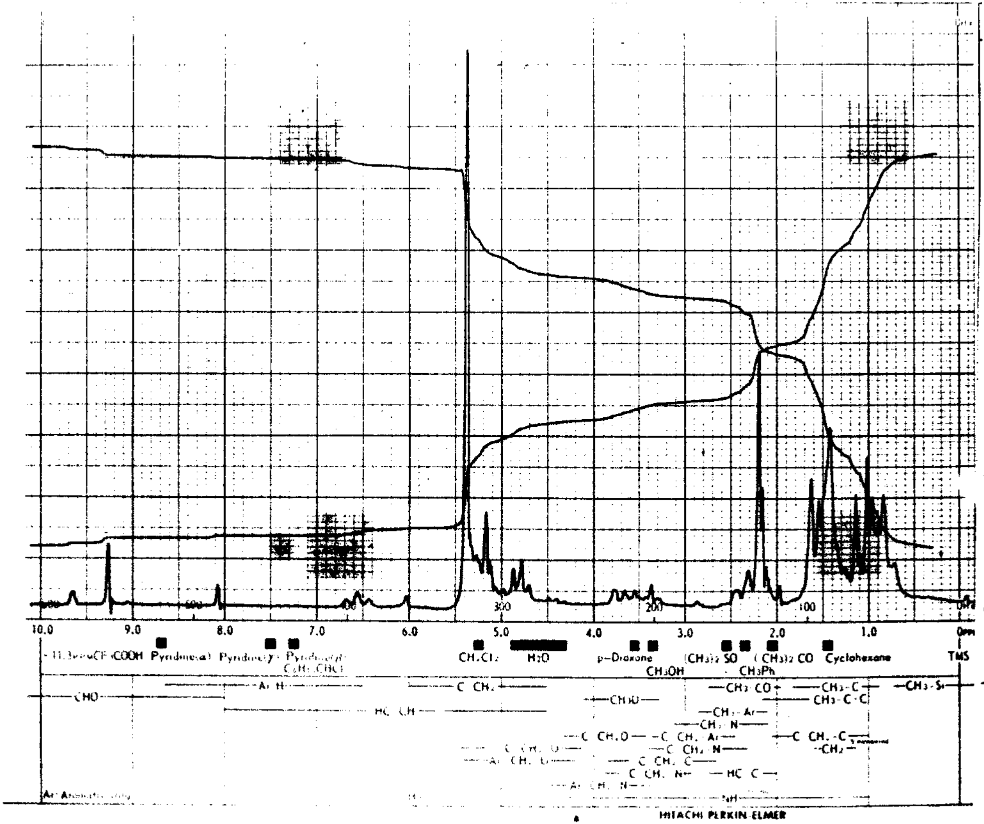
Methyl Glyoxal

Solvent: Neat

Amplitude

Spectrum: 3

Integration: 3



Spectrum No: 46

Sample:
Methyl Glyoxal

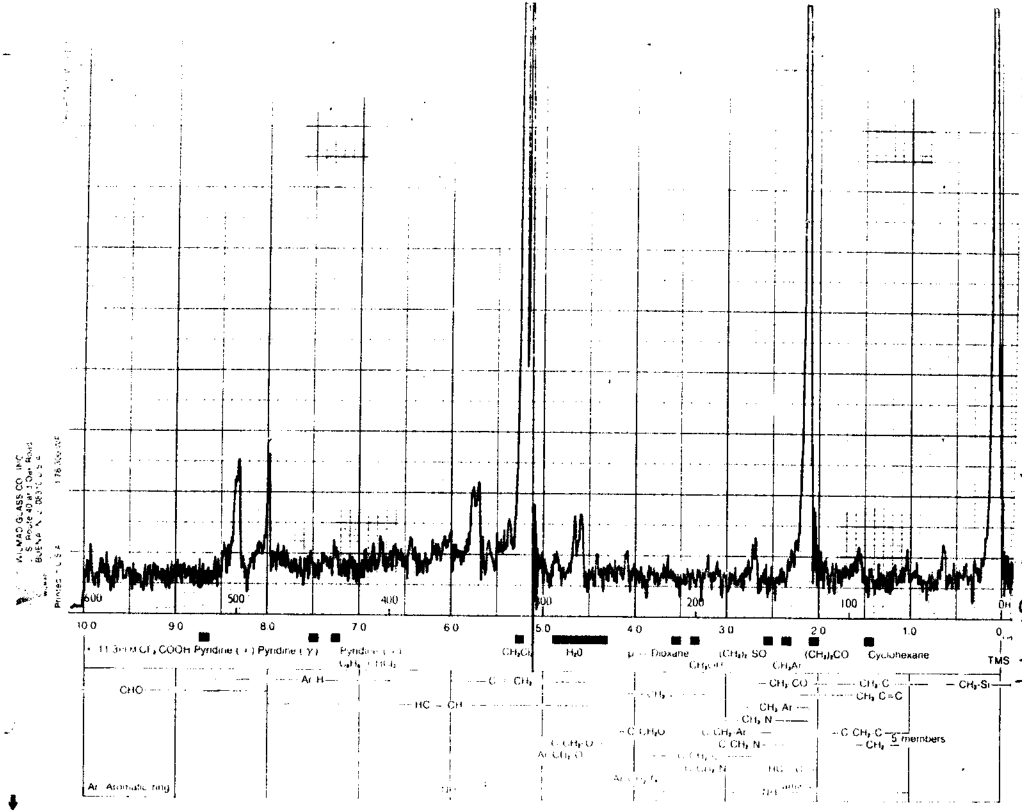
Solvent: Neat

Amplitude

Spectrum: 3

Integration: 2

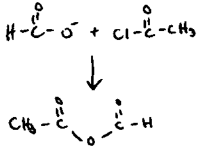
CHART NO. 435-7… PRINTED IN U.S.A.



WILMAD GLASS CO. INC
U.S. Route 40 at Oak Road
BUENA, N.J. 08310 U.S.A.
Printed in U.S.A.
176 WGNF

Spectrum No: 47

Sample :

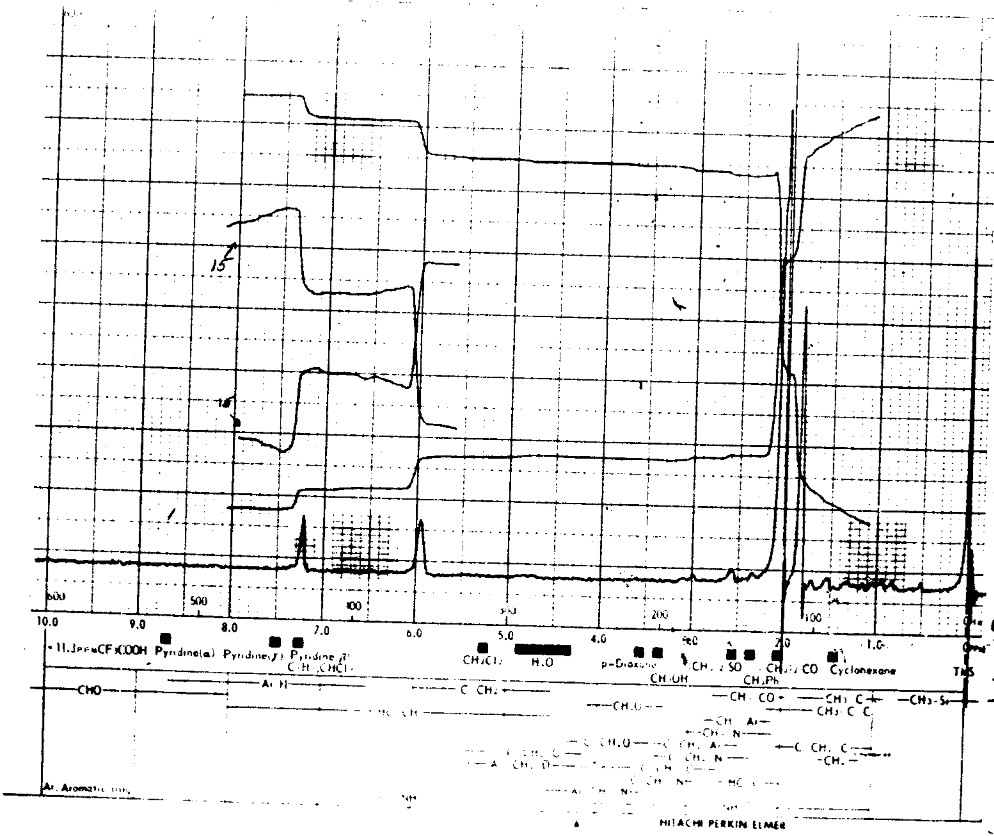

$H-\overset{O}{\overset{\|}{C}}-O^- + Cl-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-H$

Solvent: CCl4

Amplitude

Spectrum: 15

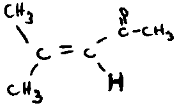
Integration: ___



Spectrum No: 48

Sample :

Mesityl Oxide

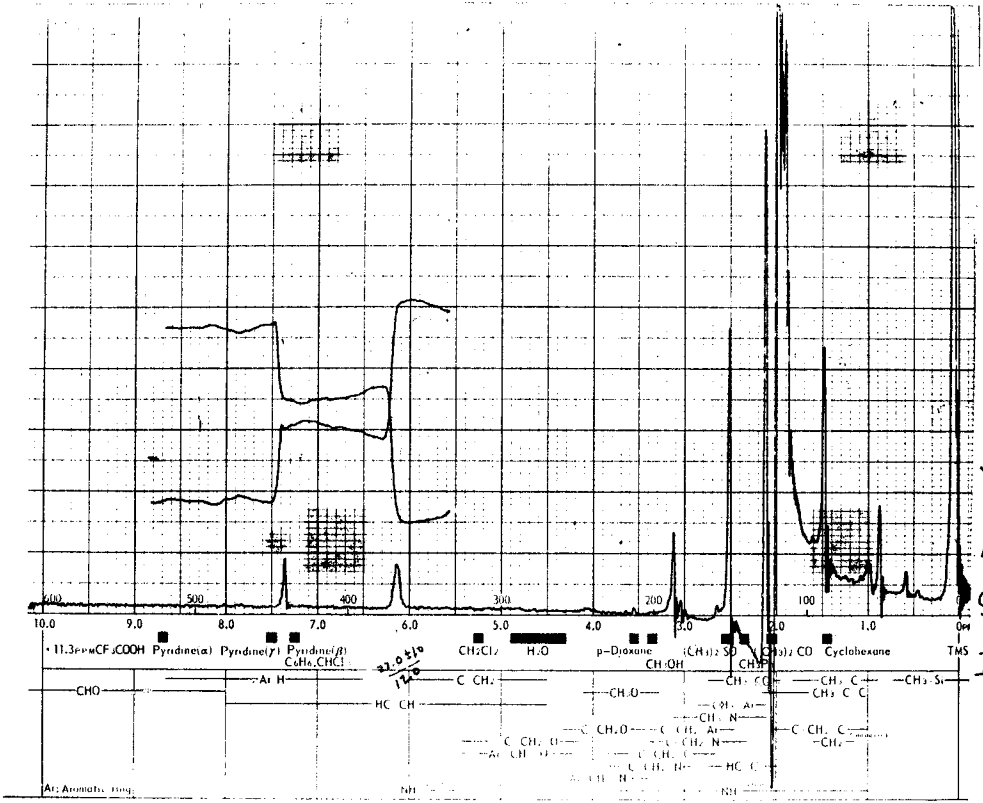


Solvent: CCl4

Amplitude

Spectrum: 9

Integration: 11

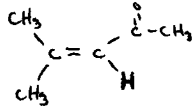


HITACHI PERKIN ELMER

CHART NO. 435-7204 PRINTED IN U.S.A

Spectrum No: 49

Sample:
Mesityl Oxide

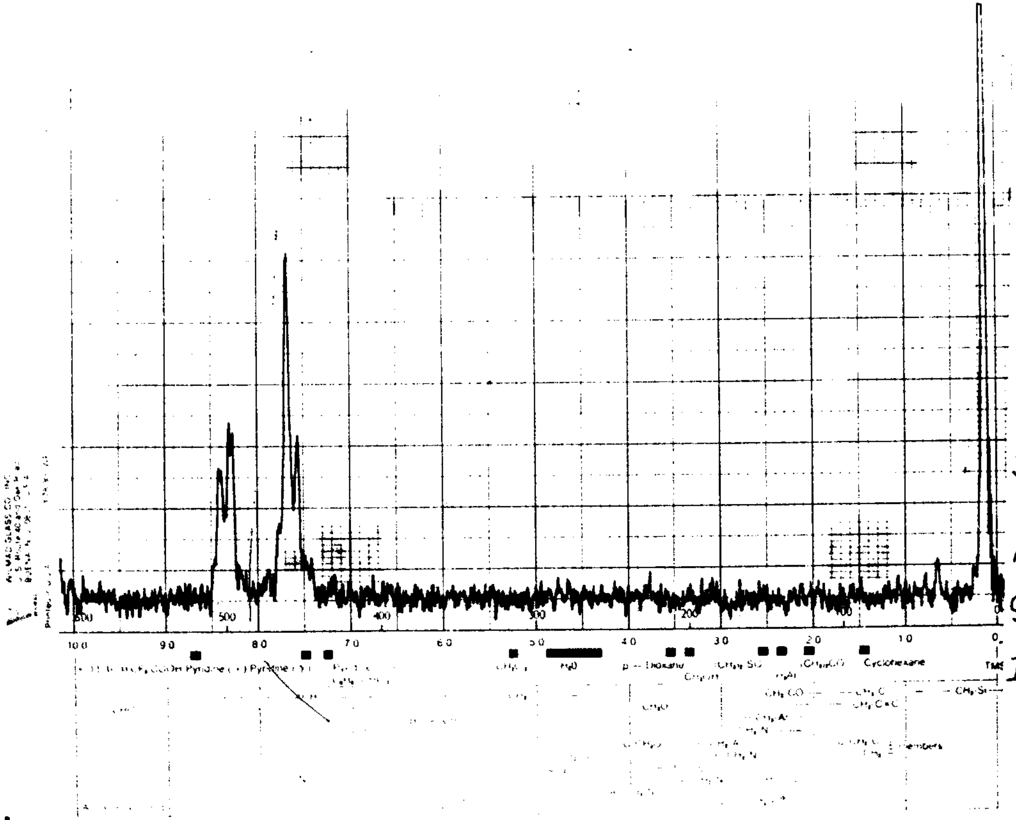


Solvent: CH_3CN

Amplitude

Spectrum: 8

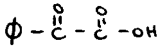
Integration: 15



Spectrum No: 50

Sample:

Phenyl Glyoxalic Acid

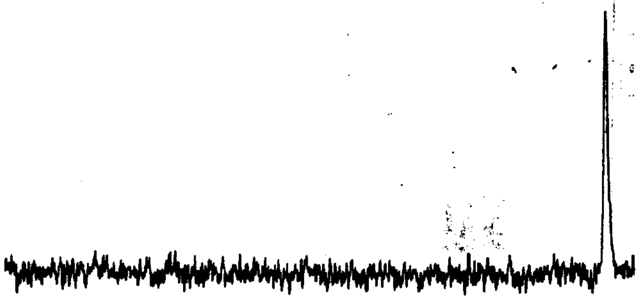

$\phi - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - OH$

Solvent: CCl₄

Amplitude

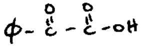
Spectrum: 15

Integration: ___



Spectrum No: 50

Sample:
Phenyl Glyoxalic
Acid



$\phi-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$

Solvent: CCl_4

Amplitude

Spectrum: 15

Integration: ___

10 - 15 PPM

END