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The effect of dimethyl sulfoxide and acetic acid on the decomposition of o-methoxy, w-diazo-acetophenone

Andrew Laurence Colb
Union College - Schenectady, NY

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THE EFFECT OF DIMETHYL SULFOXIDE
AND ACETIC ACID ON THE DECOMPOSITION
OF o-METHOXY, w-DIAZO-ACETOPHENONE

by

ANDREW LAURENCE COLB UC 1967


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Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

JUNE 1967



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This Thesis

Submitted by

Andrew Laurence Colb

Andrew Laurence Colb

to the

Department of Chemistry of Union College

in Partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

Donald E. Sheffer

DEDICATION

To Howard E. Sheffer, Ph.D., without
whose guidance and suggestions this paper
would not have been possible.

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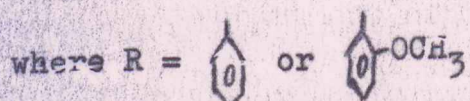
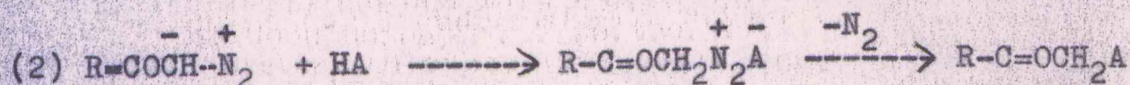
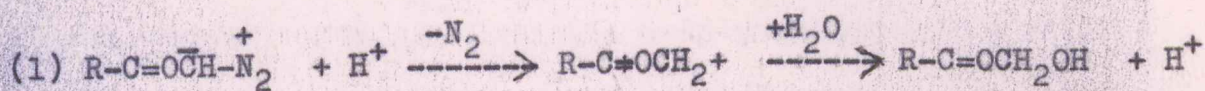
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THEORY

The acid-induced decomposition of o-methoxy, w-diazo, acetophenone might proceed by either of two pathways. Huisgen(1) postulated that the mechanism was either "catalytic" (equation 1) or "stoichiometric," (equation 2) and the differences in the mechanisms were directly related to acid concentration, nucleophilic power of the anion of the acid, and the ionic strength of the medium.



If the reaction medium contains only weakly nucleophilic species such as the bisulfate ion, upon loss of nitrogen caused by protonation of the nitrogen-bearing carbon, the nucleophilic character of the ortho ring substituent becomes important since it can effectively compete with the other nucleophiles at the carbonium ion. If a "catalytic" type mechanism predominates, the reaction may yield some cyclic product. Likewise, if the medium is sufficiently polar to effectively solvate the carbonium ion, the carbonium ion will be less

discriminatory toward nucleophilic strength and a cyclic product will be formed.

In the slightly polar medium of concentrated sulfuric or glacial acetic acid in absolute ether, the closely associated ion pair strongly favors attack only by the acidic anion to form, even with an ortho ring substituent, a straight chain product.

Sheffer(2) showed that by varying nucleophilicity both a straight chain and a six-membered ring were formed. He observed, however, that under the same conditions, o-methoxy, w-diazo acetophenone reacts only to form the cyclic ether coumaranone (benzoburanone) with no straight chain products observed.

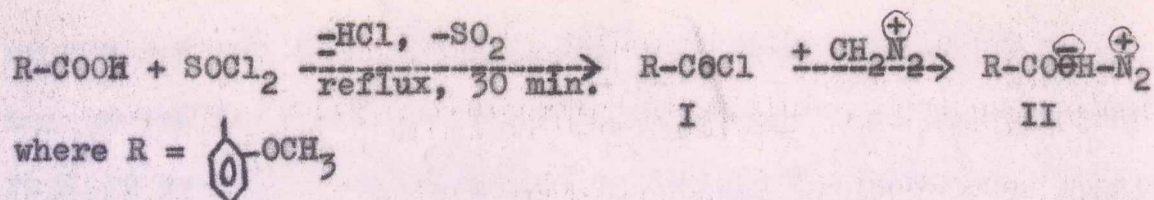
Sheffer's(2) reactions with o-methoxy, w-diazo acetophenone were carried out in ether, a non-polar medium. The aim of this researcher's study was to determine the reaction course for the decomposition of o-methoxy, w-diazo acetophenone, in a highly polar, slightly nucleophilic medium containing nucleophilic acetate ion, to form either coumaranone or a straight chain product.

EXPERIMENTAL

Bose and Yates(3) demonstrated that, in an aqueous, acidic medium, o-methoxy, w-diazo acetophenone(II) decomposes to form only cyclic coumaranone(IX). Since an aqueous reaction would not permit the formation of a straight chain product, dimethyl sulfoxide, a highly polar compound with no ionizable protons, was chosen as the solvent for all the reactions studied.

Two distinct, but related, reactions were carried out in DMSO (as dimethyl sulfoxide will be henceforth abbreviated). First a Lewis acid, boron trifluoride was reacted in DMSO with II. The acid for the second reaction was acetic acid. The acetic acid reaction was also carried out in DMSO. One of the sidelights of the boron trifluoride reaction was to determine if the DMSO would, itself, cause a reaction with II, thereby destroying its use as a solvent. Since boron trifluoride has no nucleophilic group, the only possible nucleophilic species are the methoxy oxygen and the sulfoxide oxygen. If products appeared which contained evidence of DMSO interaction, e.g. the formation of a stable $-\text{CH}_2-\text{O}-\overset{+}{\text{S}}(\text{CH}_3)_2$ grouping or the formation of coumamanone before the water was added, DMSO would have been an ineffective solvent.

Of all the reactants in the two major reactions, only the diazoketone(II) had to be synthesized; the others were readily available. That compound was synthesized in two steps from o-methoxy benzoic acid according to the following sequence:



About 0.30 moles of acid chloride (33 ml.) were already available, having been prepared by this researcher for a previous experiment. This brownish liquid was redistilled in vacuo at 142°C at 17mm-Hg. The boiling point of the pale-yellow, pungent-smelling distillate was in accordance with the literature value.⁽⁴⁾ Of the 0.25 moles of I remaining after distillation, 0.15 moles (20 ml.) were set aside for reaction with diazomethane which was then prepared, in situ, from the method suggested by Sheffer.⁽⁵⁾

An efficient condenser (at least 60 cm. long) is fitted with an adapter to which is sealed a length of 9 mm tubing extending nearly to the bottom of a five-liter, round-bottomed flask which serves as a distillation receiver. The receiver should be closed with a two-holed cork, with drying tube attached if anhydrous diazomethane is desired. The receiver is placed in a well mixed ice--salt bath and sufficient dry ether (about 100 ml.) is added to cover the tip of the adapter tube.

In a five-liter, round-bottom flask are placed three liters of U. S. P. grade ether, 232 ml. of diethylene glycol monoethyl ether, and 336 ml. of 30% sodium hydroxide solution. This mixture is cooled to 0°C before starting. When this temperature is reached, 72 gms. of bis(N-methyl, N-nitroso) terephthalimide are added in one portion.

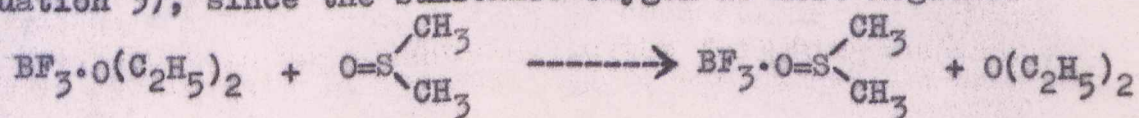
The flask is immediately transferred to a heating mantle and connected by a gooseneck to the condenser. The reaction mixture is heated just sufficiently to distill about two liters of ether in two hours. An 80% yield is average.

After the reaction mixture had turned white, the heating mantle was turned off, ice was added to keep the distillate

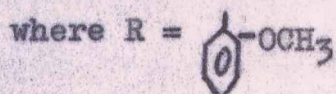
at 0°C and for five minutes, the 0.15 moles of acid chloride was poured into the ethereal diazomethane. Nitrogen gas was rapidly evolved. The reaction mixture was allowed to stand overnight and to return to room temperature.

REACTANTS	moles	gms.	ml.	mol. wt.	b.p.
o-methoxy, benzoyl chloride	0.15	25.5	20.0	170.6	145 ¹⁷
diazomethane	0.45	gas		42.0	-23
PRODUCTS	expected yield, gms.			actual yield	
o-methoxy, w-diazo, acetophenone	29.8			did not isolate	

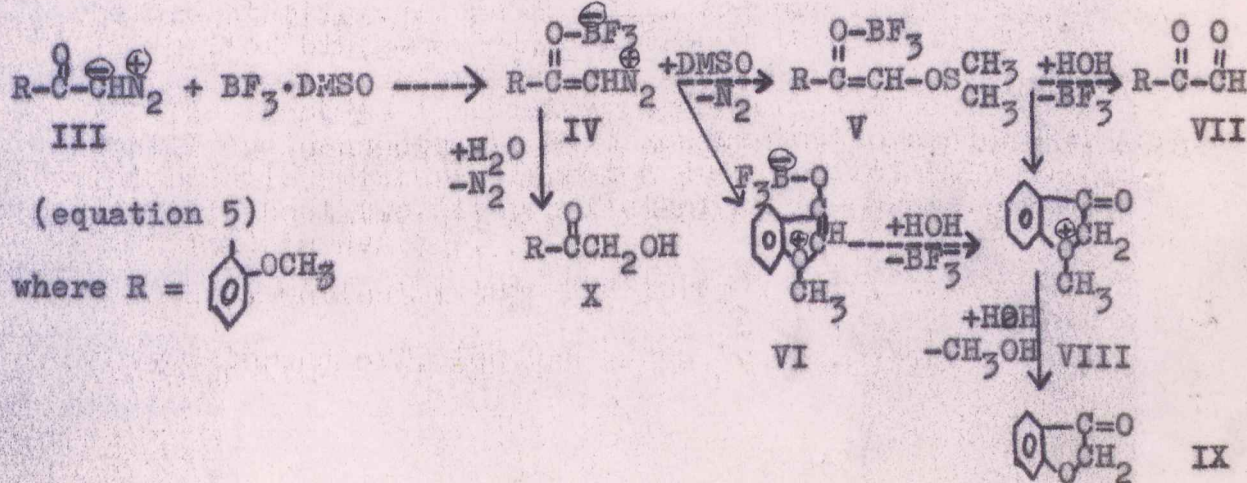
After the evolution of nitrogen had stopped, the ether solution was first filtered, to remove polyethylenes formed from excess diazomethane, and then evaporated, in vacuo, heating with a mantle the flask containing the diazoketone only sufficiently to compensate for the heat loss due to ether evaporation. To the viscous, dark-orange diazoketone, 0.2 moles (14 ml.) of DMSO were added. Likewise 0.2 moles of DMSO were added to 0.075 moles (8.88 ml.) of freshly distilled boron trifluoride etherate. The purpose of this addition of excess DMSO was the reduction of the concentration of available ether, whose non-polar effects might alter or affect the reaction course. Upon addition of the DMSO to the boron trifluoride, a violent reaction ensued, considerably heating the reaction vessel. The reaction was probably a substitution of the ether adduct by the DMSO (equation 3), since the sulfoxide oxygen is more negative



(Lewis basic) than the ether oxygen. Whether or not the newly formed coordination complex would be so stable as to be unreactive was not known at the time. However, the reaction was continued. That boron trifluoride was reacted in less than the theoretical molar proportions was a consequence of both the instability of the diazoketone and the reactivity of the fluorines. If some of the diazoketone had indeed decomposed, then the excess of boron trifluoride would favor a fluorine for hydrogen substitution in the ensuing reaction to form unwanted by products. (equation 4)



With the DMSO solutions prepared and chilled to 0°C, the diazoketone was added to the boron trifluoride from a dropping funnel over the course of one hour. Nitrogen was evolved as each drop of diazoketone reacted. A reaction mechanism, as postulated by Sheffer, was modified to account for the DMSO solvation effects. (equation 5)



If DMSO plays no role in the reaction intermediates except as a solvent, the reaction will proceed from IV to X with the formation of the acyl alcohol. If DMSO reacts to substitute for the nitrogen by either an S_N1 -type mechanism or a concerted S_N2 -type mechanism, the the reaction will proceed to intermediate V. Whether the glyoxal or oxonium intermediate is then formed on addition of water depends upon the nucleophilic strength of the methoxy oxygen and upon the exact role of DMSO. If DMSO actually forms the carbon-oxygen bond, then phenyl glyoxal is the probable product. If, however, intermediate V is simply a DMSO solvated carbonium, it will immediately upon formation react to form the oxonium intermediate VIII which will yield coumaranone upon hydrolysis. A third course of reaction might be dependent upon the formation of VI as an intermediate as the nitrogen leaves. By hydrolysis with water of the boron trifluoride complex at the oxygen atom and of the methyl group at the oxonium ion, coumaranone would be formed, via intermediate VIII.

When water, in excess, was added to the reaction flask after a day had elapsed to allow the reaction to go to completion, a redish oil separated. Ether was added to affect a clean separation and extraction. The red layer dissolved in the ether. The ether layer was first washed twice with water and then washed three times with sodium bicarbonate(5%) to neutralize any remaining acid. The water layers were returned to the original water solution; the bicarbonate layers were

discarded. The ether was again washed with water and the wash discarded. Evaporation of the ether left orange and red crystals of indeterminate melting point. When recrystallized from benzene, a sharp melting point of 98°-99°C was obtained, and the product was identified as coumaranone by comparison to a known infrared spectrum. The original water layer was washed with ether, which, when evaporated, showed crystals similar to those in the original ether layer. The water layer was then evaporated in vacuo. Neither the distillate nor the residue produced a precipitate when treated with 2,4-dinitrophenylhydrazine.

At this time it was realized that one of the reasons for the lack of the appearance of compounds other than coumaranone might be the interference of any excess DMSO. DMSO is soluble in water, ethanol, ether, acetone, and ethyl acetate. Phenyl glyoxal is soluble in water, alcohol, ether and chloroform. There were no literature references on solubilities or derivatives of the o-methoxy substituted phenylglyoxal.

Since not all of the diazoketone had been used in the initial reaction, the reaction was repeated under the same conditions. The purpose of this was to employ a different separation scheme. While the reaction products were extracted with ether and washed with sodium bicarbonate, it was observed that, in this experiment, the bicarbonate layer became redish. When acid was added to a small aliquot, a yellow color reappeared, but it appeared paler than the yellow of the original reaction mixture.

In the determination of the water layer, a continuous extraction system was constructed and run for about thirty hours. At the end of that time, the ether layer of the collected extract was dark orange. After being dried with anhydrous sodium sulfate, the ether was evaporated. A yellow liquid and yellow specks of solid remained.

On the vapor pressure chromatograph, a known solution of coumaranone 1% in ether was tested to determine retention times. The ether peak appeared after 1.2 boxes, the coumaranone peak after 9.0 boxes. All VPC samples, including the known, were run in 50 μ portions, with amplification at 1x, helium pressure at 10 psi, and column temperature at 220°C. The ether concentrate (not the extract, but the original ether layer) yielded two peaks corresponding to ether and coumaranone at 1.1 and 9.0 boxes, respectively. The ether extract from the water layer showed only the ether peak at 1.1 boxes. An NMR of the ether extract showed no phenyl-group hydrogens, but yielded two peaks slightly downfield from TMS. The peaks were assumed to be ether. A standard coumaranone sample in CHCl_3 (chloroform) was tested on the Perkin-Elmer infrared spectrophotometer. The IR confirmed the previous results obtained with the VPC and NMR.

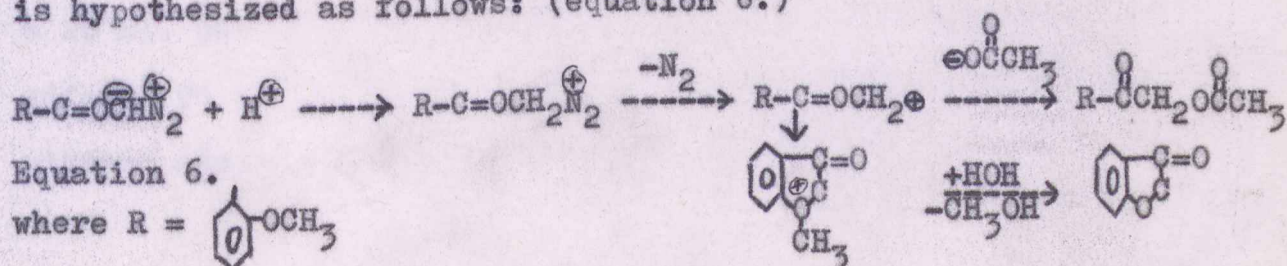
The water layer remaining after the continuous extraction was tested with 2,4 DNP. No precipitate resulted, and glyoxal formation seemed to be absent in the reaction. The analysis of spectral data will be found in the spectra section of this paper.

The second major reaction, the decomposition of o-methoxy, w-diazo acetophenone with acetic acid in DMSO was performed twice. In the first reaction, the 0.1 mole of acid chloride remaining from the boron trifluoride-initiated decomposition was reacted with about 0.32 moles of diazomethane prepared as before with the following changes in reactant quantities and reaction conditions.

2000 ml. flask
1200 ml. ether
180 ml. diethylene glycol.
monoethyl ether

240 ml. 30% NaOH
72 gms. bis(N-methyl,
N-nitroso) terephthalimide

The theoretical yield of diazomethane is 0.4 moles and an expected yield of 0.32 moles (80%) was assumed for the reaction molar ratio. The theoretical yield of diazoketone was ~~is~~ then 0.1 mole of 16.8 gms. It was not isolated, but rather reacted immediately with glacial acetic acid. As in the decomposition with boron trifluoride, the diazoketone and glacial acetic acid were both dissolved in 0.2 moles of DMSO. Heat was evolved upon addition of DMSO to the acetic acid which was present in a molar ratio of 4:1 with the diazoketone. The purpose of the large molar ration was to provide the optimum conditions for nucleophilic attack of the acetate ion, i.e. its presence in high concentrations. The reaction mechanism is hypothesized as follows: (equation 6.)



As the acetic acid was added to the diazoketone, nitrogen was evolved as previously observed. The nitrogen was collected, and its volume measured. The collection apparatus consisted of two, 1000 ml. graduated cylinders filled with water and inverted in a large beaker with water covering only the bottom of the cylinders. A rubber hose from the reaction flask was placed half-way up a cylinder. As one cylinder filled, the hose was quickly transferred to the other cylinder. At the end of a day, the following measurements had been taken:

	Cylinder 1	Cylinder 2
volume of cylinder, initial	10 ml.	40 ml.
volume of cylinder, final	970 ml.	480 ml.
volume of gas collected	960 ml.	440 ml.

The reaction flask volume was about 500 ml, of which 100 ml was reaction liquid, leaving 400 ml. for gas. The vapor pressure of water at room temperature, the solubility of nitrogen in water at room temperature, and the solubility of nitrogen in the reaction mixture were all neglected in the final determination. The total volume of gas collected was about 1800 ml. The volume of one mole of any gas (ideal) at STP is 22.4 liters; the volume for 0.1 mole is 2.24 liters. The yield is therefore $\frac{(1800)}{2240} \times 100 = 80\%$.

After the completion of the reaction, 70 ml. of liquid remained in the flask. This was divided into a 50 ml. and a 20 ml. portion. To the 50 ml. aliquot, 100 ml of water was added. To the 20 ml. aliquot, 20 ml. of ethanol was added, the mixture stoppered and put aside.

In the aliquot to which water was added, a yellow solid immediately precipitated, leaving a yellow filtrate. This system was then filtered, weighed, and tested on the melting point apparatus. The melting range was 69°-78°C. The wet weight was 11.7 gms. A wet weight of 1.5 gms of the precipitate was recrystallized from ethanol-water with a subsequent melting point of 83°-85°C. This was recrystallized again from hot, absolute ethanol when it was realized that the precipitate was only slightly soluble in cold ethanol or methanol, but very soluble in their hot solutions. Three crops of crystals were obtained. The first had a melting range of 94-96°C, the second 95°-97°C, and the third 96.5-98°C.

The remainder of the precipitate was dried and recrystallized from methanol. Table 1. shows the recrystallization data.

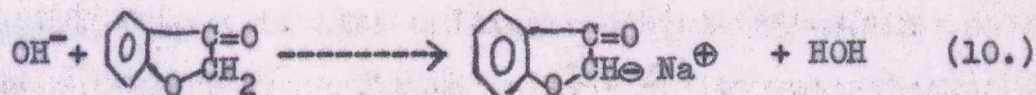
Crop #	melting range	weight
1	94-95°C	0.8 gm.
2	92-94°C	0.7 gm.
3	94.5-96°C	0.31 gm.

TABLE 1.

The second crop of the 1.5 gm. aliquot (m.p. 95-97°C) was recrystallized from methanol and an NMR spectra taken. The singlet at 276 cps at sweep width 1000 cps (2.3 ppm) unmistakably represents the $-O-CH_2-\overset{!}{C}=O$ hydrogens, the only hydrogens in the compound coumaranone aside from the ring hydrogens. At 3.5-4.0 cps the aromatic hydrogen splitting lines appeared.

From their reaction to dilute sodium hydroxide (5%) by turning a deep red, all three crops were determined to be coumaranone, in various stages of purity. This hydroxide

reaction, which is hypothesized as follows (equation 10.), is related to the coupling of coumaranone at the furanone ring hydrogens with organic bases to form dyes.



This reaction proved to be most useful for rapid determination of the presence of coumaranone, since the red hue of the organic anion is very intense.

The yellow mother liquor was extracted three times with ether. The ether layer was then extracted three times with bicarbonate solution (5%). The bicarbonate extract was acidified, reextracted three times with ether, dried, and evaporated. A brown tar remained, smelling strongly of acetic acid. The ether layer was then extracted with sodium hydroxide. Subsequent evaporation of the remaining ether layer led to brown-orange crystals of melting range 41°-65°C. To the crystals, two drops of methanol were added and the solution decanted from the remaining crystals which were clear. The crystals were rinsed with ether and melted at 65.5°-66°C. An IR spectrum was taken and it proved to be identical with coumaranone! The discrepancy of the melting points is inexplicable.

The hydroxide extract was acidified and ^Xextracted again with ether. The ether was then dried and evaporated. A dark brown liquid and solid remained. This product was placed on an alumina-packed chromatogram column. Benzene was the

initial elutant. The solvent was varied in ionic strength from the original benzene to water while twenty-five samples were taken. The following table (table 2.) describes the results. Infrared spectra were run on the contents of the


<u>Bottle #</u>	<u>Solvent</u>	<u>Color of eluted portion</u>
1-5	benzene	clear
6-8	50% benzene	
	50% ethyl acetate	pale yellow
9-15	ethyl acetate	yellow
16-18	ethyl acetate + acetone	yellow
19-24	absolute ethanol	dark yellow
25	water	red

(Table 2.)

first and last bottles. Although the colors were different, the spectra were identical. Both spectra corresponded exactly to the standard spectra of coumaranone.

Since the effects of the excess acetate ion on the oxonium intermediate had not been studied in the first reaction, another sample of o-methoxy, w-diazo acetophenone was prepared and decomposed with acetic acid in a 4:1 molar ratio. Two-tenths moles of acid chloride, prepared as previously described, were added to about 0.6 moles of diazomethane, prepared in situ. Acetic acid, 0.8 moles (48 ml), in 30 ml of DMSO were then added to the resulting diazoketone in DMSO. The reaction was allowed to stand for 24 hours before the excess acetic acid was evaporated in vacuo at 32-35°C. About 30 ml. of DMSO was then evaporated from the reaction mixture at 79^a-81°C (16mm-Hg). The remaining liquid was divided into two equal aliquots. To the first aliquot, water was added immediately. Both yellow and red precipitates were formed. The second aliquot was allowed to

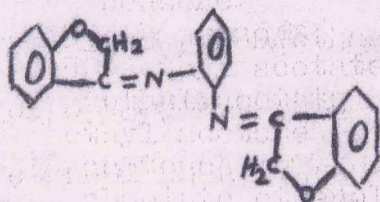
stand, stoppered, for three days. At the end of that time, red crystals were observed in the flask.

The crystals from the anhydrous mixture were filtered and recrystallized from methanol. They melted sharply at 97°C, and their IR spectrum was identical to that of coumaranone. Since water had not been added, there was strong evidence that the oxonium ion was indeed an intermediate and that solvation was the only DMSO reaction at the carbonium-type ion. That is, a DMSO reaction intermediate -C(=O)CH₂-O-S(CH₃)₂ does not form. The unstable oxonium ion is probably immediately cleaved by the acetate ions in solution to form coumaranone and methyl acetate.

To the mother liquor remaining after filtration of the anhydrous layer, water was added slowly. Fine, red crystals appeared immediately and, as more water was added, the solution started to turn yellow. By use of a buret, water was added just to the point of color change. The solution was again filtered, and the red crystals recrystallized from methanol; their spectra showed them to be coumaranone. Water was then added, in excess, to form a yellow solution. By the same process of filtration and recrystallization, the character of the yellow crystals was also determined as coumaranone.

By extraction procedures and use of the IR spectrophotometer, the two different types of crystals in the first aliquot were also analyzed. Both types of crystals were coumaranone. The use of ortho-phenylenediamine for use in making derivatives

was considered, since it is generally specific to α -diketones, a possible reaction product. However, it was not used for two reasons. First, no o-methoxy phenylglyoxal was available with which to make a standard derivative. Since coumaranone also has a keto group, two moles of it might react with the amine to form



The feasibility of separation of the two possible derivatives either by extraction with base of the coumaranone-coupled product or by column chromatographic methods was not studied, but has distinct possibilities of success.

SPECTRAL ANALYSIS

The infrared spectra of coumaranone proved invaluable in the qualitative determination of reaction products. Determination was made by comparison of the spectrum of the unknown to the spectrum of the known. The major coumaranone peaks were assigned as follows (Table 3.) (Graphs 1a, 1b).

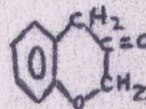
<u>Frequency (cm⁻¹)</u>	<u>Assignment</u>
3000	=C-H stretch
1720	C=O upward shift in frequency caused by loss of coplanarity because of ortho substitution
1612	C=C stretch
1460-1480	C=C stretch
1320	Ar-O-C
1295	C=O stretch, C-H out of plane deformation
1180	C=O stretch C-H out of plane deformation
1140	C=O stretch C-H out of plane deformation
1100	C-H out of plane deformation
1015	not assigned
995	not assigned
837	not assigned

Vibrations at 770-735 cm⁻¹ which are expected for vibrations on an ortho-substituted ring were observed in only some of the spectra studied. Their absence has not been accounted for.

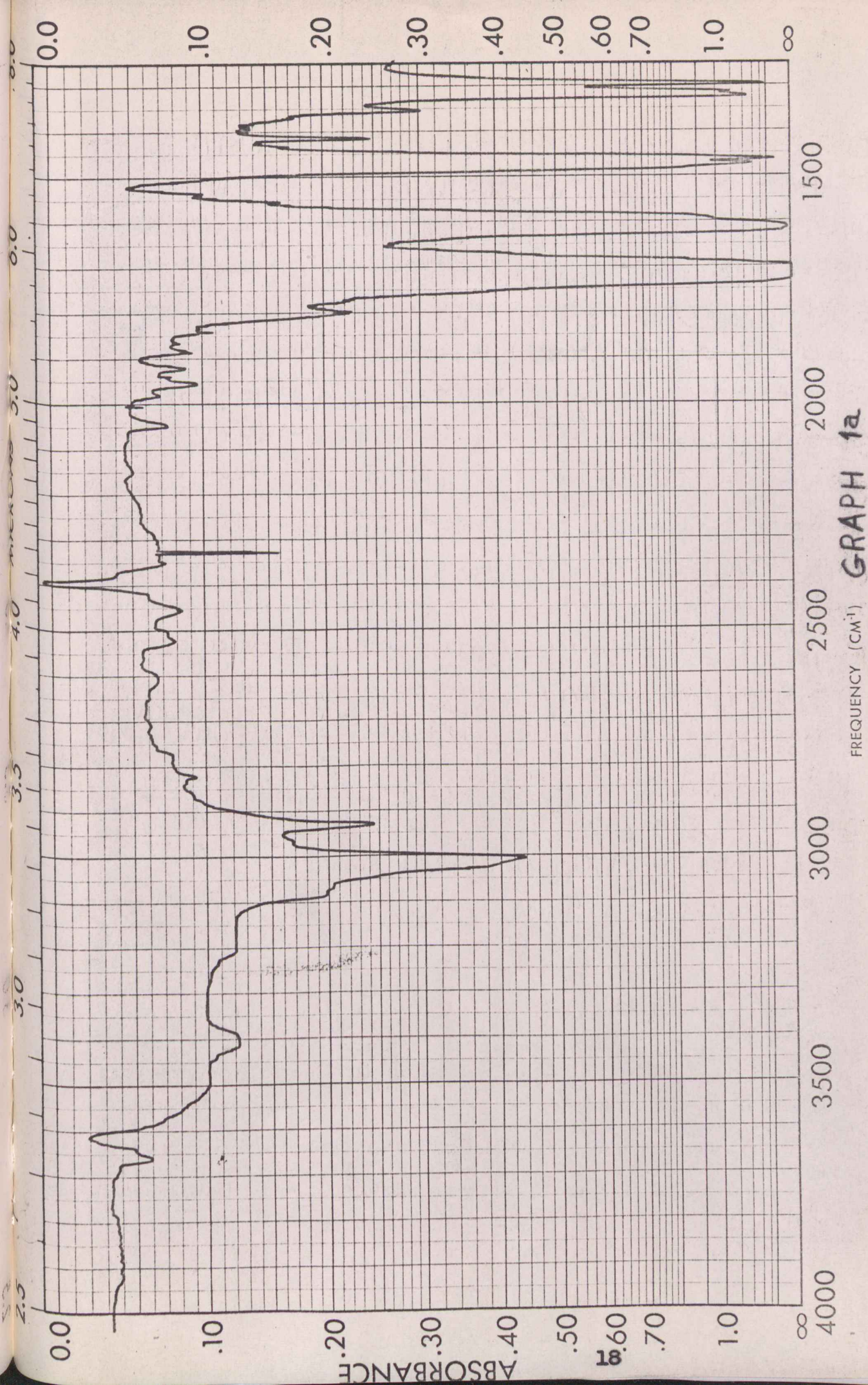
* * *

Using a sweep width of 1000 cps, the NMR spectrum showed the expected aromatic hydrogen splitting in the region of 3.4-3.9 ppm. A singlet was observed at 2.3 ppm (276 cps) (Graph 2).

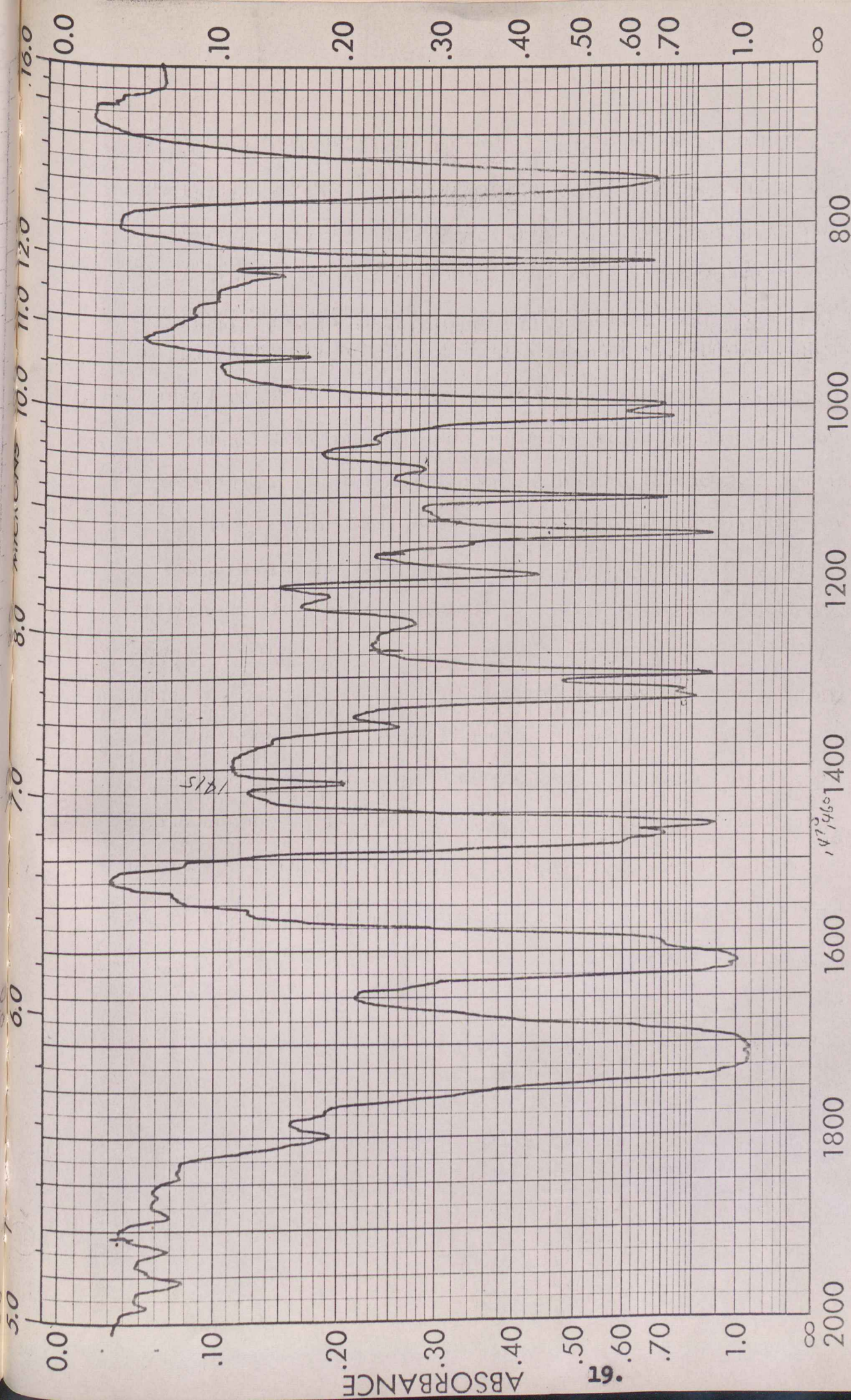
Coumaranone has only two equivalent hydrogens besides the aromatic ring hydrogens. The assignment for the representative singlet was taken from Sheffer⁽²⁾. He reported a tau value of 5.68 for the peak of -COCH₂O- in chromanone-3,



corresponds with the value of 276 cps at sweep width 1000 cps.



SAMPLE <u>Coumaranone</u>	CURVE NO. _____	SCAN SPEED <u>12.5</u>	OPERATOR <u>clb</u>
ORIGIN _____	CONC. _____	SLIT <u>2</u>	DATE <u>11/25/66</u>
SOLVENT <u>CHCl₃</u>	CELL PATH _____	REMARKS _____	
10%	REFERENCE _____		



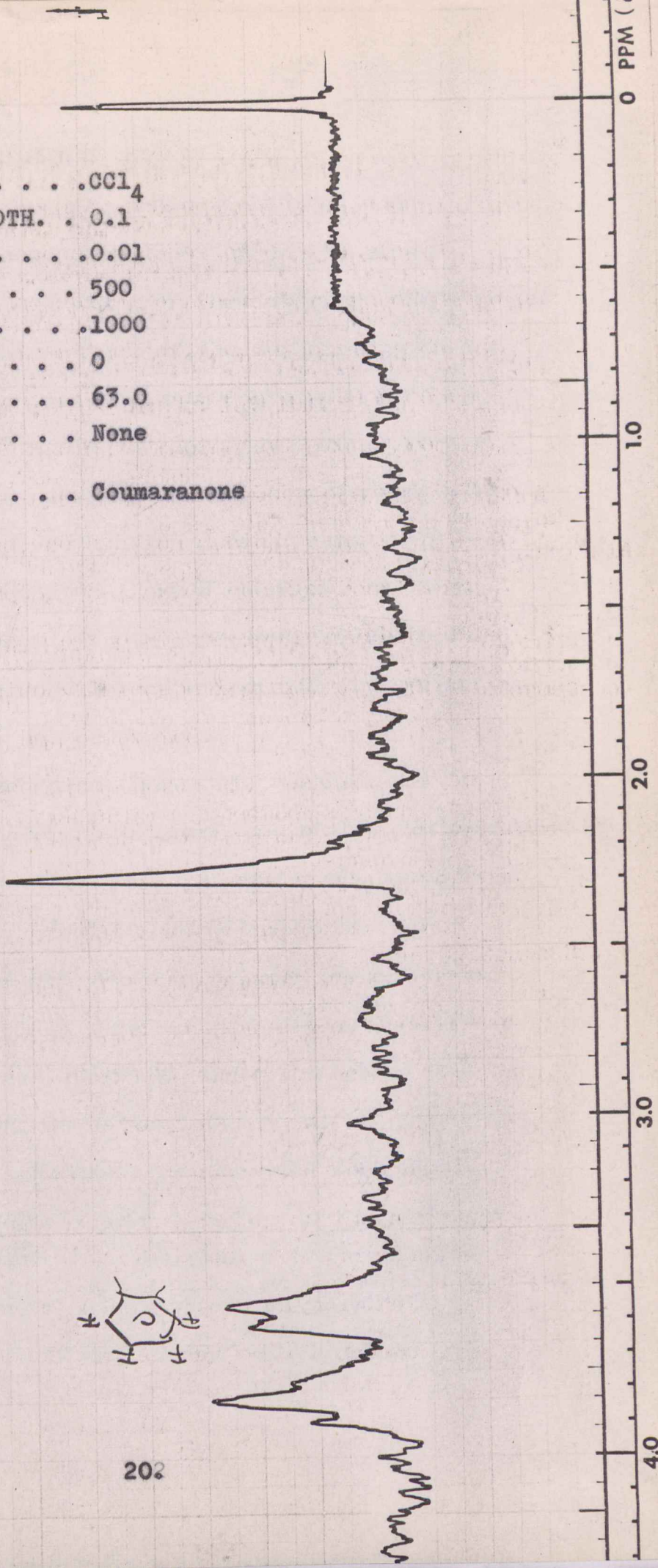
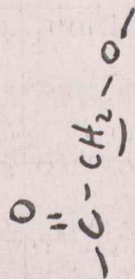
GRAPH 1b

SAMPLE <u>Polystyrene</u>	CURVE NO. _____	SCAN SPEED <u>25</u>	OPERATOR <u>calb</u>
ORIGIN _____	CONC. _____	SLIT <u>25</u>	DATE <u>11/25/66</u>
SOLVENT _____	CELL PATH _____	REMARKS _____	

SOLVENT. CCl₄
FILTER BANDWIDTH. . 0.1
R. F. FIELD. 0.01
SWEEP TIME. 500
SWEEP WIDTH. 1000
SWEEP OFFSET. 0
SPECTRUM AMP. 63.0
INTEGRAL AMP. None

SAMPLE. Coumaranone

GRAPH 2



CONCLUSION

Since coumaranone is the only product obtained when o-methoxy, w-diazo acetophenone is decomposed with glacial acetic acid, a concerted mechanism for the departure of nitrogen followed by the nucleophilic attack of the methoxy oxygen is indicated. The acetate ion in DMSO solution has been shown to be sufficiently active to cleave the methyl group from the oxonium ion. Since the oxonium ion had been cleaved before the addition of water, the acetate ion, which might have been tied up as an acetate-dimethyl sulfoxide complex resulting in the observed intense heat of solution, was available as a nucleophile. With no nucleophile competing with the methoxy group, no mechanism could be postulated.

If a non-concerted mechanism (pure S_N1) mechanism prevailed, then an acetate ester should form due to the nucleophilicity and availability of the acetate ion. No ester was discovered in the reaction products. Further, if the reaction was catalytic, then, as water was added, α -hydroxy acetophenone should appear as a product by attack of the OH⁻ on the carbonium ion. No alcohol was detected. Thus it appears that the proximity of the nucleophilic methoxy oxygen to the nitrogen-bearing carbon provides a route for a concerted mechanism. The methoxy oxygen attacks the active carbon as the nitrogen, a good leaving group, departs, leading only to the oxonium intermediate. When water is added, it can only hydrolyze the methyl group from the oxygen, if any methyl groups had

been left uncleaved by the lack of sufficient acetate ion, and precipitate the coumaranone which is more soluble in DMSO than in water.

The DMSO reacts similarly to the aqueous medium as described by Bose and Yates(3). Apparently, the nucleophilicity of acetic acid plays no role except to effect the methyl group cleavage and supply the hydrogen to protonate the carbanion portion of the inner diazonium salt.

To determine whether the decomposition always follows a concerted mechanism, the reaction might be carried out in a medium of very low polarity, e.g. benzene or cyclohexane, where ion-pair formation would be more favorable than solvated ions. The use of a very strong nucleophilic anion of an acid, such as I^- in HI, might also provide a key to the mechanism.

The decomposition of the diazoketone, carried out at an asymmetric center such as in o-methoxy, w-diazo, w-methyl acetophenone might aid in reaction course determination because of its stereospecific geometry. However, by this researcher's method of diazoketone preparation, the asymmetric diazoketone would involve preparation of $CH_3-\overset{\ominus}{C}-\overset{\oplus}{CHN_2}$ which, even if easily prepared, could tautomerize to $\overset{\ominus}{CH_2}-CH_2-\overset{\oplus}{N_2}$, resulting in unwanted (non-asymmetric) diazoketones.

BIBLIOGRAPHY

1. Huisgen, R.; Angew. Chem. 67, 442 (1955).
2. Sheffer, H. E. and J. A. Moore; J. Organic Chem. 28, 129 (1963)
3. Bose, A. J. and P. Yates; J. Am. Chem. Soc. 74, 4703 (1952)
4. Handbook of Chemistry and Physics; 46th ed.; Chemical Rubber Publishing Co.; page C-193; (1965)
5. From the notes of H. E. Sheffer