

5-31-1974

Reactions of perchloro-1,2-dimethylene cyclobutane with amines

Robert James Smith
New Jersey Institute of Technology

Follow this and additional works at: <https://digitalcommons.njit.edu/theses>

 Part of the [Chemical Engineering Commons](#)

Recommended Citation

Smith, Robert James, "Reactions of perchloro-1,2-dimethylene cyclobutane with amines" (1974). *Theses*. 2159.

<https://digitalcommons.njit.edu/theses/2159>

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Theses by an authorized administrator of Digital Commons @ NJIT. For more information, please contact digitalcommons@njit.edu.

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

REACTIONS OF PERCHLORO-1,2-DIMETHYLENE CYCLOBUTANE
WITH AMINES
BY
ROBERT JAMES SMITH

A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

This thesis is to be used only with due regard to the rights of the author(s). Bibliographical references may be noted, but passages must not be copied without permission of the College and without credit being given in subsequent written or published work.

Newark, New Jersey
1974

ABSTRACT

Perchloro-1,2-dimethylene cyclobutane was reacted with primary amines forming cyclic amidinium salts. Their structures were elucidated by the performance of various spectral analyses.

APPROVAL OF THESIS
REACTIONS OF PERCHLORO-1,2-DIMETHYLENE CYCLOBUTANE
WITH AMINES

BY

ROBERT JAMES SMITH

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

MAY, 1974

PREFACE

I would like to express my sincere thanks and gratitude to Dr. David Kristol whose unselfish help made my work realizable and also to my wife, Susan.

TABLE OF CONTENTS

INTRODUCTION.....	1
Syntheses of Small Ring Chloro- carbons.....	2
Reactions of Perchloro-1,2-dimethylene Cyclobutane.....	6
Other Related Syntheses and Reactions.....	8
Reactions of Halocarbons with Nucleophiles.....	13
EXPERIMENTAL PROCEDURE.....	18
DISCUSSION OF RESULTS.....	28
CONCLUSION.....	34
FIGURES.....	35
REFERENCES.....	46

LIST OF FIGURES

FIGURE	I	*****	Infrared Spectrum of Dimethoxy-t-butyl Adduct
FIGURE	II	*****	Infrared Spectrum of a New Amidinium Salt
FIGURE	III	*****	Infrared Spectrum of t-butylamine Hydrochloride
FIGURE	IV	*****	Infrared Spectrum of Cyclopentylamine Adduct
FIGURE	V	*****	Infrared Spectrum of Cyclohexylamine Hydrochloride
FIGURE	VI	*****	Infrared Spectrum of Cycloheptylamine Adduct
FIGURE	VII	*****	Infrared Spectrum of Cyclooctylamine Adduct
FIGURE	VIII	*****	NMR Spectrum of Cyclopentylamine Adduct
FIGURE	IX	*****	NMR Spectrum of Cycloheptylamine Adduct
FIGURE	X	*****	NMR Spectrum of Cyclooctylamine Adduct
FIGURE	XI	*****	Mass Spectrum of Cyclopentylamine Adduct

INTRODUCTION

The study of the syntheses and reactions of chlorocarbons is a relatively new and unexplored area of organic chemical research. One reason for the existence of this unexplored frontier is the great investigative interest levied on the syntheses and reactions of the hydrocarbons because of both their greater availability and applicability to modern laboratory techniques, such as nmr and mass spectroscopy. Reactions of organic compounds which contain few heteroatoms, such as chlorines, yield simple, readily characterized compounds when reacted with monofunctional reagents. By contrast, the reactions of polyhalo compounds may yield polyfunctional molecules produced by a variety of substitutions, additions and eliminations which may occur simultaneously.

Reactions of small ring chlorocarbons may have three results. First, the reaction may result in ring closure creating various bicyclic compounds. Second, the reaction may result in ring expansion whereby a small ring chlorocarbon may increase in size and at the same time become more stable by relieving angle strain within the ring. Third, the reaction may result in ring opening creating a host of acyclic products. However, reactions involving

chlorocarbons may effect significant changes in the functional groups attached to the compounds because of the great abundance of reactive sites.

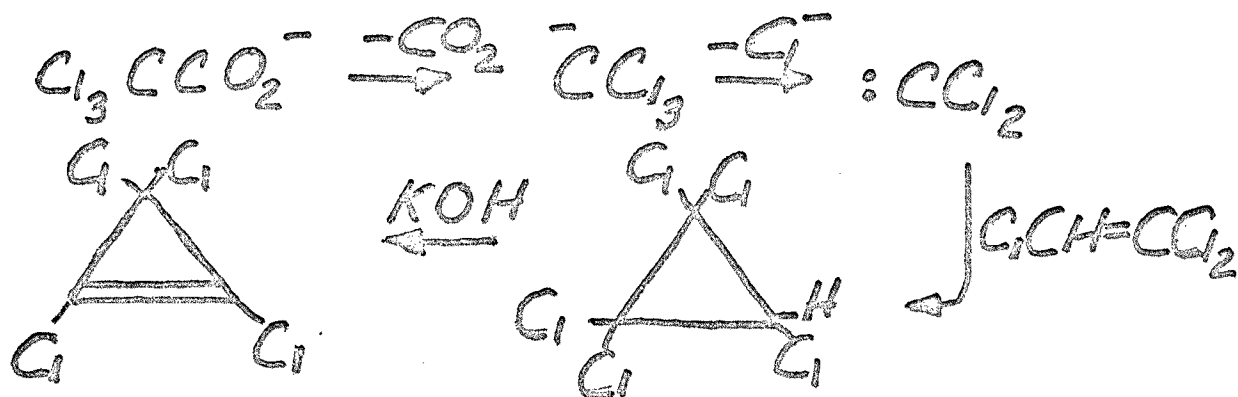
Reactions involving chlorocarbons usually occur under milder conditions than their sister hydrocarbons because of the more polarized carbon-chlorine bond as opposed to the carbon-hydrogen bond. It is for this reason that a greater variety of reactions occur with chlorocarbons than with hydrocarbons. For instance, substitution and elimination reactions occur more readily with chlorocarbons than with their corresponding hydrocarbons.

Up to recent times, reactions with chlorocarbons have generally been limited to reactions with Lewis Acids or to free radical reactions. Very little work has been done on nucleophilic substitutions of chlorocarbons which is the topic of my thesis.

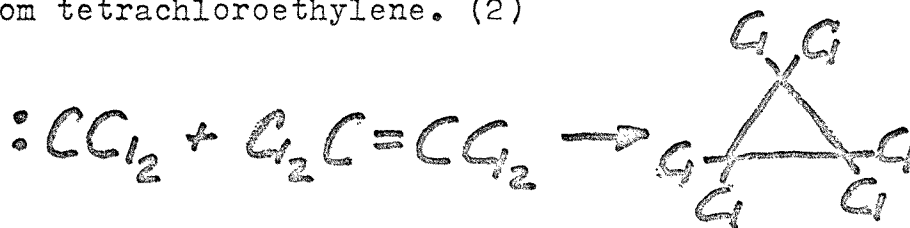
Syntheses of Small Ring Chlorocarbons

The availability of small ring chlorocarbons have significantly increased because of recent developments in organic chemical research. For example, dichlorocarbene (produced by thermal decarboxylation of sodium tri-

chloroacetate) and trichloroethylene reacted together to produce pentachlorocyclopropane. Dehydrohalogenation of the latter afforded tetrachlorocyclopropene. (1)



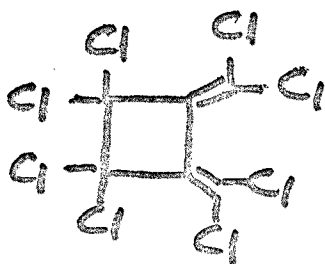
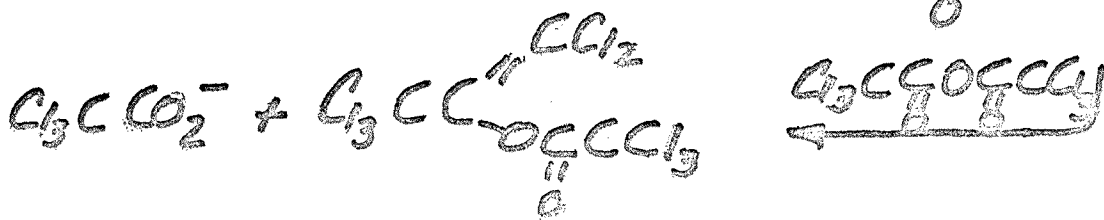
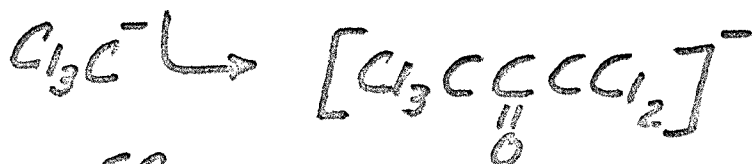
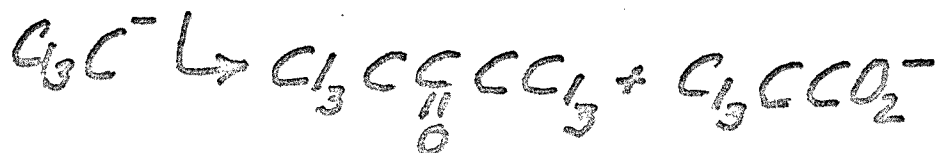
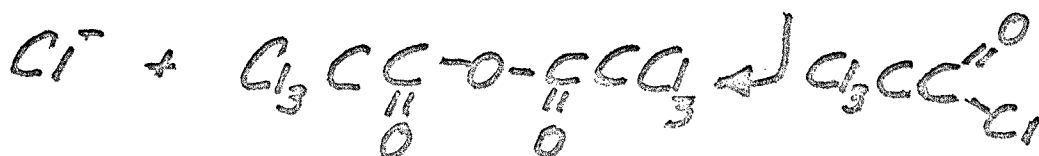
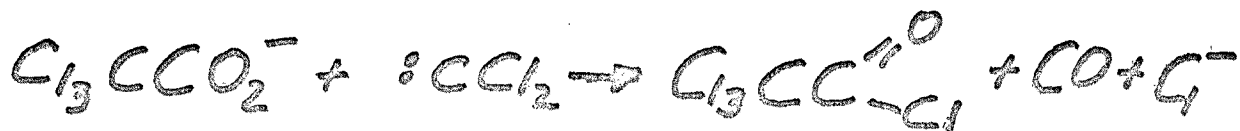
Hexachloropropane was prepared in a similar manner from tetrachloroethylene. (2)



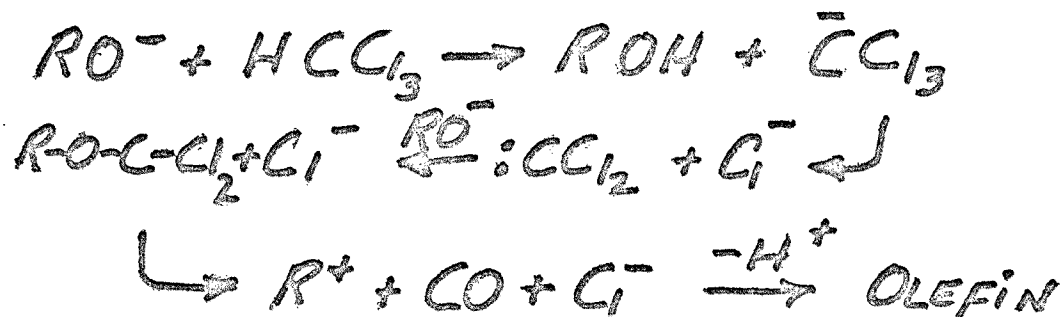
Perchlorocyclobutene was synthesized by treatment of the more readily accessible perfluorocyclobutene with aluminum chloride and gaseous hydrogen chloride. (3)

Small amounts of trichloroacetic anhydride, carbon tetrachloride, perchloroisopropenylacetate and perchloro-1,2-dimethylene cyclobutane were extracted from the decarboxylation reaction of sodium trichloroacetate run without the presence of a species which would react with either

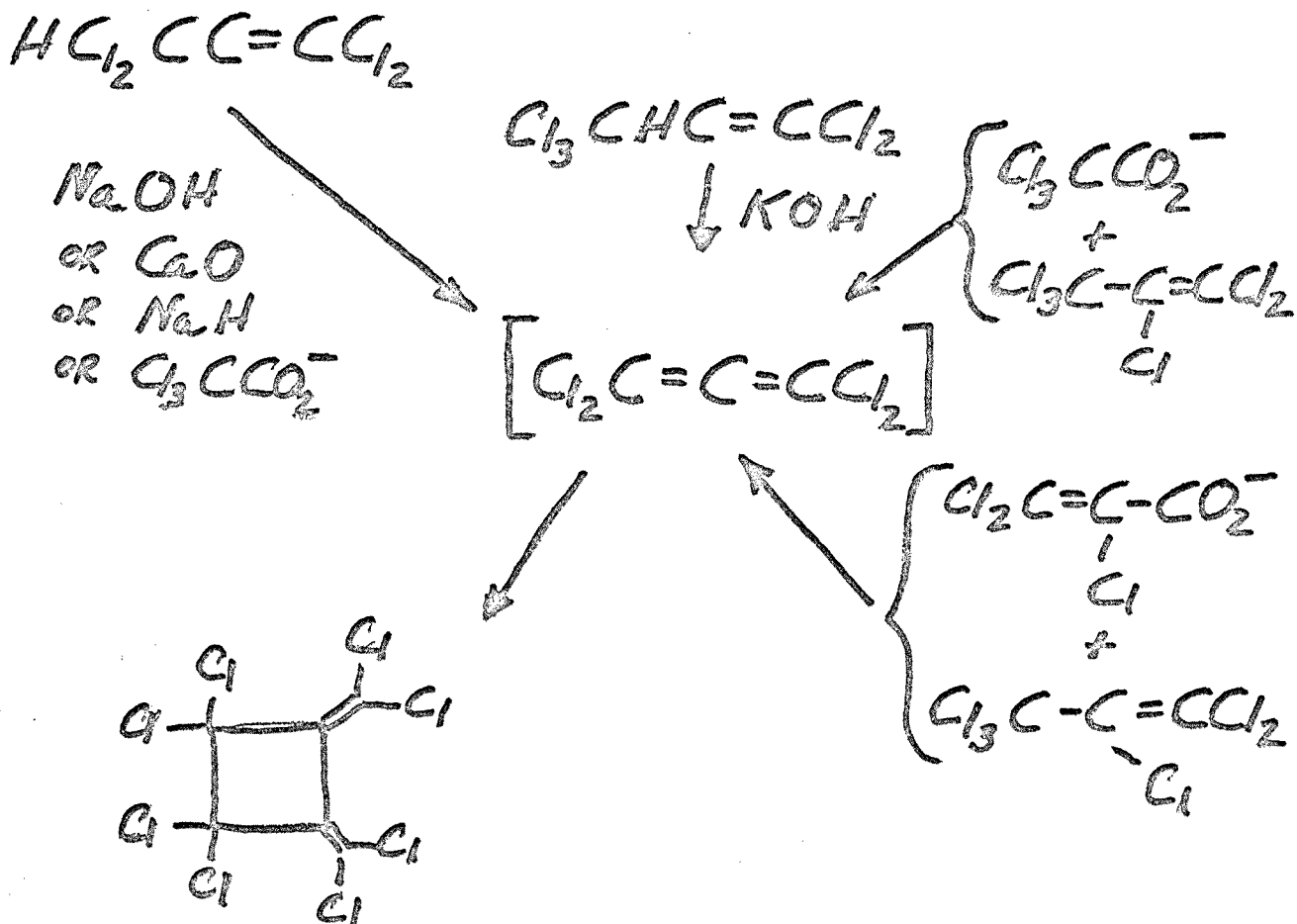
$:CCl_2$ or CCl_3^- . (4) The following mechanism was proposed to account for the products:



Although the reaction of dichlorocarbene with trichloroacetate ion to yield carbon monoxide and trichloroacetyl chloride is an unusual step, Wagner believed this step was the most likely one for the generation of the carbon monoxide observed. He noted that Hine (5) had pointed out that the electrophilic nature of $:CCl_2$ would make a reaction with an anion unlikely. Hine postulated the following reaction to explain the formation of carbon monoxide and an olefin in the alkaline alcoholysis of chloroform. (6)

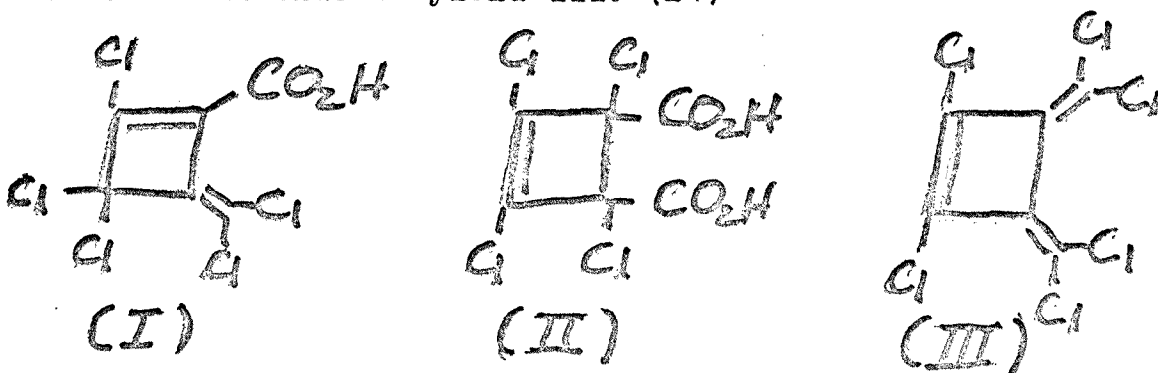


Perchloro-1,2-dimethylene cyclobutane, which is the chlorocarbon that is reacted with amines in my thesis, was synthesized in much higher yield from 1,1,2,3,3-pentachloropropene by treatment with sodium hydride (7), calcium oxide (8), potassium hydroxide (9), or sodium trichloroacetate in refluxing 1,2-dimethoxyethane. (10) Perchloro-1,2-dimethylene cyclobutane may be prepared from pentachlorocrotonoyl chloride and sodium carbonate (11), 1,1,3,3,3-pentachloropropene and potassium hydroxide (12), or sodium trichloroacrylate and hexachloropropene. (13)



Reactions of Perchloro-1,2-Dimethylene Cyclobutane

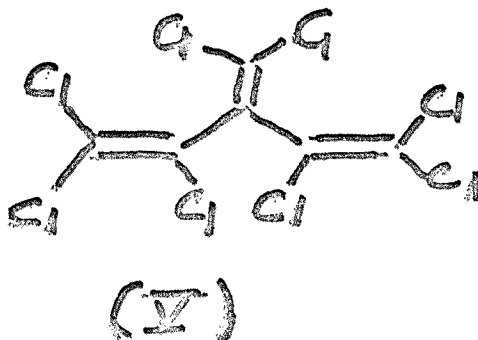
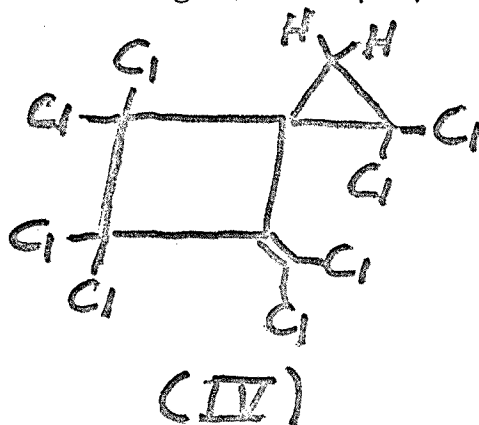
Only a few reactions of perchloro-1,2-dimethylene cyclobutane have been reported. It has been reacted with either sulfuric acid or potassium hydroxide to yield I, with fuming nitric acid to yield II, and with a mixture of aluminum chloride to yield III. (14)



Roedig postulated that the oxidation and rearrangement of perchloro-1,2-dimethylene cyclobutane to II may have proceeded via a trichloromethyl substituted intermediate because he isolated chloropicrin(trichloronitromethane) from the reaction mixture. This emphasized the complexity of the reaction, but did not explain its exact course.

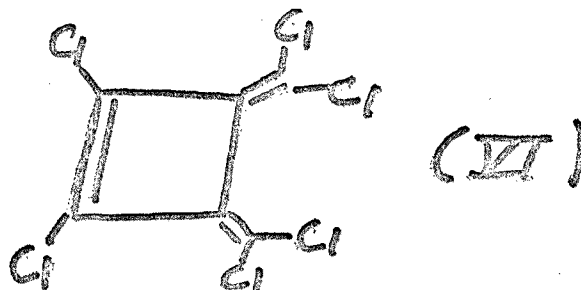
When perchloro-1,2-dimethylene cyclobutane was treated with an ethereal solution of diazomethane, only one double bond was found to react, and the spiro compound IV was produced. (15)

At 230^o, perchloro-1,2-dimethylene cyclobutane was reported to rearrange to V. (16)

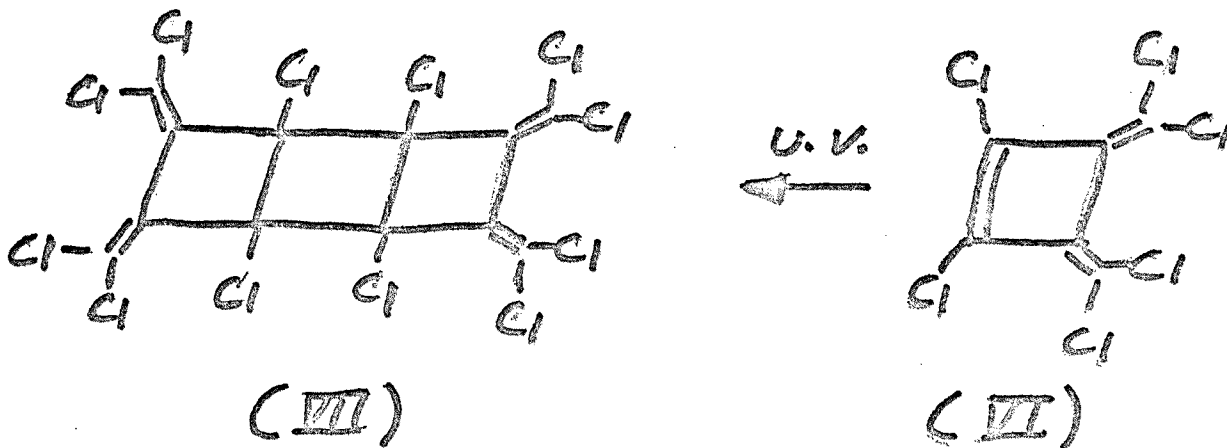


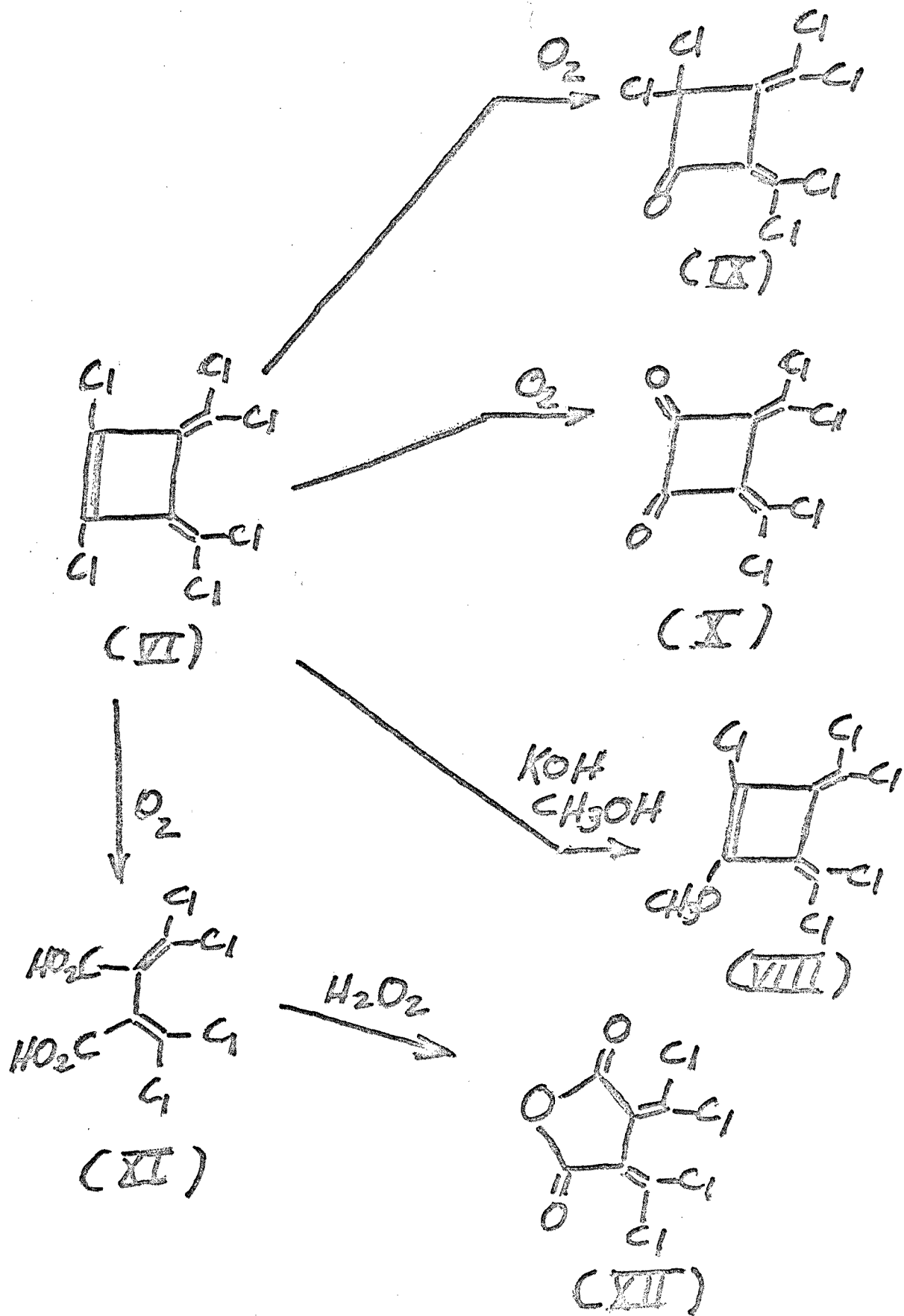
Other Related Syntheses and Reactions

VI, which is closely related to perchloro-1,2-dimethylene cyclobutane, has been reported to undergo dimerization, nucleophilic substitution and oxidation.

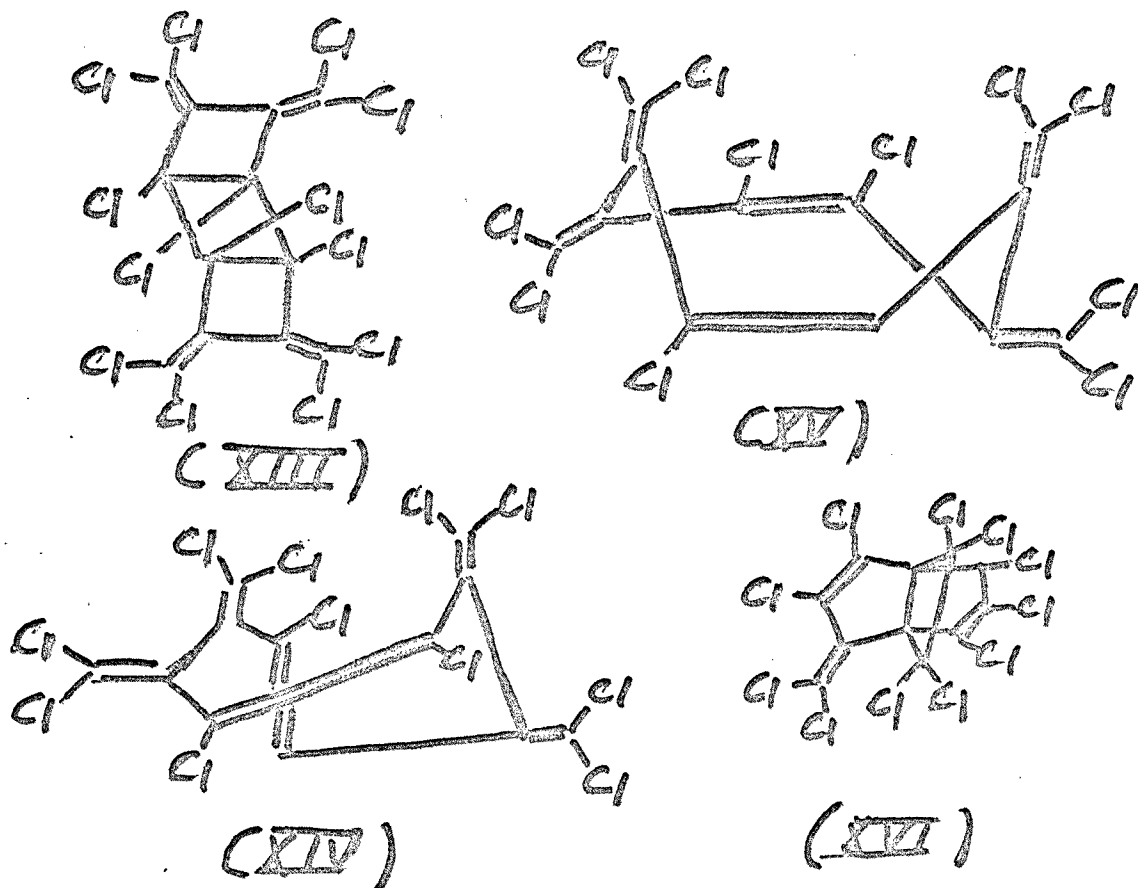


Under the influence of ultraviolet irradiation, VI dimerized to VII. (17) Upon treatment with methanolic potassium hydroxide, VI was converted to the methyl ether VIII, which in turn could be oxidized to IX, X, and XI. (18) VI itself was oxidized to IX, X, XI and XII by molecular oxygen in the presence of carbon tetrachloride. (19)



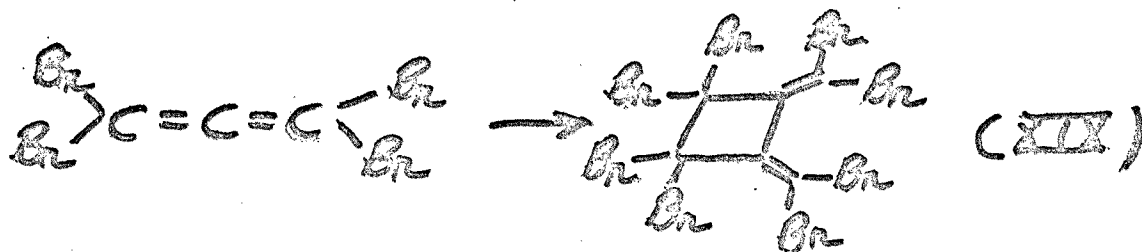
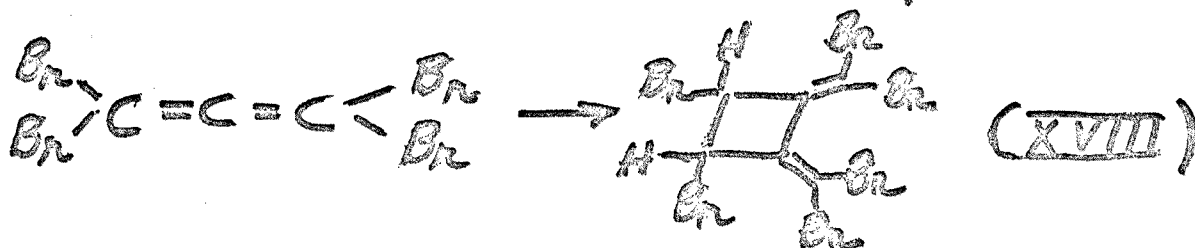
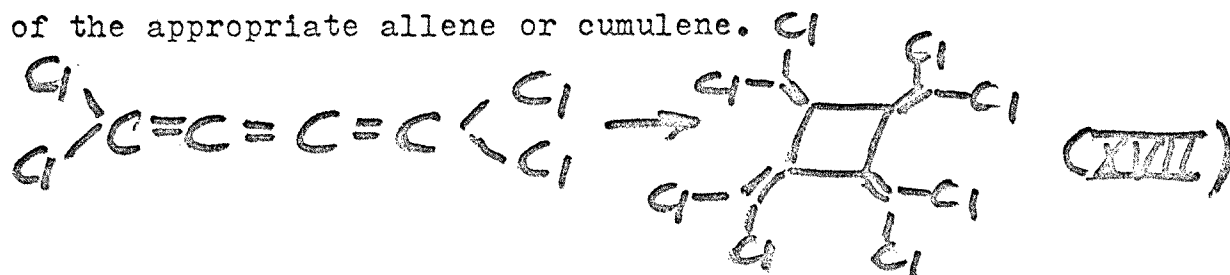


Through a detailed study of its pyrolysis, VI yielded XIII at 160°, XIV and XV at 190°, and XVI at 250°. (20)

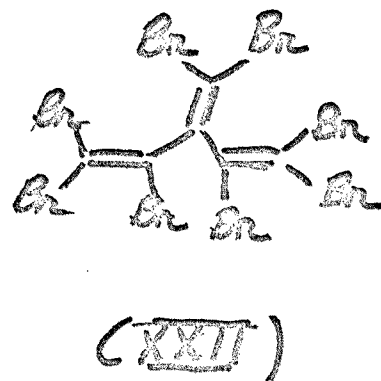
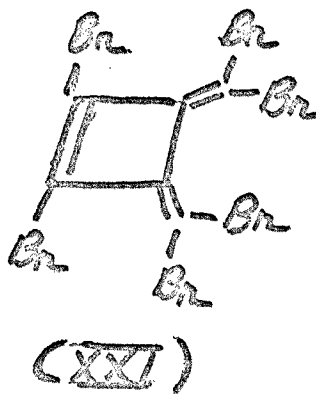
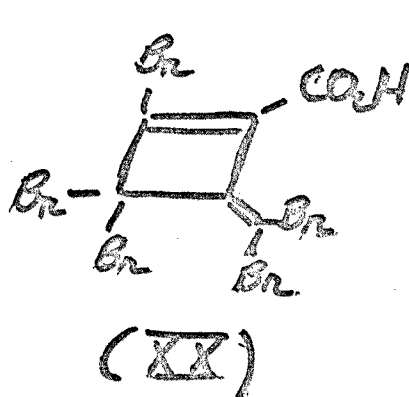


XIV and XV differ in their ring conformations even though they have identical bonding arrangements. Since these conformations are not readily interconvertible, XIV and XV are distinct compounds at room temperature. At 250°, however, XV is converted to XIV.

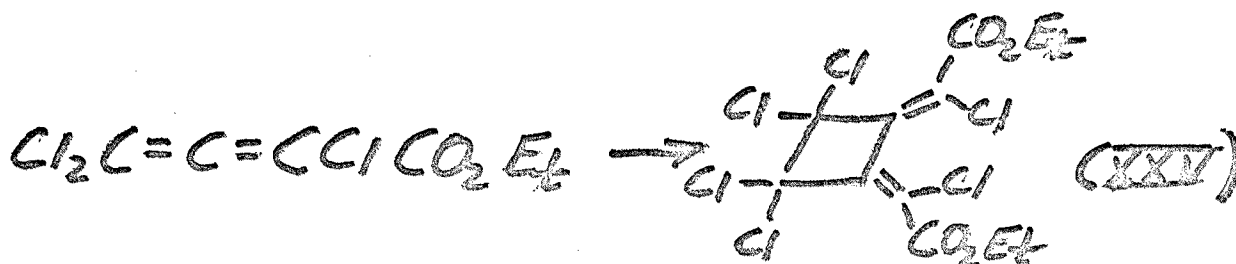
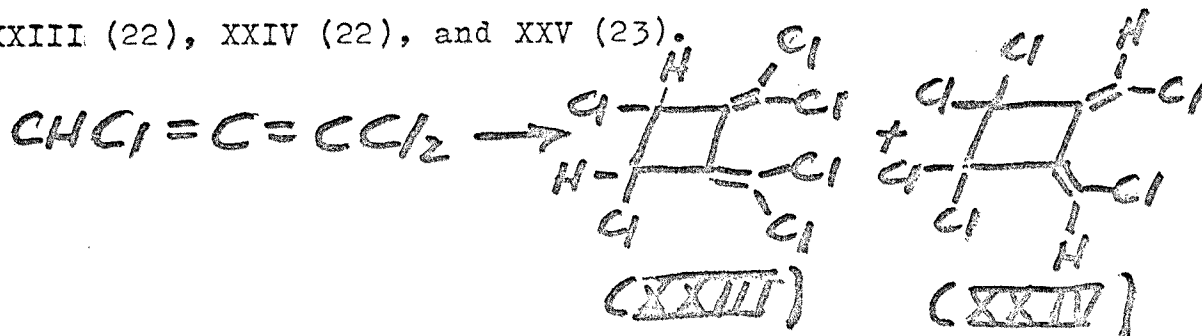
XVII, XVIII and XIX were each prepared by dimerization of the appropriate allene or cumulene.



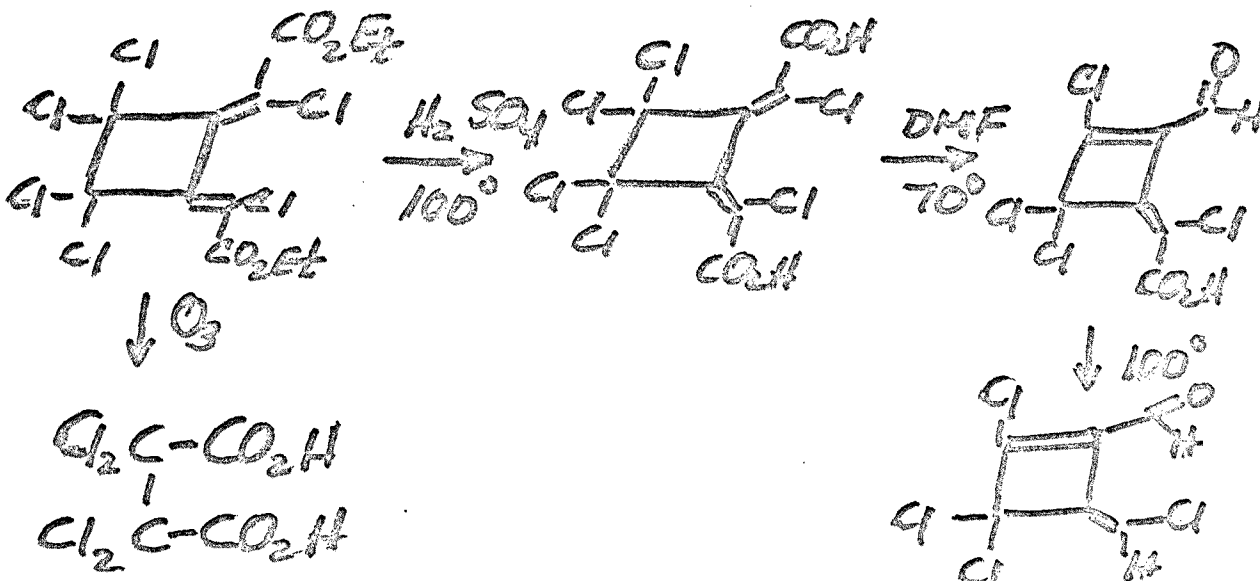
XIX reacted with sodium bicarbonate to yield XX and with aluminum to yield XXI. Upon vigorous heating, XIX yielded XXII. (21)



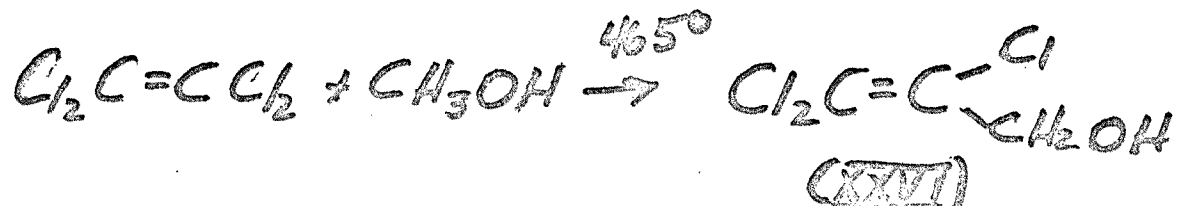
Dimerization of the appropriate chloroallene yielded
XXIII (22), XXIV (22), and XXV (23).



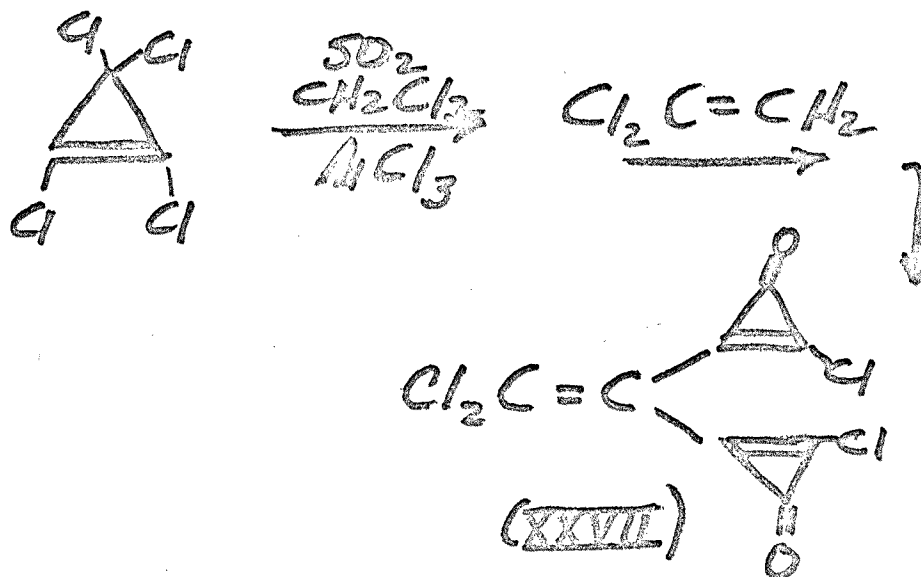
XXV was found to undergo oxidation and hydrolysis. The hydrolysis product was decarboxylated in two steps, the first of which presumably proceeded with allylic rearrangement via a "Vilsmeier complex" (24) that upon hydrolysis yielded the aldehyde acid. The experimental conditions for this decarboxylation were not reported.



Tetrachloro ethylene reacted with methanol to yield the unusual substitution product XXVI. (25)

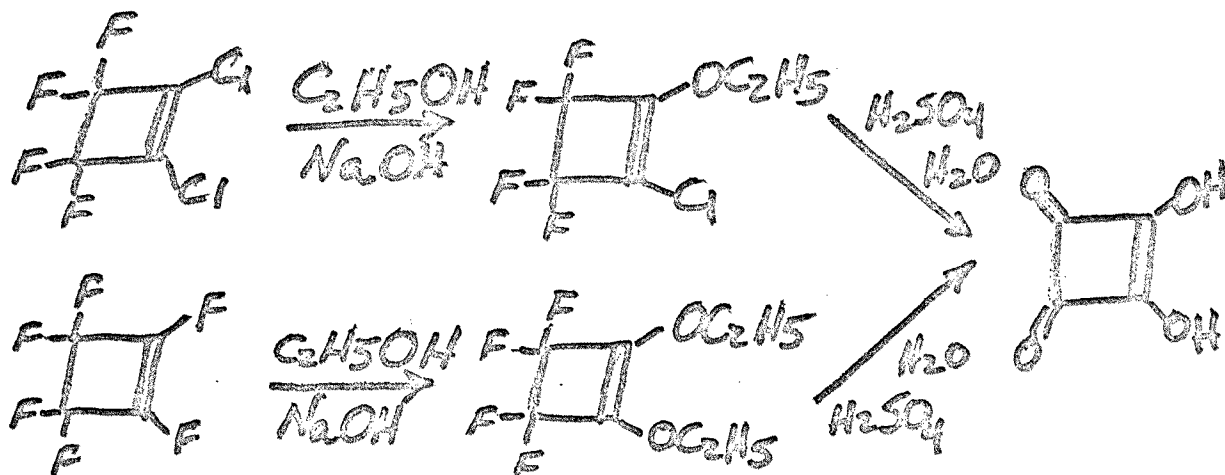


Tobey reported XXVII as end product of a reaction using tetrachlorocyclopropane. (26)

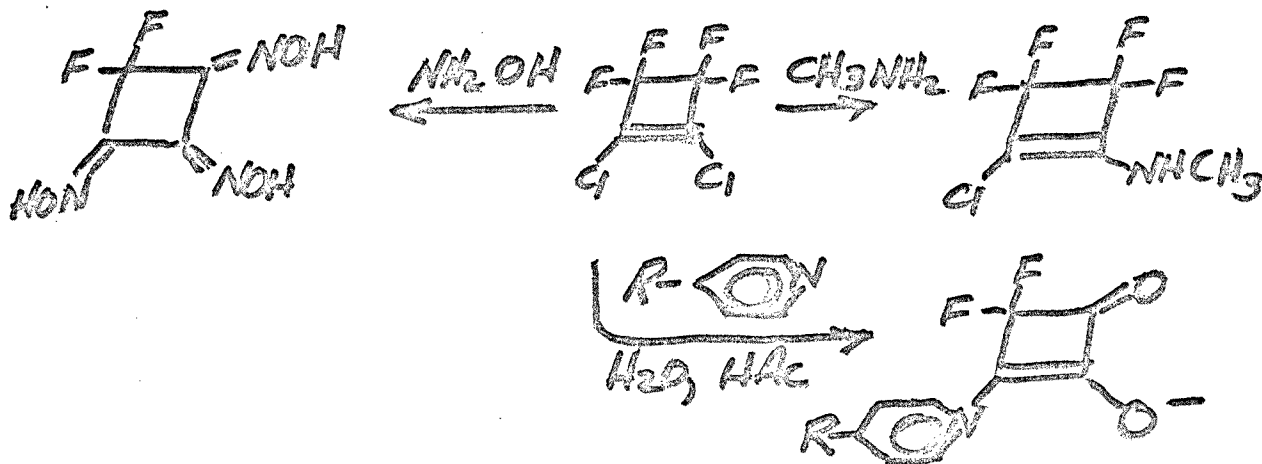


Reactions of Halocarbons with Nucleophiles

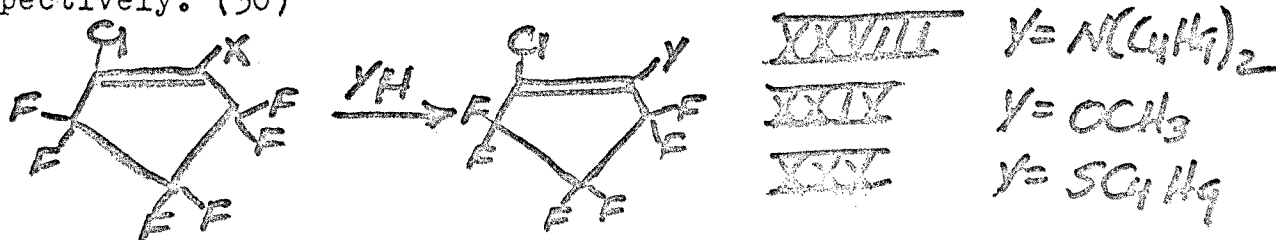
Reactions of polycarbons with nucleophilic reagents, although infrequent, have yielded some very unusual products. Squaric acid was synthesized via two different paths involving nucleophilic substitution of a polyhalogen compound. (27)



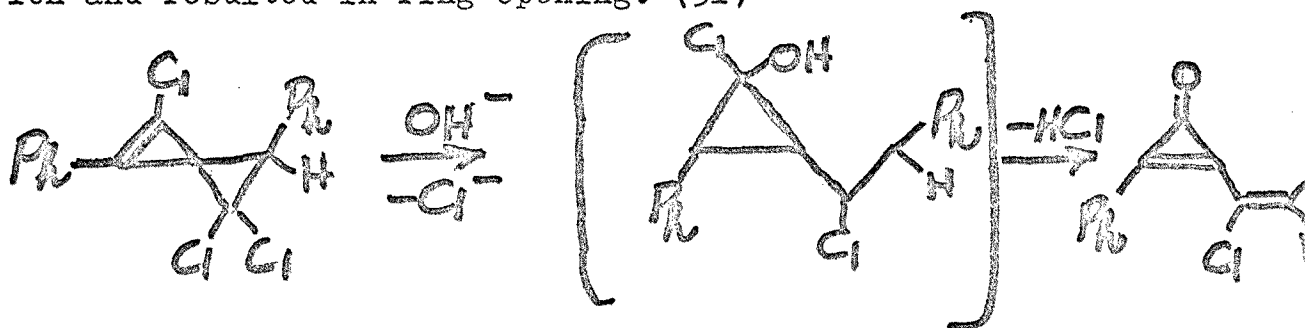
Perchlorocyclobutenes have been reacted with methylamine or hydroxylamine (28) to yield simple substitution products, and with substituted pyridines to yield betaines. (29)



Perhalocyclopentenes also reacted with nucleophiles giving substitution products XXVIII, XXIX and XXX when reacted with di-n-butylamine, methanol and n-butyl mercaptan, respectively. (30)

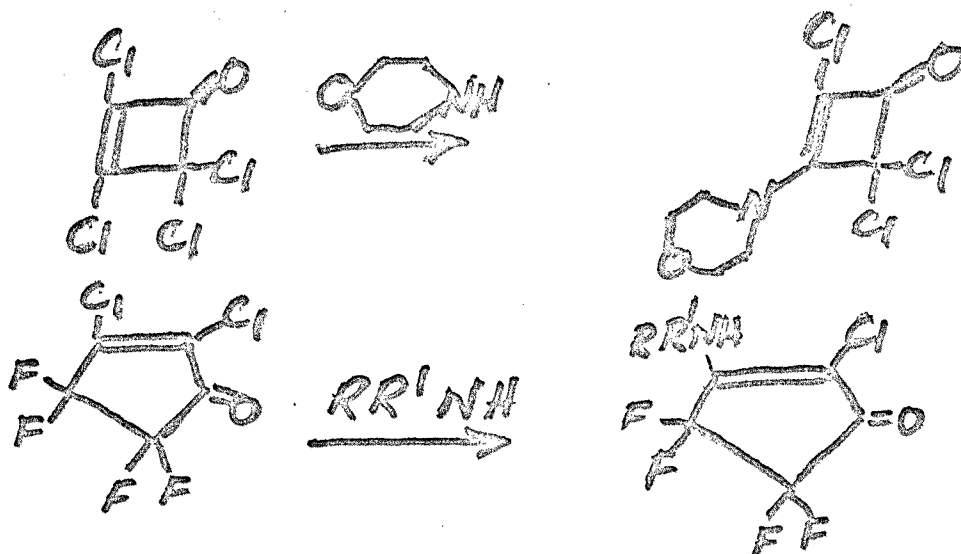


In the nucleophilic substitution of a halogen compound, the attack by a nucleophile is not necessarily limited to the carbon bearing the halogen which is being displaced. The following reaction evidenced attack at the carbon not attached to the leaving group by the nucleophile hydroxide ion and resulted in ring opening. (31)

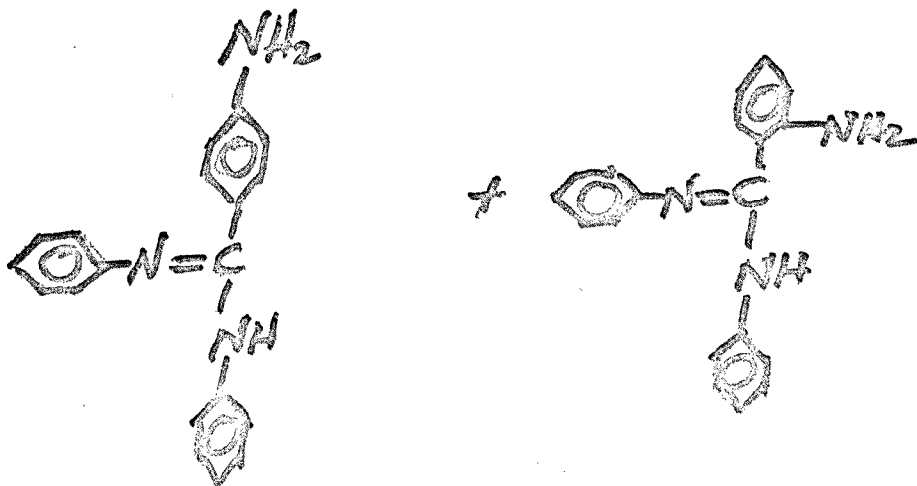


Numerous examples of substitution with various nucleophiles resulting in simultaneous ring opening were observed in the reactions of tetrachlorocyclopropene. Acyclic products were produced when reacting alcoholic ammonia, water and alcohols with tetrachlorocyclopropane. Although the mechanisms were not reported, the suggestion was that the first step in each reaction was the addition to the double bond to give a cyclopropane, which then underwent ring opening to give the observed products. (32)

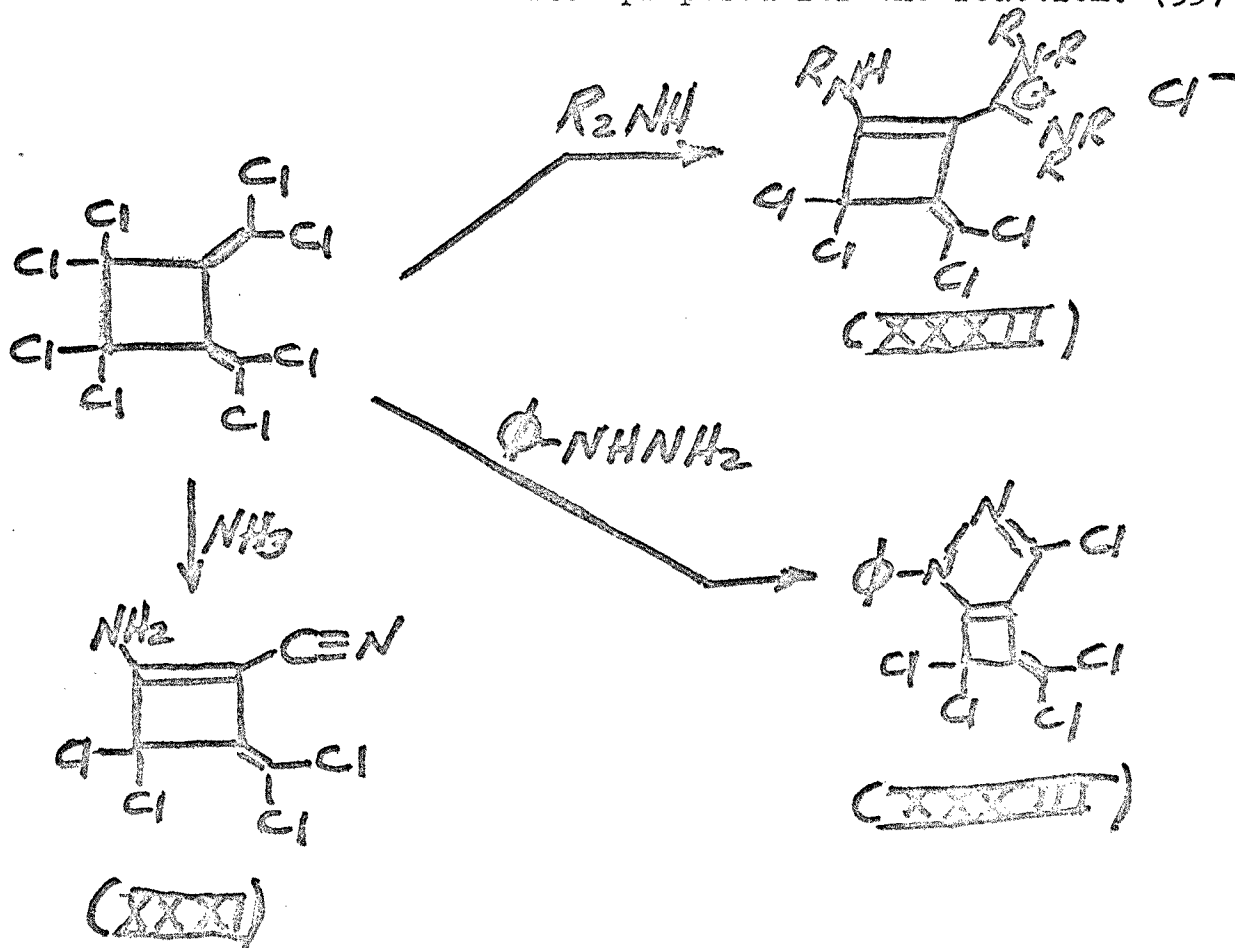
Nucleophilic substitutions of polyhalogenated molecules occur readily when other functional groups are present. The reactions of amines with chlorinated cyclic ketones have been observed to occur under milder conditions. (33)



Even chlorocarbons that are generally considered unreactive toward nucleophilic substitution have been reported to react with amines. Carbon tetrachloride has long been known to react with aniline to yield pararosanine and amidines. (34) This reaction was run in a sealed tube at 170° for thirty hours. It is possible that the reaction involved a homolytic process. Many reactions of carbon tetrachloride with amines have subsequently been shown to be initiated by free radicals.



Perchloro-1,2-dimethylene cyclobutane was readily reacted with ammonia to yield 2-amine-3,3-dichloro-4-dichloromethylene-1-cyanocyclobutene (XXXI) and with primary or secondary aliphatic or aromatic amines to yield N-substituted 2-alkyl (or aryl) amine-3,3-dichloro-4-dichloromethylenecyclobutenyl-carboxamidinium chlorides. (XXXII) The reaction of perchloro-1,2-dimethylene cyclobutane with phenylhydrazine proceeded with cyclization to give a cyclobutenopyrazole. (XXXIII) Kristol and Shapiro studied the spectroscopic properties of these products and of the transformation products derived from them. A mechanism was also proposed for the reaction. (35)



EXPERIMENTAL PROCEDURE

Approximately twelve fold excesses of t-butylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, and cyclooctylamine were separately reacted with perchloro-1,2-dimethylene cyclobutane. An experimental method and a statement of results are fully outlined in the following discussion for each of the above reactants.

In the reaction of t-butylamine and perchloro-1,2-dimethylene cyclobutane, a twenty fold excess of t-butylamine (40.90 gms, 58.6 mls) was added to a 1000 ml separatory funnel containing 200 ml of anhydrous ethyl ether. Similarly, 0.0281 mole of perchloro-1,2-dimethylene cyclobutane (10.0 gms) was prepared in a 500 ml erlenmeyer flask containing 200 mls of anhydrous ethyl ether. While stirring magnetically the contents in the erlenmeyer flask, the contents in the separatory funnel were added drop wise at first. After a couple of minutes, a cloudy precipitate started to appear in the erlenmeyer flask. The addition of the solution in the separatory funnel was quickened after ten minutes until about one-half hour later the entire solution had been added. At this point the contents in the erlenmeyer flask had turned a deep yellow color and was kept stirred overnight.

The contents in the flask were then suction filtered

to yield a solid weighing 12.34 gms. This solid consisted of t-butylamine hydrochloride and t-butylamine adduct. In order to remove the t-butylamine hydrochloride, this solid was placed in a 250 ml erlenmeyer flask containing an excess of chloroform. The contents in the flask were suction filtered to yield a solid weighing 12.27 gms. This solid was identified as the t-butylamine hydrochloride because it was not soluble in chloroform. The filtrate from the second suction filtering was rotary evaporated to dryness. The solid recovered was then placed in a 250 ml erlenmeyer flask containing an excess of hexane. The contents of this flask were suction filtered to yield a solid weighing 0.40 gm and identified as the t-butylamine adduct. The remaining t-butylamine adduct was recovered from rotary evaporating the filtrate from the first suction filtering. A tan greasy sludge resulted at dryness. To this sludge was added 60 ml of chloroform and a few boiling stones. The contents were then brought to reflux and hexane was added slowly at first and later more quickly until about 500 ml had been added. The contents were then allowed to reflux for approximately one hour. After the hour the flask was stoppered and refrigerated. After three days a solid precipitated and the contents of the flask were suction filtered to yield a solid weighing 5.91 gms. An exact operation was performed on the filtrate as described above to recover a solid weighing 1.82 gms. This solid was identified as the t-butylamine adduct and the total amount recovered was 8.13 gms

To isolate the product, dimethoxy-t-butyl adduct, 13.4 gms of t-butyl adduct were placed in a 250 ml erlenmeyer flask containing 50 ml of methanol. To the contents of this flask were added 6.4 gms of sodium methoxide (four fold excess) prepared in 50 ml of methanol. The contents of the flask were then allowed to stand for two weeks. After such time the contents were suction filtered to yield a solid weighing 1.665 gms. This solid was identified as the dimethoxy-t-butyl adduct.

In the reaction of dimethoxy-t-butyl adduct and dilute hydrochloric acid, a new amidinium salt was produced. Into a 1000 ml erlenmeyer flask containing 350 ml of dimethoxyethane was added 6.24 gms of dimethoxy-t-butyl adduct. To this solution was added 150 ml of methanol and then 150 ml of distilled water. Next was added 30 ml of 6M hydrochloric acid which immediately turned the solution yellow. The contents of the flask were then allowed to stand. Later suction filtering yielded a solid weighing 2.849 gms.

The product, t-butylamine hydrochloride, was also isolated by adding 2.6 gms of the amidinium salt as described above to a 125 ml erlenmeyer flask containing 100 ml of 6M hydrochloric acid and 25 ml of concentrated hydrochloric acid. The contents were stirred constantly and the solution at first was a light yellow and then progressively deepened

in color until it reached an intense yellow. It was then stoppered and kept stirred overnight. The contents were then transferred from the flask to a 500 ml round bottom flask and rotary evaporated initially at 33°C and gradually up to a constant temperature of 40°C. The collecting vessel was placed in an ice bath to help forward the stripping of the acid solution. A greasy yellowish solid remained. Small traces of hydrochloric acid were evaporated from the flask by blowing nitrogen gas through the flask. A small amount of methanol was added to the flask which dissolved the greasy solid. Then a small amount of hexane was poured into the flask. The entire contents of the flask were then transferred to a 125 ml erlenmeyer flask containing a few boiling stones. The solution was allowed to reflux and small quantities of chloroform were added to the mix until a precipitate occurred. The solution was still kept refluxing while small quantities were added of hexane to further knock out any product. Afterwards the solution was suction filtered to yield a yellowish solid weighing 0.1 gm. The filtrate was rotary evaporated at a constant temperature of 38°C to yield a slightly reddish liquid. To this liquid was added 50 ml of methanol turning the resulting solution slightly yellow. The contents were then placed in a 25 ml erlenmeyer flask containing some boiling stones and brought to reflux. At reflux small amounts of chloroform were added until a precipitate started to form. At this point refluxing was stopped and the flask

was placed in an ice-bath for a few minutes. The contents were then suction filtered to yield a solid weighing 0.37 gm. This solid was placed in a 125 ml erlenmeyer flask containing 25 ml of methanol and the contents were then brought to reflux after adding a few boiling stones. At reflux small quantities of chloroform were added until a precipitate occurred. At this point ^{the flask} was placed in a water bath to cool. The contents were then gravity filtered to yield a white crystalline solid weighing 0.19gm. Its melting point was 290-295° C. This solid was identified as t-butylamine hydrochloride.

In the reaction of cyclopentylamine and perchloro-1,2-dimethylene cyclobutane, a twelve fold excess of cyclopentylamine (0.118 mole, 10 gms, 6.9 mls, 85 MW) was added to a 1000 ml separatory funnel containing 200 ml of freshly distilled ethyl ether from LiAlH_4 . At the same time a solution of perchloro-1,2-dimethylene cyclobutane (0.01 mole, 3.56 gms, 356 MW) and 200 ml of freshly distilled ethyl ether were prepared in a 500 ml erlenmeyer flask. While the contents of the erlenmeyer flask were magnetically stirred, the solution in the separatory funnel was added drop by drop at first. After about a couple of minutes, a cloudy precipitate started to appear in the erlenmeyer flask. The addition of the solution in the separatory funnel was quickened after ten minutes

until about one-half hour later the entire solution had been added. At this point the contents in the erlenmeyer flask had turned a deep yellow color and was kept stirred overnight.

The contents in the flask were then suction filtered to yield a white precipitate weighing 8.0 gms and approximately 350 ml of filtrate (reddish in color). This white precipitate was placed in a 250 ml erlenmeyer flask containing 100 ml of distilled water. The contents were stirred and then suction filtered to yield a solid weighing 6.088 gms. This procedure of washing with distilled water was repeated until two consecutive weighings occurred. At this point the solid weighed 4.785 gms. This process removed cyclopentylamine hydrochloride. This solid was then placed in a 250 ml beaker along with a few boiling stones. Approximately 50 ml of chloroform was added to the beaker at which time the contents dissolved completely. This beaker was placed on a hot plate and the contents were brought to reflux. At reflux small amounts of hexane were added as the volume of the contents in the beaker diminished because of the refluxing operation. Hexane was continually added (150 ml) until a cloudy precipitate appeared. The beaker was removed from the hot plate and allowed to cool to room temperature. When cooled the contents in the beaker were suction filtered and washed with hexane to yield a white solid weighing 3.577 gms. Its melting point range was 246-250°C. It was identified as cyclopentylamine adduct.

In the reaction of cyclohexylamine and perchloro-1,2-dimethylene cyclobutane, a ten fold excess of cyclohexylamine (0.10 mole, 9.9 gms, 12.3 ml, 99 MW) was added to a 1000 ml separatory funnel containing 200 ml of freshly distilled ethyl ether. Similarly 3.56 gms of perchloro-1,2-dimethylene cyclobutane were added to a 500 ml erlenmeyer flask containing 200 ml of freshly distilled ethyl ether from LiAlH_4 . Then while the contents in the flask were stirred, the contents in the separatory funnel were added drop by drop at first. Shortly the contents in the flask became a little cloudy. Then the contents in the separatory funnel were added more quickly until about one-half hour later the entire contents in the separatory funnel were added. By this time the solution in the flask was a deep yellow. It was then kept stirred overnight. Upon coming back the next day the solution had evaporated leaving a solid weighing 6.15 gms. This solid was placed in a 250 ml erlenmeyer flask containing 150 ml of chloroform. The contents of the flask were then gravity filtered to yield a solid weighing 0.131 gms. Supposedly this solid should have been the cyclohexylamine hydrochloride because of its insolubility in chloroform. The resulting filtrate was then brought to reflux along with a few boiling stones. At reflux small amounts of hexane were added at first and gradually increased until a cloudy precipitate started to appear. At this point heating was discontinued

and the flask was allowed to cool to room temperature. When cool the solution was suction filtered and washed with small amounts of hexane to yield a crystalline solid weighing 2.994 gms. Supposedly this solid should have been the cyclohexylamine adduct. The melting point range of this crystalline white solid was 208-210°C.

In the reaction of cycloheptylamine and perchloro-1,2-dimethylene cyclobutane, a twelve fold excess of cycloheptylamine (0.12 mole, 13.584 gms, 9.2 ml, 113.2 MW) was placed in a separatory funnel containing 200 ml of freshly distilled ethyl ether. Similarly 3.56 gms of perchloro-1,2-dimethylene cyclobutane (0.01 mole, 356 MW) was added to a 500 ml erlenmeyer flask containing 200 ml of freshly distilled ethyl ether from LiAlH_4 . Then while the contents of the flask were being magnetically stirred, the contents in the separatory funnel were added drop by drop at first and gradually more quickly until about forty-five minutes later the entire contents of the separatory funnel were added. Initially the contents in the flask became cloudy and later turned a deep yellow. It was kept stirred for two days. This solution was then gravity filtered to yield a white solid weighing 9.42 gms. This solid was washed with 50 ml of distilled water and the resulting solution was suction filtered to yield a solid weighing 10.0 gms (wet with water). This solid was then placed in a 250 ml erlenmeyer flask containing

50 ml of chloroform and a few boiling stones. This solution was then brought to reflux. At reflux small amounts of hexane were added until a precipitate appeared. At this point heating was stopped and the flask was allowed to cool to room temperature. When cool the solution was gravity filtered to yield a white solid weighing 4.43 gms. This solid was identified as cycloheptylamine adduct. The melting point range was 270-275°C.

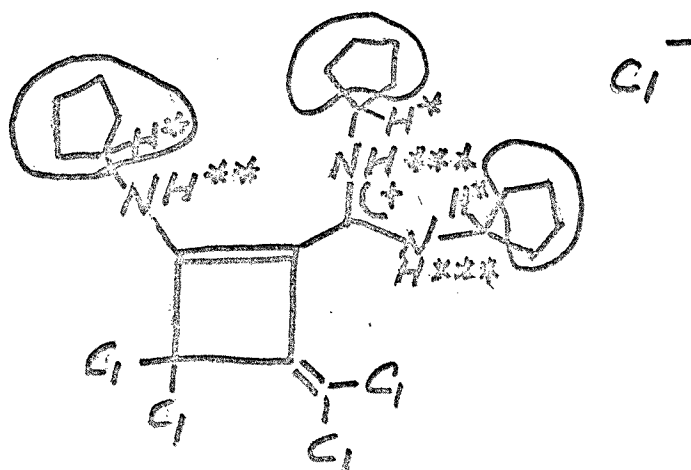
In the reaction of cyclooctylamine and perchloro-1,2-dimethylene cyclobutane, twelve fold excess of cyclooctylamine (15 gms, 10.13 ml, 127.23 MW) was added to a 1000 ml separatory funnel containing 200 ml of freshly distilled ethyl ether from LiAlH_4 . Similarly 3.56 gms of perchloro-1,2-dimethylene cyclobutane (0.01 mole, 356 MW) was placed in a 500 ml erlenmeyer flask containing 200 ml of freshly distilled ethyl ether. Then while the contents of the flask were being magnetically stirred, the contents in the separatory funnel were added drop by drop at first and gradually more quickly until about one-half hour later the entire contents of the separatory funnel were added. Initially the contents in the flask became cloudy and later turned a deep yellow. It was kept stirred for two days. This solution was then suction filtered to yield a solid weighing 7.322 gms. The solid was next placed into a 250 ml beaker along with about 100 ml of distilled water. The resulting

solution was suction filtered to yield a wetted solid weighing 6.407 gms. Again the solid was placed into the beaker containing 100 ml of distilled water. This solution was suction filtered to yield a wetted solid weighing 5.739 gms. This operation was repeated until two consecutive weighings resulted. This occurred at a weighing of 4.600 gms. To this solid was then added about 25-30 ml of chloroform. The resulting solution was gravity filtered to remove dirt particles. This solution was then brought to reflux. At reflux small quantities of hexane were added until a precipitate appeared. Heating was stopped and the flask was allowed to cool to room temperature. When cool the solution was suction filtered to yield a white granular solid weighing 2.275 gms. This solid was identified as cyclooctylamine adduct. Its melting point range was 280-285°C.

DISCUSSION OF RESULTS

Samples of cyclopentylamine adduct, cycloheptylamine adduct and cyclooctylamine adduct were sent out for elemental analyses to PCR, Inc., Gainesville, Florida. For cyclopentylamine adduct, the calculated percentages were: C 50.24%, H 6.02%, N 8.37%, Cl 35.36%. The actual percentages found were: C 50.27%, H 6.11%, N 8.33%, Cl 36.63%. For cycloheptylamine adduct the calculated percentages were: C 55.32%, H 7.22%, N 7.17%, Cl 30.28%. The actual percentages found were: C 55.28%, H 7.24%, N 7.09%, Cl 30.34%. For cyclooctylamine adduct the calculated percentages were: C 57.35%, H 7.70%, N 6.69%, Cl 28.25%. The actual percentages found were: C 57.45%, H 7.71%, N 6.62%, Cl 28.03%.

FIGURE VIII is a nmr spectrum of cyclopentylamine adduct whose structure is depicted below.



On inspection there appears to be one large peak centered around 8.2 τ and three smaller peaks centered around 6.2 τ , 5.8 τ , and 1.2 τ , respectively. The large peak represents the aliphatic hydrogens contained in the rings and designated as circled hydrogens. The areas under the three smaller curves are in a ratio of 2:1:2. Each area represents the number of hydrogens. The peak at 6.2 τ represents the hydrogen which is attached to a carbon that is attached to a positive nitrogen and designated as H^* . The peak at 5.8 τ represents a hydrogen attached to a non-positive nitrogen and designated as H^{**} . The peak at 1.2 τ represents the hydrogen that is attached to a positive nitrogen and designated as H^{***} . Although the hydrogen designated H^x appears to resemble H^* , it is attached to a carbon which is attached to a non-positive nitrogen and it falls at 8.2 τ and not 6.2 τ . The peak at 2.6 τ represents a trace amount of deuterio chloroform which is used as the solvent in the nmr spectrum. FIGURES IX and X represent nmr spectra of cycloheptylamine adduct and cyclooctylamine adduct, respectively. Although not as definitive as FIGURE VIII, they do show the large peak centered at 8.4 τ and 8.5 τ representing the aliphatic ring hydrogens. They also both show a slight rise in the curves centered between 6 and 7 τ representing amine hydrogens. However, what these spectra do not show

are any peaks centered around 2-3 μ and 3-5 μ which represent aromatic and vinylic species.

FIGURES IV, VI and VII show infrared spectra for cyclopentylamine adduct, cycloheptylamine adduct and cyclooctylamine adduct, respectively. All three have very broad band absorption around 3000 cm^{-1} which is a combination of C-H absorption, C-N absorption, and the very diffuse absorption of the amidinium. All have a sharp peak at 1700 cm^{-1} and a broad peak at 1600 cm^{-1} which represent the three double bonds in the molecules. The sharp peak probably represents the double bond within the four-membered ring. The broad peak is a combination of the double bond attached to the two chlorines and the amidinium partial double bond. Around 1400 cm^{-1} there is heavy absorption of the C-H bond. At 930 cm^{-1} C=C bond absorbs. All three spectra show an intense peak at $820\text{-}830\text{ cm}^{-1}$ which is characteristic of C-Cl bond. These three compounds as shown by their spectra are closely related and belong to one family.

FIGURES III and V show infrared spectra for t-butylamine hydrochloride and cyclohexylamine hydrochloride, respectively. Both show very broad absorption centered around 3000 cm^{-1} which reflects the C-H and NH_3^+ absorption. They also show a very intense peak at 2050 cm^{-1} which is character-

istic ammonium chloride absorption. At 1400 cm^{-1} there is strong absorption of C-H. However, in both spectra there is no absorption at $820\text{-}830\text{ cm}^{-1}$ which signifies no C-Cl bonds. There is an ionic chlorine but it is not attached to any carbon atom in the molecule. By comparison of these two spectra, it can be seen that t-butylamine hydrochloride is much simpler than cyclohexylamine hydrochloride because of fewer peaks. This results by the fact that in cyclohexylamine hydrochloride there are different types of C-H bonds around the molecule and in t-butylamine hydrochloride there is only one C-H bond.

FIGURE I shows the infrared spectrum of dimethoxy-t-butyl adduct. There appears no broad absorption centered about 3000 cm^{-1} as in the previous spectra. This results from the fact that this compound has no positively charged nitrogen. Instead this compound shows two peaks in this range. At 3250 cm^{-1} C-N absorption occurs and at 2900 cm^{-1} C-H absorption occurs. Similarly around 1700 cm^{-1} there are three peaks for the three double bonds in the molecule. Between $1200\text{-}1350\text{ cm}^{-1}$ numerous peaks forming a slight parabolic shape appear which characterizes a C-O-C bond. The triple peak at 1400 cm^{-1} for C-H absorption is also characteristic for ester compounds. Since there appears no intense peak around 820 cm^{-1} , chlorines were knock off

the ring by OCH_3 . Dimethoxy-*t*-butyl adduct is an example of an amidine.

FIGURE II is an infrared spectrum of an amidinium salt resulting from reacting the amidine, dimethoxy-*t*-butyl adduct, with dilute hydrochloric acid. The spectrum shows the reappearance of the broad absorption band centered about 3000 cm^{-1} which is a blend of C-H, C-N, and positively charged nitrogen absorption. Again the two peaks that were characterized in the infrared spectra of cyclopentylamine adduct, cycloheptylamine adduct, and cyclooctylamine adduct to signify the three double bonds in the molecule reappeared.

FIGURE XI is the mass spectrum for cyclopentylamine adduct. The mass number calculated for this compound was 463 (3 N, 29 H, 21 C, 4 Cl₃₅). Shrader stated that isotopic clusters of four chlorines had a certain pattern. He showed the first peak to be smaller than the second peak, the third peak to be smaller than the first and second peaks, the fourth peak to be smaller than the third peak, and the fifth peak to be smaller than the fourth peak. (36) On one end of the spectrum two chlorines in succession are kicked out from the compound as can be evidenced by peaks at mass numbers 429 and 394. On the other end of the spectrum there are peaks at mass numbers 69 and 84 which signify expulsion of a cyclopentyl

group and a cyclopentyl amine group, respectively. Not much can be said about what occurs in the intermediate range because the mechanism of disintegration becomes unclear. However, the expulsion of two chlorines from one end of the spectrum and the formation of cyclopentyl and cyclopentylamine groups occurring at calculated mass numbers clearly points to the structure assigned as being correct.

CONCLUSION

This thesis helped to further advance the findings of many researchers who reacted polyhalogenated cyclic carbon compounds with cyclic amines to form various amidinium salts. Even though the primary cyclic amines used in my thesis were bulky, steric effects did not inhibit formation of the salts. In fact these products were relatively stable as evidenced by their elevated melting points.

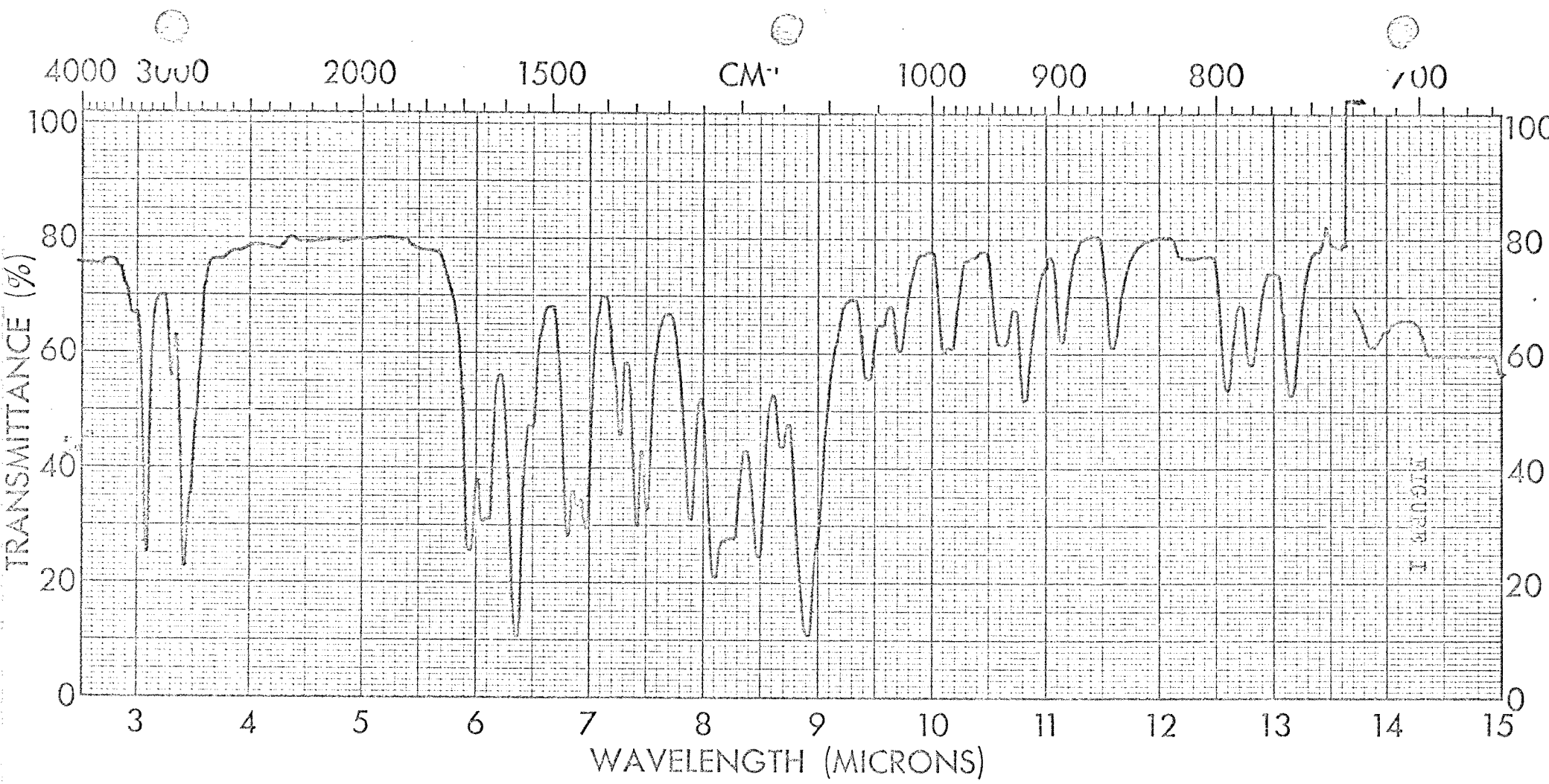


FIGURE 1

SPECTRUM NO. <i>solid</i>	ORIGIN	LEGEND	REMARKS
SAMPLE PG 31 LUEZI		1.	
<i>Veratrilol</i>	PURITY	2.	
<i>solid</i>	PHASE	DATE 3-1-71	
	THICKNESS	OPERATOR R. Smith	

SPECTRO-TECH INC. 55

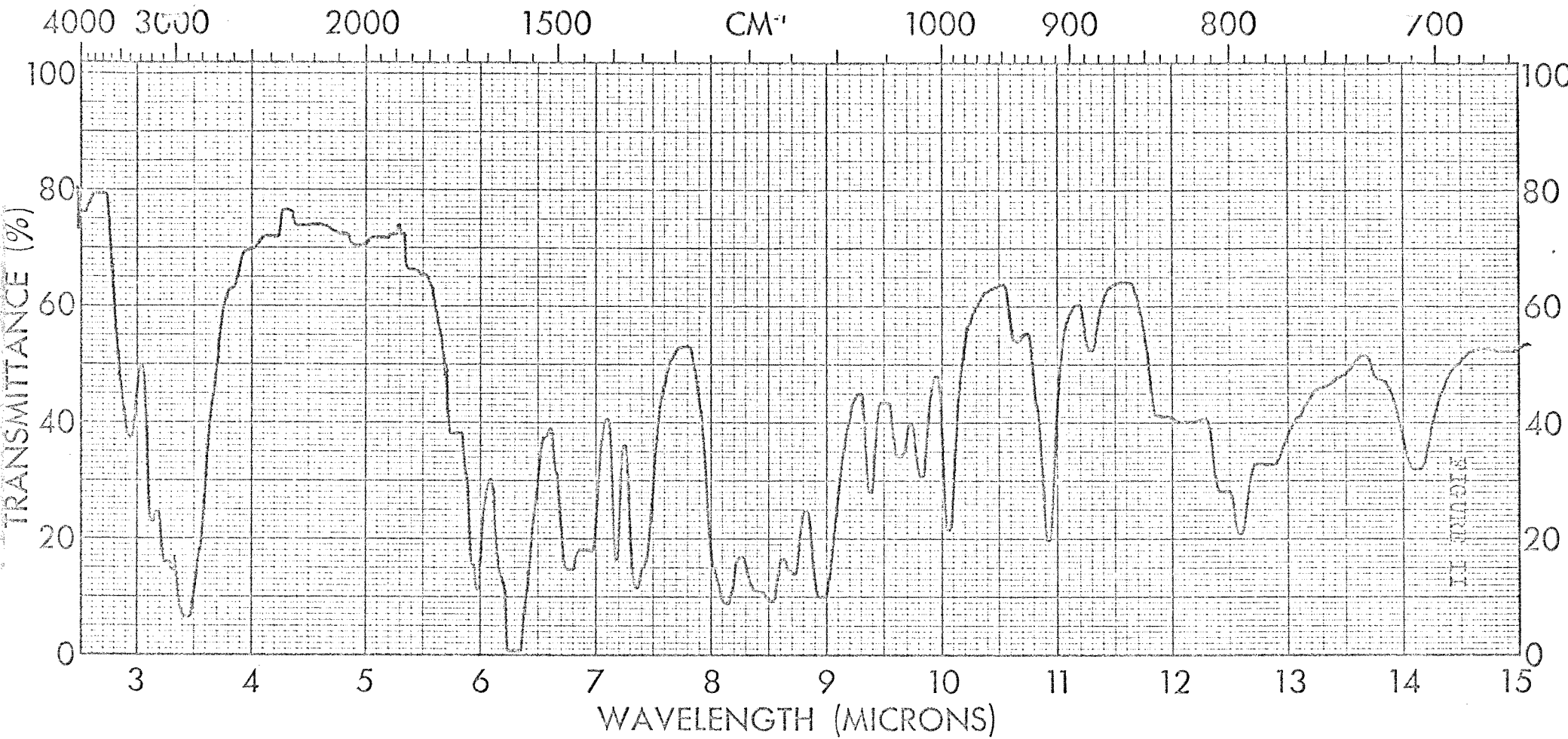
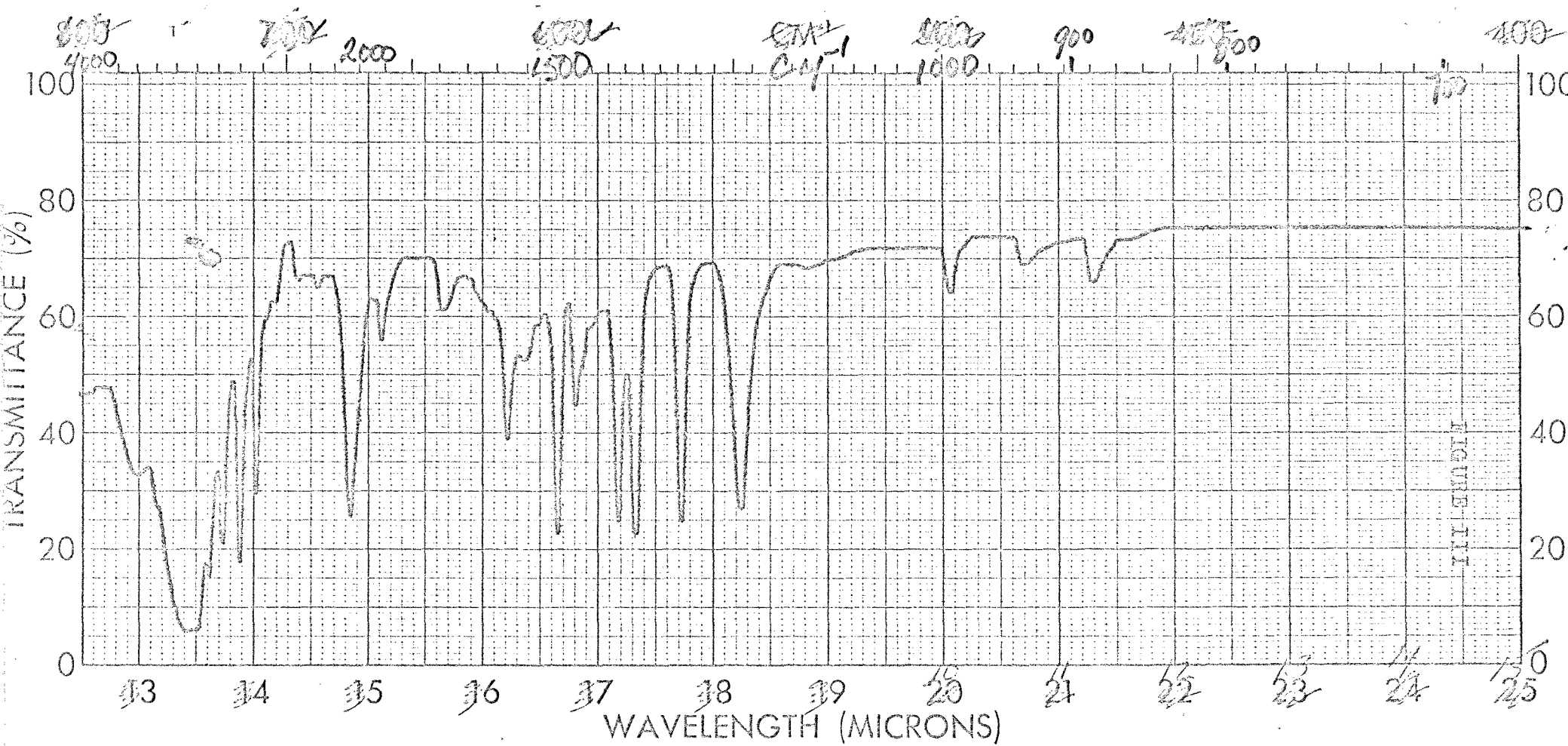


FIGURE 11

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE <i>SOLID</i> PAGE 35 LINE 9	<i>NEW ANIDINIUM</i> <i>SALT</i>	1.	<i>(+HCl)</i>
<i>TRIP # 1</i>	PURITY	2.	
	PHASE	DATE <i>3-1-71</i>	
	THICKNESS	OPERATOR <i>R. SMITH</i>	

SPECTRUM NO. 36



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE SOLID PAGE 41 LINE 19	t-BUTYL AMINE HYDROCHLORIDE	1.	
TRIAL #2	PURITY CH_3 CH_2 CH_3	2.	
	PHASE CH_3 NH_3^+	DATE 3-19-71	
	THICKNESS 01	OPERATOR R. SMITH	

SILENCING IN...
 SAMPLE...
 37

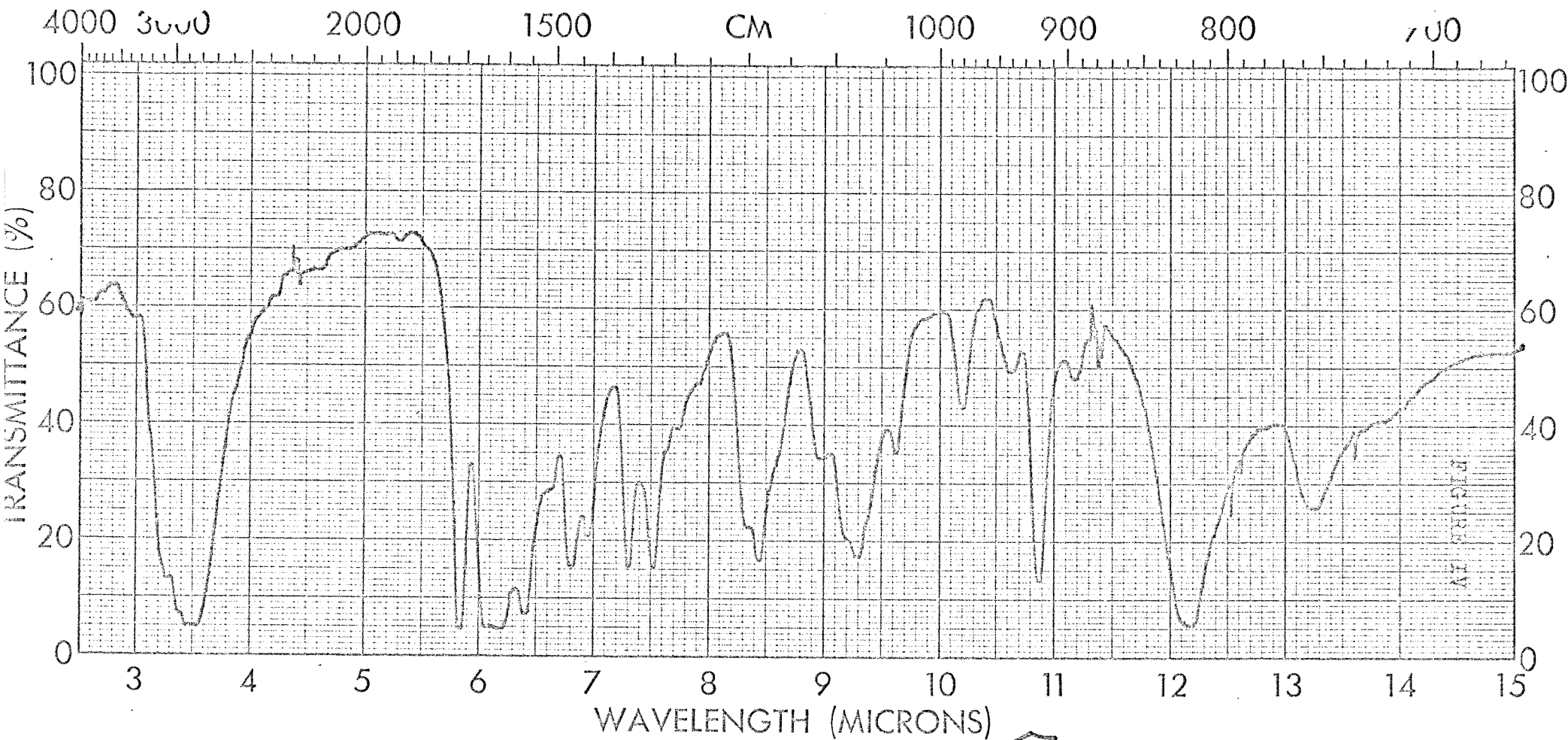
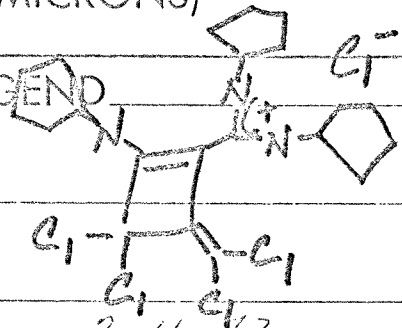
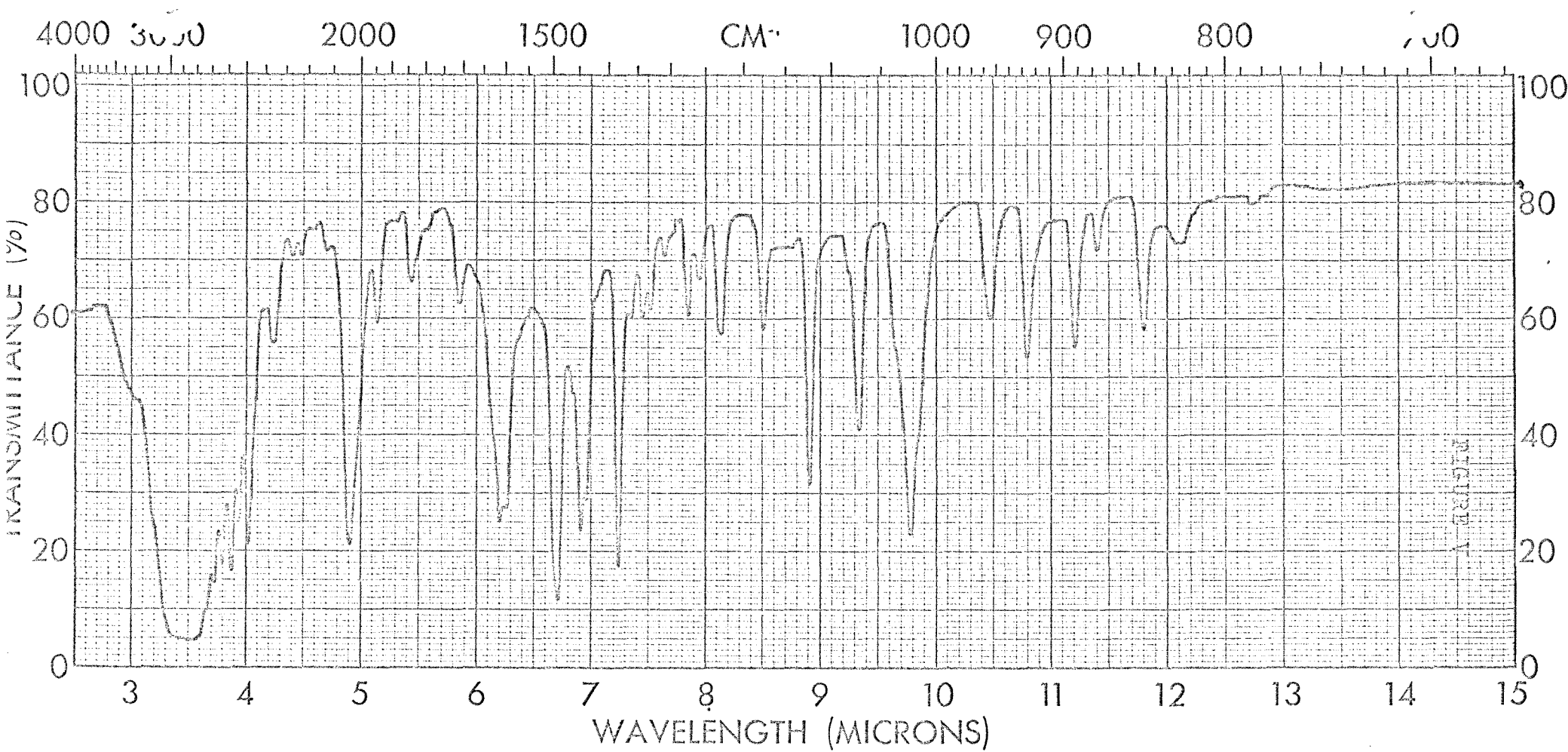


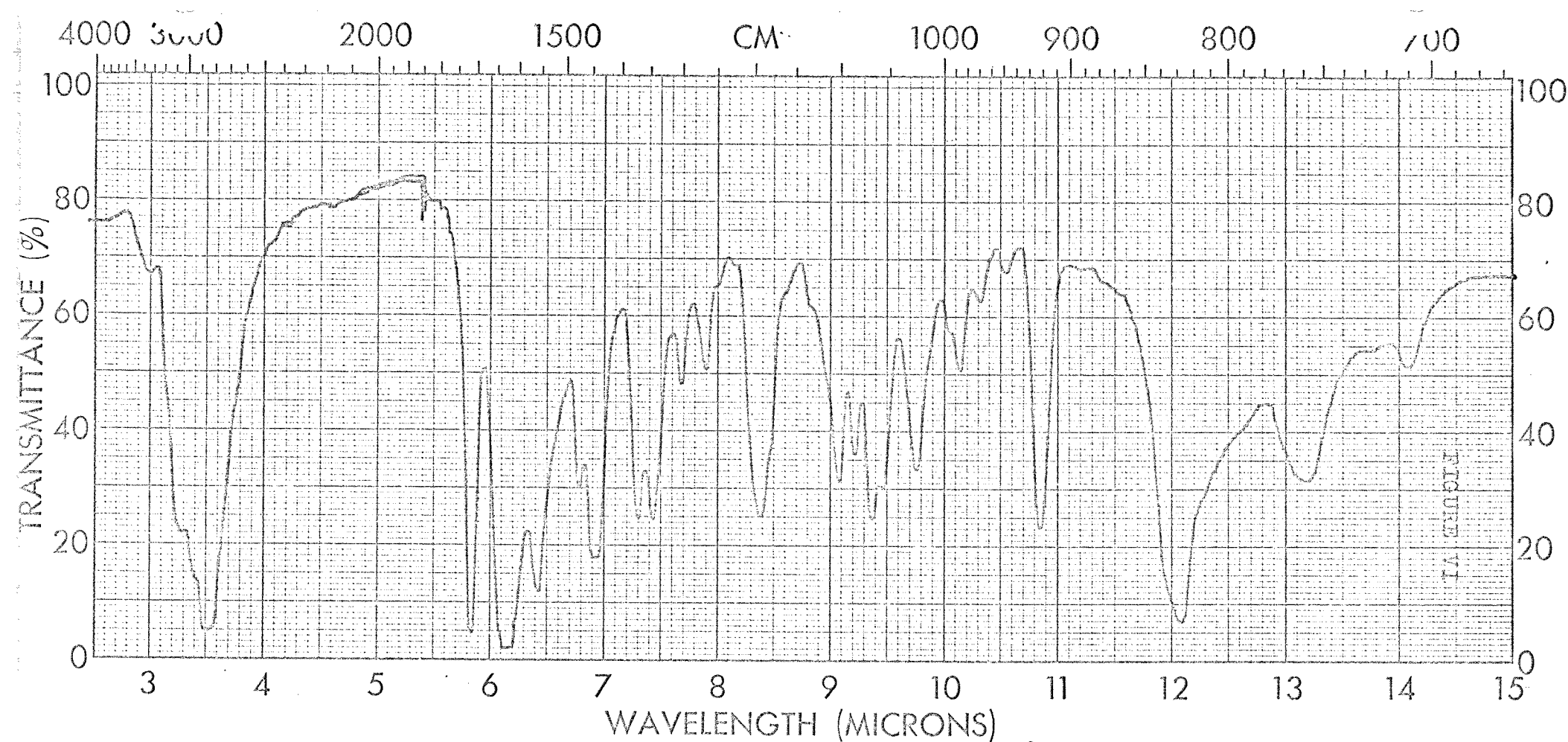
FIGURE 1A

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE <u>Solid 77-16</u>	<u>CYCLOPROPANONE ADDUCT</u>	1. 	
<u>(Cyclopropane)</u>	PURITY	2. <u>2-4-72</u>	<u>5mg solid</u>
	PHASE	DATE <u>1-5-72</u>	<u>200mg KBr</u>
	THICKNESS	OPERATOR <u>P. SMITH</u>	



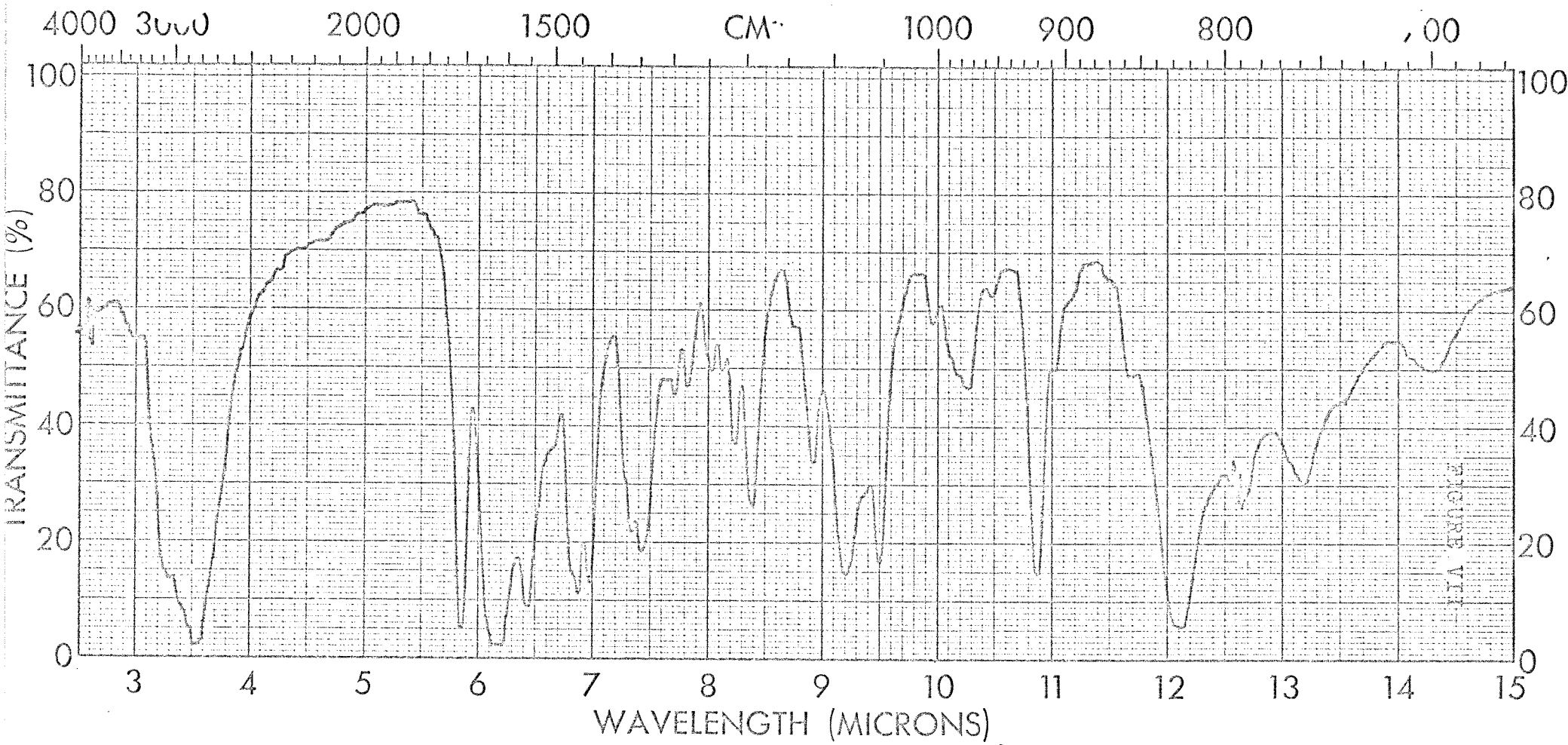
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE SOLIDS 77-30	CYCLOHEXYL AMINE HYDROCHLORIDE	1.	54g solid
(C/16/Hex/μ)	PURITY	2.	200mg KBr
	PHASE <chem>C1CCCCC1[NH3+].[Cl-]</chem>	DATE 2-4-72 1-15-72	
	THICKNESS 1	OPERATOR R. S. H. H.	

SPECTRUM NO. 59



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	
SAMPLE <u>Solids 79-5</u>	<u>CYCLOHEPTYLAMINE</u>		<u>546 Solids</u>	
<u>(Cycloheptyl)</u>	<u>ADDUCT</u>		<u>200MG KBr</u>	
PURITY			<u>DATE 2-4-72</u>	<u>TRIAL #2</u>
PHASE			OPERATOR <u>R. Smith</u>	<u>SAME LABEL AS TRIAL #1</u>
THICKNESS				

SPECTRUM NO. 40



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE <i>SOLID 7A-19</i>	<i>cyclohexylamine adduct</i>	<ol style="list-style-type: none"> 	
<i>(cyclohexane)</i>	PURITY	DATE <i>2-4-72</i>	<i>549g solid 200 mg KBr</i>
PHASE	THICKNESS	OPERATOR <i>R. Smith</i>	

SPECTRUM NO. 41

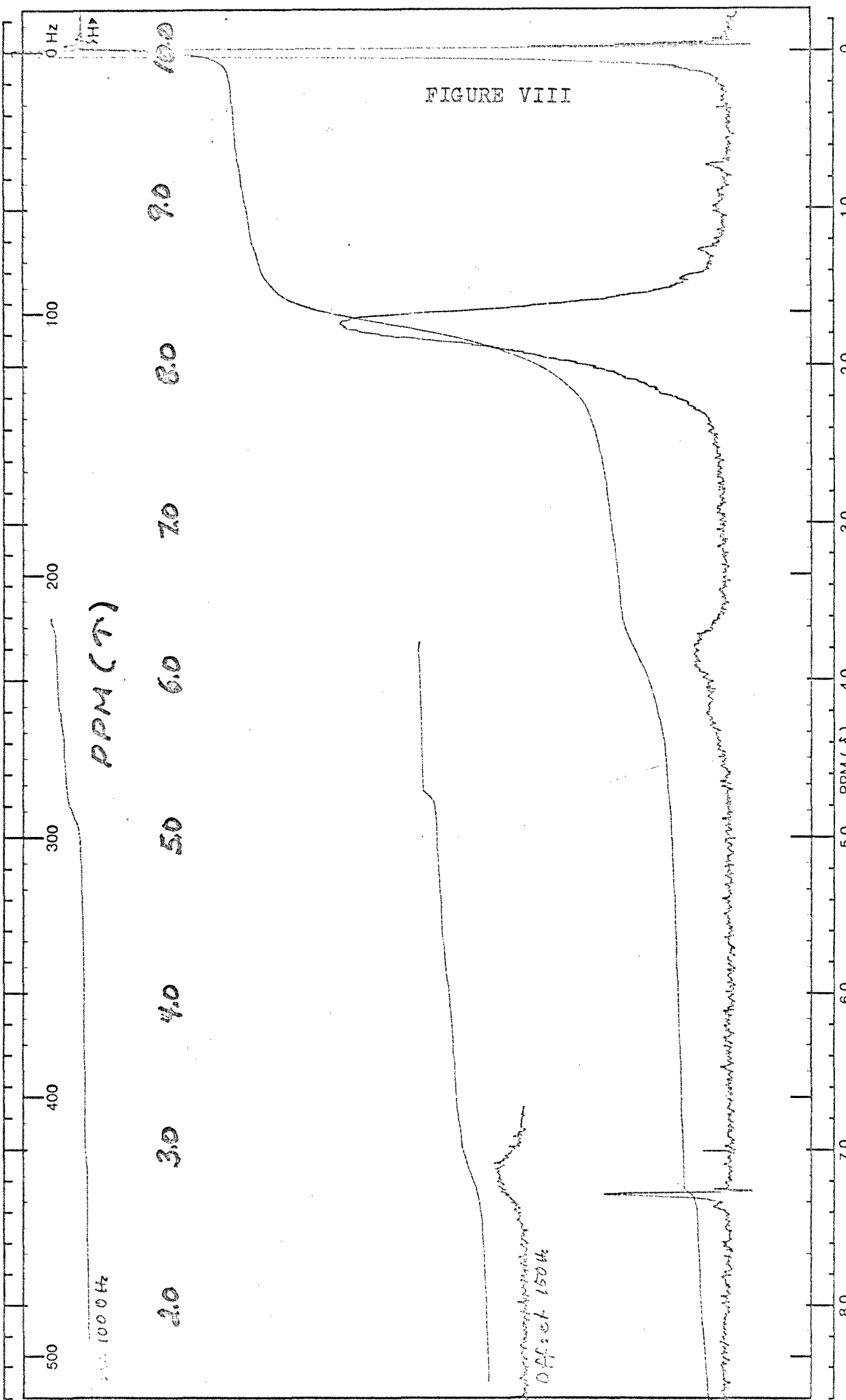


FIGURE VIII

PPM (τ)

0 Hz

100

200

300

400

500

2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0

100.0 Hz

Offset 150 Hz

REMARKS:

③

SAMPLE:

AUTO (250)
(500)

MANUAL

SWEEP TIME (SEC): 50.23
SWEEP WIDTH (Hz): 23.50 [100] [250] [500]

INTEGRAL AMPLITUDE: 12.5-3.5 FILTER: 1 2 3 4 5 6 7 8

SPINNING RATE (RPS): 44

RF POWER LEVEL: 0.06

SOLVENT: CDCl₃

Cyclohexylamine
ADUVER

42

60 MHz NMR
SPECTRUM NO.

R/M

OPERATOR

DATE: 3-15-74

THOMPSON PACKARD INC.

SOLVENT $CDCl_3$

FILTER BAND WIDTH 2 cps

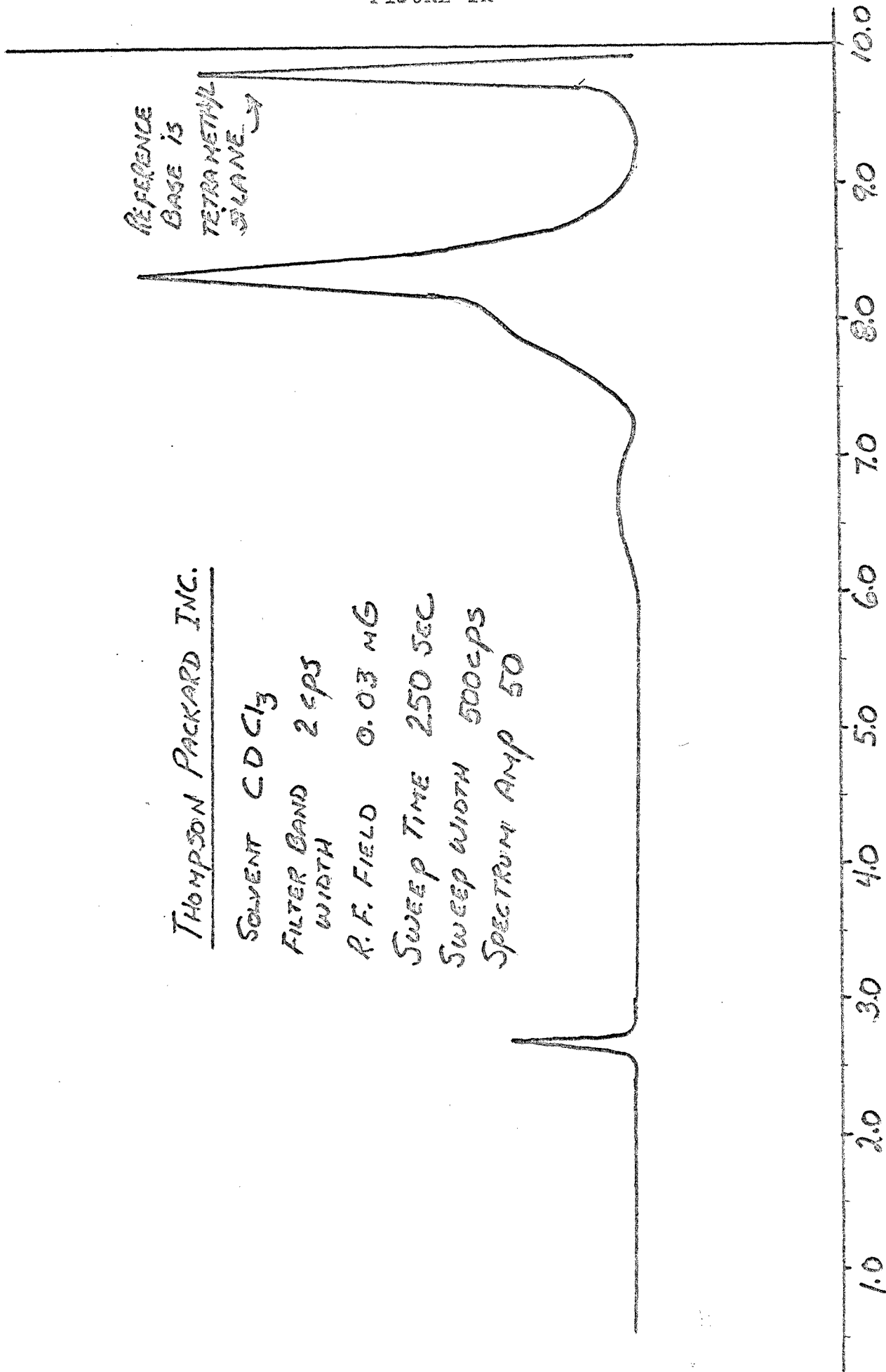
R. F. FIELD 0.03 MG

SWEEP TIME 250 SEC

SWEEP WIDTH 500 cps

SPECTRUM AMP 50

REFERENCE
BASE IS
TETRAMETHYL
SIANE



PPM (T)

SAMPLE 85-17

DATE 3-1-74

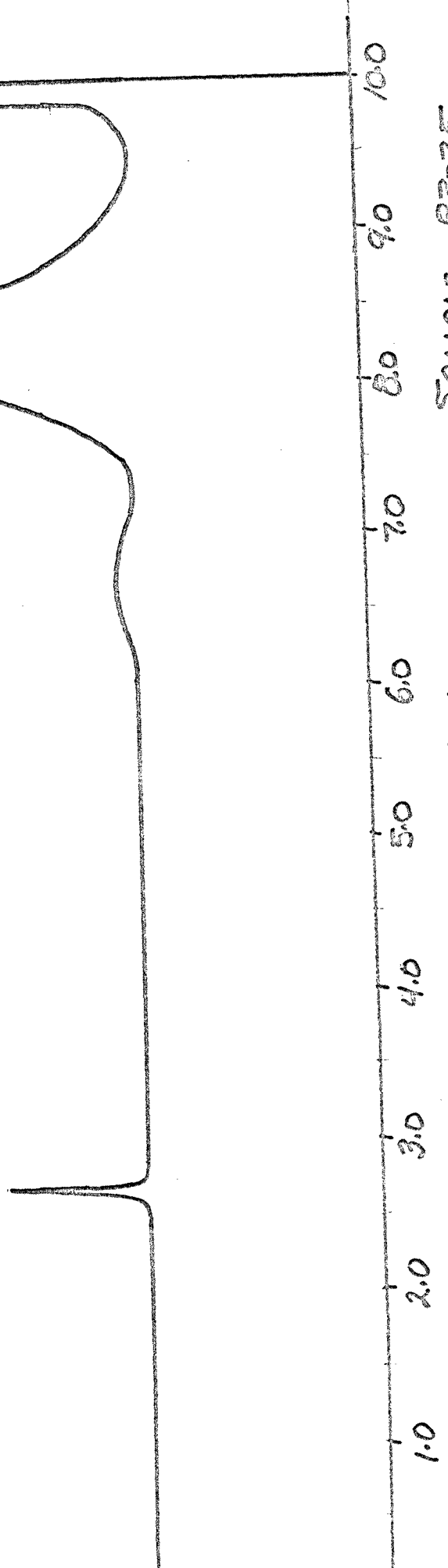
OPERATOR D. T.

FIGURE X

REFERENCE BASE
IS TETRAMETHYL
SILANE

THOMPSON PACKARD INC.

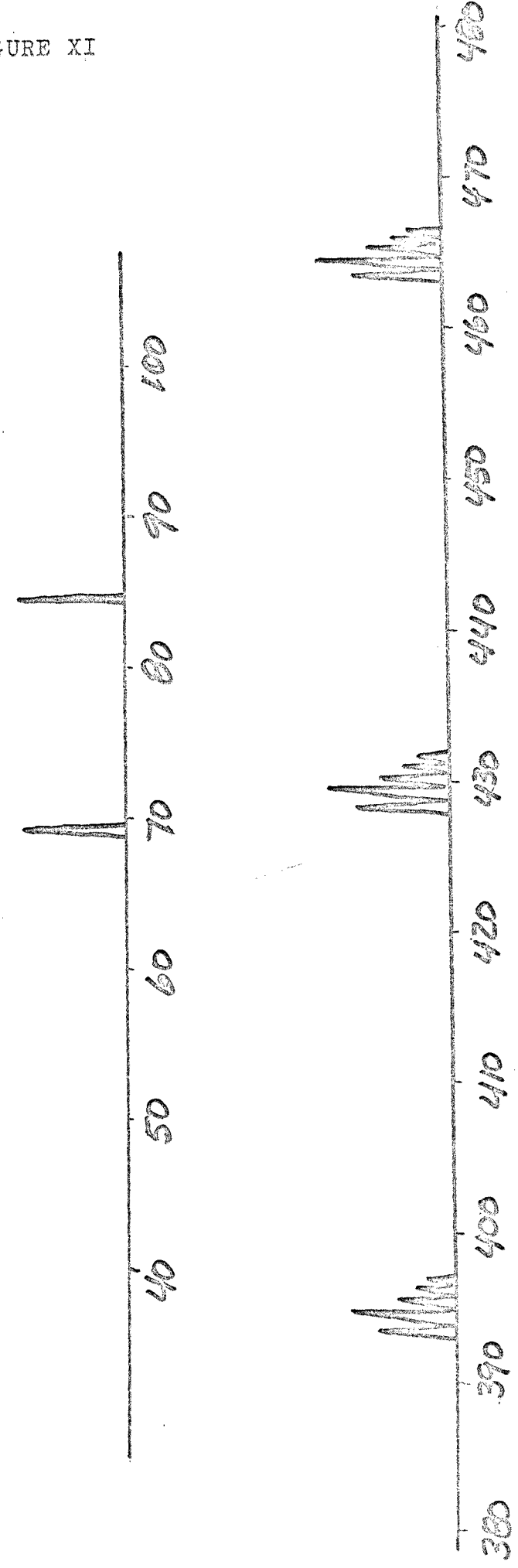
SOLVENT $CDCl_3$
FILTER BAND WIDTH 2 cps
R.F. FIELD 0.03 MG
SWEEP TIME 250 SEC
SWEEP WIDTH 500 cps
SPECTRUM AMP. 50



SAMPLE B3-25
DATE 3-1-74
OPERATOR D. T.

FIGURE XI

MASS SPECTRUM FOR CYCLOPENTYLAMINE ADDUCT



MASS NUMBERS

REFERENCES

- (1) Tobey, S.W. and West, R., Tetrahedron Letters 1179 (1963).
- (2) Fields, E.K. and Meyerson, S., J. Org. Chem. 28, 1915 (1963).
- (3) Solomon, W.C., Dee, L.A. and Schults, D.W., J. Org. Chem. 31, 1551 (1966).
- (4) Wagner, W.M. and Kloosterziel, H., Rec. Trav. Chim. 81, 947 (1962).
- (5) Hine, J., Pollitzer, E.L. and Wagner, H., J. Am. Chem. Soc. 75, 5607 (1953).
- (6) Hine, J., J. Am. Chem. Soc. 72, 2438 (1950).
- (7) Roedig, A. and Bischoff, F., Naturwiss. 49, 448 (1962).
- (8) Pilgrim, K. and Korte, F., Tetrahedron Letters 883 (1962).
- (9) Roedig, A., Markel, G. and Heinrich, B., Angew. Chem. 75, 88, (1963).
- (10) Wagner, W.M. and Kloosterziel, H., Rec. Trav. Chim. 81, 925 (1962).
- (11) Moahs, G., Angew. Chem. 75, 451 (1963).
- (12) Roedig, A., Bischoff, F., Heinrich, B. and Markel, G., Ann. 670, 8 (1963).
- (13) Wagner, W.M. and Vriesman, L., Rec. Trav. Chim. 82, 517 (1963).
- (14) Roedig, A., Bischoff, F., Heinrich, B. and Markel, G., Ann. 670, 8 (1963).
- (15) Roedig, A. and Heinrich, B., Chem. Ber. 100, 3716 (1967).
- (16) Moahs, G., Angew. Chem. 75, 451 (1963).

- (17) Mano, K., Kusuda, K., Fujino, A. and Sakan, T., Tetrahedron Letters, 489 (1966).
- (18) Fujino, A. and Kusuda, K., Bull. Chem. Soc. Jap. 39, 160 (1966).
- (19) Kusuda, K. and Mano, K., Bull. Chem. Soc. Jap. 40, 1188 (1967).
- (20) Mano, K., Kusuda, K. and Fujino, A., Tetrahedron Letters, 1375 (1968); Furusaki, A. and Nitta, I., Tetrahedron Letters, 1379 (1968).
- (21) Roedig, A., Markel, G. and Schaller, H., Ann. 710, 7 (1968).
- (22) Roedig, A. and Detzer, N., Angew. Chem Int. Ed. 7, 471 (1968).
- (23) Roedig, A. and Detzer, N., Angew. Chem. Int. Ed. 7, 472 (1968).
- (24) Jutz, G., Mueller, W. and Mueller, E., Chem. Ber. 99, 2479 (1966).
- (25) Volkenshtein, Y.B., Besprozyanniji, M.A., et. al., Izv. Akad. Nauk. S.S.S.R., 2609 (1972).
- (26) Tobey, S.W., Chemical Abstracts 77, 19254
- (27) Cohen, S., Lacher, J. and Park, J.D., J. Am Chem. Soc. 81, 3480 (1959).
- (28) McBee, E.T. and Turner, J.J., J. Org. Chem. 30, 3698 (1965).
- (29) Ellzey, S.E. and Guice, W.A., J. Org. Chem. 31, 1300 (1966).
- (30) Frank, A.W., J. Org. Chem. 31, 1917 (1966).
- (31) Dehmlow, E., Chem. Ber. 100, 2779 (1967).
- (32) Tobey, S.W. and West, R., Tetrahedron Letters, 1179 (1963).

- (33) Moahs, G. and Hegenberg, P., Angew. Chem. 78, 927 (1966);
Sweeney, R.F., Veldhuis, B. and Gilbert, E.~~B.~~, et. al.,
J. Org. Chem. 31, 3174 (1966).
- (34) Hartung, E., J. Chem Soc. 113, 163 (1918); Chemical
Abstracts 12, 1378 (1918).
- (35) Kristol, D. and Shapiro, R., J. Org. Chem. 38, 1470
(1973).
- (36) Shrader, Stephen R., Introductory Mass Spectrometry.
Boston: Allyn and Bacon, Inc., 1971, p. 21