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Synthetic approaches to specifically labeled dimethyl-dideuterionaphthalenes

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UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

Synthetic Approaches to Specifically Labeled Dimethyldideuterionaphthalenes

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

chem

by Armand J. Scatena MS 1977

By Armand J. Scatena
(Student's signature)

Approved by William B Martin, Jr.
Thesis advisor

Approved by
Committee on Graduate Studies

Date June 1977

Synthetic Approaches to Specifically Labeled Dimethyldideuterionaphthalenes

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by

Armand J. Scatena

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Chemistry

Union College
January, 1977

DEDICATION

I wish to express my gratitude to Dr. William B. Martin, whose advice and guidance contributed significantly to the completion of this thesis.

Recognition is also due to Schenectady Chemicals, Inc. for the use of their analytical instruments.

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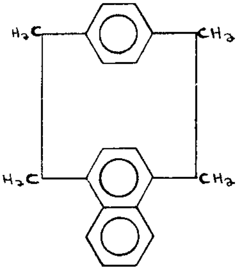
ABSTRACT

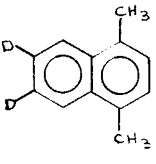
The purpose of this work was the study of synthetic approaches to specifically labeled deuterated 1,4-dimethylnaphthalenes. Alkylation of ortho- and para-dibromobenzenes eventually led to the formation of some 1,4-dimethylnaphthalene although deuteration was rather poor. Under the conditions employed, much isomerization of Friedel-Crafts products resulted. Not only did the bromines rearrange intramolecularly, but substantial rearrangement of the alkylating moiety may also have occurred. The major products of these reactions were dibromophenylcyclohexanes. It appears from the products obtained by the methods employed in our work that specific monodeuteration rather than specific dideuteration should be used to attain the desired products.

INTRODUCTION

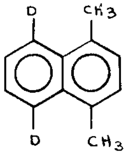
The reason for undertaking the synthesis of the dimethyldideuterionapthalenes (II, III and IV) stems from interest in assigning coupling constants* to various portions of the benzo- [2.2] - paracyclophane molecule (I)



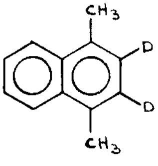
I



II



III



IV

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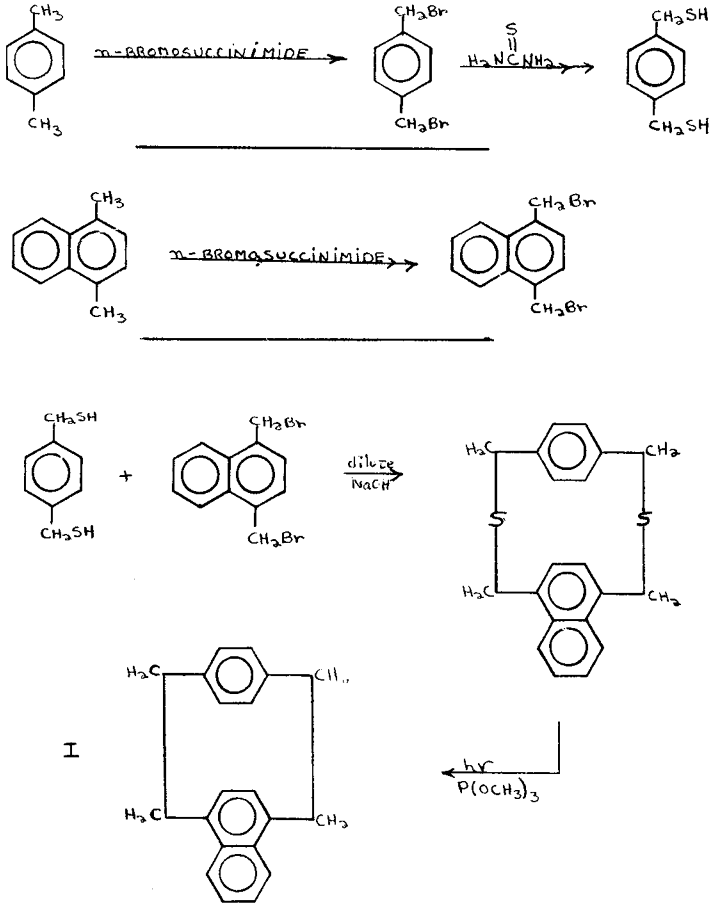
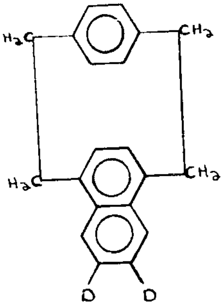
*Some NMR coupling constants on a related dithiabenzoparacyclophane have been determined by Begley [4] and differ from those expected from literature. ESR coupling constants are to be correlated with those of undeuterated I.

The subsequent syntheses for making specifically labeled dideuterio-benzo- 2.2 -paracyclophanes would proceed analogously to the following scheme:

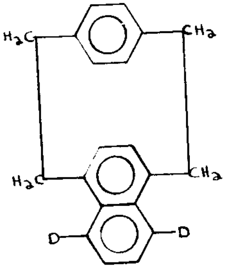


I

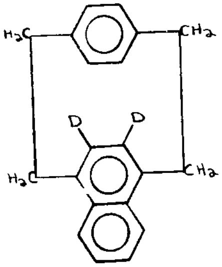
The dimethyldideuterionapthalenes are to be used later to synthesize the dideuteriobenzo- [2.2] - paracyclophanes (V, VI and VII), which will yield the unequivocal assignment of the coupling constants in the naphthalene moiety of the benzoparacyclophane radical anion.



V



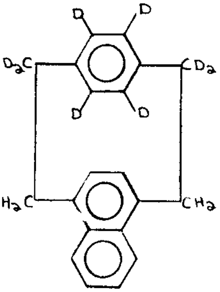
VI



VII

Initial work in this area was done by Professors F.Gerson and W. Martin. [1,2,3] From this and yet unpublished work, it was assumed that better accommodation of the odd electron would be expected in the naphthalene portion of this sandwich-like compound. Thus, small coupling constants are expected in the benzene portion of the molecule. Initial ESR and ENDOR (electron nuclear double resonance spectroscopy) studies have been made by Gerson and Martin. Confirmation of their assignment of coupling constants is possible by substitution of deuterium for hydrogen in specific locations.

Work on the synthesis of 2, 2, 4, 5, 7, 8, 9, 9-octadeuteriobenzo- [2.2]-paracyclophane (VIII) has been initiated by Begley and Martin[4] to confirm the assignment of the presumably small coupling constants to the benzene portion of the molecule.

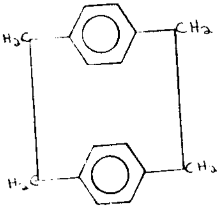


VIII

Thus benzoparacyclophanes V, VI and VII would be used to measure the coupling constants of the naphthalene portion of the radical anion of the molecule in order to map the electron densities in the orbital bearing the single electron.

HISTORICAL AND SYNTHETIC APPROACH

The first reported paracyclophane was discovered by Brown and Farthing[5] while examining polymers prepared by low pressure pyrolysis of p-xylene. They noticed that a chloroform extraction of the polymer yielded a mixture of low molecular weight compounds containing traces of an acetone-insoluble fraction having a melting point of 285°C. The structure of this compound was determined by x-ray diffraction to be that of [2.2] - paracyclophane(IX)which they named "di-p-xylene".



IX

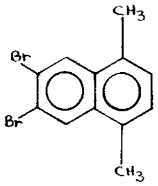
Brown and Farthing failed in future attempts to prepare this novel compound. The first successful synthesis of a paracyclophane was reported by Cram and Steinberg.[6] Since then, Cram has published numerous papers in the Journal of the

American Chemical Society on paracyclophane chemistry.

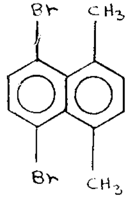
In 1951 Cram originally defined a paracyclophane as a class of compounds in which "two benzene rings are rigidly held in a face to face position by methylene bridges in the para position".[6]

Our interest lies in benzo- [2.2]-paracyclophane (I). As stated earlier, we are interested in confirming the assignment of coupling constants in the molecule. The work done by Begley and Martin[4] will either confirm or refute the assignment of the coupling constants in the benzene portion of the molecule. The dimethyl-dideuterionaphthalenes (II, III and IV) will be used in the synthesis of the dideutriobenzo- [2.2]-paracyclophanes (V, VI and VII), which will either confirm or refute the assignment of the coupling constants in the naphthalene portion of the molecule.

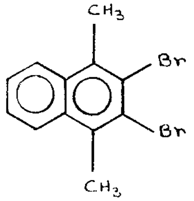
A search of the literature showed us that the dimethyldideuterionaphthalenes(II, III, IV) had not been previously synthesized. It was decided to try and make II, III and IV from their dibromo counterparts[7] (X, XI and XII), none of which have been previously synthesized.



X

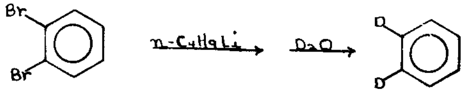


XI



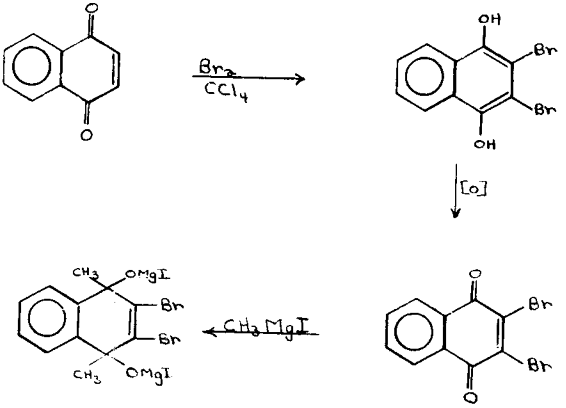
XII

To be sure that the bromine atoms would exchange for deuterium atoms and yield the desired compounds, it was decided to first try o-dibromobenzene as a model case. The following reaction was carried out and deuteriobenzene was obtained in trace amounts.



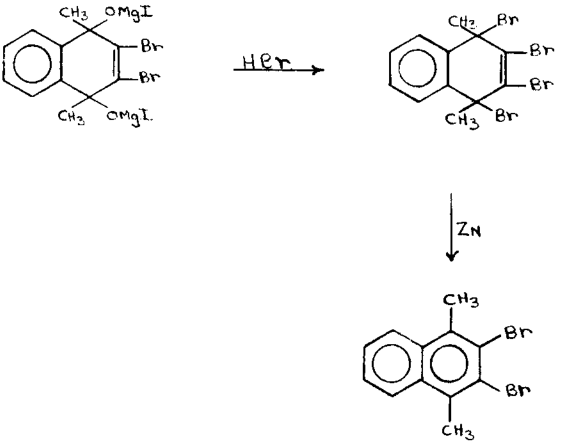
(1)

A proposed route of synthesis of 1,4-dimethyl-2,3-dideuterionaphthalene began with the bromination of naphthoquinone, followed by treatment with Grignard reagent.[8]



(2)

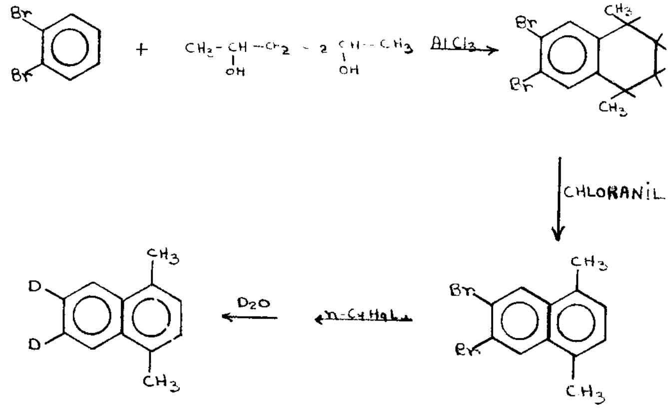
The intermediate was then to be treated with HBr and zinc metal to give the desired dibromide.



(2')

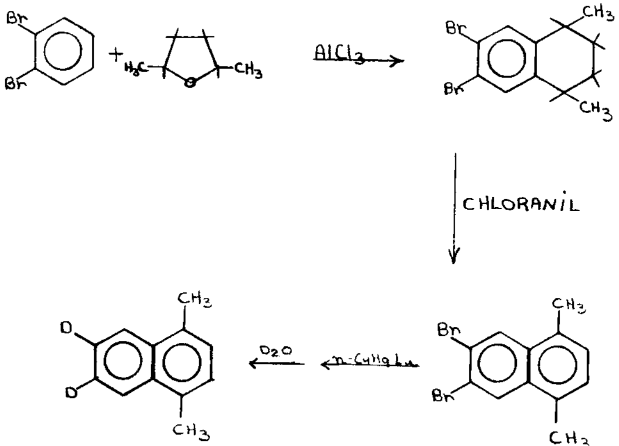
As a model case, naphthoquinone was treated with methyl magnesium iodide, HBr and zinc metal (2 and 2').
The desired product (1,4-dimethylnaphthalene) was not obtained.

The following reaction sequences were the proposed routes for synthesis[9,10] of 1,4-dimethyl-6,7-dideuterionaphthalene(II).


Br
Br
CH2-CH-CH2-2CH-CH3
OH
OH
AlCl3
Br
Br
CH3
CH3
CHLORANIL
CH3
Br
Br
CH3
n-C4H9Li
D2O
CH3
D
D
CH3

II

(3)

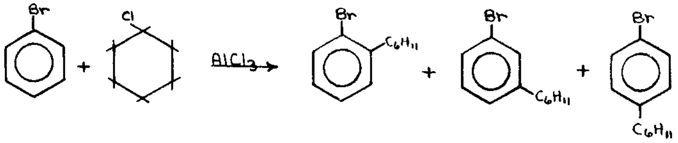

Br
Br
H3C
CH3
O
AlCl3
Br
Br
CH3
CH3
CHLORANIL
CH3
Br
Br
CH3
n-C4H9Li
D2O
CH3
D
D
CH3

(4)

II

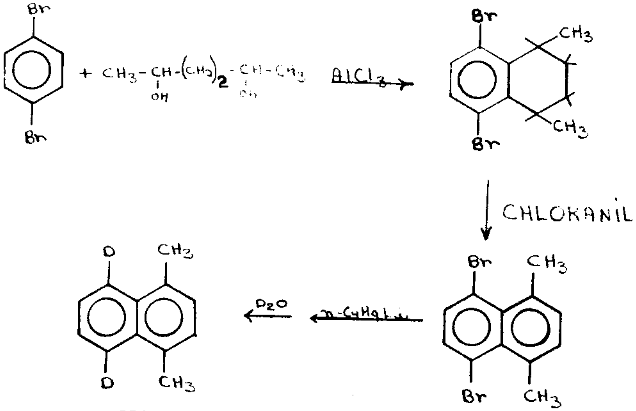
The Friedel-Crafts alkylation of aromatic rings is historically too well documented to review here. Reference is made only to Chapter 1, Volume III of "Organic Reactions" by C. C. Price (John Wiley, New York (1946)) and to the series of volumes of "Friedel Crafts and Related Reactions" by Olah (Interscience, New York (1964)). In "Organic Reactions", several references for alkylation of monobromobenzene are given.[22,23,24,25,26,27]

A typical sequence was to treat the bromobenzene with the appropriate alkyl halide and Al Cl_3 at about room temperature. The Al Cl_3 was later destroyed with water and after drying, the products were fractionated.



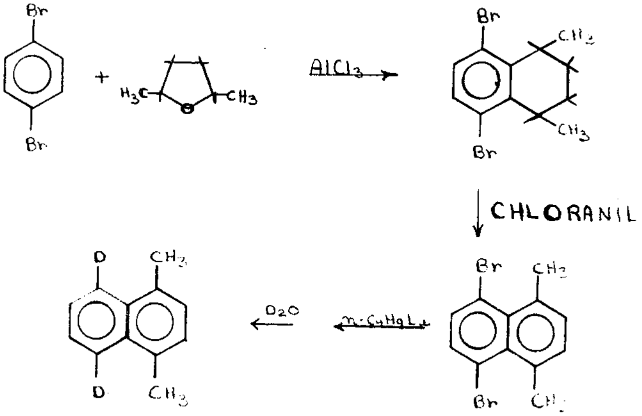
In this thesis, the concern was with the difunctionality of the cyclic ether or the diol causing linear combination of three or more substituents. Therefore, at the time of planning, cyclohexane was chosen to be what seemed an inert solvent which would optimize cyclization of the two reactants.

The following reaction sequences were proposed for the synthesis of 1,4-dimethyl-5,8-dideuterionaphthalenes (IV) [9,10]



(5)

III

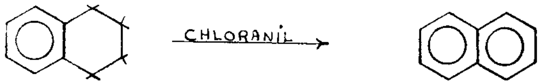


(6)

III

As a model case for the aromatization via chloranil,[11,12,13] an attempt to convert tetralin to naphthalene was made.

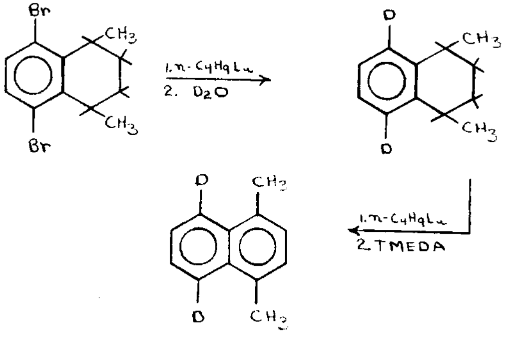
(7)



In the model case, only 40% of the tetralin was converted to naphthalene. When, however, the dimethyldibromotetralins were treated with chloranil, no aromatization was apparent.

An alternate method of aromatization was tried using n-butyl lithium and tetramethylethylendiamine [14](TMEDA).

(8)



III

This method of aromatization offered some conveniences in that subsequent treatment with n-butyl lithium and TMEDA could be made without having to first separate the product, thus combining the deuteration and the aromatization.

EXPERIMENTAL

Model Case:o-Dideuteriobenzene[7](1) Into an oven dried 25 ml reaction flask containing 2.6 g.(0.01 moles) of o-dibromobenzene(Eastman 3914) were slowly added 9 ml (0.02 moles) of 2 [illegible]-butylithium in hexane(Alfa 44109). There was a noticeable evolution of heat. After the solution was allowed to stand for one hour with an attached reflux condenser, 0.7 ml(0.035 moles) of deuterated water(D_2O) (Silanor 99.7 atom %) were added and the reaction was allowed to stand overnight. After 20 hours, 10 ml of water were added to the reaction mixture in order to neutralize any residual n-butyllithium. The reaction mixture was then acidified with concentrated hydrochloric acid and extracted with 20 ml of anhydrous ethyl ether. The ether extract was then injected into a gas chromatograph. The separation of dideuteriobenzene from 1-bromo-2-deuteriobenzene, d_1-phenol and 1-bromobutane was carried out on two different chromatographic columns: 1) a 6 ft. x 1/4 in.-10% silicone oil DC-710 on Chromosorb W at 90°C and, 2) a 6 ft. x 1/4 in.-15% SE30 + 10% Carbowax 20M on Chromosorb W at 100°C. The chromatographic analysis indicated that only trace amounts of the dideuteriobenzene had been formed. Utilizing a GC-mass spec, a mass spectrum (figure 1) of the supposedly dideuteriobenzene was obtained. The mass spectrum indicates that the product formed was monodeuteriobenzene and not dideuteriobenzene. An infrared spectrum(figure 2-2A) of the hexane mixture was taken before the ether extraction was made.

Model Case: 1,4-Dimethyl Naphthalene[8](2 and 2')

Into a 100 ml reaction flask containing 20 ml of dry tetrahydrofuran were added 0.68 g.(0.028 moles) of finely divided magnesium and 4.0g.(0.028 moles) of iodomethane(Eastman 164). The iodomethane was added with the aid of an additional 10 ml of dry tetrahydrofuran. The mixture was heated gently until all of the magnesium was consumed. Then, a solution of 2.21g. (0.14 moles) of naphthoquinone(Eastman P1704) in 25 ml of dry tetrahydrofuran was added to the reaction mixture. The mixture was then heated and held at reflux temperature for one hour. During refluxing, the reaction mixture became blue-green in color. After refluxing, the reaction mixture was concentrated to dryness in vacuo using a Buchi rotovapor-R apparatus. Then, 10 ml of 48% hydrobromic acid were cautiously added to the residue. To this solution was added 50 ml of ethanol and 2.0g. of zinc metal. The solution was stirred at room temperature with an attached reflux condenser for 72 hours. The ethanol was then removed in vacuo using a Buchi rotovapor-R apparatus. Then, 100 ml of a 1:1(V/V) benzene-ether solution was used to extract the product from the residue. The benzene-ether solution was then gravity filtered and washed with two 50 ml portions of 5% NaOH solution. The benzene-ether solution was again gravity filtered and then placed in a fume hood under a current of air to remove the benzene-ether. The extraction yielded a brown solid. Inspection of an infrared spectrum of the solid(figures 3-3A) and injection of the benzene-ether solution into a chromatograph showed that no 1,4-dimethylnaphthalene had been formed.

Model Case-Naphthalene [11,12,13](7) To a solution of 2.6g. (0.02 moles) of tetralin(Fisher T-72) in 50 ml of p-xylene (AR) were added 9.8g(0.04 moles) of chloranil(Eastman P603). The mixture was refluxed for five hours and then cooled and gravity filtered. Analysis of the mixture was carried out by gas chromatography. Columns used in the analysis were a 6 ft. x 1/8 in.-10% UCW-98 at 120°C and a 6 ft. x 1/4 in.-15% SE-30+ 10% Carbowax 20M at 175°C. Standard solutions of naphthalene and tetralin were used to identify the components. On the UCW-98 column, the tetralin had a retention time of 300 seconds and the naphthalene a retention time of 320 seconds. Injection of the mixture yielded fused peaks. On the SE-30-carbowax 20M column, the tetralin had a retention time of 161 seconds and the naphthalene had a retention time of 247 seconds. A comparison of the ratio of areas showed the tetralin to naphthalene conversion to be only 40% complete.

1,4-Dimethyl-5,8 dibromonaphthalene or isomer[9](5) To a solution of 24.9g.(0.106 moles) of p-dibromobenzene(Eastman P474) in 175 ml of dry distilled cyclohexane were added 48.75g. (0.369 moles) of Al Cl3(Fisher A-575) with stirring. Then at room temperature, 12.5 g.(0.106 moles) of 2,5-hexanediol (Aldrich H1 190-4) were added dropwise with an addition funnel over a period of forty minutes. The initial reaction temperature was 24°C. At the end of the addition of the diol the reaction temperature was 30°C. The addition funnel was washed with 25 ml of dry, distilled cyclohexane. Then, the reaction was allowed to proceed at room temperature with stirring for 70 hours. The color of the reaction changed sequentially from white(initially) to green (after 30 minutes) to yellow (after four hours) to brown (after 70 hours). After 70 hours, ice was added to the reaction mixture in order to decompose the excess $Al\ Cl_3$. The organic layer was then separated from the aqueous layer by means of a separatory funnel. The cyclohexane was removed from the organic layer by distillation, leaving a brown, oil -like liquid. Injection of the brown liquid into a gas chromatograph revealed that the liquid contained more than one component. The liquid was vacuum distilled under approximately 5 mm pressure. Four different fractions were collected: 1) undistilled residual material (IR-figures 4-4A), 2) a 48°-60°/ca. 5 mm fraction (IR-figures 5-5A), 3) a 60°-102°C/ca. 5 mm fraction (IR-figures 6-6A) and 4) a 120°-130°C/ ca. 5 mm fraction (11% of the reaction products by weight, IR figures 7-7A) whose GC curve showed three major peaks. This high boiling fraction was analyzed by gas chromatography on a 6 ft. x 1/8 in. 10% UCW-98 column at 200°C. This fraction contained two major components, each of which was collected in a glass coil cooled with ice at the outlet of the chromatograph's thermal conductivity detector.

An infrared spectrum (figures 8-8A and 9-9A), a nuclear magnetic resonance spectrum (figures 10 and 11) and a mass spectrum (figures 12 and 13) were taken on each of these components. In addition to these two major components, a small amount of a third, minor component was collected. A nuclear magnetic resonance spectrum(figure 14) and a mass spectrum(figure 15) were taken on this minor component. It was assumed that these three components which were obtained from the higher boiling fraction were isomers of dimethyldibromotetralin. Thus, to a solution of 2.0g.(0.063 moles) of the high boiling fraction in 50 ml of p-xylene (AR) were added 3.42 g.(0.0139 moles) of chloranil. This mixture was refluxed under a nitrogen atmosphere for 18 hours. After refluxing, the mixture was gravity filtered and washed with one 25 ml portion of 10% aqueous NaOH and five 25 ml portions of tap water. The p-xylene was removed in vacuo using a Buchi rotovapor-R apparatus. The remaining amber colored liquid was identified by infrared (figures 16-16A and 17-17A) and by chromatographic analysis to be the starting material.

1,4-Dimethyl-5,8-dibromo-1,2,3,4-tetrahydronaphthalene or Isomer[10](6). To a solution of 23.6g.(0.1 moles) of p-dibromobenzene in 200 ml of dry, distilled cyclohexane were added 46.2g.(0.35 mole) of Al Cl3 with stirring. Then, 10g. (0.1 moles) of 2,5-dimethyltetrahydrofuran(Pfaltz and Bauer) were added dropwise with an addition funnel over a period of ninety minutes at room temperature. The reaction temperature climbed from 24°C to 33°C during the addition. After the addition of 2,5-dimethyltetrahydrofuran was completed,the reaction temperature dropped to 28°C. The color of the reaction changed sequentially from white to green to yellow to brown(after four hours). The reaction was allowed to proceed at room temperature with stirring for 24 hours. After 24 hours, ice was added to the reaction mixture to decompose the Al C13. The organic layer was then separated from the aqueous layer by means of a separatory funnel. The organic layer was then distilled to remove the cyclohexane leaving only a brown oily liquid behind. An IR spectra and a GC curve of the brown, oily liquid were taken. The GC curve revealed that the brown, oily liquid contained more than one component. This material was vacuum distilled under approximately 5 mm pressure. The vacuum distillation yielded four fractions: 1) undistilled, residual material (IR-figures 18-18A), 2) a 46°C-56°C/ca. 5 mm fraction (IR-figures 19-19A), 3) a 111°C/ca. 5 mm fraction (IR-figures 20-20A) and 4) a 126°C/ca. 5 mm fraction (IR-figures 21-21A). The 126°C fraction was chromatographed on a 6 ft. x 1/8 in. 10% UCW-98 column at 200°C. The curve revealed one major component which represented 60% of the fraction. This component was collected in a glass coil cooled with ice at the outlet of the chromatograph's thermal conductivity detector. An infrared spectrum(figures 22-22A), a nuclear magnetic resonance spectrum (figure 23) and a mass spectrum(figure 23-A)were taken on this component.

1,4-Dimethyl-6,7-Dibromo-1,2,3,4-tetrahydronaphthalene or Isomer[10](4) To a solution of 11.8g.(0.05 moles) of o-dibromobenzene in 150 ml of cyclohexane were added 19.8 g.(0.15 moles) of Al Cl_3 with stirring. To this solution was added a solution of 5.0g.(0.05 moles) of 2,5-dimethyltetrahydrofuran in 50 ml of cyclohexane. The 2,5-dimethyltetrahydrofuran solution was added dropwise by means of an addition funnel over a period of 45 minutes. The addition was carried out at room temperature. The reaction temperature climbed from 23°C to 30°C during the addition. The reaction was allowed to proceed at room temperature for 24 hours. The reaction color again changed sequentially from white to green to yellow to brown. After 24 hours, ice was added to the reaction mixture to decompose the Al Cl_3. The organic layer was separated from the aqueous layer in a separatory funnel and distilled to remove the cyclohexane. Again, only a brown oily liquid remained. This liquid was vacuum distilled under approximately 5 mm pressure. Four fractions were collected: 1) Undistilled residue (IR-figures 24-24A), 2) a 52-56°C/ca. 5 mm fraction (IR-figures 25-25A), 3) a 62°C/ ca. 5 mm fraction (IR-figures 26-26A) and 4) a 106°C-114°C fraction (IR-figures 27-27A). The fraction collected at 106°-114°C was injected into a gas chromatograph containing a 6 ft. x 1/8 in. 10% UCW-98 column at 200°C. The chromatographic curve revealed that the 106°-114°C fraction contained three major components, each of which was collected in a glass coil cooled with ice at the outlet of the chromatograph's thermal conductivity detector. An infrared spectrum (figure 28-28A) and a GC-mass spectrum (figures 29A, 29B, 29C, 29D and 29E) were taken on the first component. An infrared spectrum(figures 30-30A) a proton nuclear magnetic resonance spectrum(figure 31), a C^{13} nuclear magnetic resonance spectrum(figure 32) and a mass spectrum (figure 33) were taken on the second component. An infrared spectrum(figures 34-34A), a nuclear magnetic resonance spectrum (figure 35) and a mass spectrum were taken on the third component.

1,4-Dimethyl-5,8-deuterionaphthalene or Isomer[14](8) To a solution of 2.0 g.(0.006 moles) of dimethyldibromotetrahydronaphthalenes (the mixture of high boiling isomers obtained from the reaction of p-dibromobenzene and 2,5-hexanediol) in 25 ml of dry distilled cyclohexane were added 6.5 ml of 22% n-butyllithium in hexane. The reaction mixture was refluxed for one hour with a #5A molecular sieve drying tube attached. After one hour, the reaction mixture was cooled and 0.5 ml(0.025 moles) of D_2O were added. The reaction mixture was allowed to stand for 24 hours. After 24 hours, the reaction mixture was treated with a #5A molecular sieve (to remove any traces of D_2O) and gravity filtered. Then, 15 ml of tetramethylethylenediamine (TMEDA) (Eastman 8178) and 10.5 ml of 22% n-butyllithium in hexane were added to the reaction mixture and the mixture was refluxed for one hour with a #5A molecular sieve drying tube attached. After refluxing, the reaction mixture was cooled and 3.6 g.(0.025 moles) of Cd Cl_2 were added. After swirling the mixture for several minutes, it was gravity filtered. The hexane was removed from the reaction mixture in vacuo using a Buchi rotovapor-R apparatus. At this point, a nuclear magnetic resonance spectrum revealed that the mixture did not contain a large quantity of 1,4-dimethylnaphthalenes. The reaction mixture was chromatographed on a 6 ft. x 1/8 in. 10% UCW-98 column at 190°C. The reaction product was separated from the amine and collected in a glass coil cooled with ice at the outlet of the chromatograph's thermal conductivity detector. From GC analysis, it was found that this fraction contained 7% of 1,4-dimethylnaphthalene. A GC-mass spec analysis of this fraction(figures 36A and 36B) shows that 1,4-dimethylnaphthalene and not the desired 1,4-dimethyldideuterionaphthalene was the product that had formed.

Figure #1

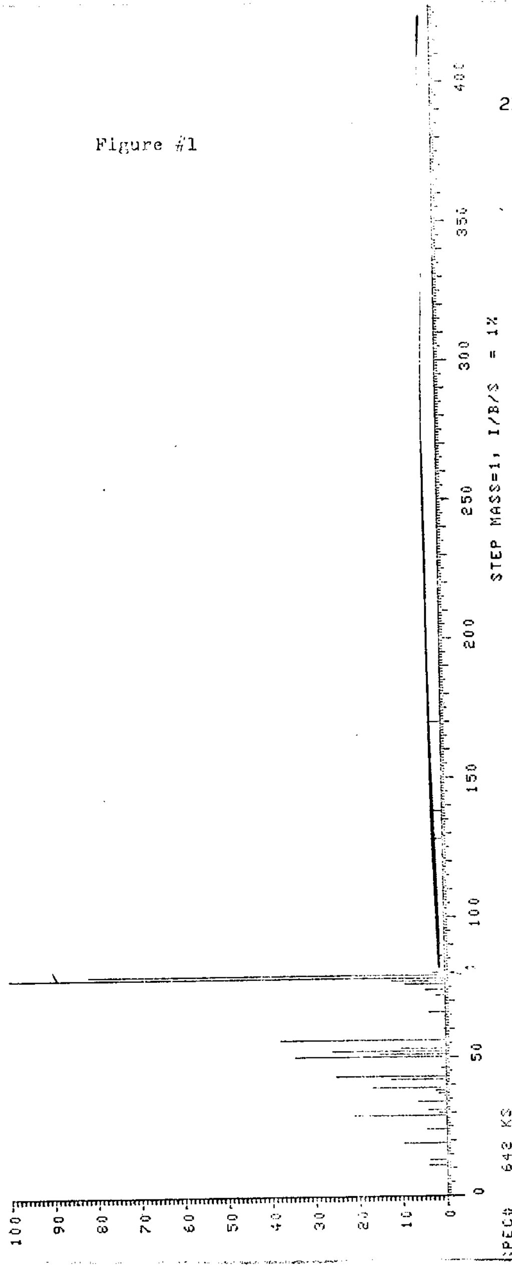


Figure #1

Mass Spectrum of
Deuterated Benzene

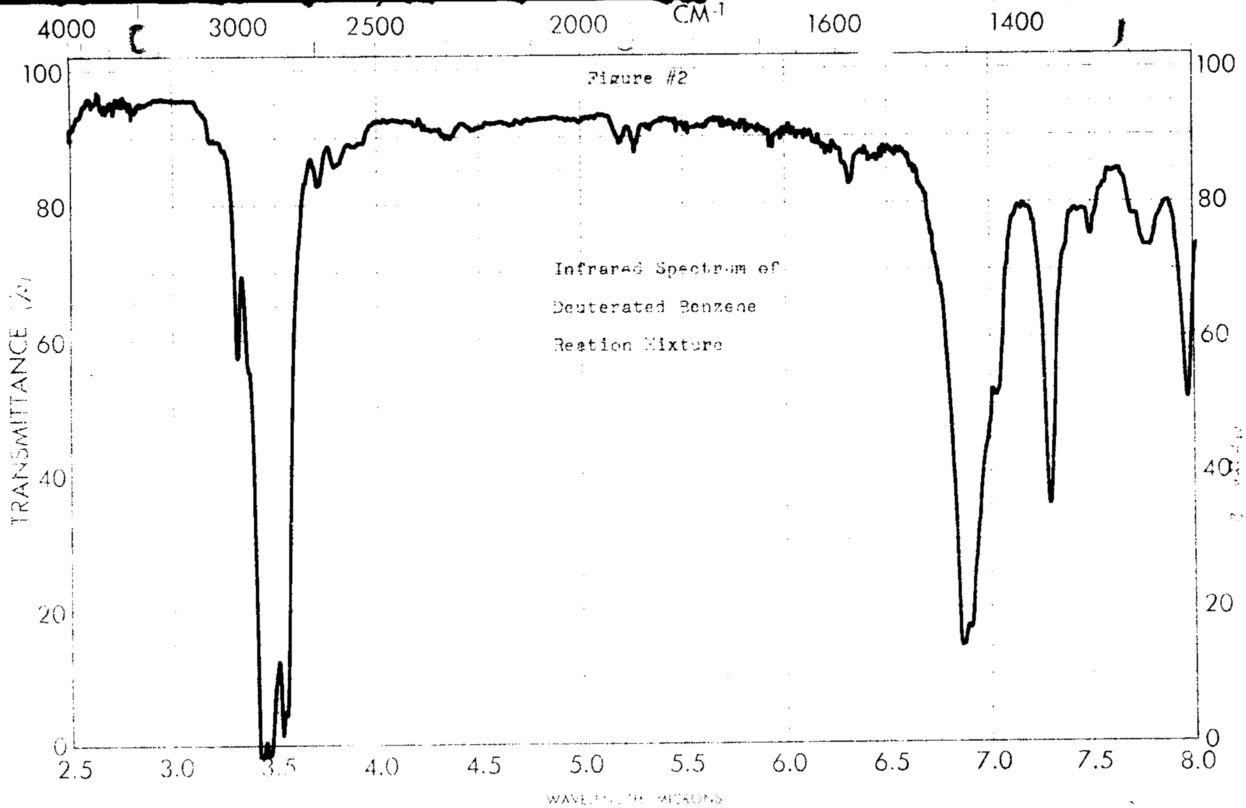


Figure #2

Infrared Spectrum of Deuterated Benzene Reation Mixture

SAMPLE #23A - Hexane-Benzene mixture
ORIGIN
SOLVENT
CURVE NO.
CONC. film on NaCl discs-Neat
CELL PATH
REFERENCE
SCAN SPEED F
SLIT N
OPERATOR
DATE 11/20/76
REMARKS

PART NO. 237-1030

PERKIN-ELMER

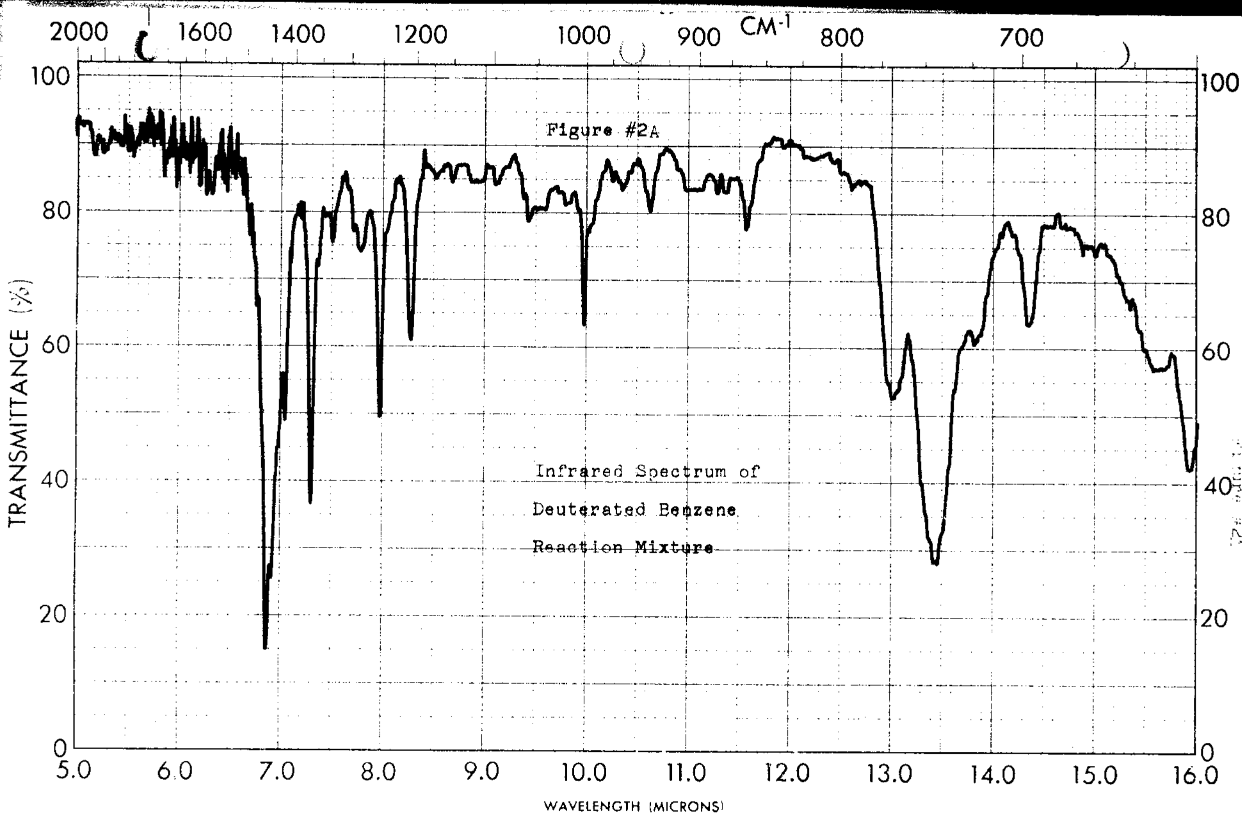


Figure #2A

Infrared Spectrum of
Deuterated Benzene
Reaction Mixture

SAMPLE Lt 73A Hexane - Benzene mixture	CURVE NO.	SCAN SPEED F	OPERATOR ajs
ORIGIN	CONC. film on NaCl disc - Neat	SLIT N	DATE 11/24/76
SOLVENT	CELL PATH	REMARKS	
	REFERENCE		

23

PART NO. 237-1031

PERKIN-ELMER

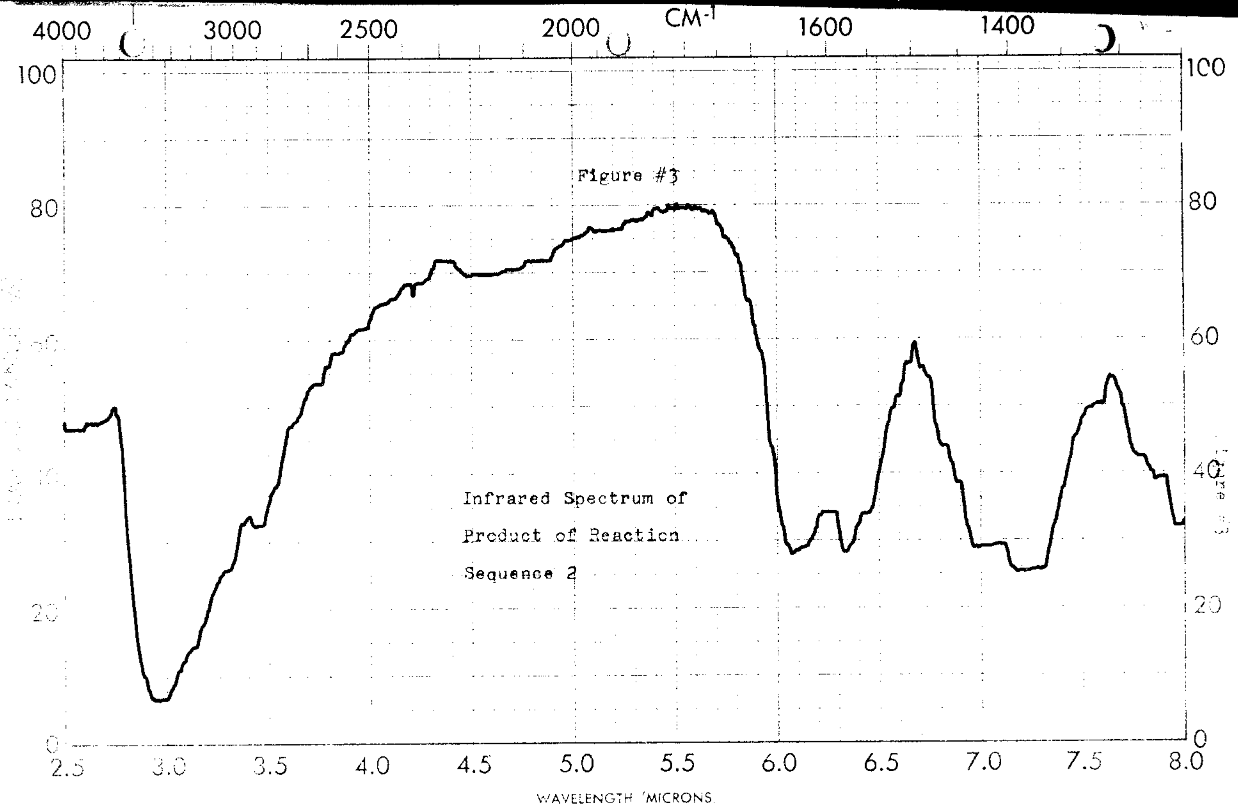


Figure #3

Infrared Spectrum of
Product of Reaction
Sequence 2

SAMPLE 21A Prep of 1,4 dimethyl Napthalene
ORIGIN
SOLVENT

CURVE NO.
CONC. 1% KBr Wafer
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR AJS
DATE 6/9/76

PART NO 237-1030

PERKIN-ELMER

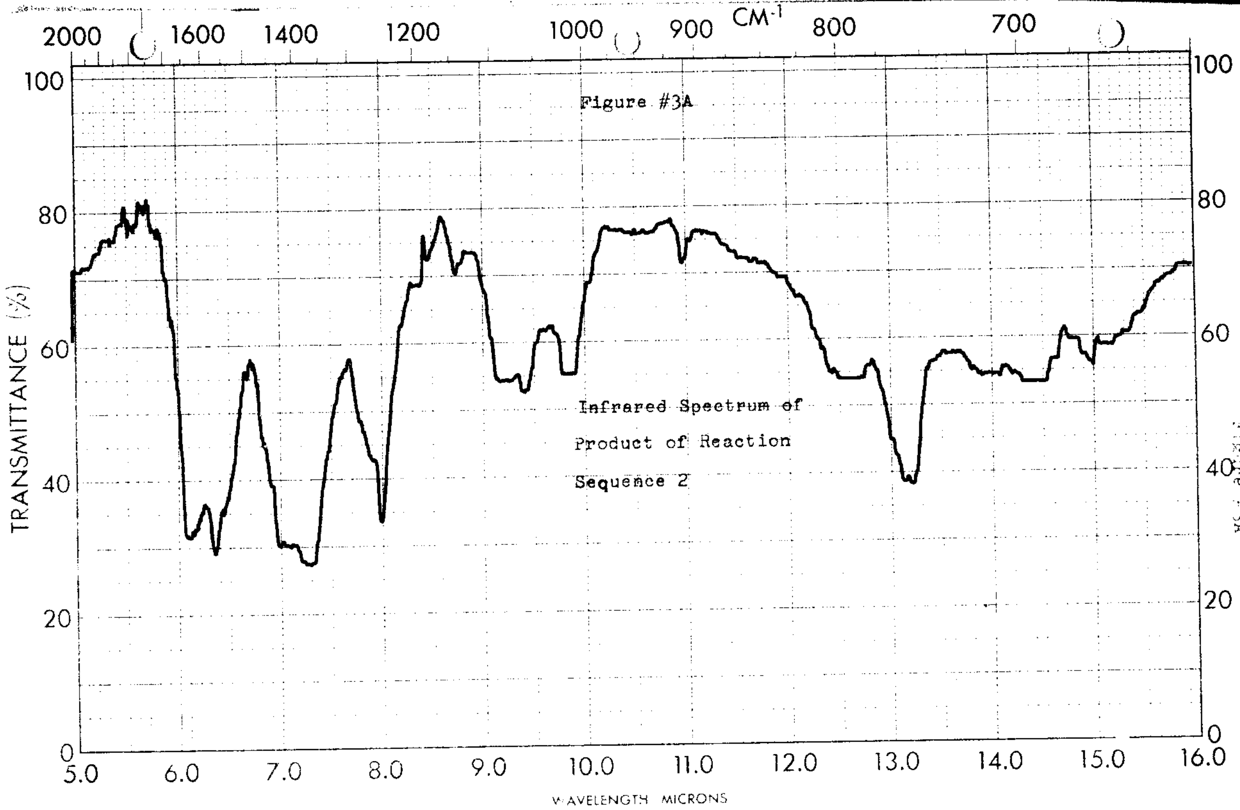


Figure #3A

Infrared Spectrum of
Product of Reaction
Sequence 2

SAMPLE 21A	CURVE NO.	SCAN SPEED F	OPERATOR ajs
	CONC. 1% KBr Wafer	SLIT N	DATE 6/9/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

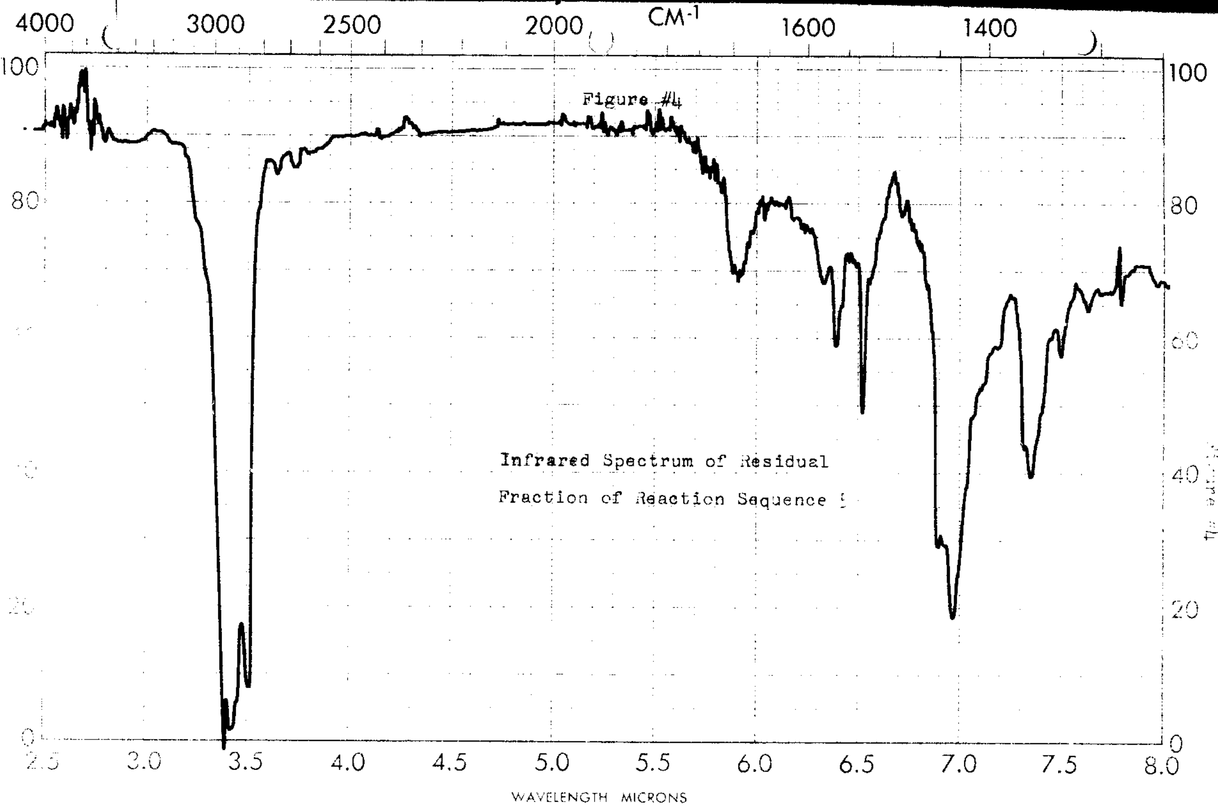


Figure #4

Infrared Spectrum of Residual

Fraction of Reaction Sequence 5

SAMPLE #24 F
Undistilled Residual Material
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc-Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajS
DATE 7/16/76

PART NO. 237-1030

PERKIN-ELMER

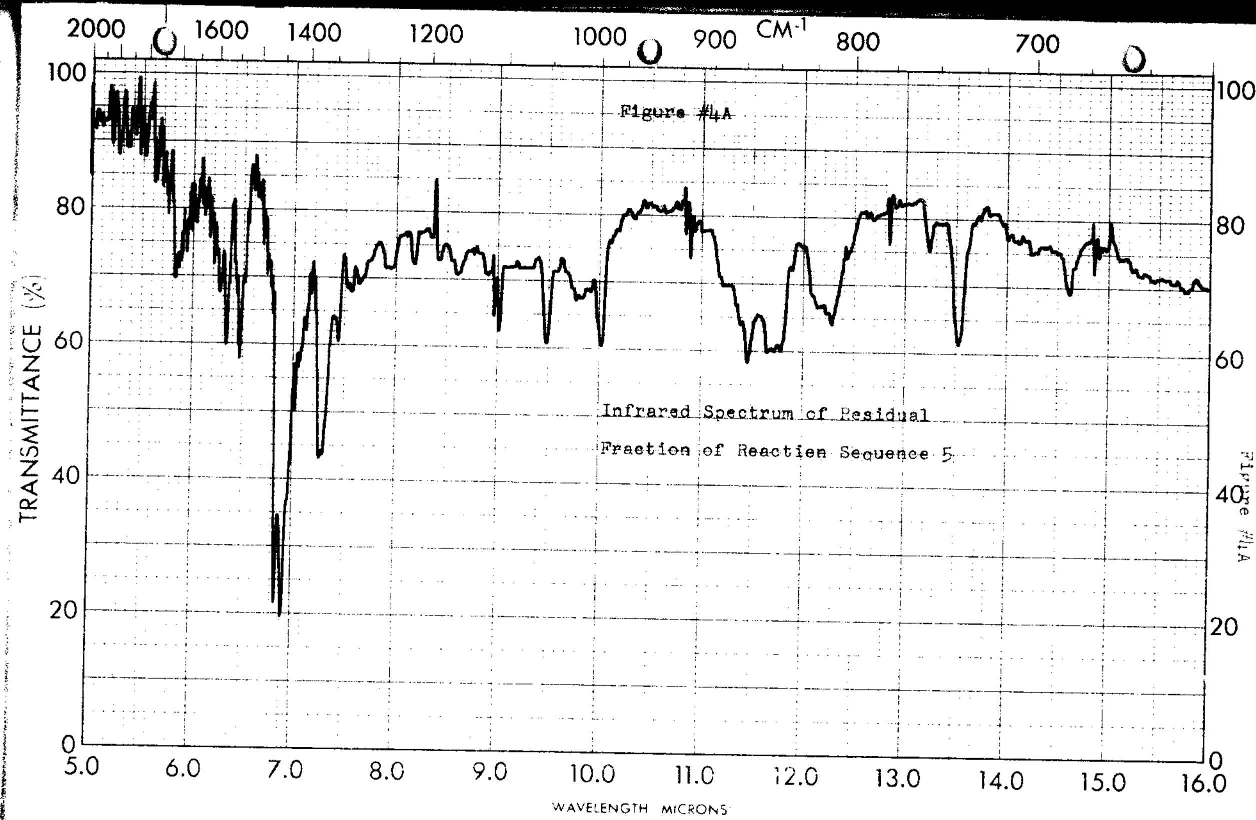


Figure #4A

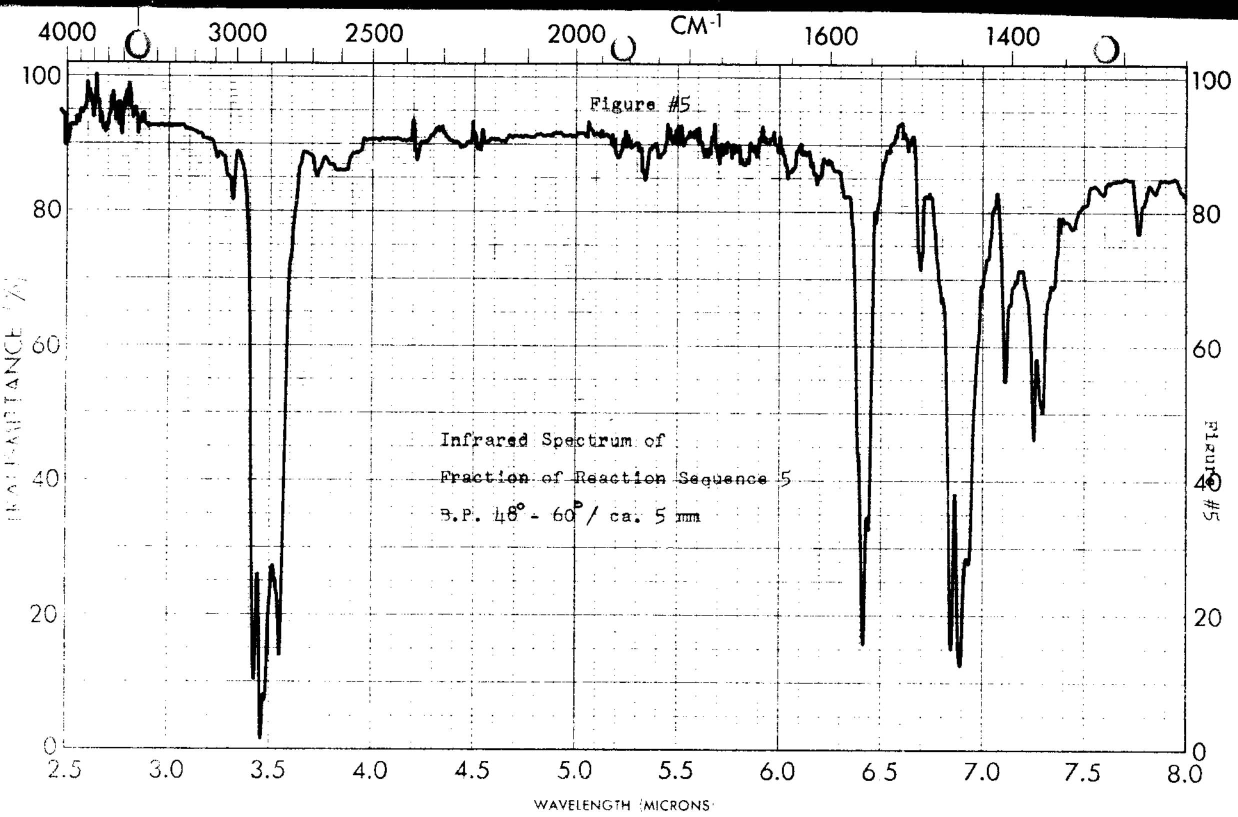
Infrared Spectrum of Residual Fraction of Reaction Sequence 5

SAMPLE #24 F
Undistilled Residual material
ORIGIN
SOLVENT
CURVE NO.
CONC. film on NaCl disc - Neat
CELL PATH
REFERENCE
SCAN SPEED F
SLIT N
OPERATOR AJS
DATE 7/16/76
REMARKS

PART NO. 237-1031

PERKIN-ELMER

Figure #5



Infrared Spectrum of

Fraction of Reaction Sequence 5

B.P. 48° - 60° / ca. 5 mm

SAMPLE #24C 48-65/5
48°-60°C / ca. 5 mm fraction
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc - neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajd
DATE 2/16/76

PART NO. 237-1030

PERKIN-ELMER

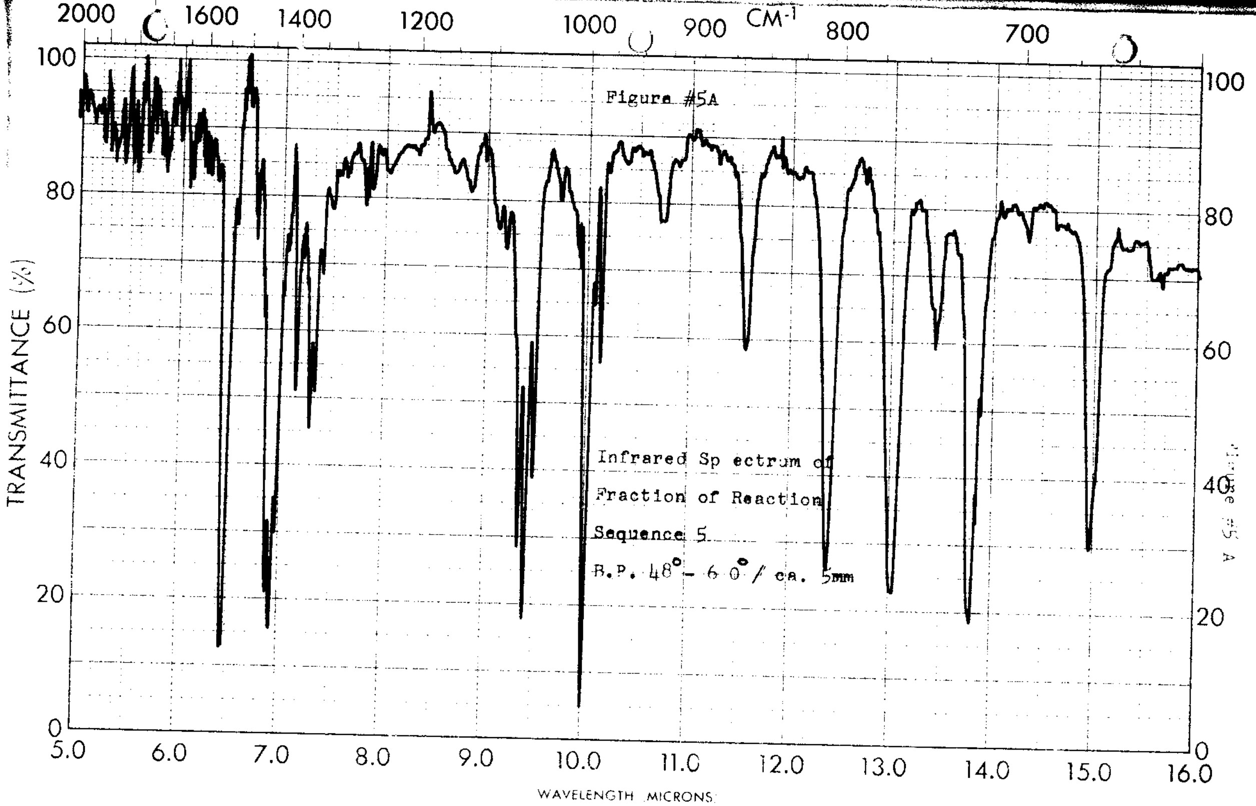


Figure #5A

Figure #5 A

Infrared Spectrum of
Fraction of Reaction
Sequence 5
B.P. 48° - 60° / ca. 5mm

SAMPLE #24C 48-60°/5
48°-60°C /ca 5mm fraction
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc - neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajd
DATE 2/16/76

PART NO. 237-1031

PERKIN-ELMER

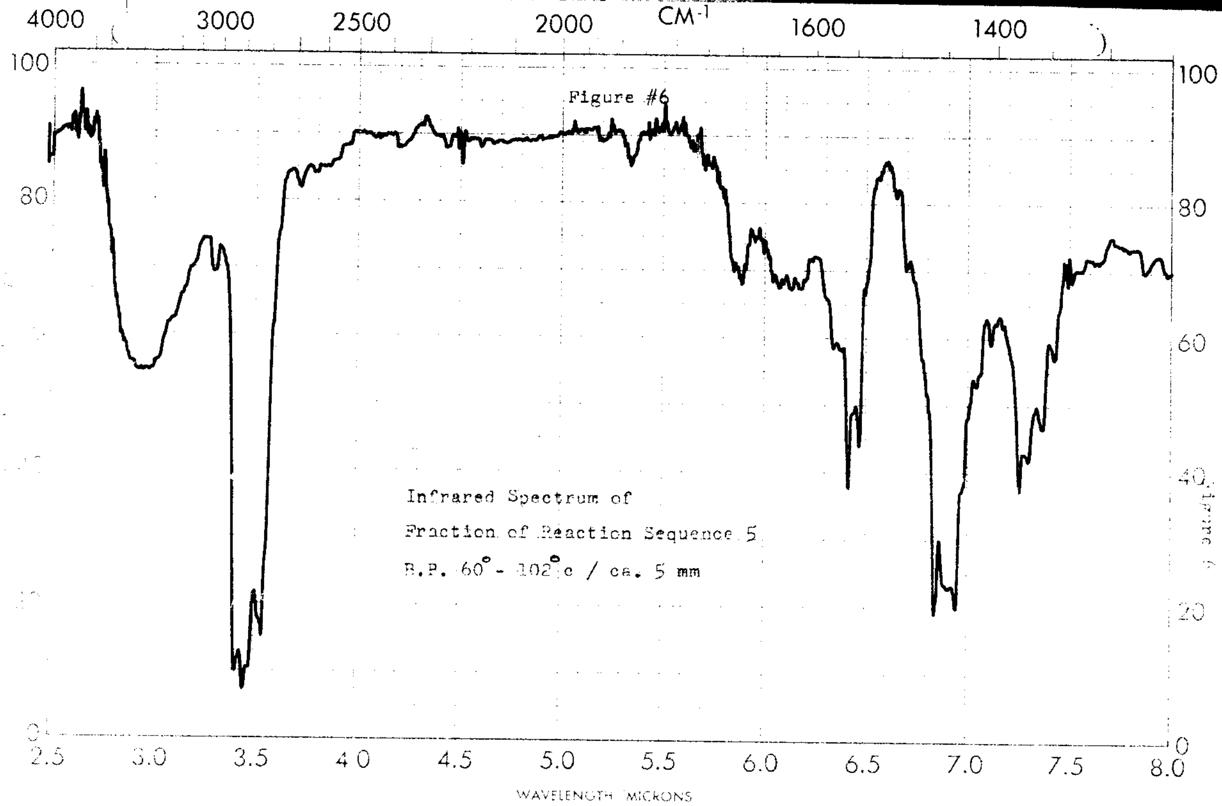


Figure #6

Infrared Spectrum of

Fraction of Reaction Sequence 5

B.P. 60° - 102°c / ca. 5 mm

SAMPLE #740
60° - 103°C /ca. 5 mm fraction
ORIGIN
SOLVENT

CURVE NO.
CONC Neat on NaCl disc - Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajl
DATE 7/16/76

30

PART NO. 221-1030

PERKIN-ELMER

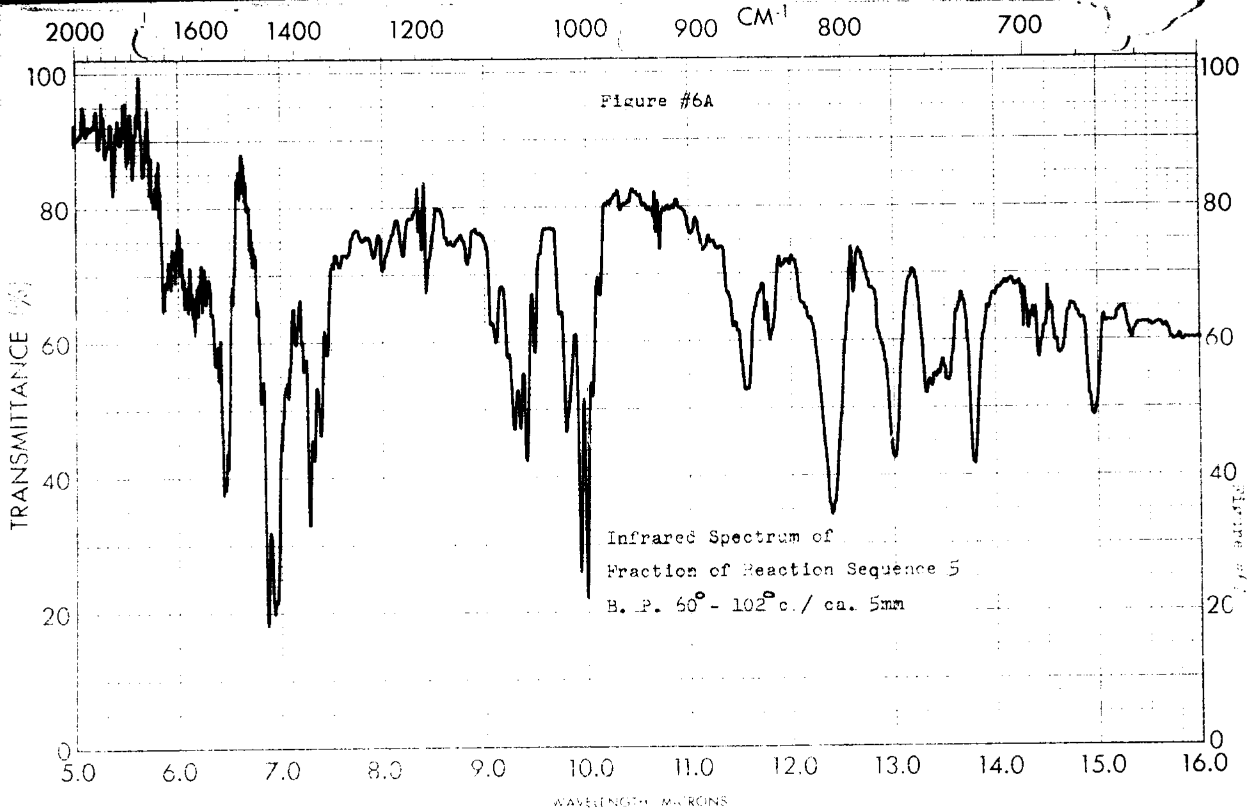


Figure #6A

Infrared Spectrum of
Fraction of Reaction Sequence 5
B. P. 60° - 102° c. / ca. 5mm

SAMPLE #34D 60°-102°C/ca. 5mm fraction	CURVE NO.	SCAN SPEED F	OPERATOR ajd
	CONC. film on NaCl disc-Neat	SLIT N	DATE 7/16/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

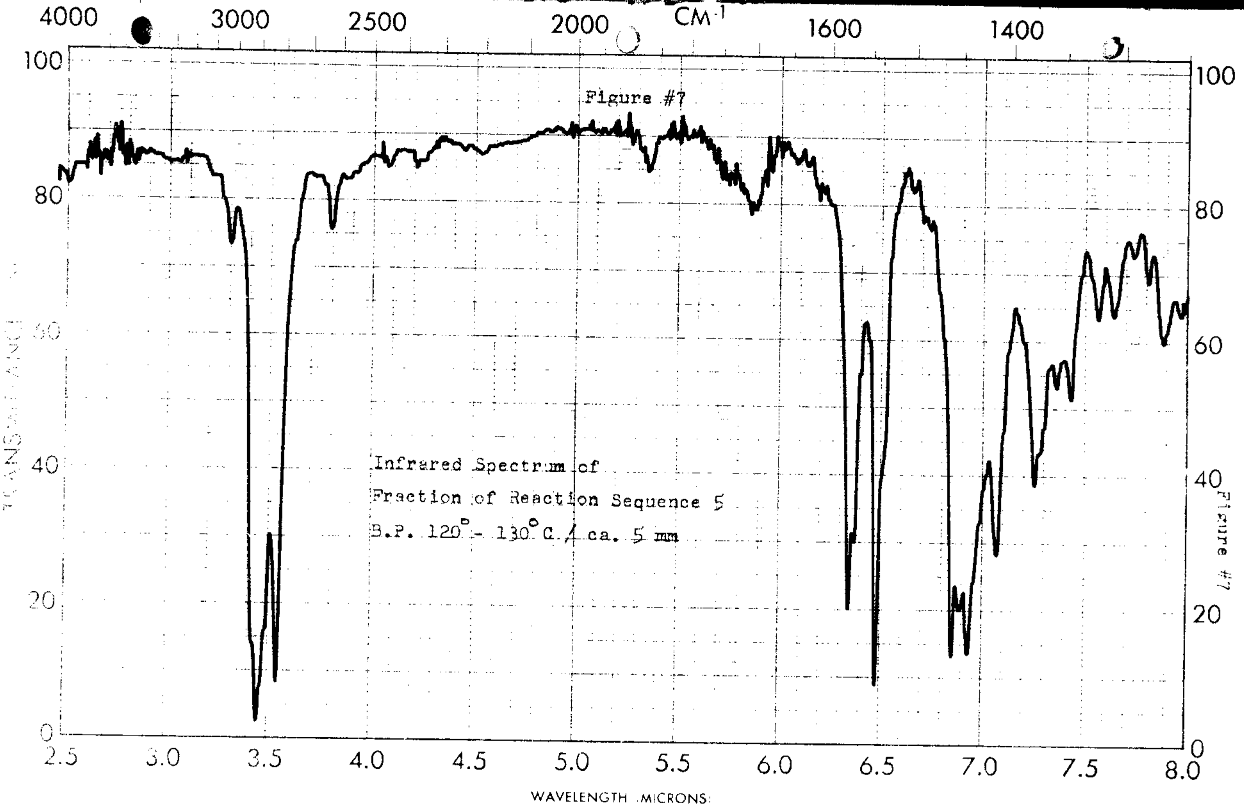


Figure #7

Infrared Spectrum of
Fraction of Reaction Sequence 5
B.P. 120° - 130° C / ca. 5 mm

Figure #7

SAMPLE #24E
120°- 130°C / ca 5 mm fraction
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc - Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N

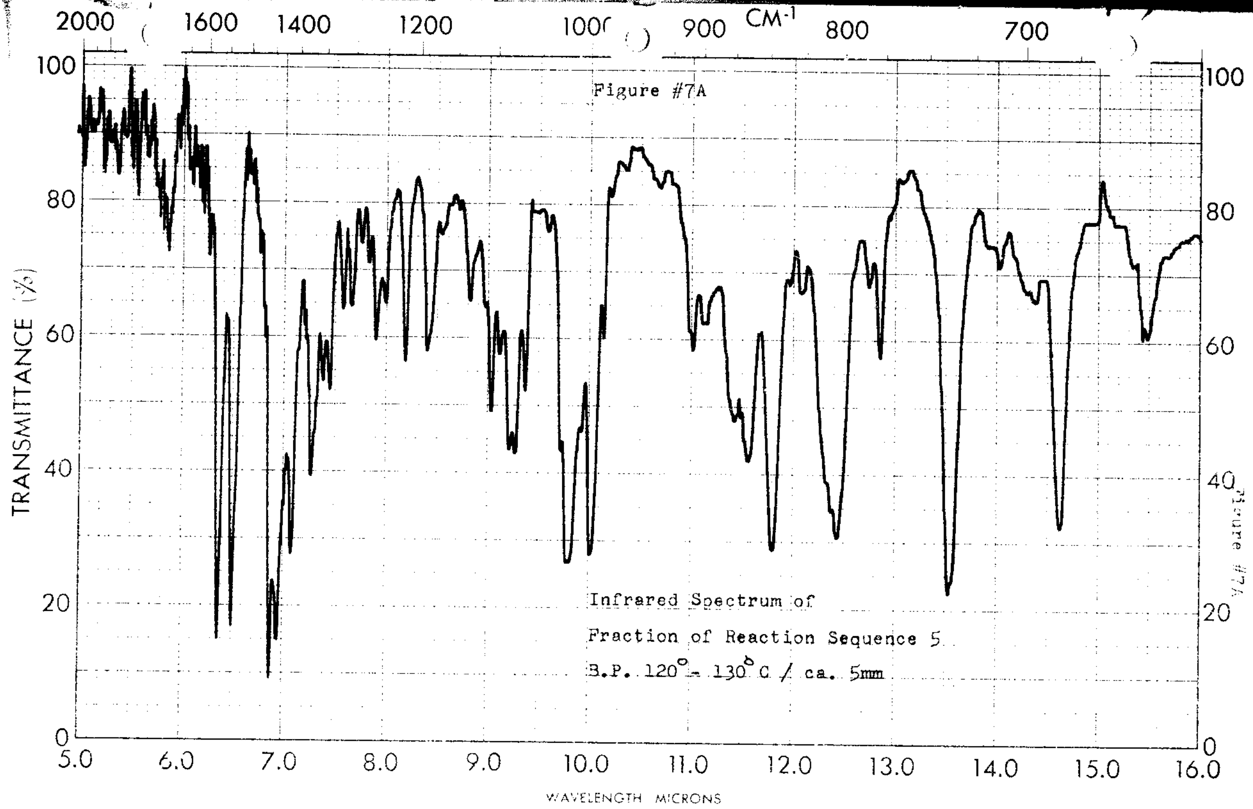
OPERATOR ajs
DATE 7/16/76

REMARKS

PART NO. 237-1036

PERKIN-ELMER

Figure #7A



Infrared Spectrum of

Fraction of Reaction Sequence 5

B.P. 120° - 130° C / ca. 5mm

Figure #7A

SAMPLE #24E

120° - 130°C /ca 5mm fract

CURVE NO

CONC. film on NaCl disc - Neat

CELL PATH

REFERENCE

ORIGIN

SOLVENT

SCAN SPEED F

SLIT N

OPERATOR ajd

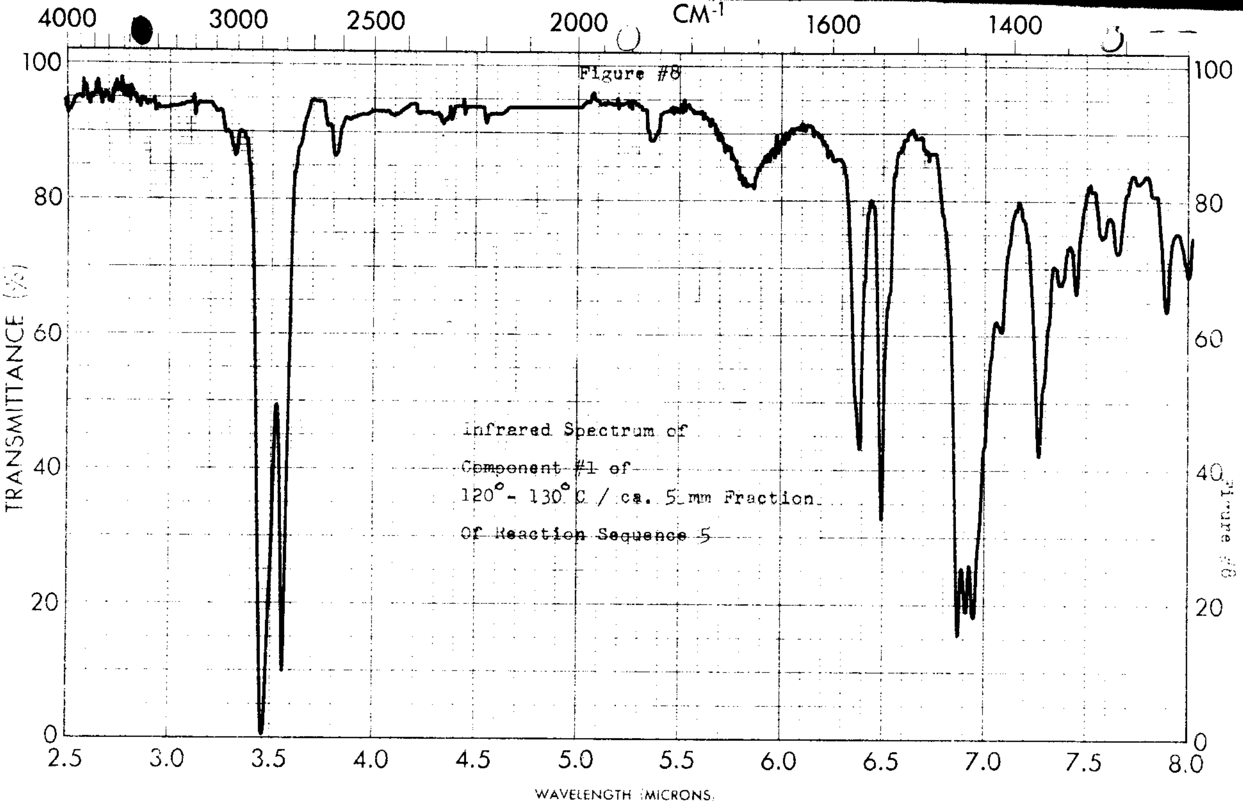
DATE 2/16/76

REMARKS

PART NO. 237-1031

PERKIN-ELMER

Figure #8



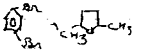
Infrared Spectrum of

Component #1 of

120° - 130° C / ca. 5 mm Fraction

Of Reaction Sequence 5

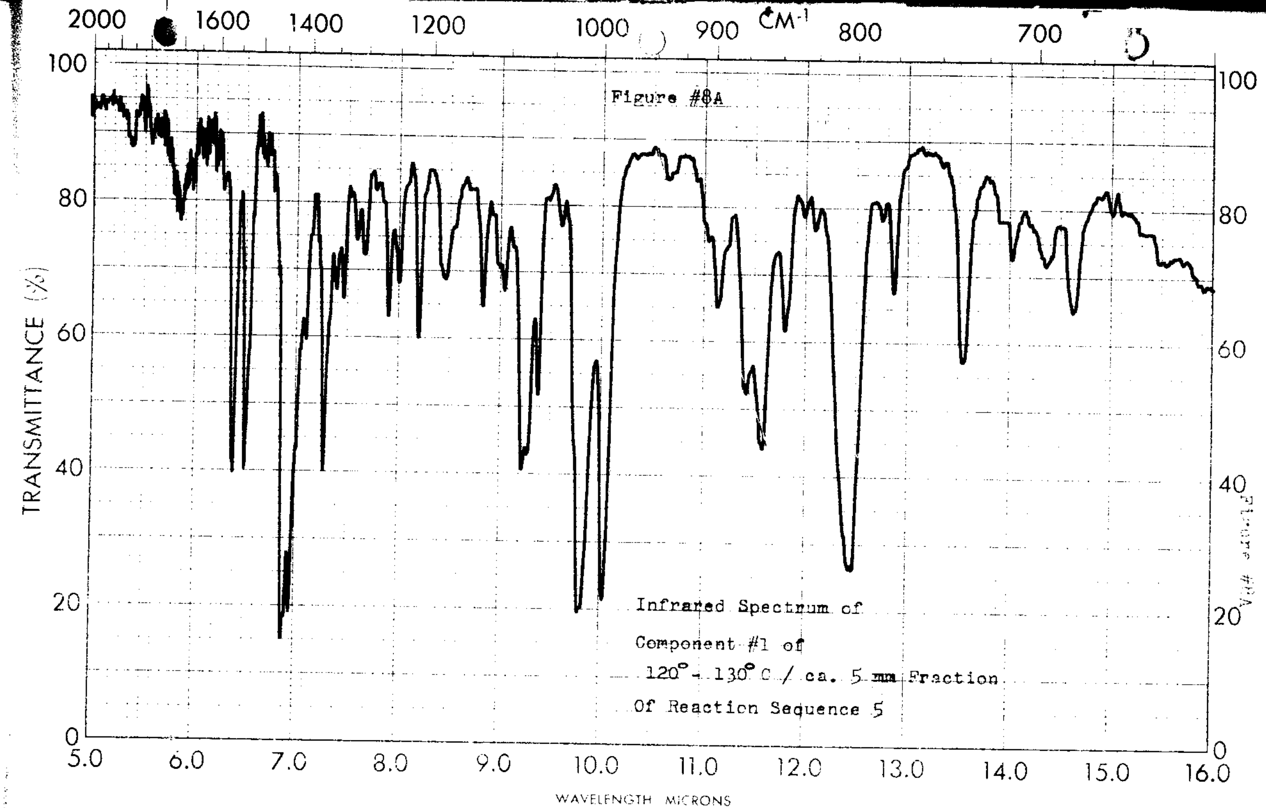
SAMPLE 24E fraction #1	CURVE NO.	SCAN SPEED F	OPERATOR a.J.D.
	CONC. film on NaCl disc - Neat	SLIT N	DATE 3/24/76
ORIGIN	CELL PATH	REMARKS React	
SOLVENT	REFERENCE		



PART NO. 237-1030

PERKIN-ELMER

Figure #8A



Infrared Spectrum of
Component #1 of
120° - 130° C / ca. 5 ~~mm~~ Fraction
Of Reaction Sequence 5

SAMPLE 24E fraction #1
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc-Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajd
DATE 8/30/76

PART NO. 237-1031

PERKIN-ELMER

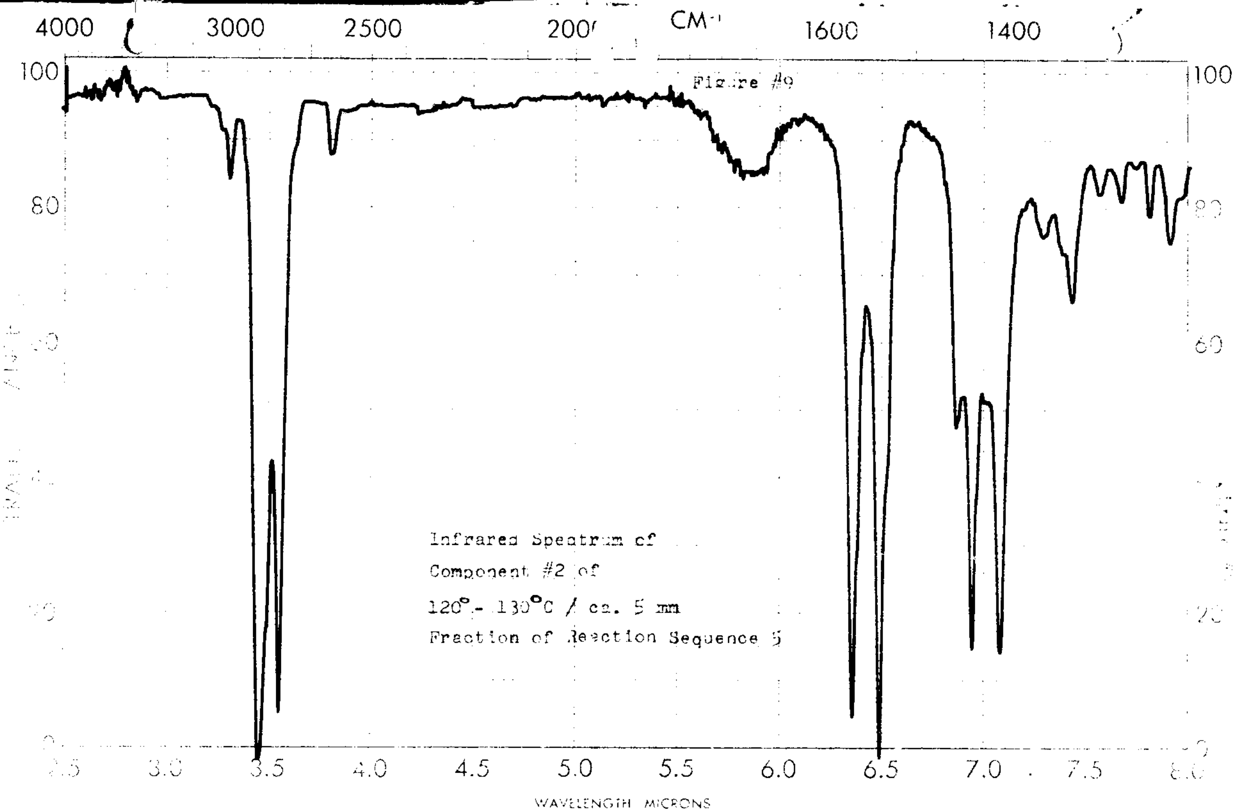


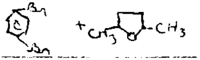
Figure #9

Infrared Spectrum of
Component #2 of
120° - 130°C / ca. 5 mm
Fraction of Reaction Sequence 5

SAMPLE 24E fraction #2
ORIGIN
SOLVENT

CURVE NO.
CONC. 1~~% in Bz~~ neat film on NaCl disc
CELL ~~PATH~~
REFERENCE

SCAN SPEED F
SLIT N
REMARKS



OPERATOR ajS
DATE 8/30/76

36

PART NO. 2

PERKIN-ELMER

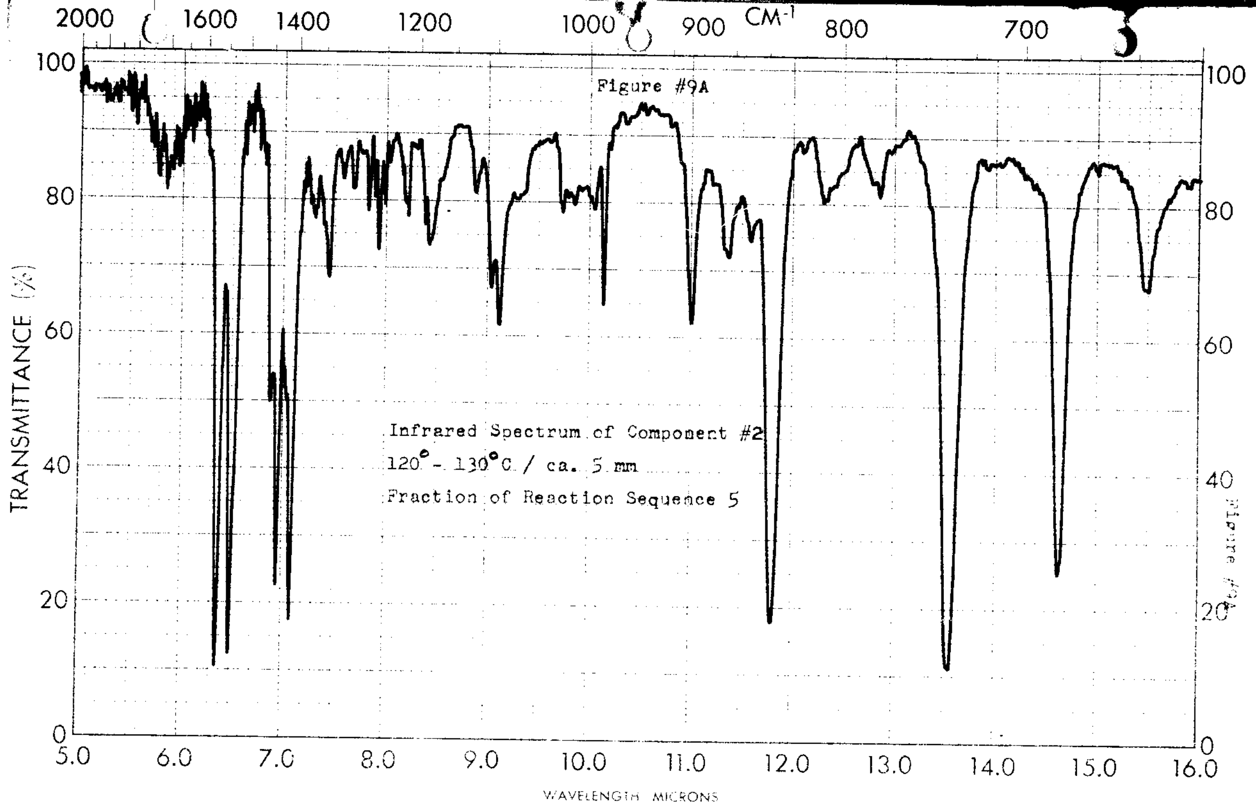
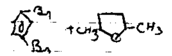


Figure #9A

Infrared Spectrum of Component #2
120° - 130°C / ca. 5 mm
Fraction of Reaction Sequence 5

Figure #9A

SAMPLE 24E fraction #2	CURVE NO.	SCAN SPEED F	OPERATOR afS
	CONC. film on NaCl disc - Neat	SLIT N	DATE 8/30/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		



PART NO. 237-1031

PERKIN-ELMER

Figure #10

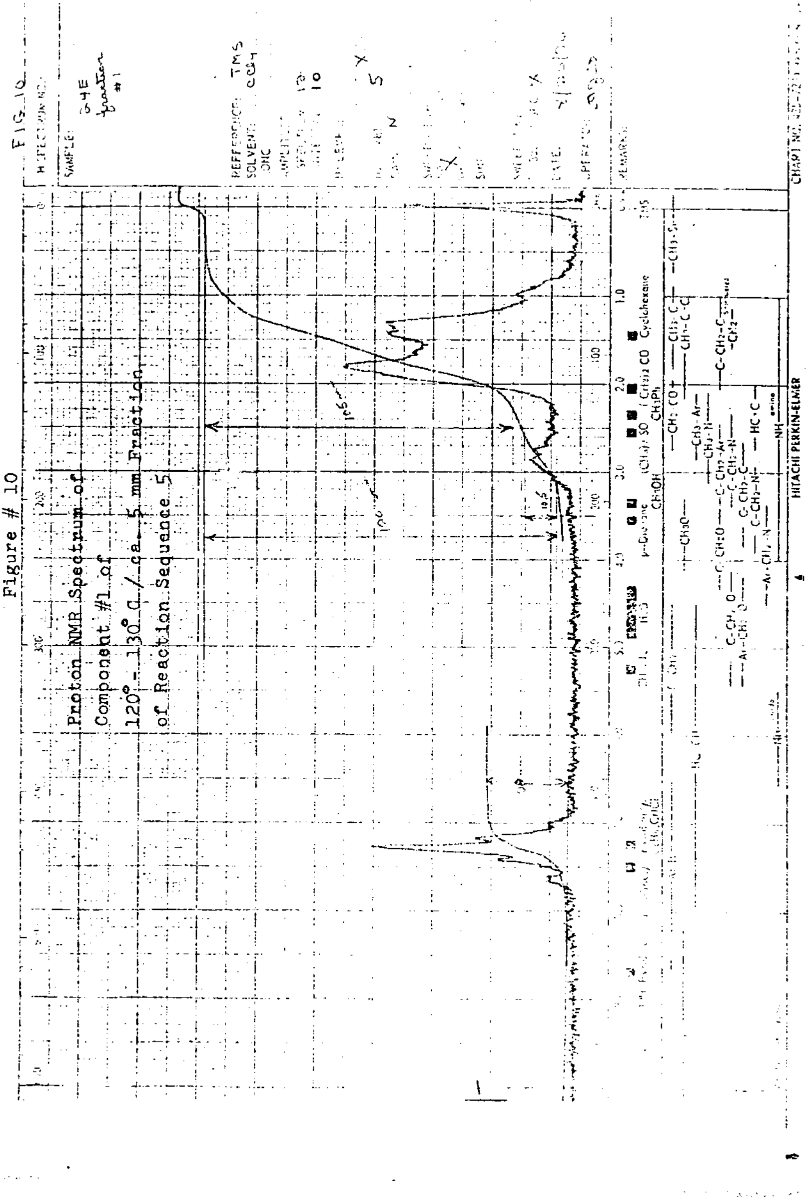
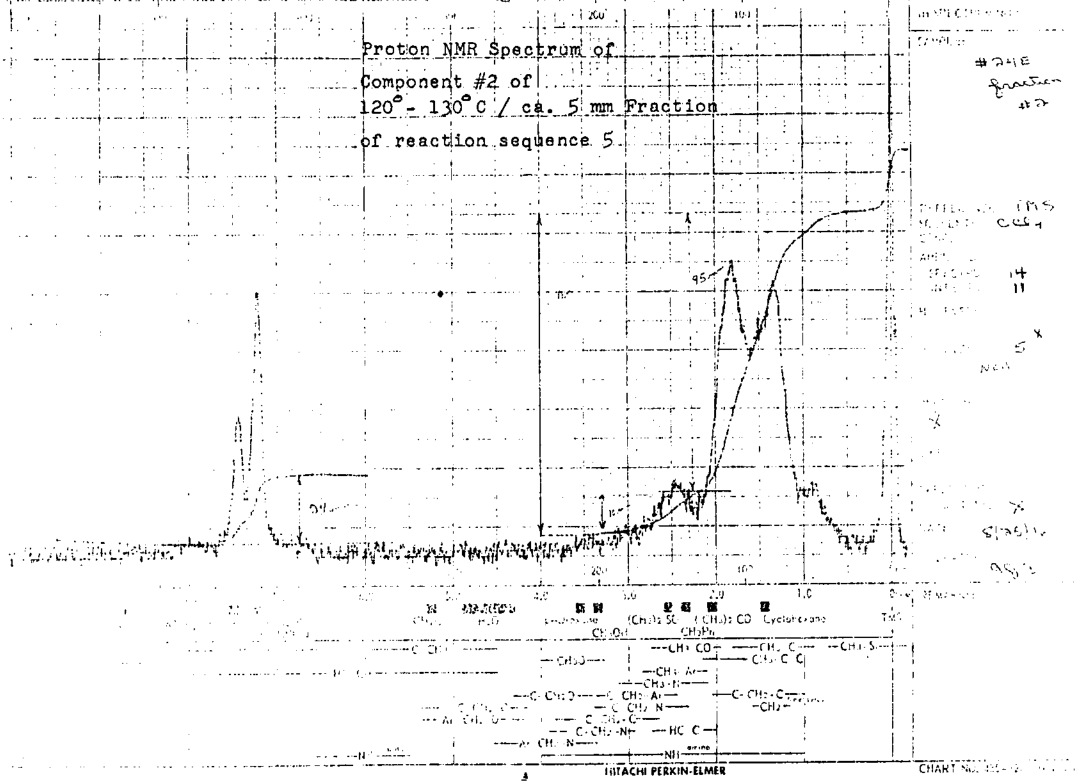


Figure # 10

Proton NMR Spectrum of Component #1 of 120° - 130° C / ca. 5 mm Fraction of Reaction Sequence 5

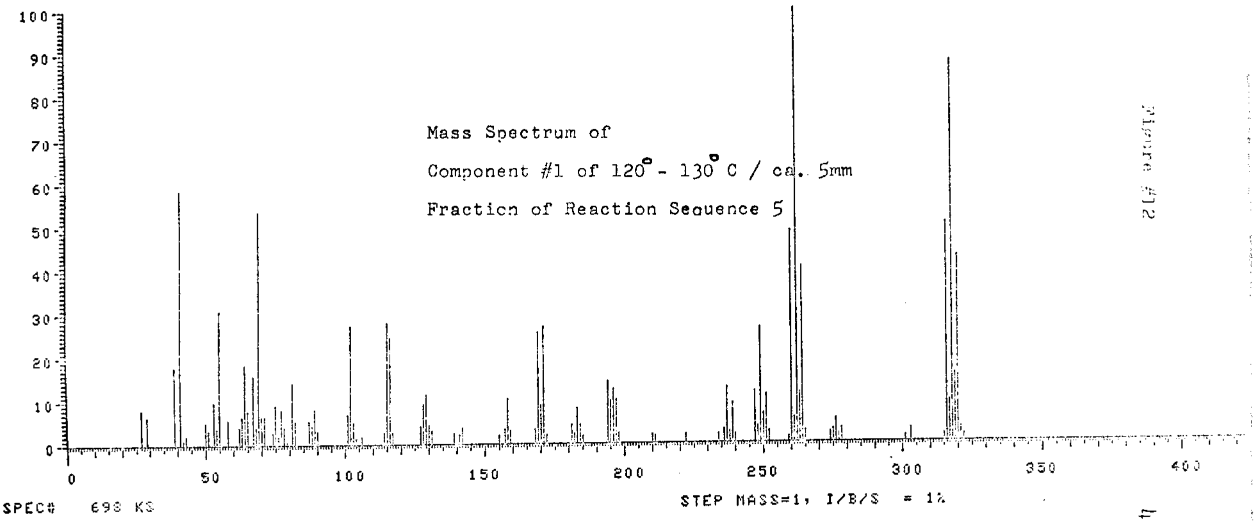
Figure #11

FIG 11



Proton NMR Spectrum of
Component #2 of
120° - 130° C / ca. 5 mm Fraction
of reaction sequence 5

Figure #12



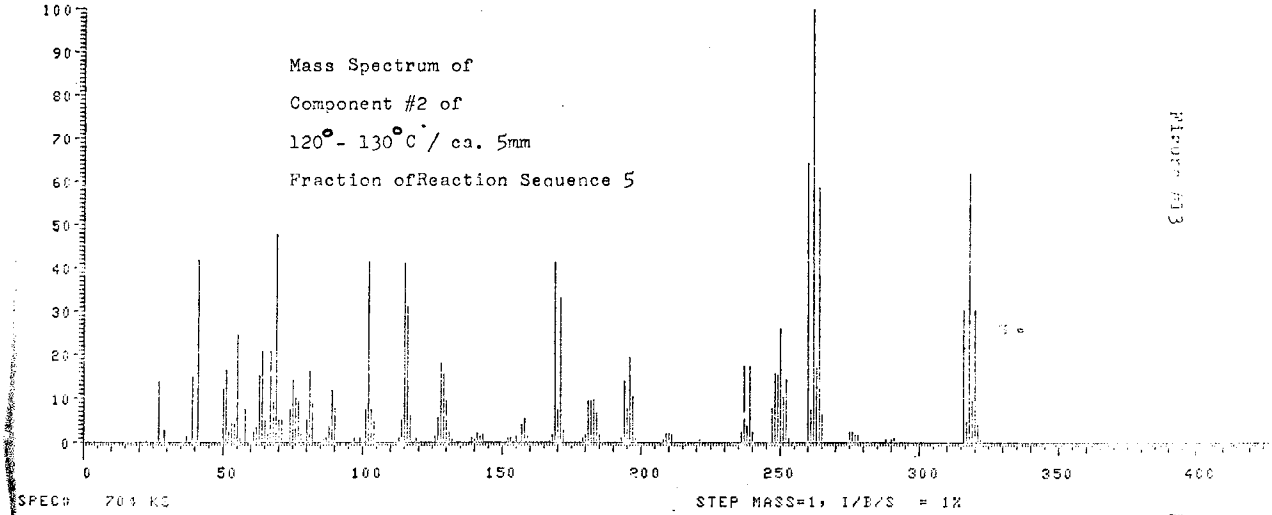
Mass Spectrum of

Component #1 of 120° - 130° C / ca. 5mm

Fraction of Reaction Sequence 5

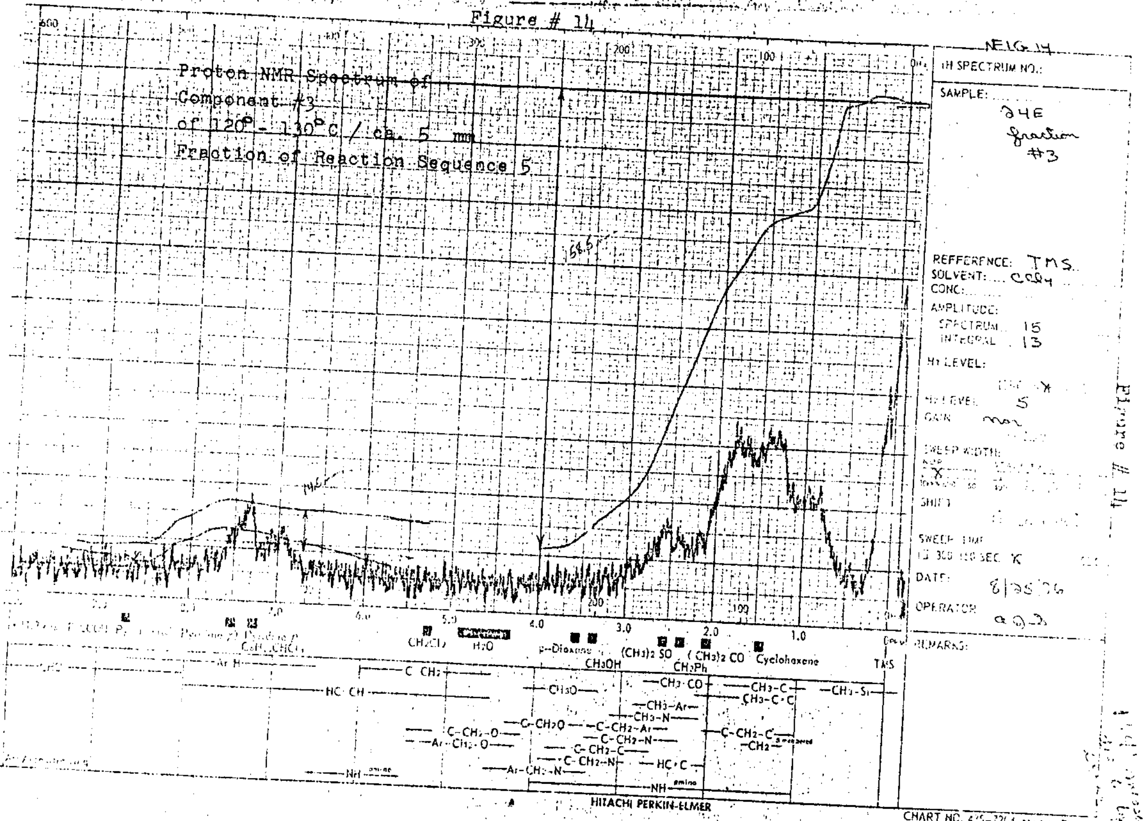
Figure #12

Figure #13



Mass Spectrum of
Component #2 of
$120^\circ - 130^\circ C$ / ca. 5mm
Fraction of Reaction Sequence 5

Figure # 14



Proton NMR Spectrum of Component #3 of 120°-130°C / ca. 5 mm Fraction of Reaction Sequence 5

Figure # 14

Mass Spectrum of

Component #3 of 120° - 130° C / ca. 5mm

Fraction of Reaction Sequence 5

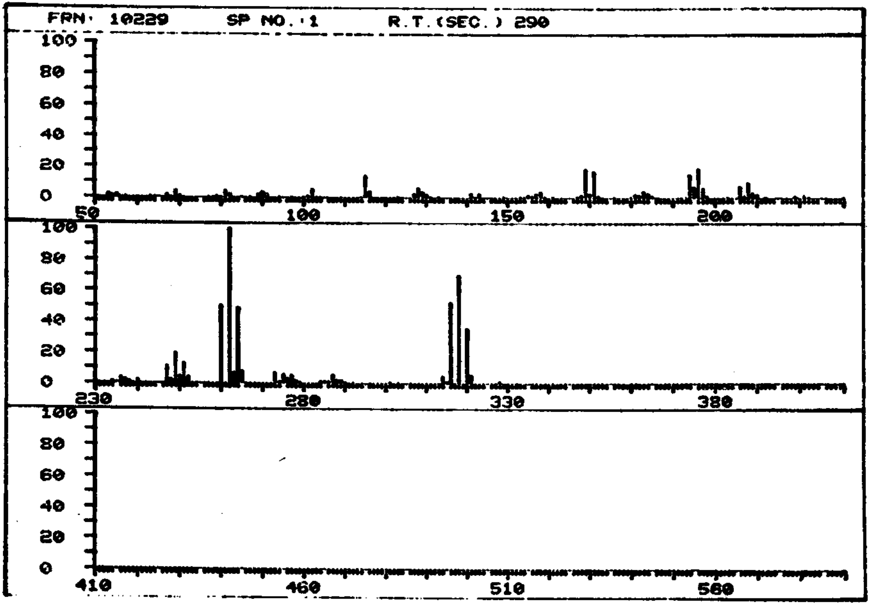
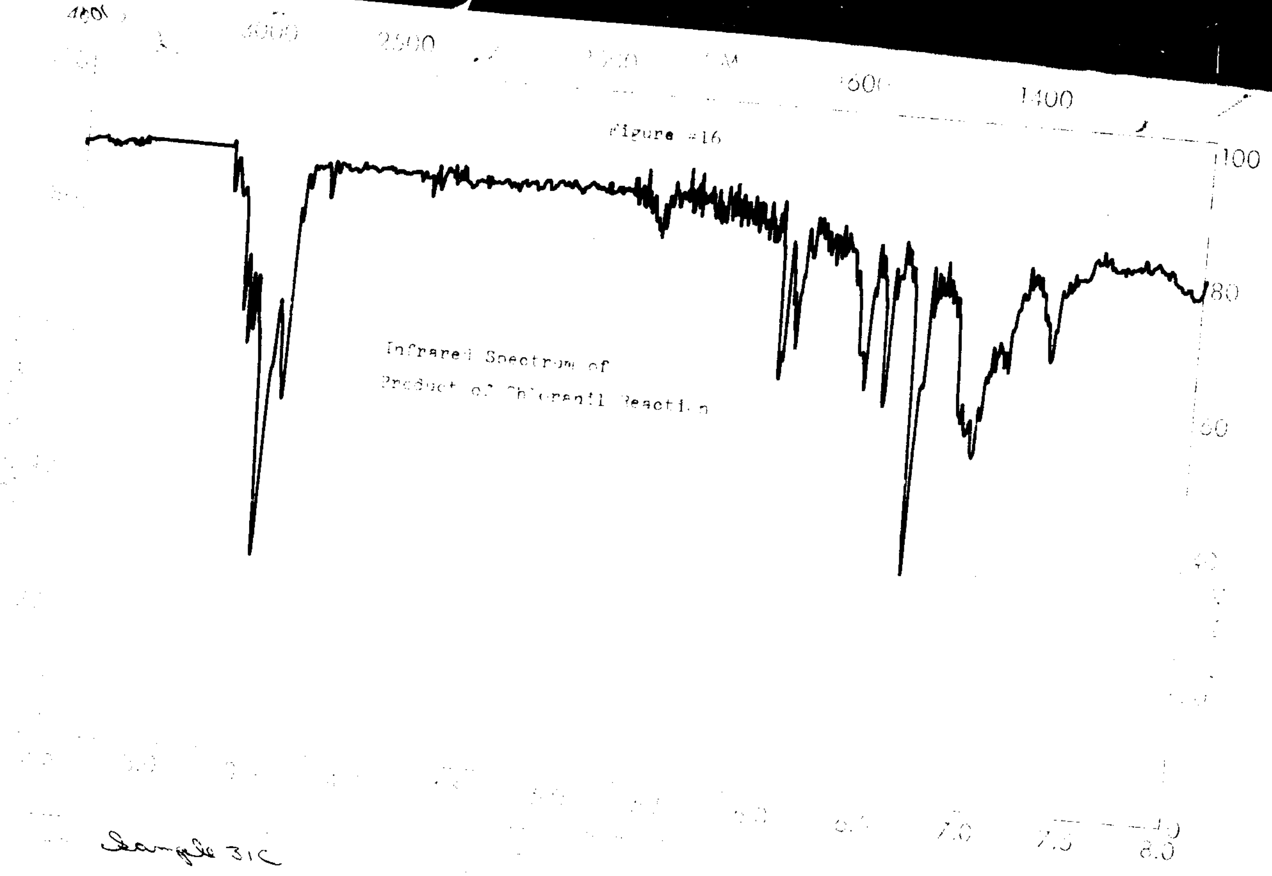


Figure #16



Infrared Spectrum of Product of Chloranil Reaction

Sample 31C

film on NaCl disc-Neat

N F

10/13/76

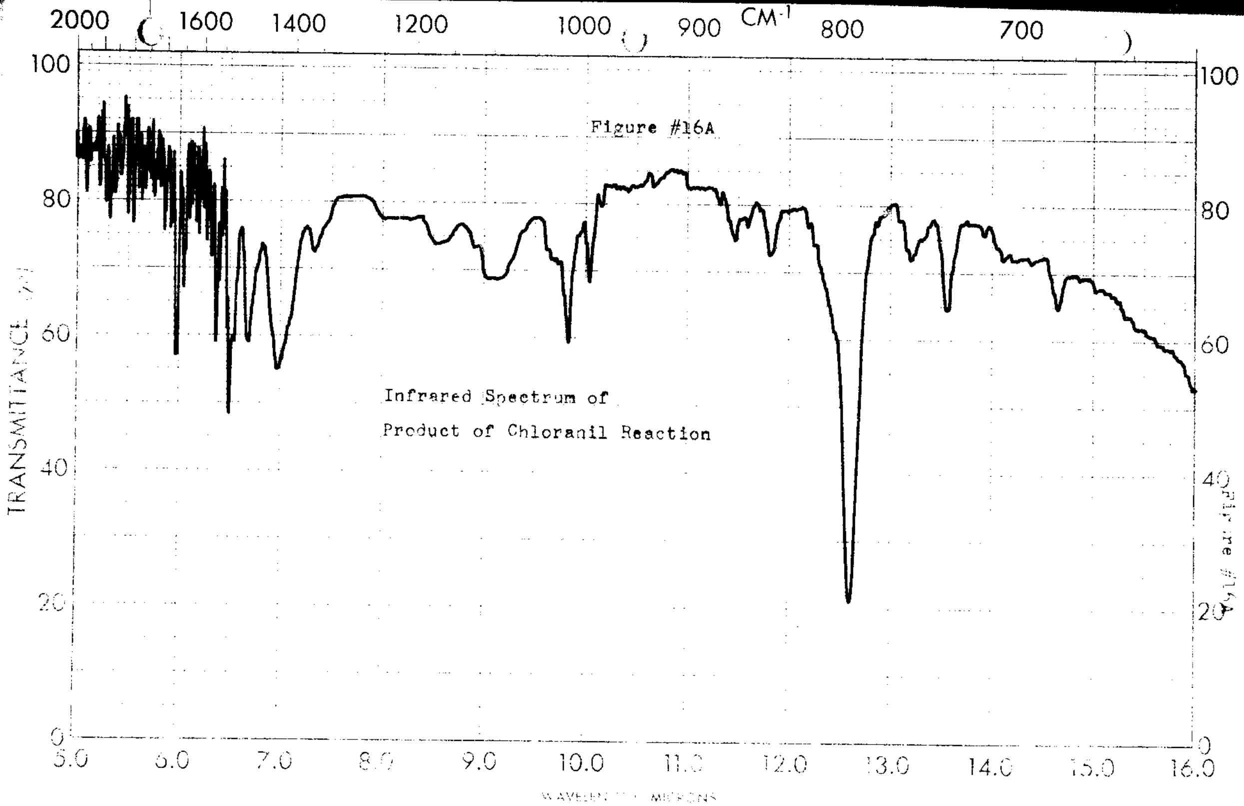


Figure #16A

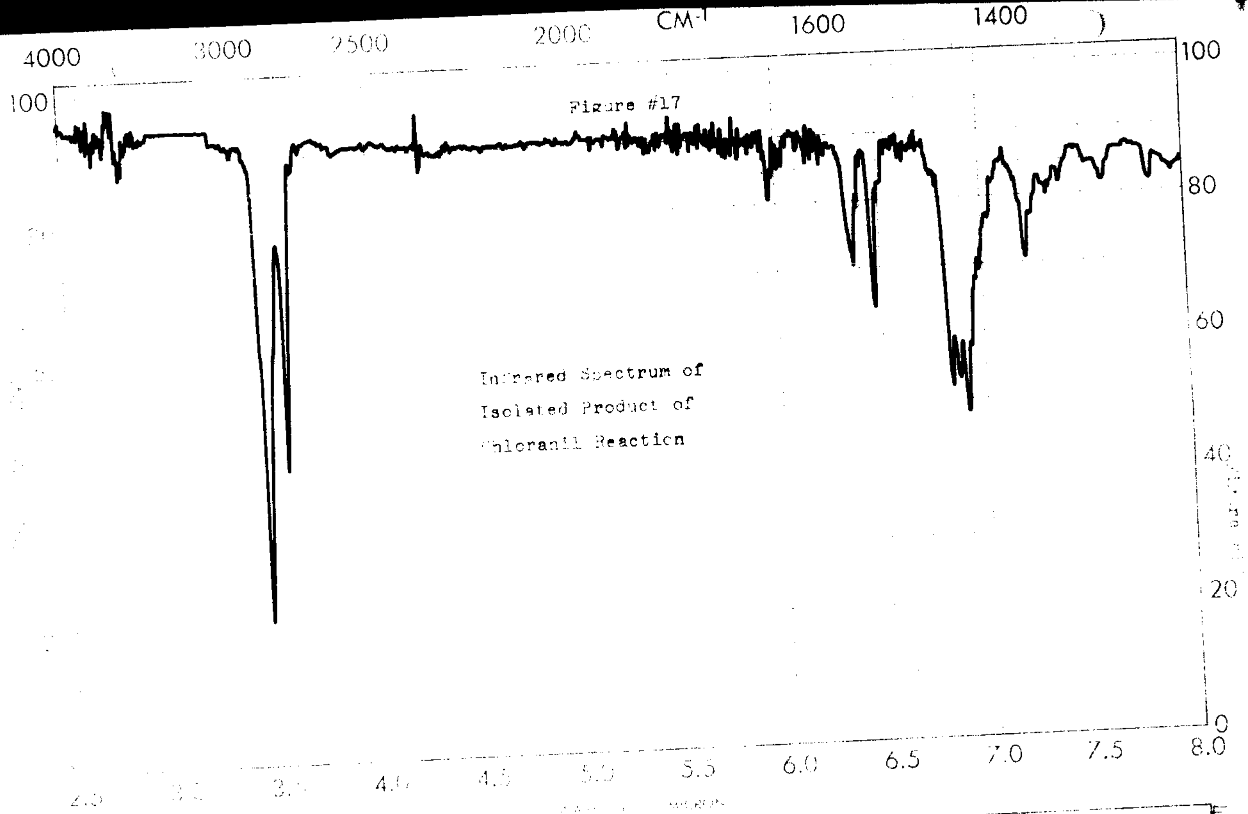
Infrared Spectrum of
Product of Chloranil Reaction

SAMPLE Sample 31C	CURVE NO.	SCAN SPEED F	OPERATOR agd
	CONC. film on NaCl disc - Neat	SLIT N	DATE 10/13/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

Figure #17



Infrared Spectrum of
Isolated Product of
Chloranil Reaction

SAMPLE Sample 31C fraction
#1
ORIGIN
SOLVENT

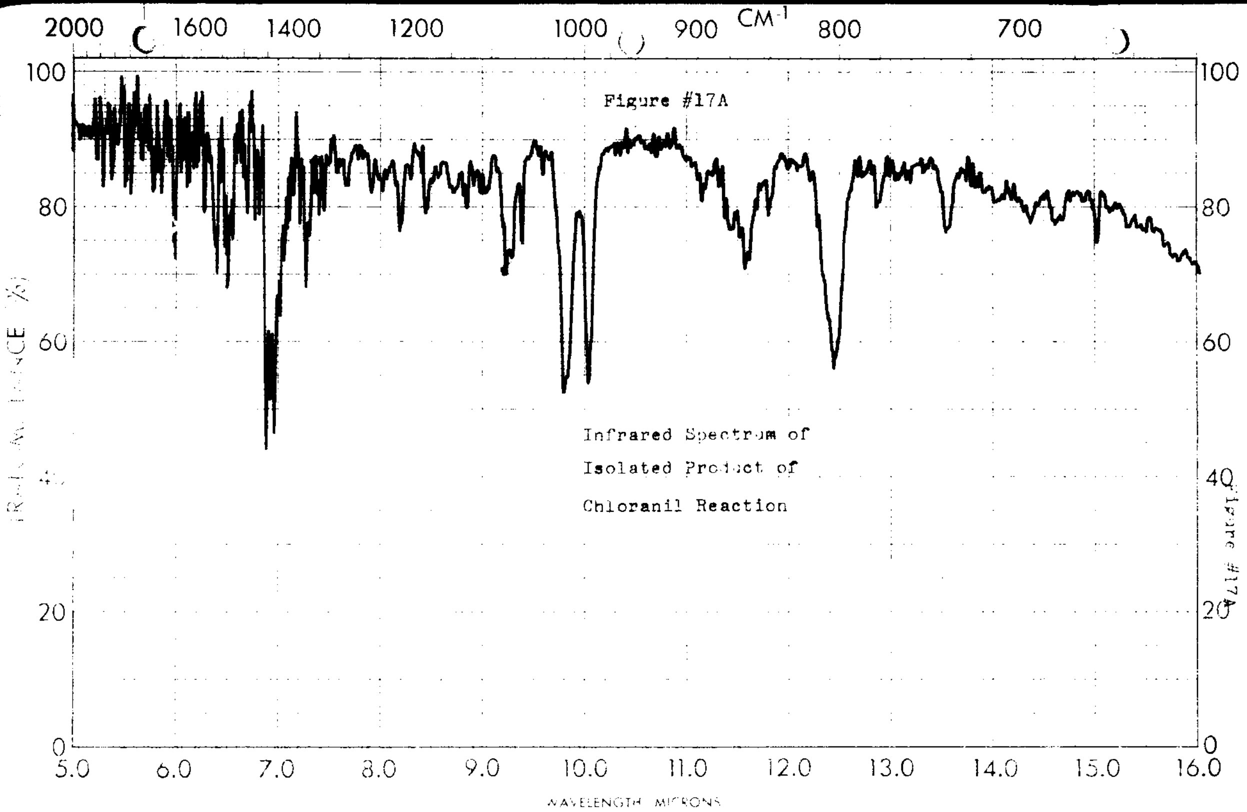
CURVE NO. Neat-film on NaCl disc
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR agd
DATE 10/13/76

PERKIN-ELMER

Figure #17A



Infrared Spectrum of
Isolated Product of
Chloranil Reaction

SAMPLE 31C fract #1	CURVE NO	SCAN SPEED F	OPERATOR ags
	CONC film on NaCl disc Neat	SLIT N	DATE 10/13/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237 1031

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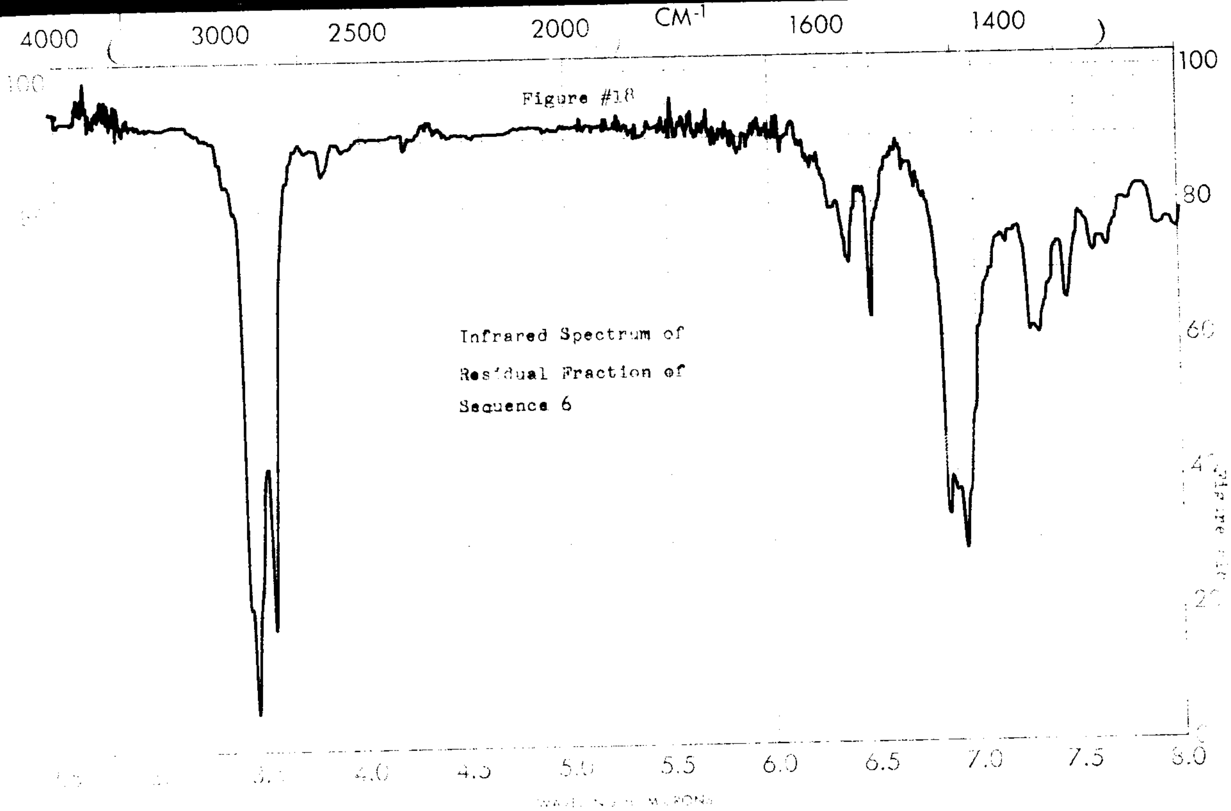
Figure #18



Infrared Spectrum of
Residual Fraction of
Sequence 6

Sample 26B
Undistilled Residue

film on NaCl disc - Neat

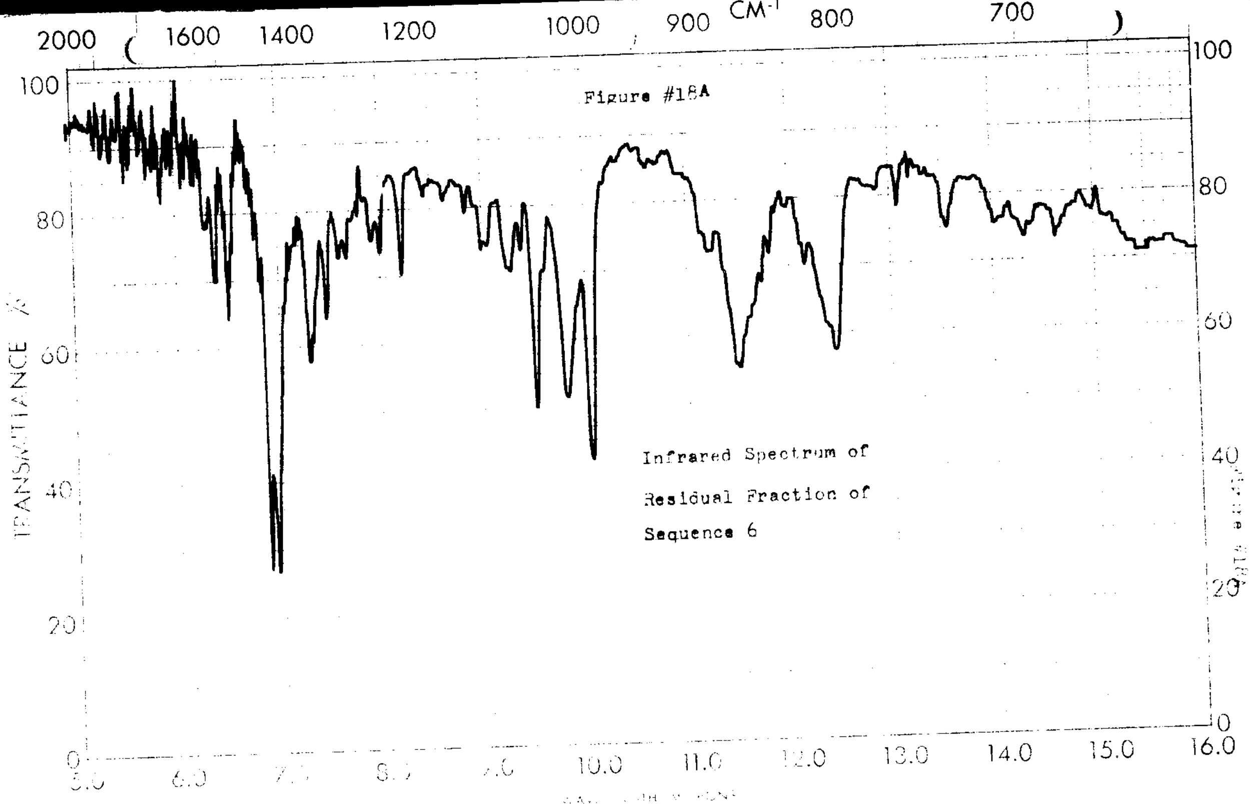
SCAN SPEED F
N

OPERATOR ajs
DATE 2/15/76

REMARKS

PERKIN ELMER

Figure #18A



Infrared Spectrum of
Residual Fraction of
Sequence 6

SAMPLE Sample #36B
Undistilled Residue

ORIGIN

SOLVENT

CURVE NO.

PHASE film on NaCl disc-Neat

REFERENCE

SCAN SPEED F
N

REMARKS

OPERATOR ajS

DATE 2/15/56

PERKIN-ELMER

PART NO. 23[illegible]31

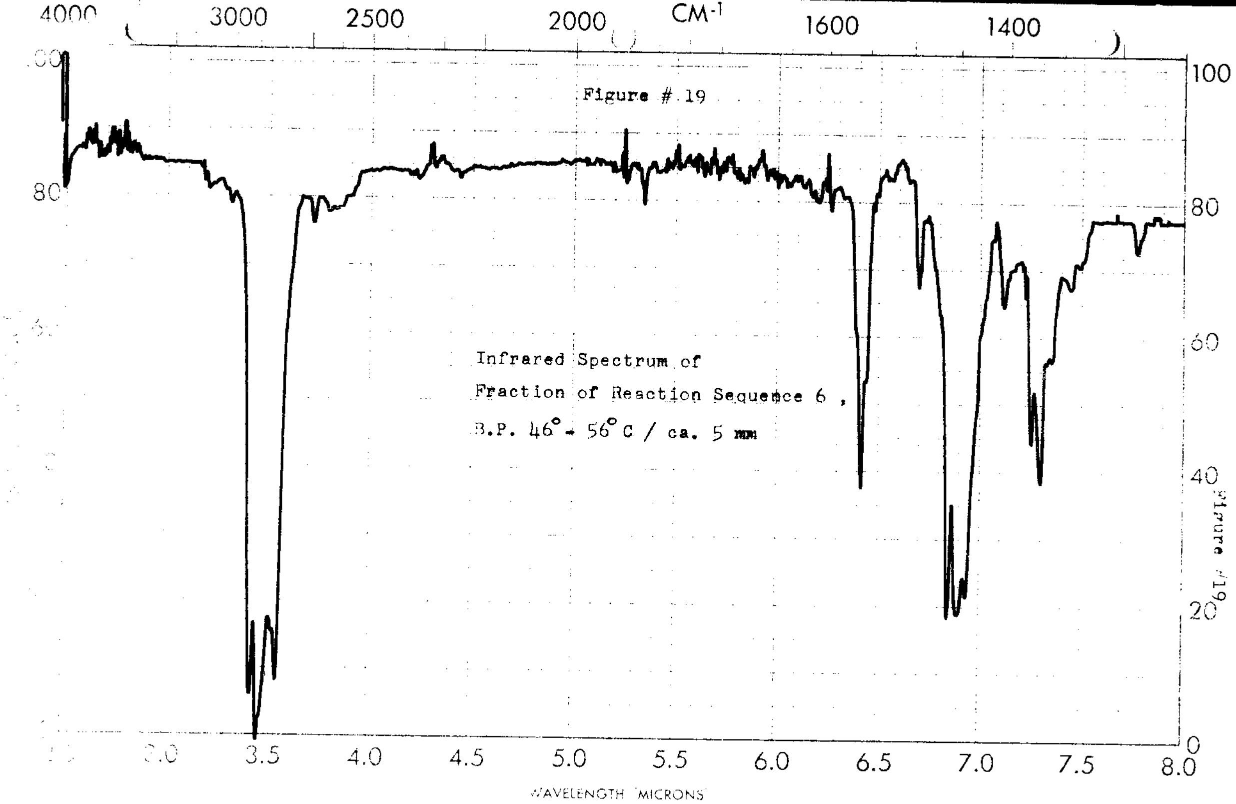


Figure # 19

Infrared Spectrum of
Fraction of Reaction Sequence 6 ,
B.P. 46° - 56° C / ca. 5 mm

Figure #19

SAMPLE Sample # 35C
46°-56°C / ca 5mm
ORIGIN
SOLVENT
PART NO. 2

CURVE NO.
CONC. film on NaCl disc - Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajd
DATE 7/15/76

PERKIN-ELMER

Figure #19A

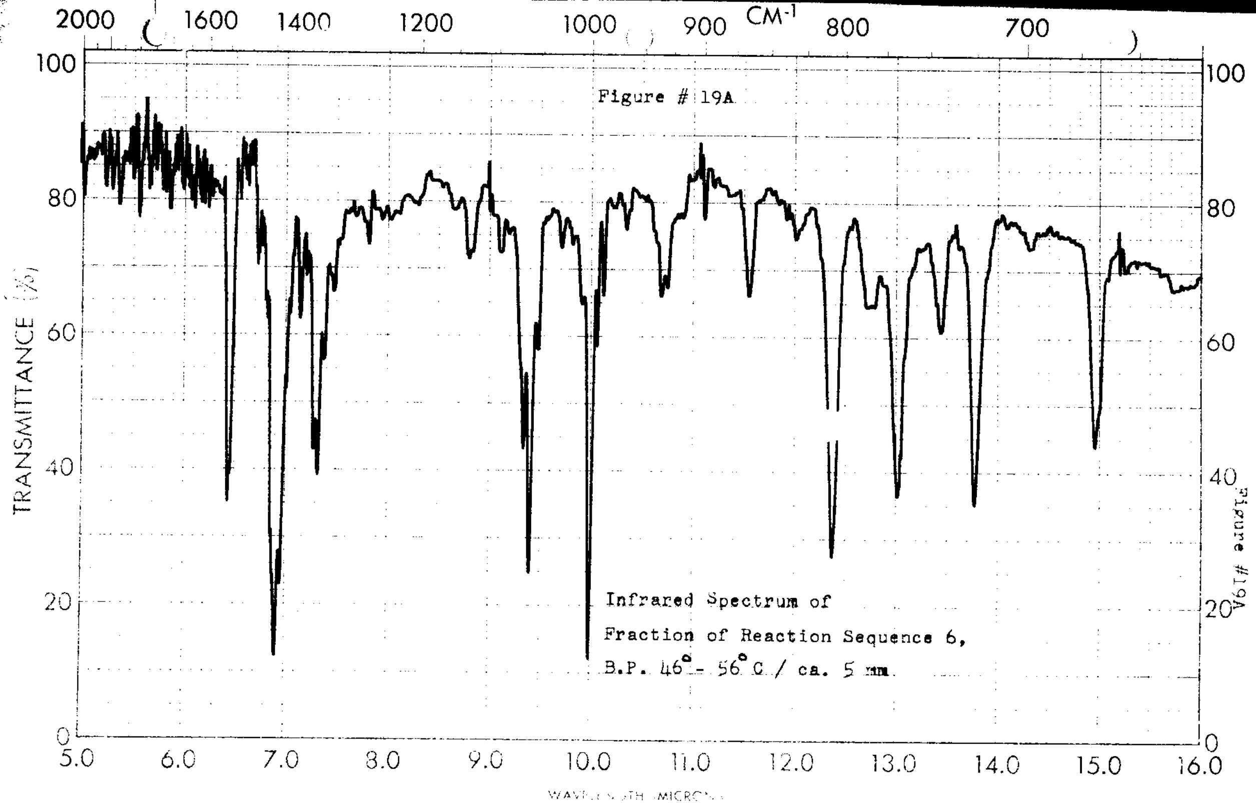


Figure # 19A

Infrared Spectrum of
Fraction of Reaction Sequence 6,
B.P. 46° - 56° C / ca. 5 mm

SAMPLE Sample #75C 46°-56°C / ca 5 mm	CURVE NO	SCAN SPEED F	OPERATOR
	CONC. film on NaCl Disc Neat	SLIT N	DATE 7/15/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

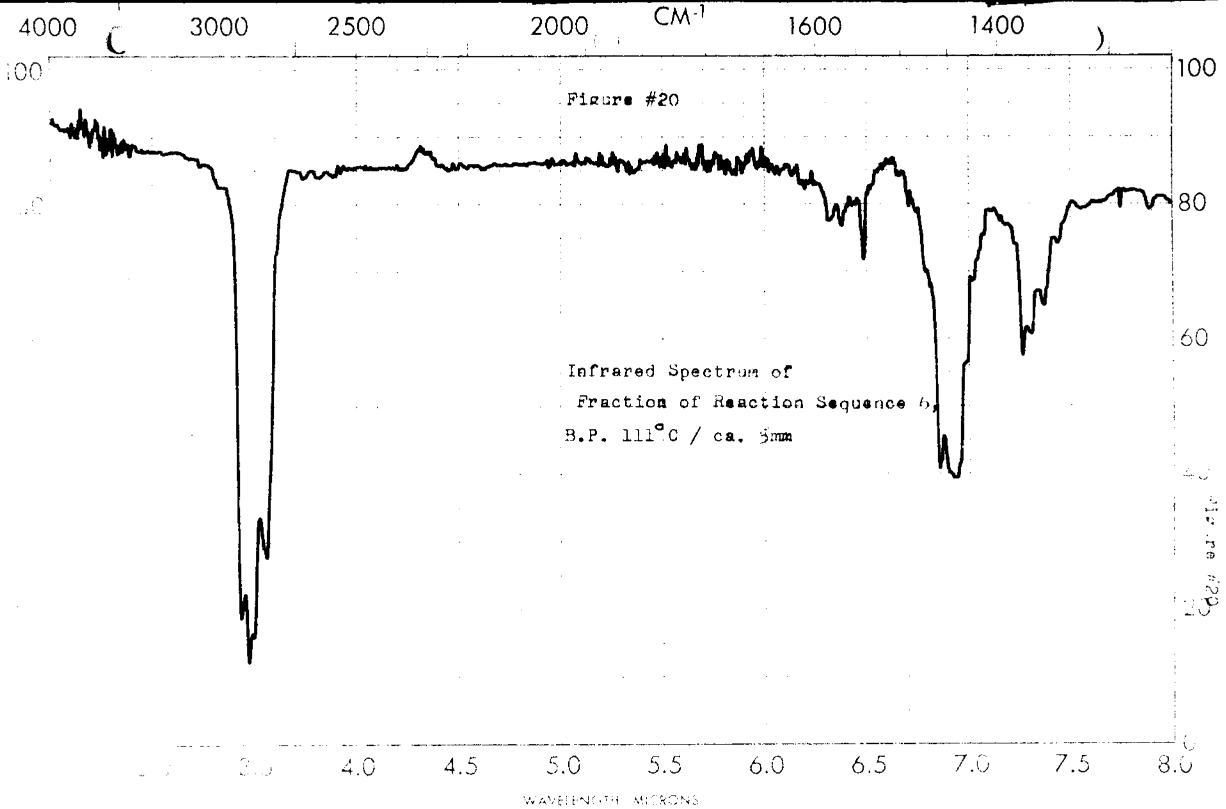


Figure #20

Infrared Spectrum of
Fraction of Reaction Sequence 6,
B.P. 111°C / ca. 5mm

Sample #35D
111°C / ca 5mm

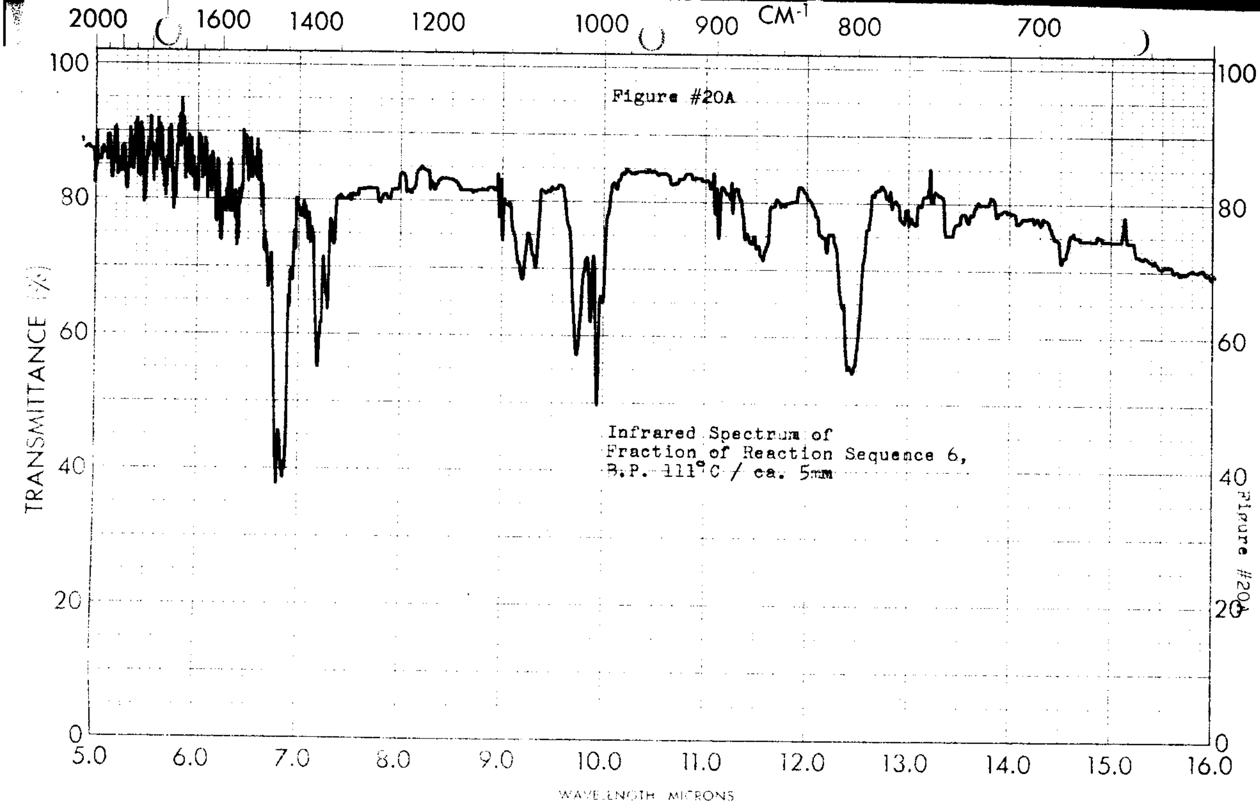
CURVE NO
CONC film on NaCl Disc-Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajz
DATE 7/15/76

PERKIN-ELMER

Figure #20A



Infrared Spectrum of
Fraction of Reaction Sequence 6,
B.P. 111°C / ca. 5mm

Figure #20A

SAMPLE #25D
111°C / ca 5mm
ORIGIN
SOLVENT

CURVE NO
CONC. film on NaCl disc - Neat
CELL PATH
REFERENCE

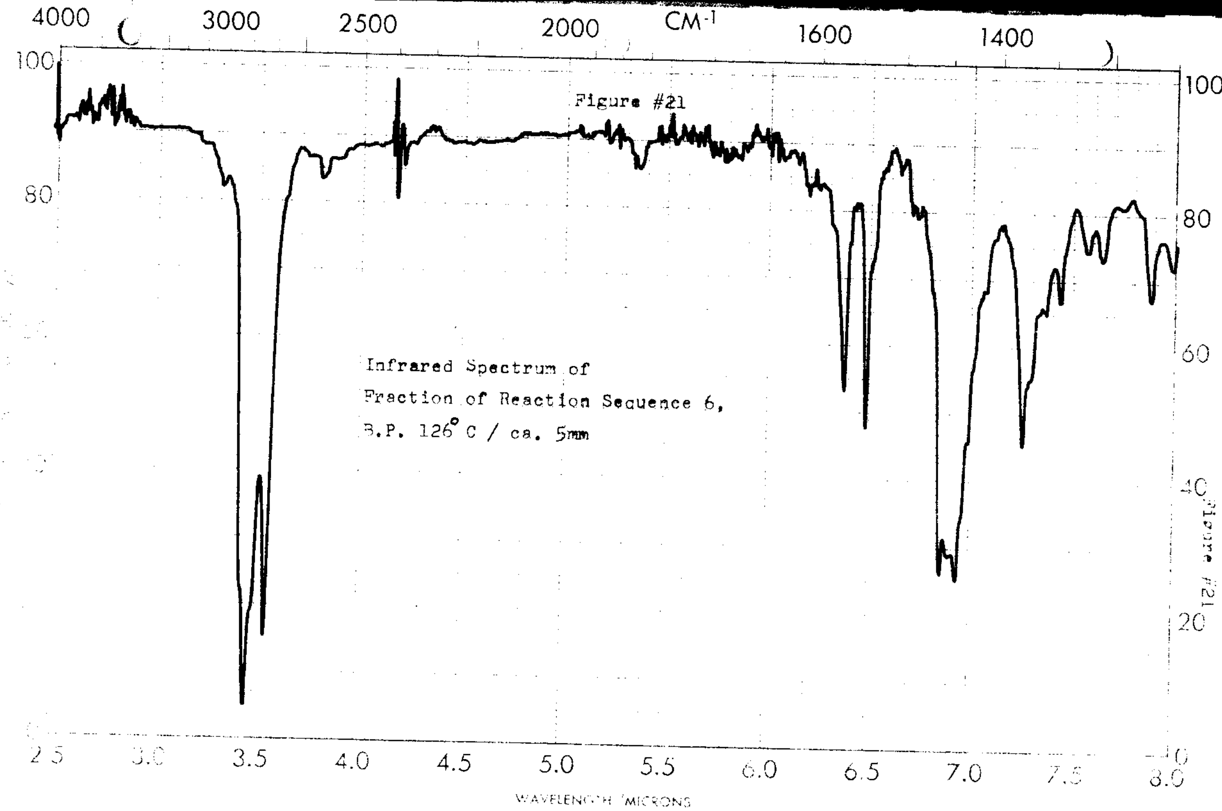
SCAN SPEED F
SLIT N
REMARKS

OPERATOR
DATE 7/15/76

PART NO. 237-1031

PERKIN-ELMER

Figure #21



Infrared Spectrum of
Fraction of Reaction Sequence 6,
B.P. 126° C / ca. 5mm

SAMPLE Sample 36A
126°C / ca 5 mm
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N
REMARKS

OPERATOR
DATE 2/15/76

PERKIN-ELMER

Figure #21

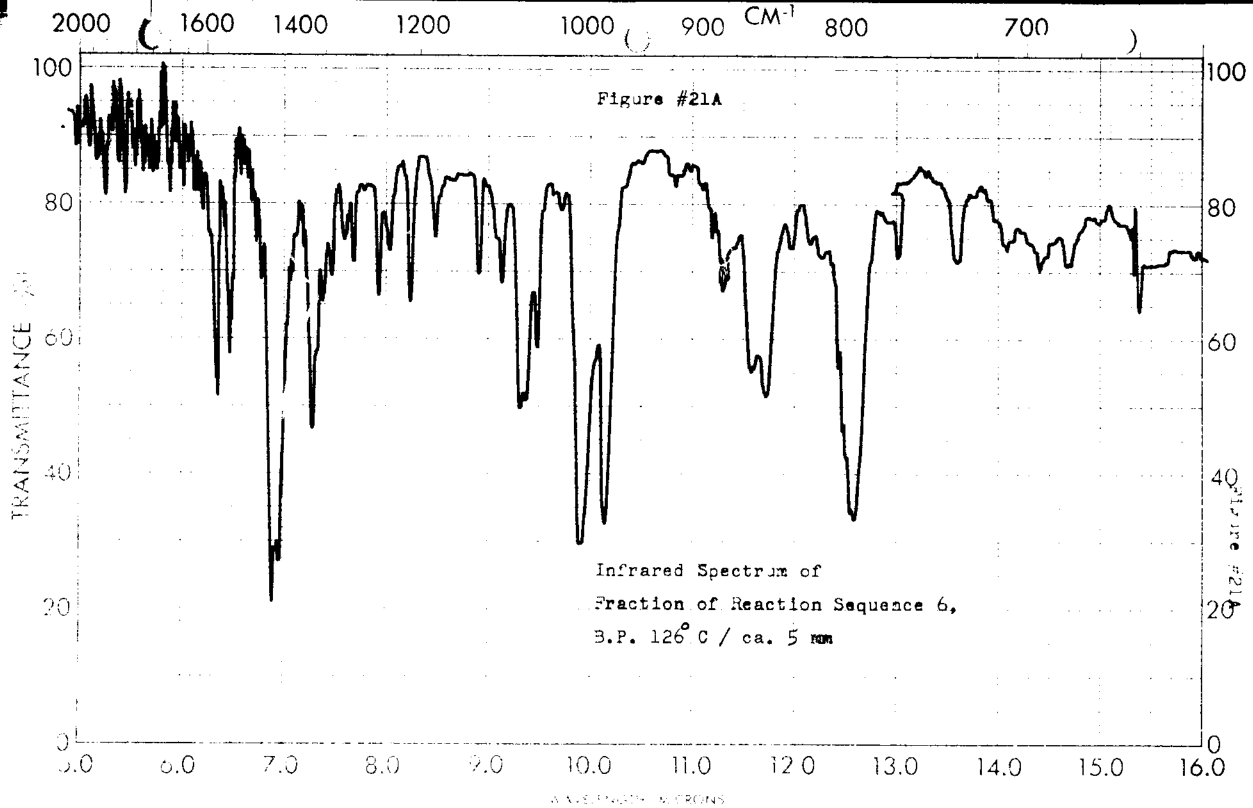


Figure #21A

Infrared Spectrum of
Fraction of Reaction Sequence 6,
B.P. 126° C / ca. 5 mm

SAMPLE Sample #26A
126°C / ca 5 mm
ORIGIN
SOLVENT
CURVE NO
CONC film on NaCl disc - Neat
CELL PATH
REFERENCE
SCAN SPEED F
SLIT N
OPERATOR a.g.d
DATE 7/15/76
REMARKS

PART NO 237 1031

PERKIN-ELMER

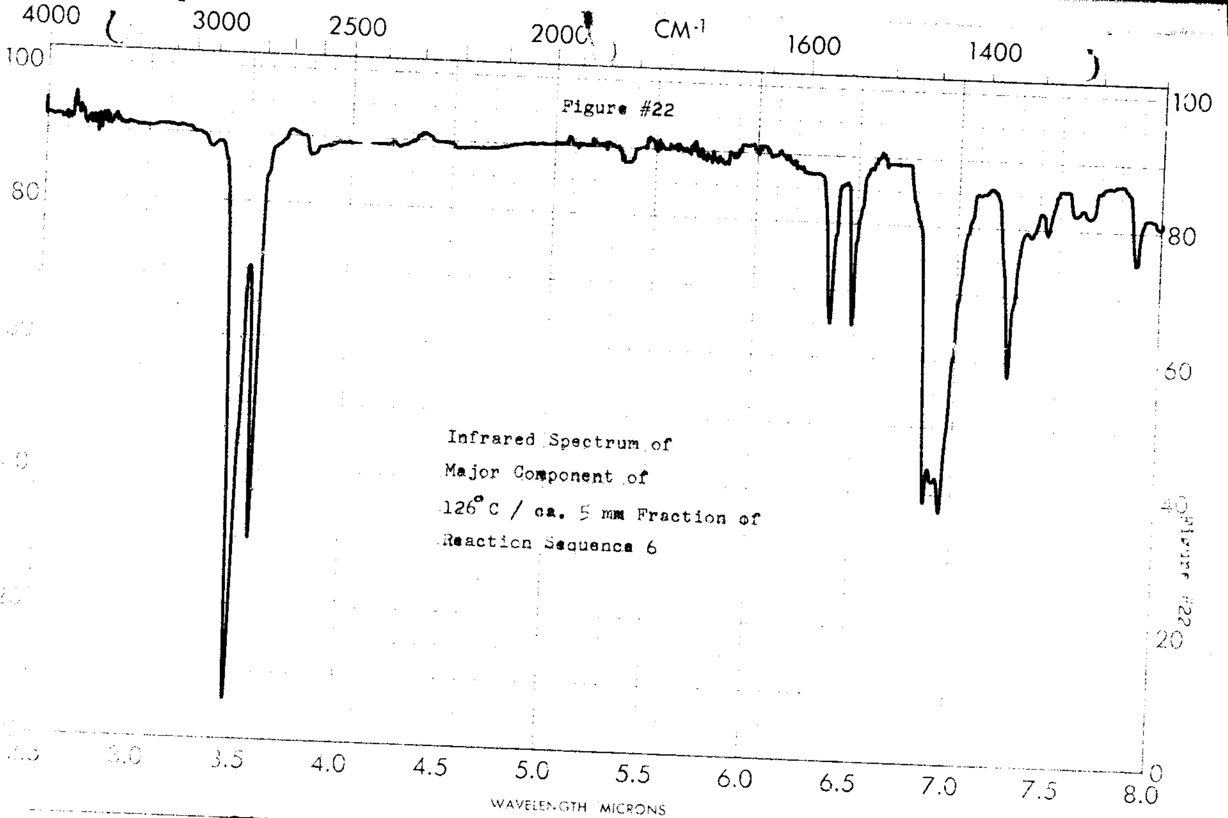


Figure #22

Infrared Spectrum of
Major Component of
126°C / ca. 5 mm Fraction of
Reaction Sequence 6

SAMPLE Sample ~~36B~~ 36C (major fraction of 36A)	CURVE NO	SCAN SPEED F	OPERATOR ajS
ORIGIN	CONC. Neat on NaCl disc - Neat	SLIT N	DATE 8/3/76
SOLVENT	CELL PATH	REMARKS	
	REFERENCE		

56

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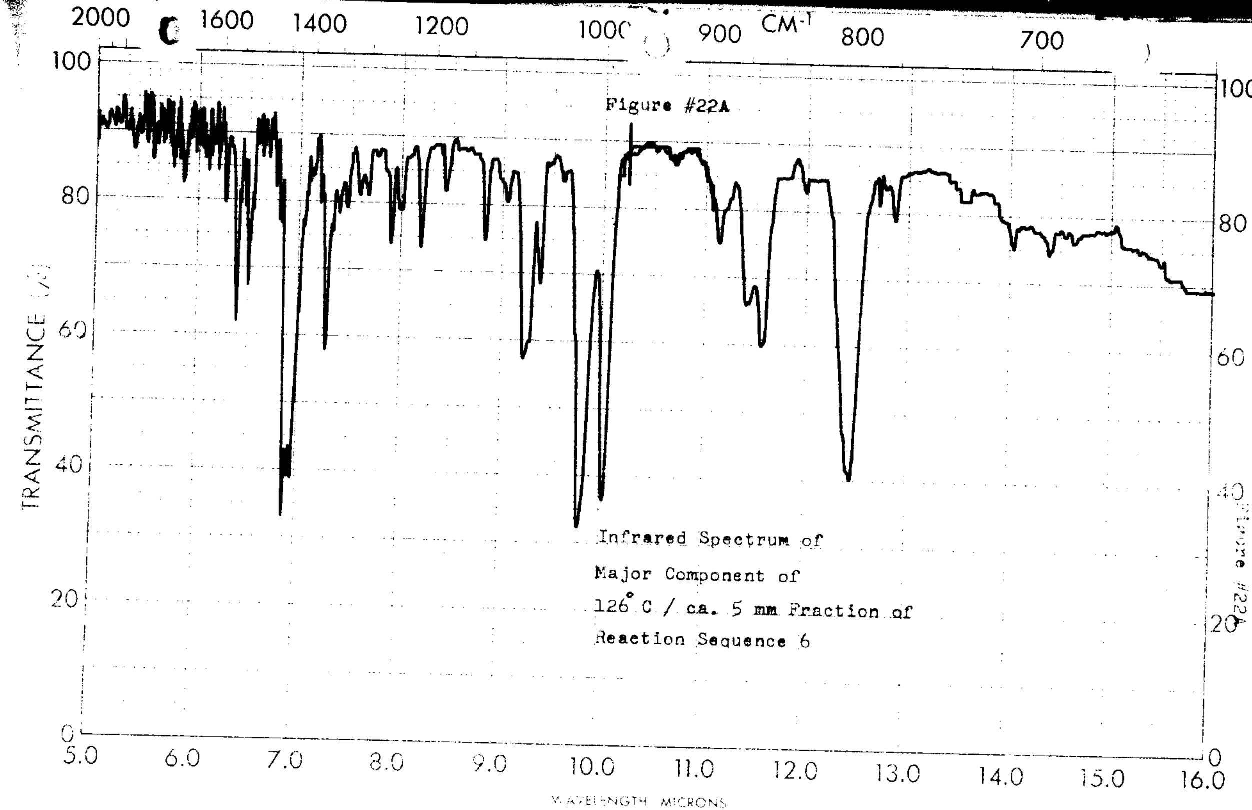


Figure #22A

Infrared Spectrum of
Major Component of
126° C / ca. 5 mm Fraction of
Reaction Sequence 6

SAMPLE Sample 26C (major fraction of 26A)
ORIGIN
SOLVENT

CURVE NO.
CONC Neat on NaCl disc-Neat
CELL PATH
REFERENCE

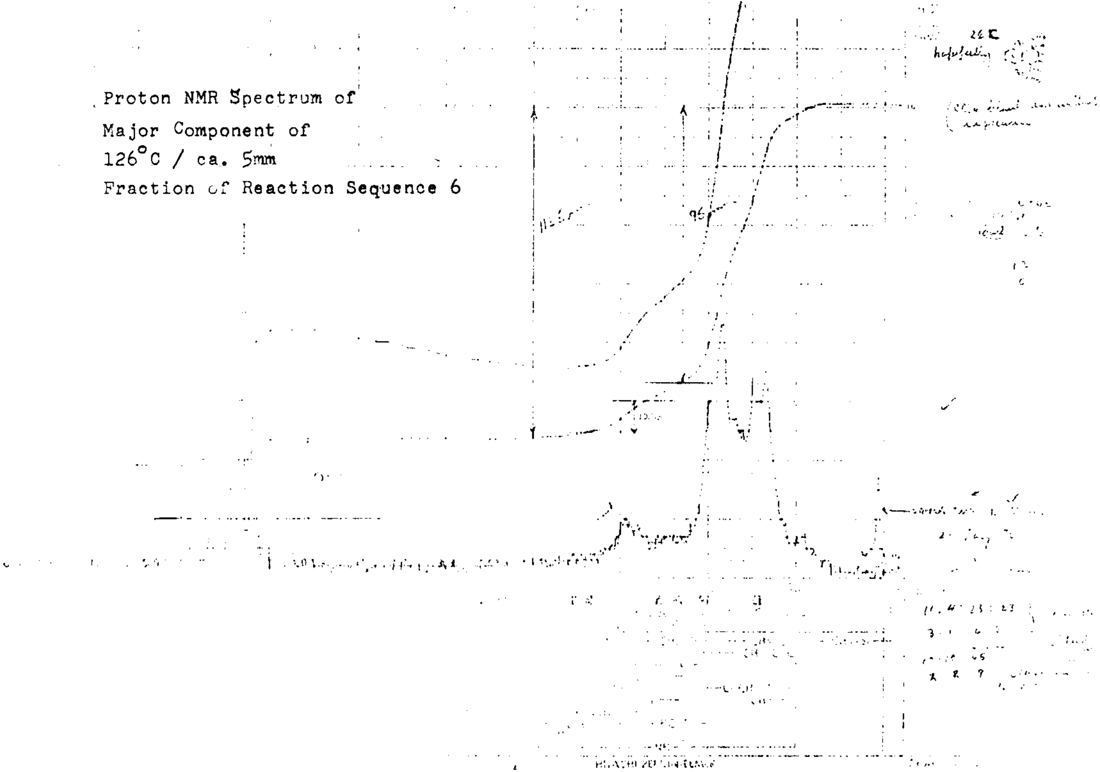
SCAN SPEED F
SLIT N
REMARKS

OPERATOR ajd
DATE 8/3/76

PART NO. 237-1031

PERKIN-ELMER

Figure #23



Proton NMR Spectrum of
Major Component of
126°C / ca. 5mm
Fraction of Reaction Sequence 6

U02 SCATENA, A.J. SYNTHETIC APPROACHES TO, etc.
S287s/1977 Science MS. 6/77 2 of 2

Figure #23A

Mass Spectrum of

Major Component of

126°C / ca. 5mm

Fraction of Reaction Sequence 6

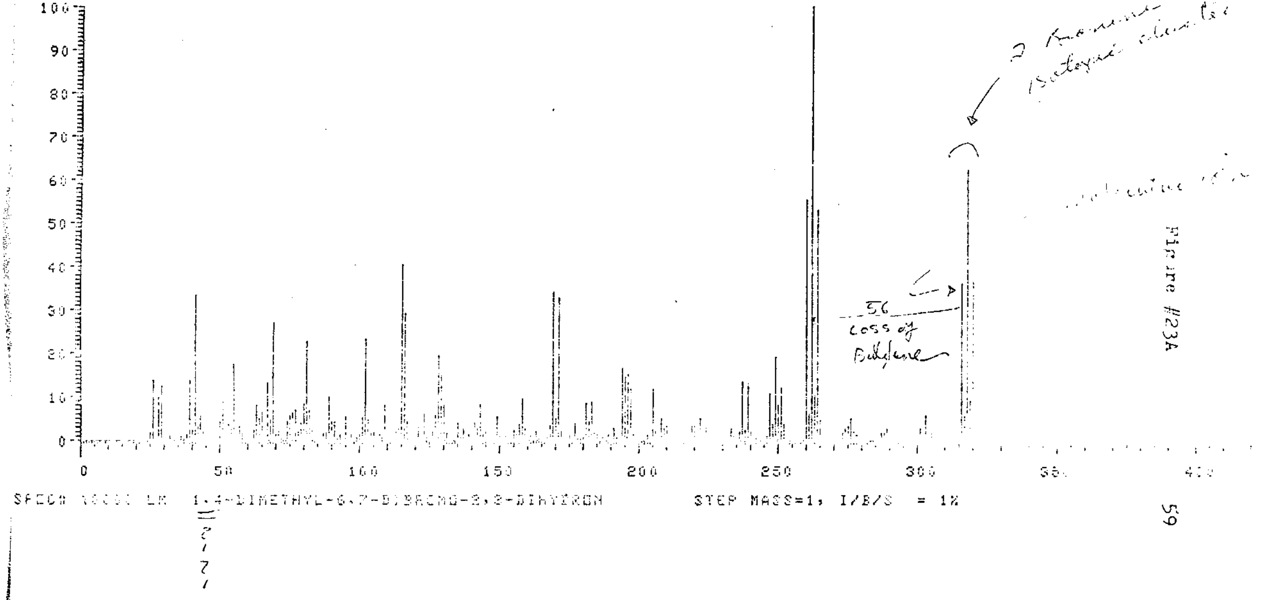


Figure #23A

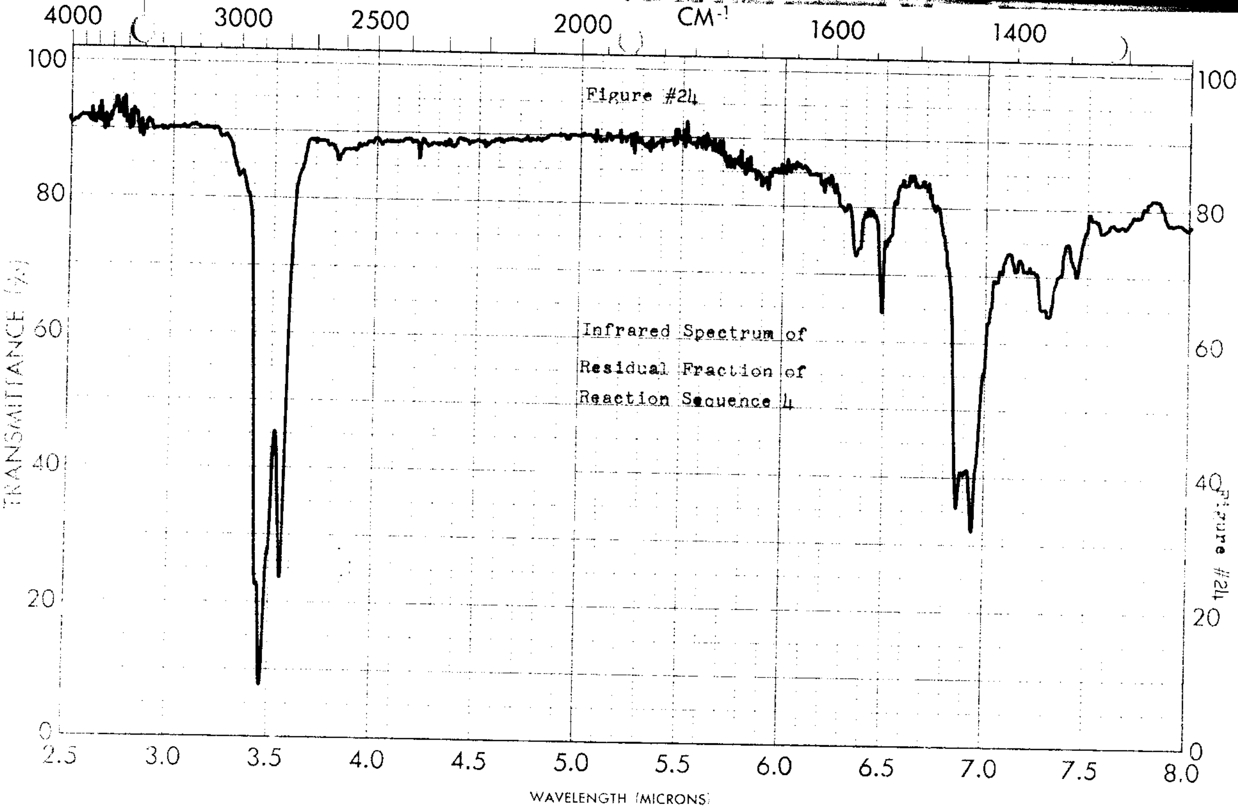


Figure #24

Infrared Spectrum of
Residual Fraction of
Reaction Sequence 4

Figure #24

SAMPLE # 27E (Residue - Undistilled material)

ORIGIN

SOLVENT

CURVE NO.

CONC. film on NaCl disc 'Nea

CELL PATH

REFERENCE

SCAN SPEED F

SLIT N

OPERATOR ajd

DATE 8/12/76

REMARKS

PART NO. 237-1030

PERKIN-ELMER

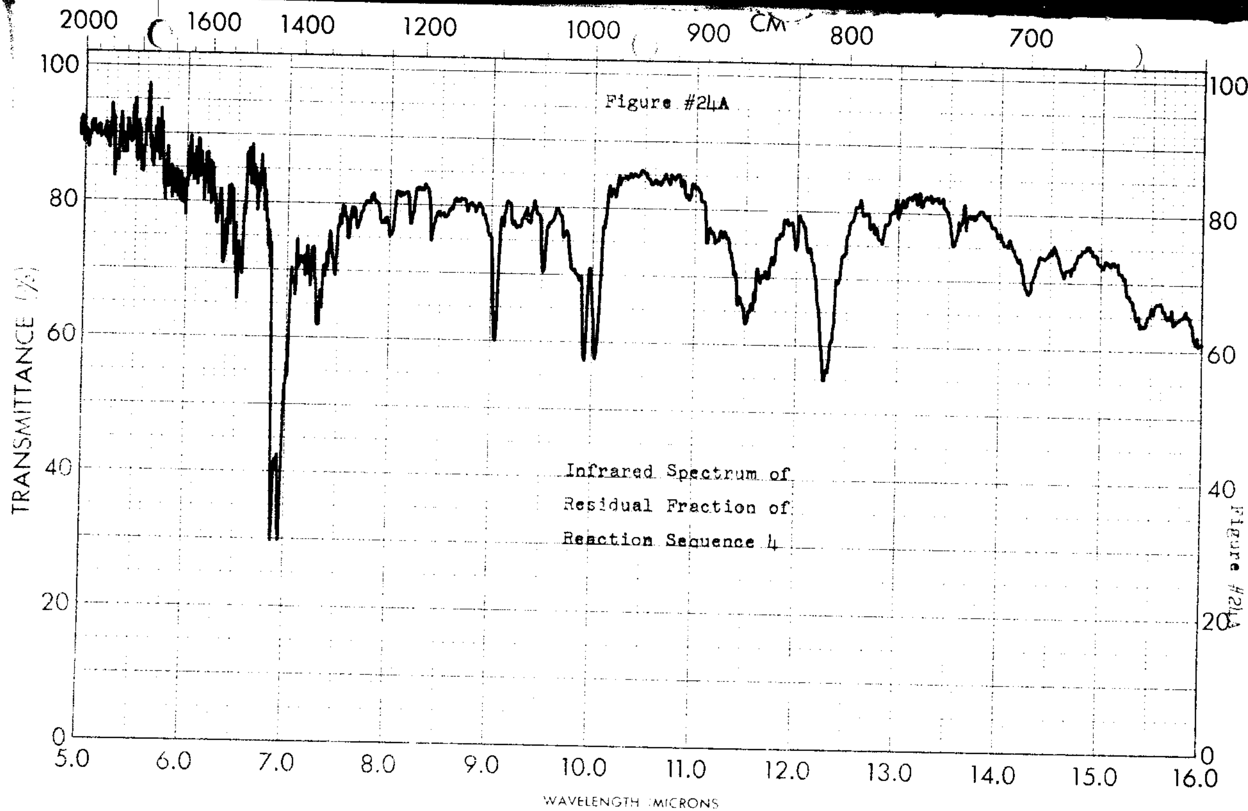


Figure #24A

Infrared Spectrum of
Residual Fraction of
Reaction Sequence 4

Figure #24A

SAMPLE 27E (~~[illegible]~~ Undistillable material
ORIGIN
SOLVENT
CURVE NO
CONC. film on NaCl disc-neat
CELL PATH
REFERENCE
SCAN SPEED F
SLIT N
OPERATOR ag
DATE 8/12/76
REMARKS

PART NO. 237-1031

PERKIN-ELMER

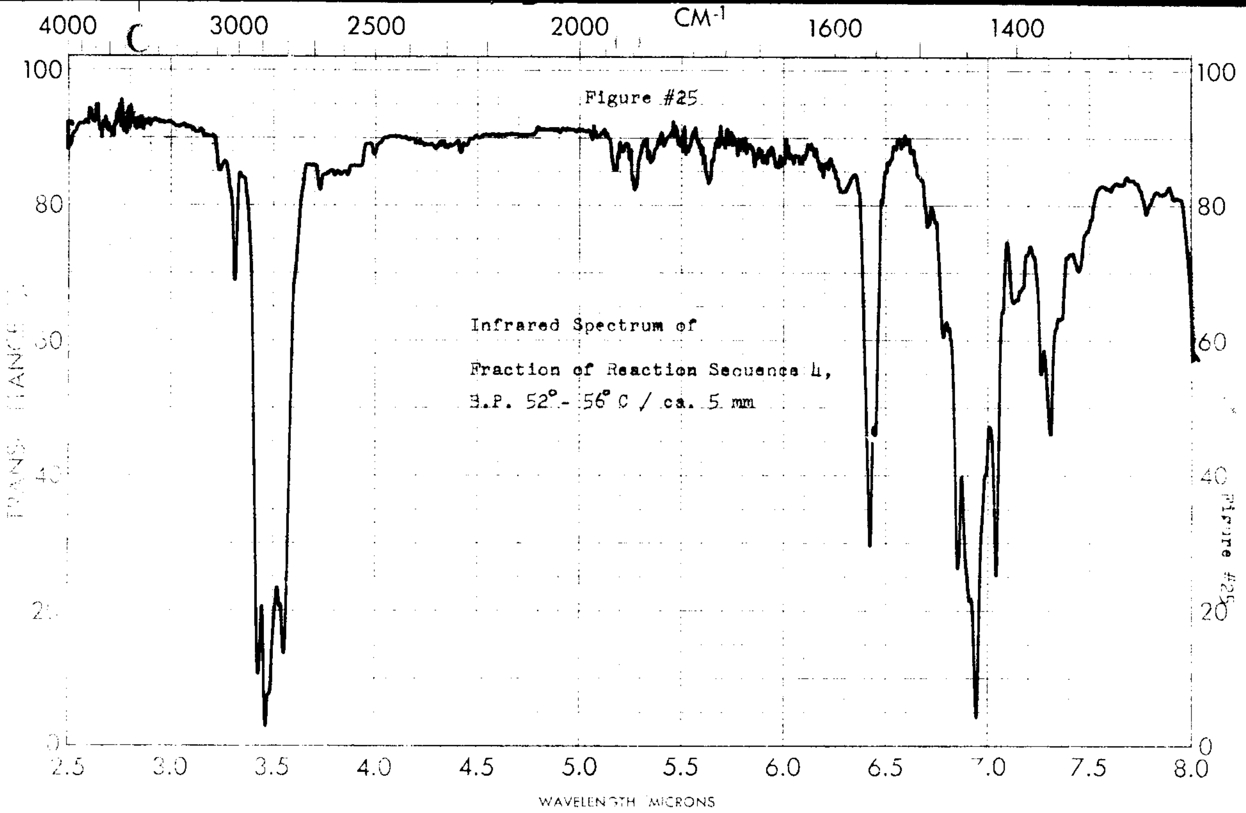


Figure #25

Infrared Spectrum of

Fraction of Reaction Sequence 4,

B.P. 52°- 56° C / ca. 5 mm

SAMPLE #27B (52-56° fraction of 27A	CURVE NO.	SCAN SPEED F	OPERATOR QJ
ORIGIN	CONC. film on NaCl disc - Neat	SLIT N	DATE 8/12/76
SOLVENT	CELL PATH	REMARKS	
	REFERENCE		

PART NO. 217-1039

PERKIN-ELMER

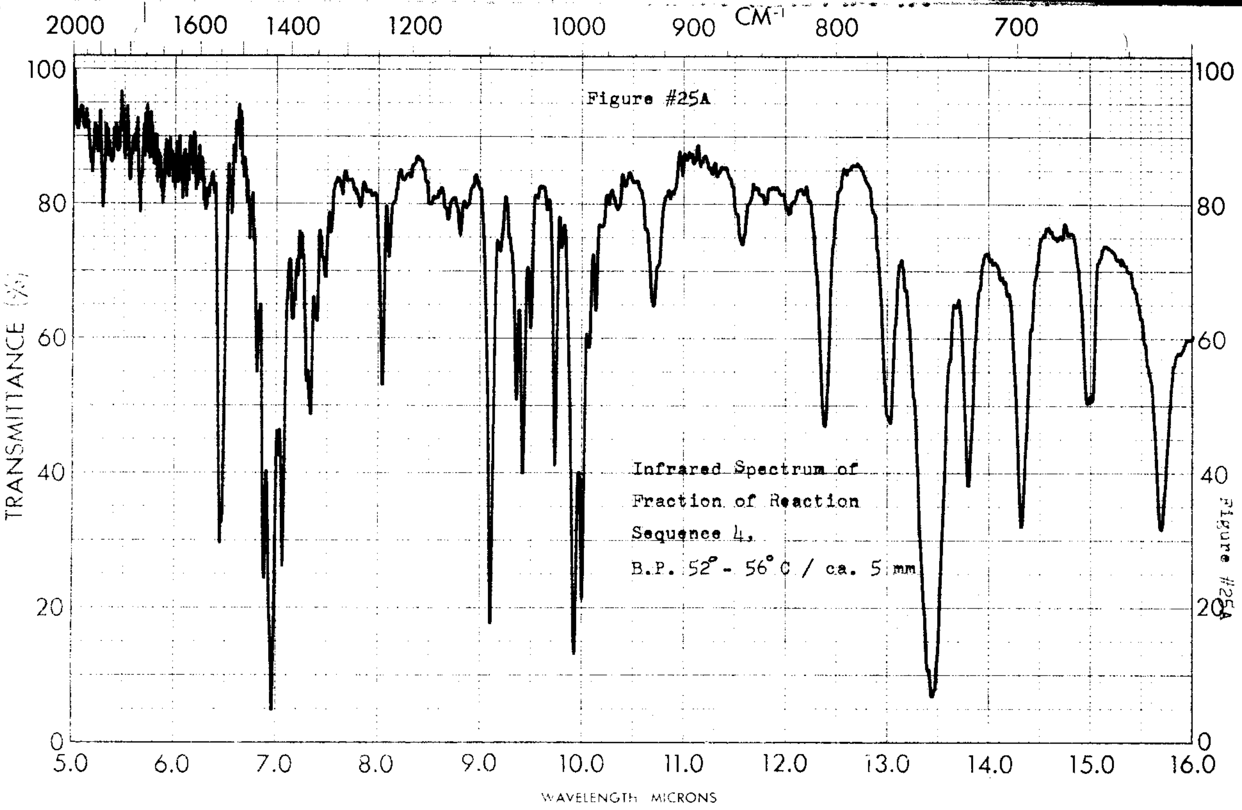


Figure #25A

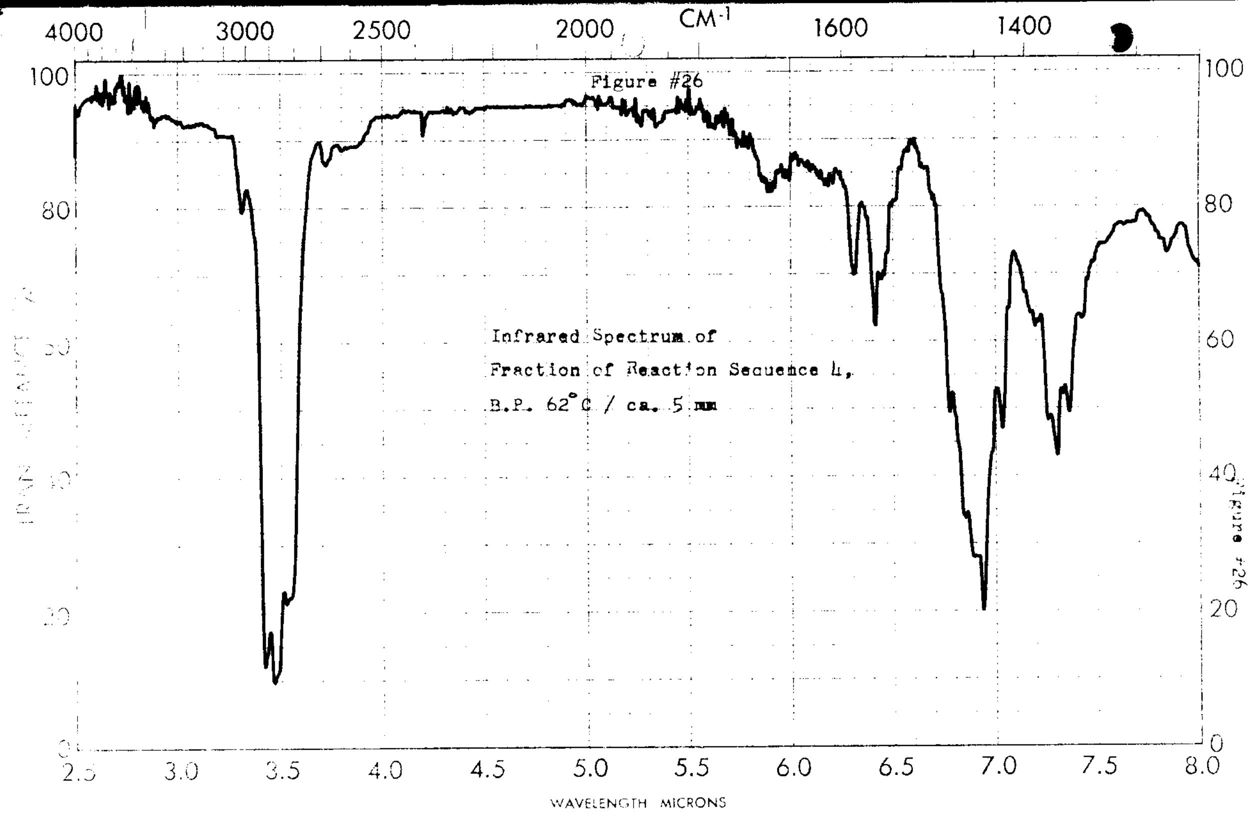
Infrared Spectrum of
Fraction of Reaction
Sequence 4,
B.P. 52° - 56° C / ca. 5 mm

SAMPLE #27B (52- 56°C fraction of 27A	CURVE NO.	SCAN SPEED F	OPERATOR ajd
	CONC. film on NaCl disc-Neat	SLIT N	DATE 8/13/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

Figure #26



Infrared Spectrum of
Fraction of Reaction Sequence 4,
B.P. 62°C / ca. 5 mm

SAMPLE #27C (62°C fraction of 27A)	CURVE NO.	SCAN SPEED F	OPERATOR ajl
ORIGIN	CONC. film on NaCl disc-Neat	SLIT N	DATE 8/12/76
SOLVENT	CELL PATH REFFRENCE	REMARKS	

ART NO 221 1030

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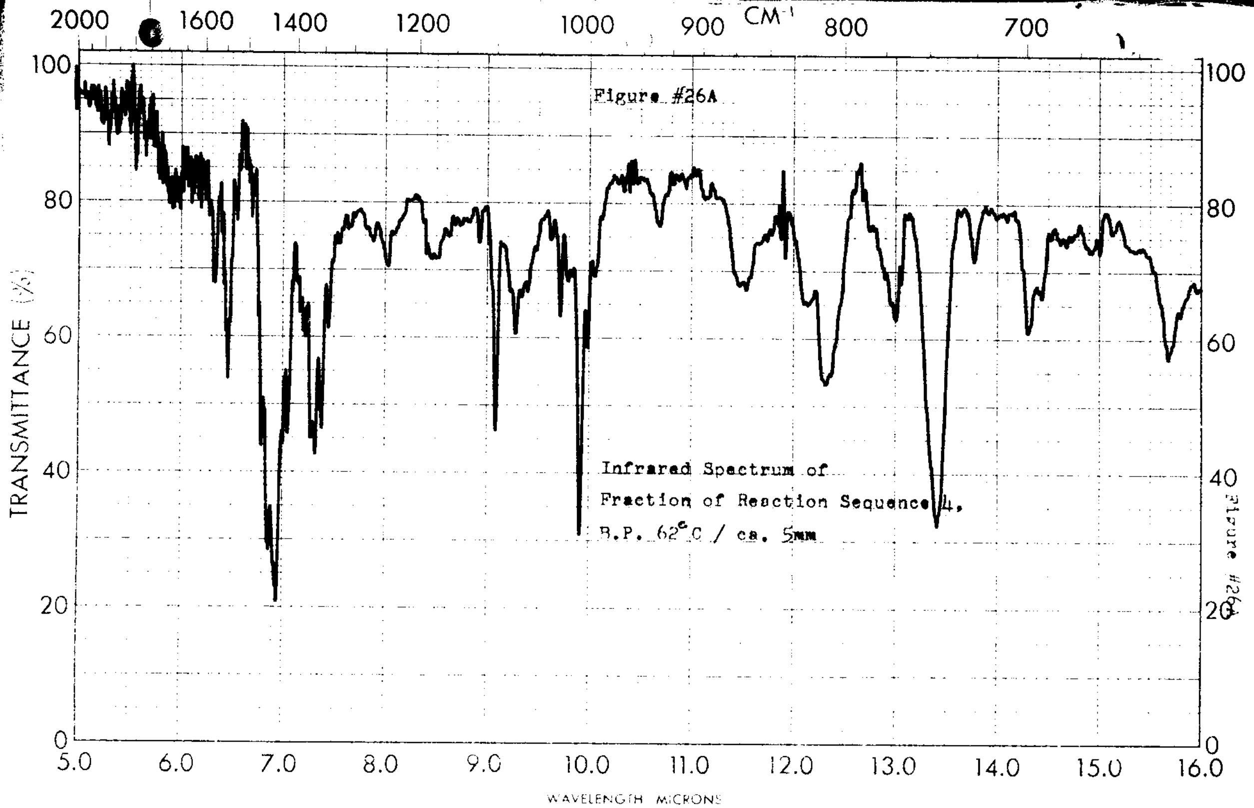


Figure #26A

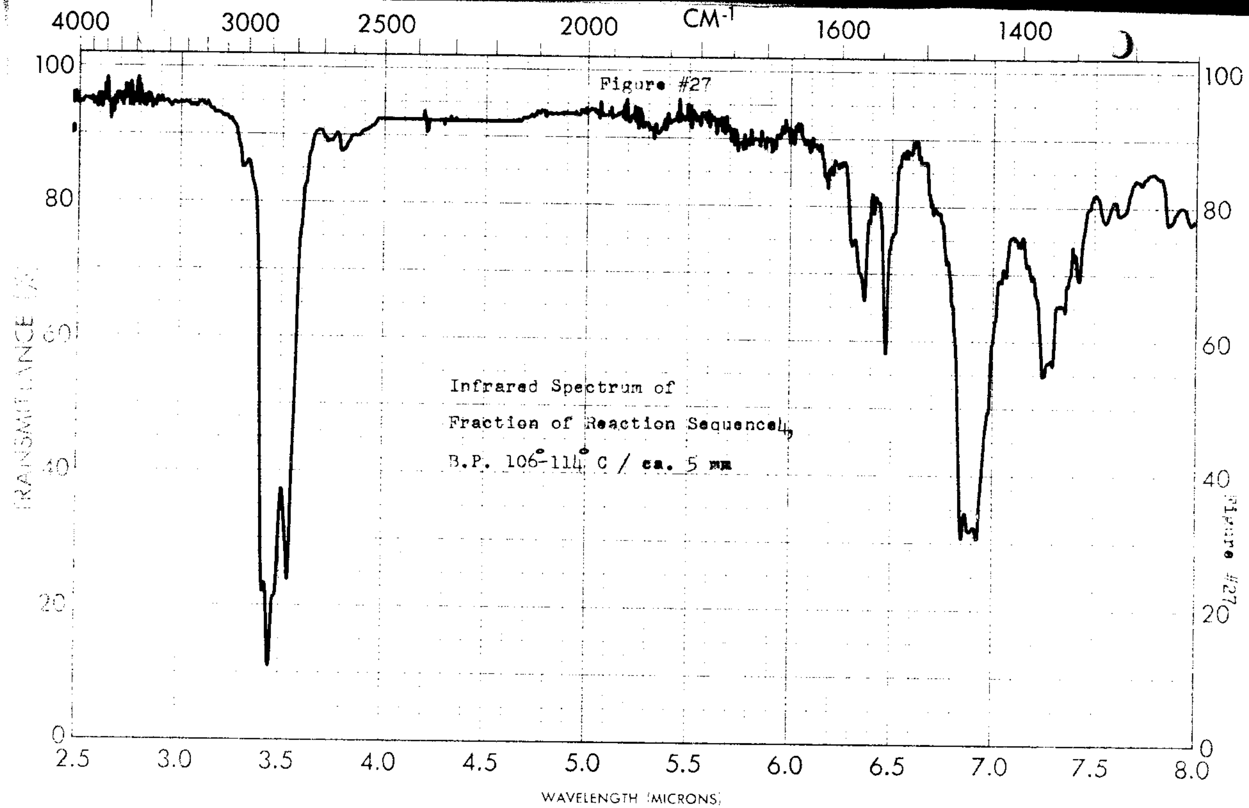
Infrared Spectrum of
Fraction of Reaction Sequence 4,
B.P. 62°C / ca. 5mm

SAMPLE #27C (62°C fraction of 27A)	CURVE NO.	SCAN SPEED F	OPERATOR agd
	CONC. film on NaCl disc-Neat	SLIT N	DATE 8/12/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

Figure #27



Infrared Spectrum of
Fraction of Reaction Sequence 4,
B.P. 106°-114° C / ca. 5 mm

SAMPLE #27D (106-114°c fraction of 27A)
ORIGIN
SOLVENT
CURVE NO.
CONC. film on NaCl disc-neat
CELL PATH
REFERENCE
SCAN SPEED. F
SLIT N
OPERATOR ajd
DATE 8/13/76
REMARKS

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PART NO. 237

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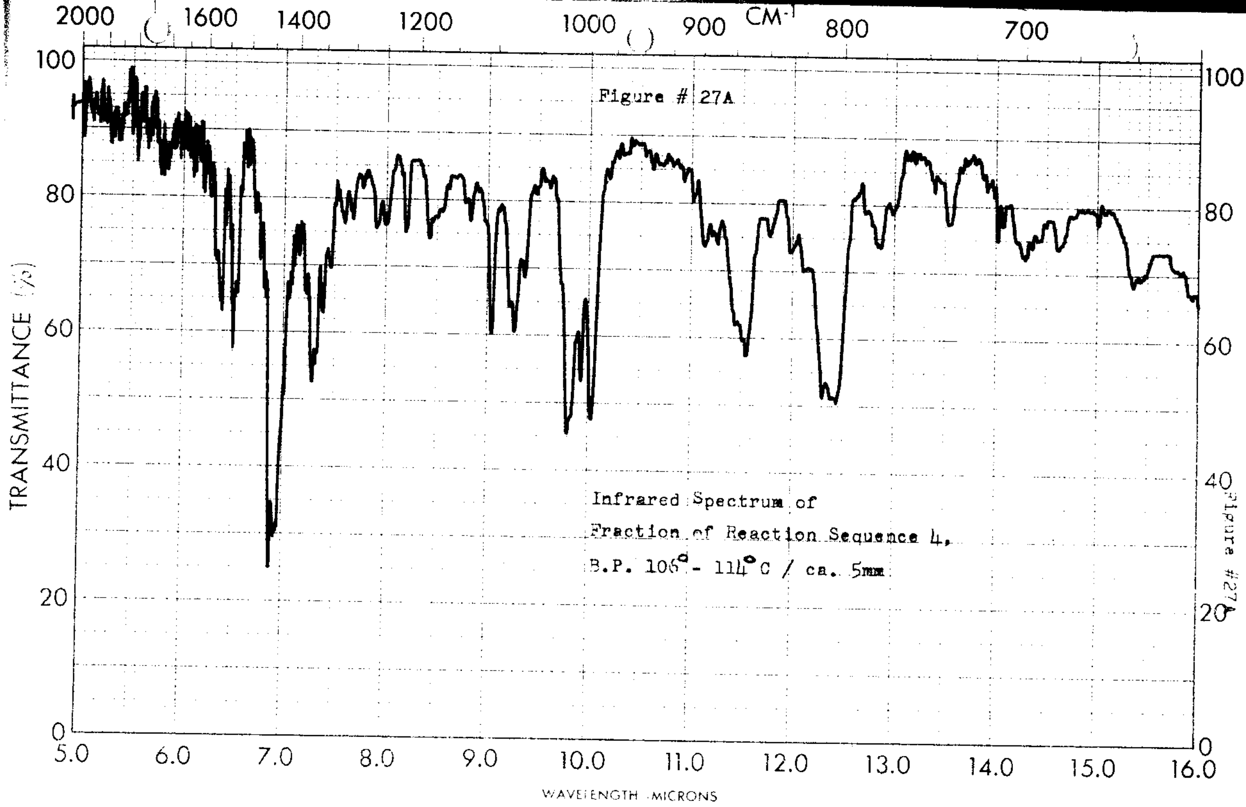
Figure # 27A



Infrared Spectrum of
Fraction of Reaction Sequence 4.
B.P. 106° - 114°C / ca. 5mm

SAMPLE #27D (106-114°c fraction of 27A)	CURVE NO.	SCAN SPEED F	OPERATOR ajd
ORIGIN	CONC. film on NaCl disc - Neat	SLIT N	DATE 8/12/76
SOLVENT	CELL PATH	REMARKS	
	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

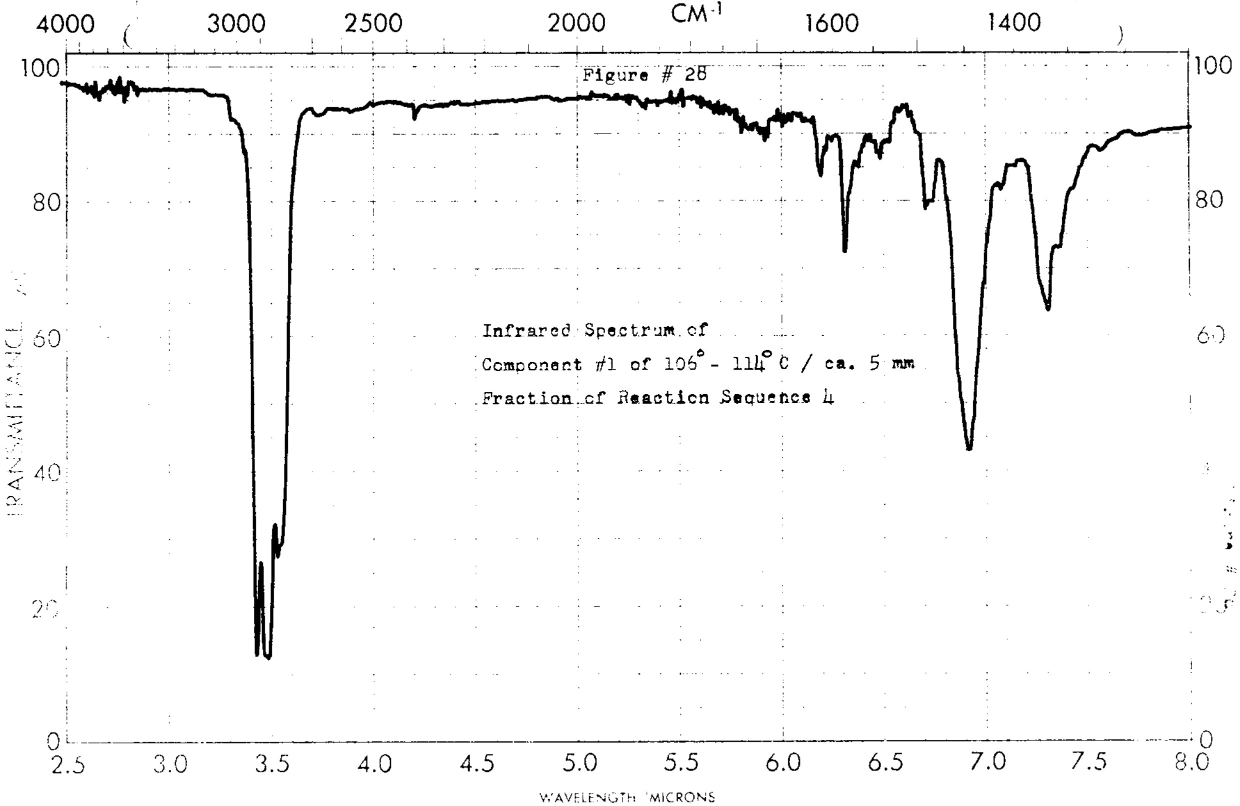


Figure # 28

Infrared Spectrum of
Component #1 of 105° - 114° C / ca. 5 mm
Fraction of Reaction Sequence 4

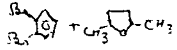
SAMPLE Sample #270 fraction #2
ORIGIN
SOLVENT

CURVE NO
CONC film on NaCl disc Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N

OPERATOR ajd
DATE 8/30/76

REMARKS



PART NO. 237-1030

PERKIN-ELMER

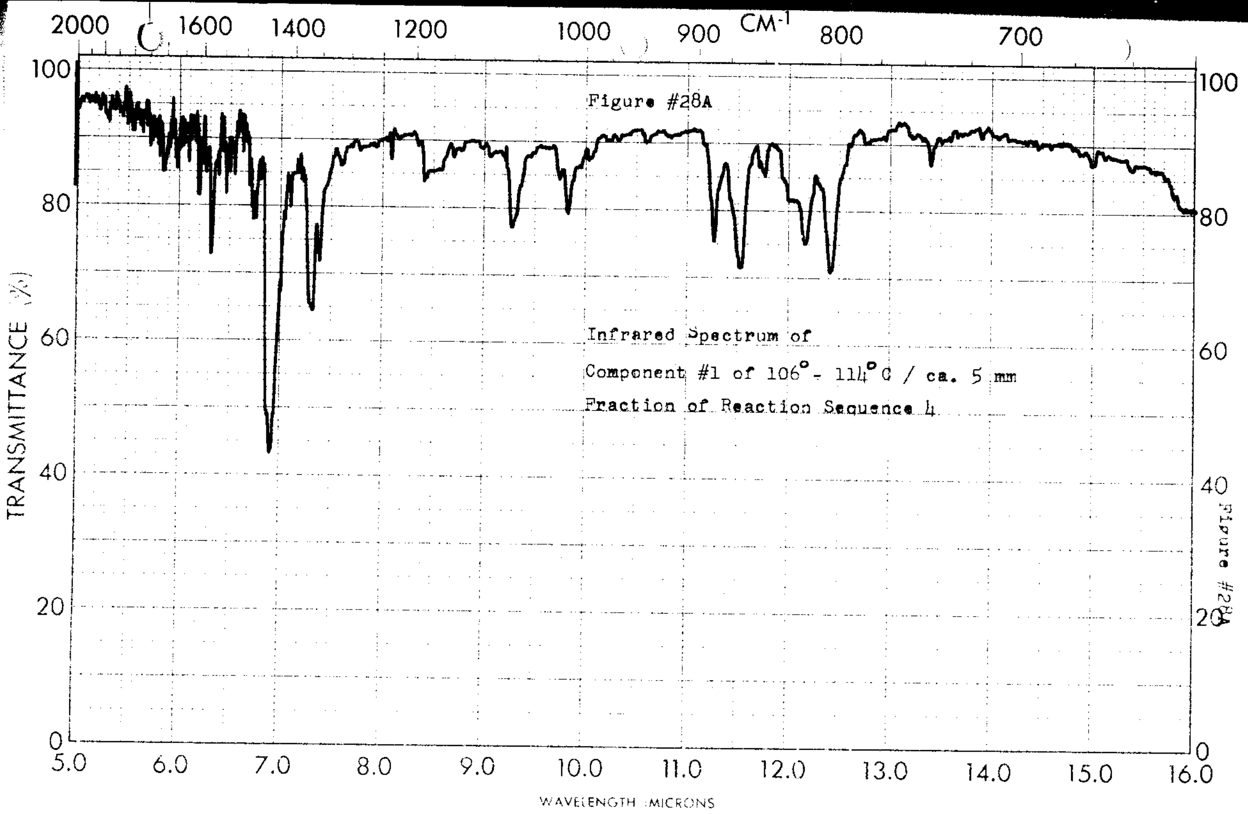


Figure #28A

Infrared Spectrum of
Component #1 of 106° - 114° C / ca. 5 mm
Fraction of Reaction Sequence 4

Figure #28A

SAMPLE Sample 370 fraction #3	CURVE NO.	SCAN SPEED F	OPERATOR ajd
	CONC. film on NaCl disc - Neat	SLIT N	DATE 8/30/76
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1031

PERKIN-ELMER

Figure #29A

GC - Mass Spectrum of Component #1 of 106 - 114 C / ca. 5mm Fraction of Reaction Sequence 4

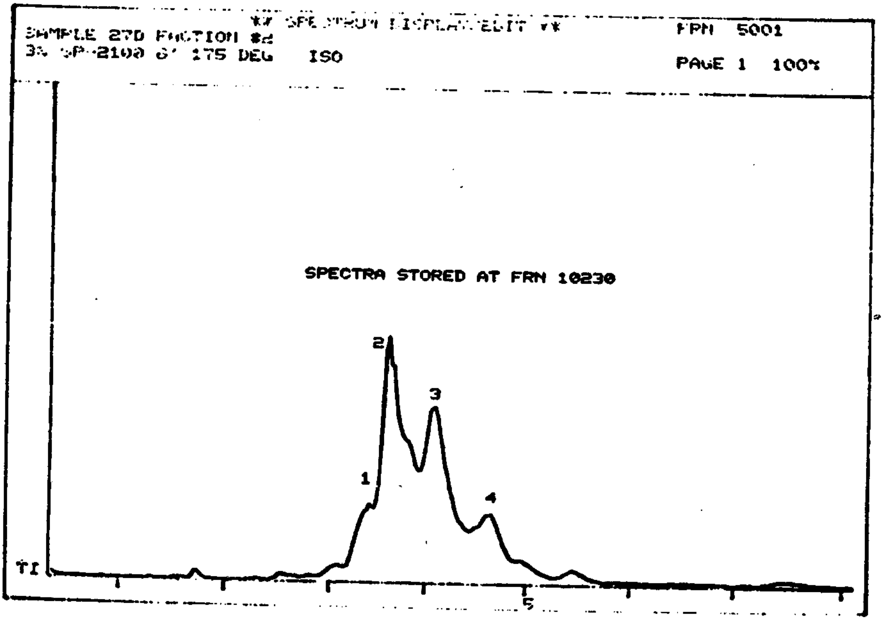


Figure #29B

GC - Mass Spectrum Cont'd.

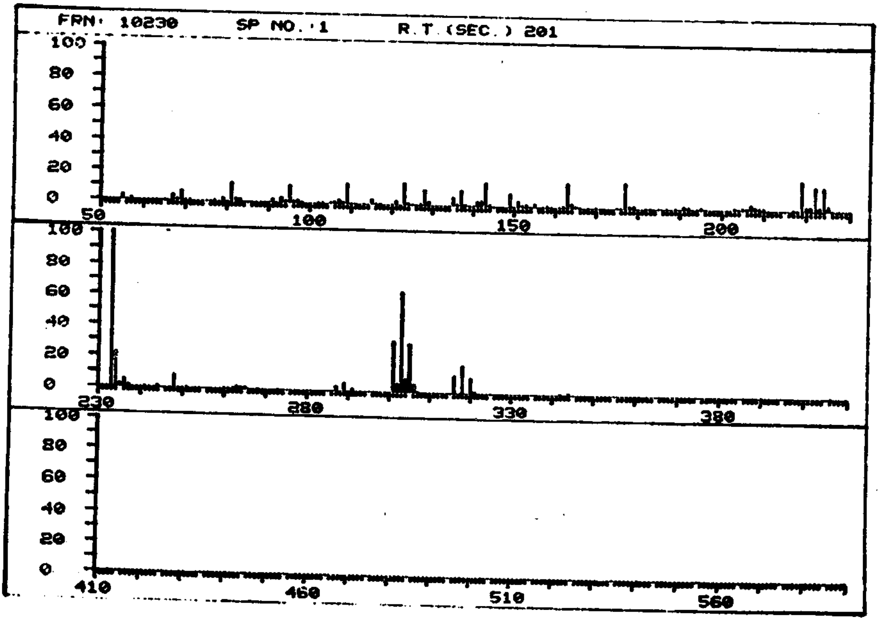


Figure #29C

GC - Mass Spectrum Cont'd.

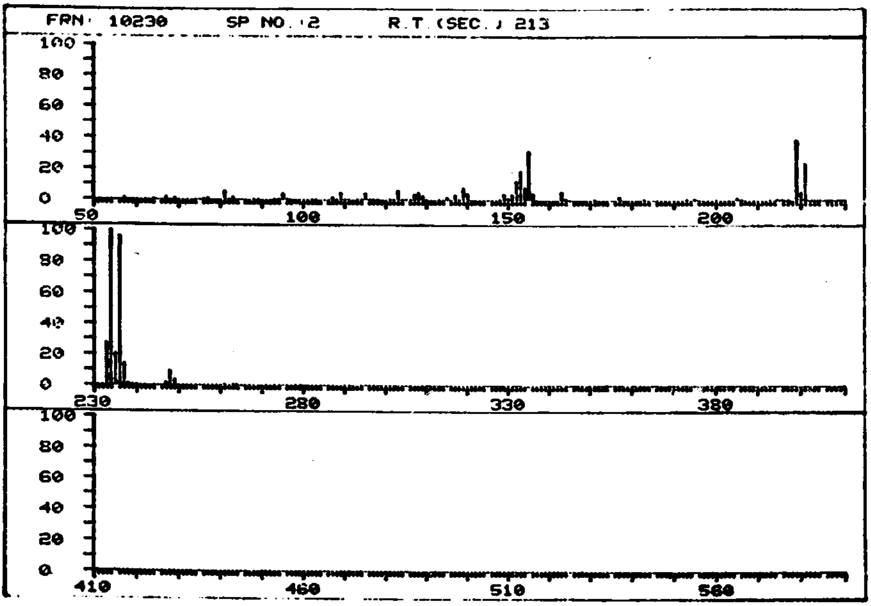


Figure #29D

GC - Mass Spectrum Cont'd.

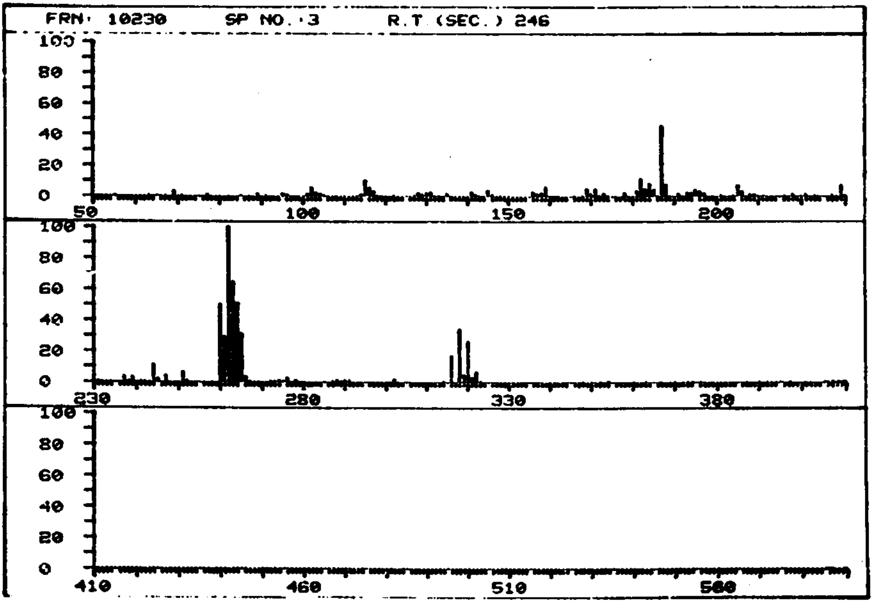
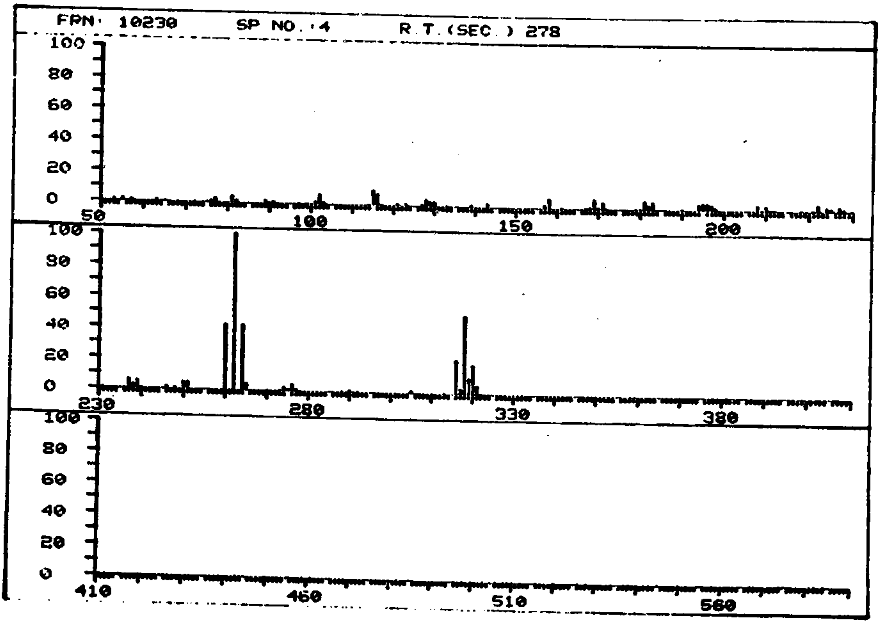


Figure #29E

GC - Mass Spectrum Cont'd.



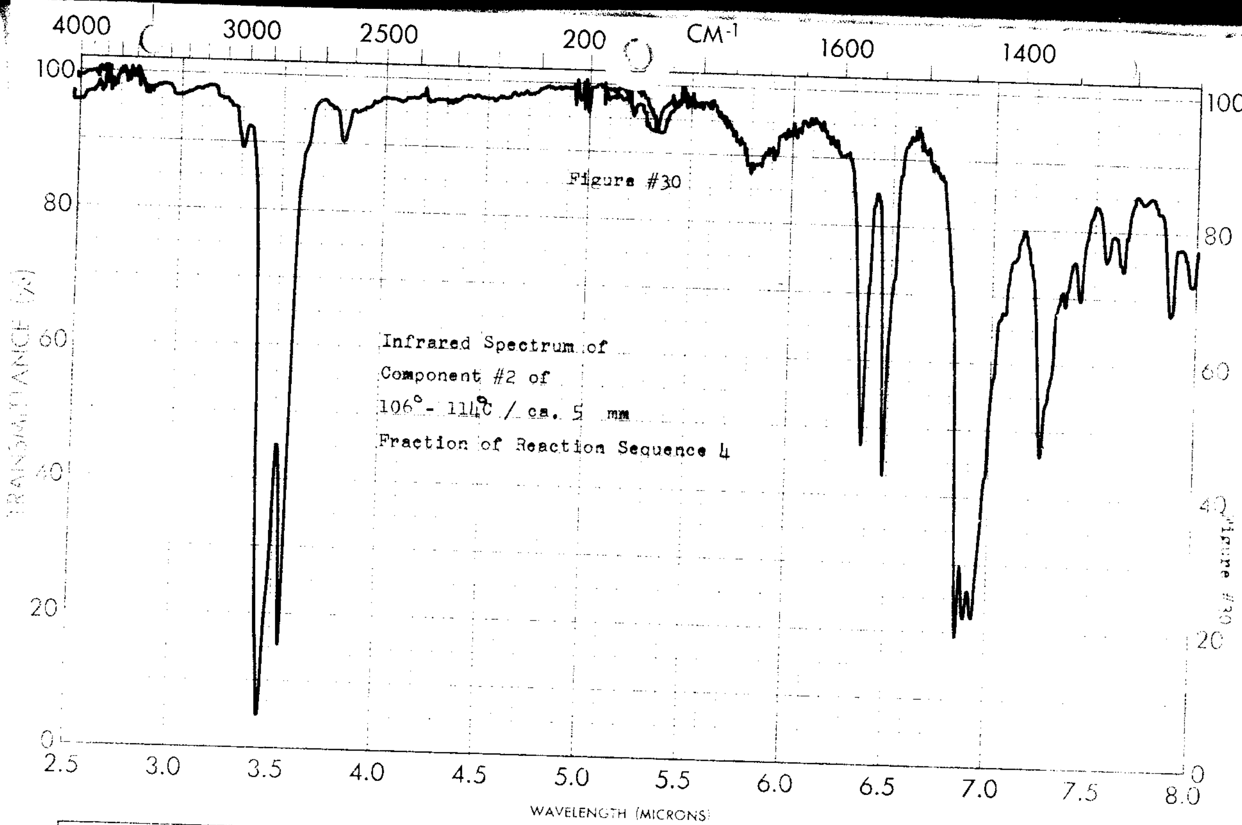
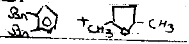


Figure #30

Infrared Spectrum of
Component #2 of
106° - 114°C / ca. 5 mm
Fraction of Reaction Sequence 4

SAMPLE Sample #270 fraction #3	CURVE NO.	SCAN SPEED F	OPERATOR ajd
ORIGIN	CONC. film on NaCl disc - Neat	SLIT N	DATE 8/30/76
SOLVENT	CELL PATH	REMARKS React	
	REFERENCE		



75

PART NO. 237-1030

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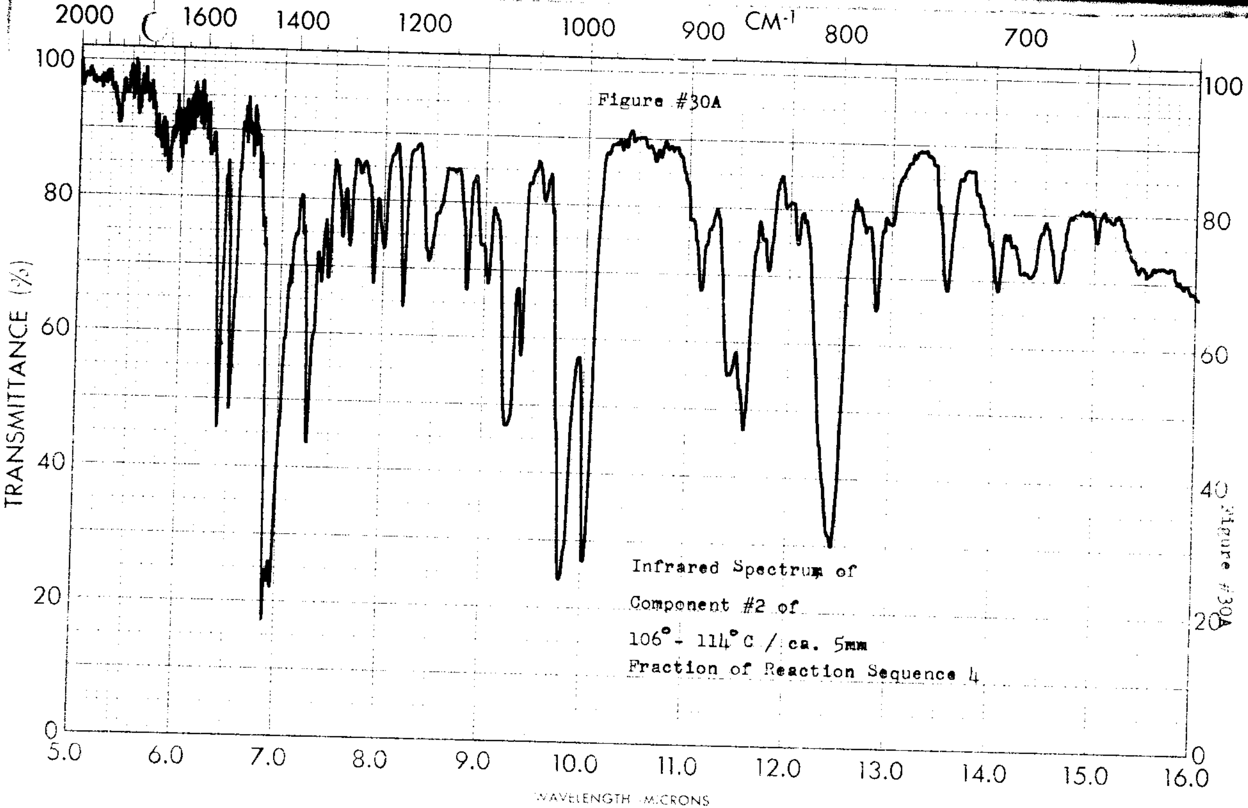

Figure #30A

Infrared Spectrum of
Component #2 of
106° - 114° C / ca. 5mm
Fraction of Reaction Sequence 4

Figure #30A

SAMPLE #27D fraction #3
ORIGIN
SOLVENT
CURVE NO.
CONC. film on NaCl disc-Neat
CELL PATH
REFERENCE
SCAN SPEED F
SLIT N
REMARKS
OPERATOR ajD
DATE 8/30/76

76

PART NO. 237-1031

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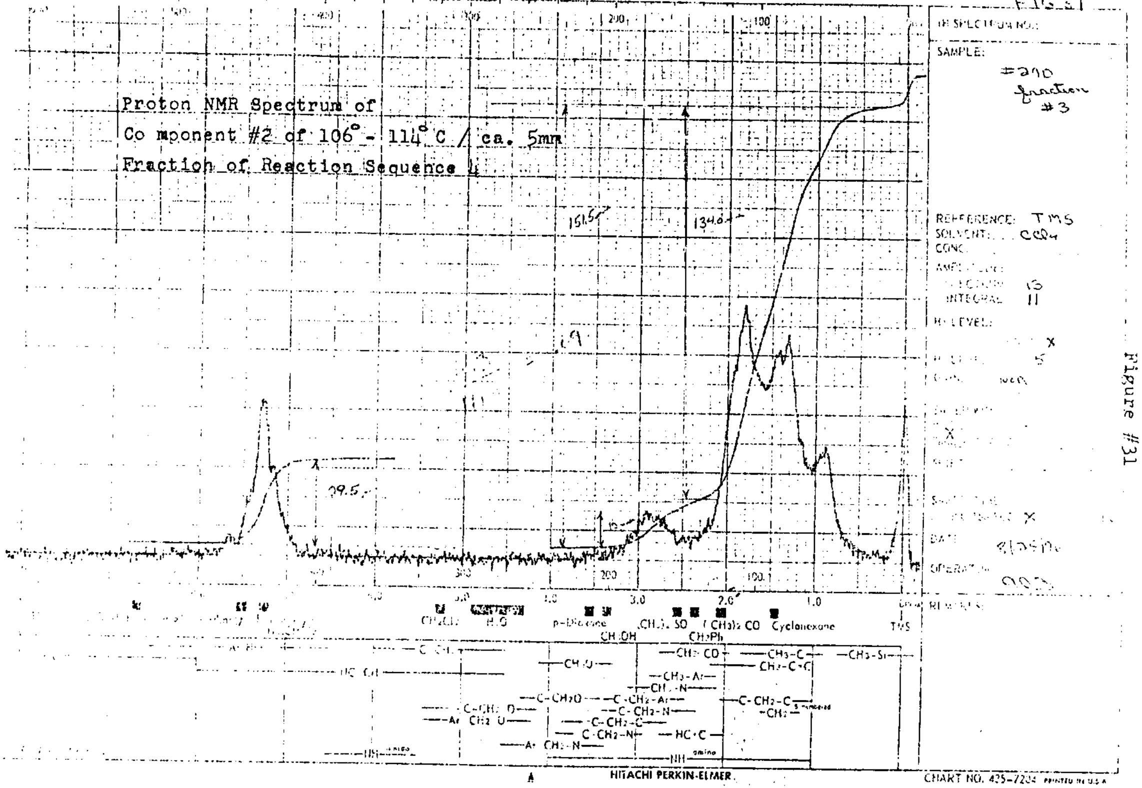
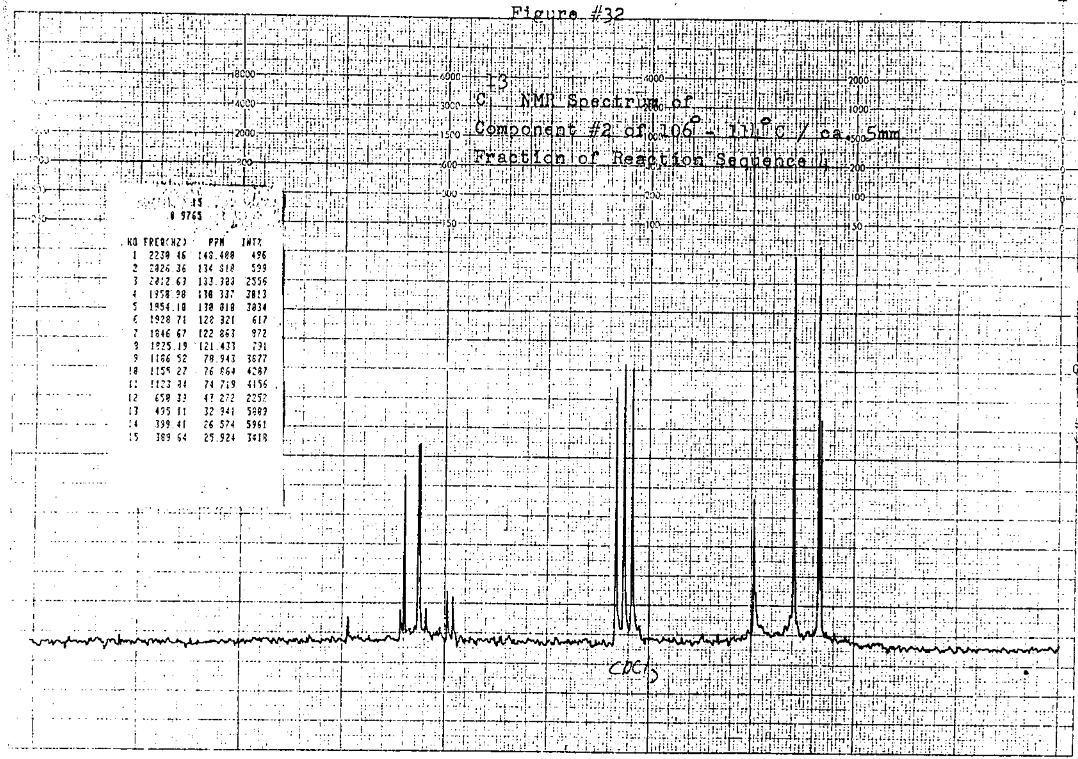
Figure #31

Figure # 31



Proton NMR Spectrum of Co mponent #2 of 106° - 114° C / ca. 5mm Fraction of Reaction Sequence 4

Figure #32



^{13}C NMR Spectrum of
Component #2 of 106° - 111°C / ca. 5mm
Fraction of Reaction Sequence 4

15
0 9765

NO	FREQ(HZ)	PPM	INT%
1	2239 46	148.400	496
2	2026.36	134 318	599
3	2012.63	133.383	2556
4	1958.98	130 337	3013
5	1954.10	130 010	3034
6	1928 71	128 321	617
7	1846 67	122 863	972
8	1825.19	121.433	731
9	1186 52	78.943	3677
10	1155 27	76 864	4287
11	1123 84	74 719	4156
12	658 33	47 272	2252
13	495 11	32 941	5889
14	399.41	26 574	5961
15	389 64	25.924	3418

Figure #32

FX-60
CHART NO.
SAMPLE 27 D Fract #3

SOLVENT CDCl3 10
CONCENTR.
REFERENCE TMS
TEMPERATURE RT

NUCLEUS
OBS C 13
LOCK
H 1
OFFSET
35.500
47.100
8
5
#142
20
5000
7000
5
32c
DECOUPLING
60 H
LOCK
low S
6 - 25
DATE 12/1/78
OPERATOR SC
REMARKS

JEOL LTD.

Figure #33

Component #2 of
106 - 114 C / ca. 5mm
Fraction of Reaction Sequence 4

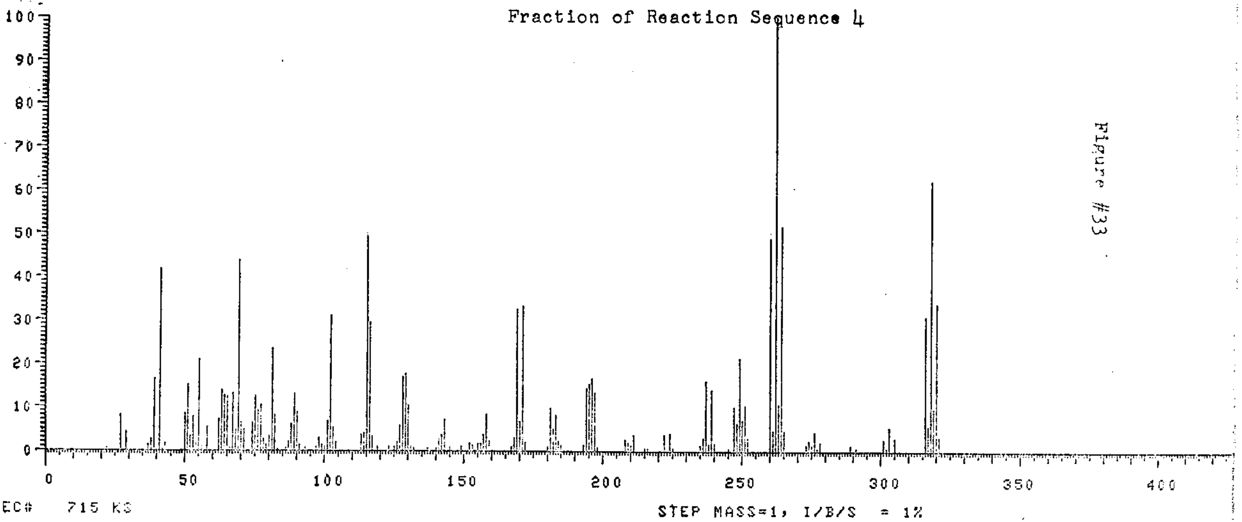
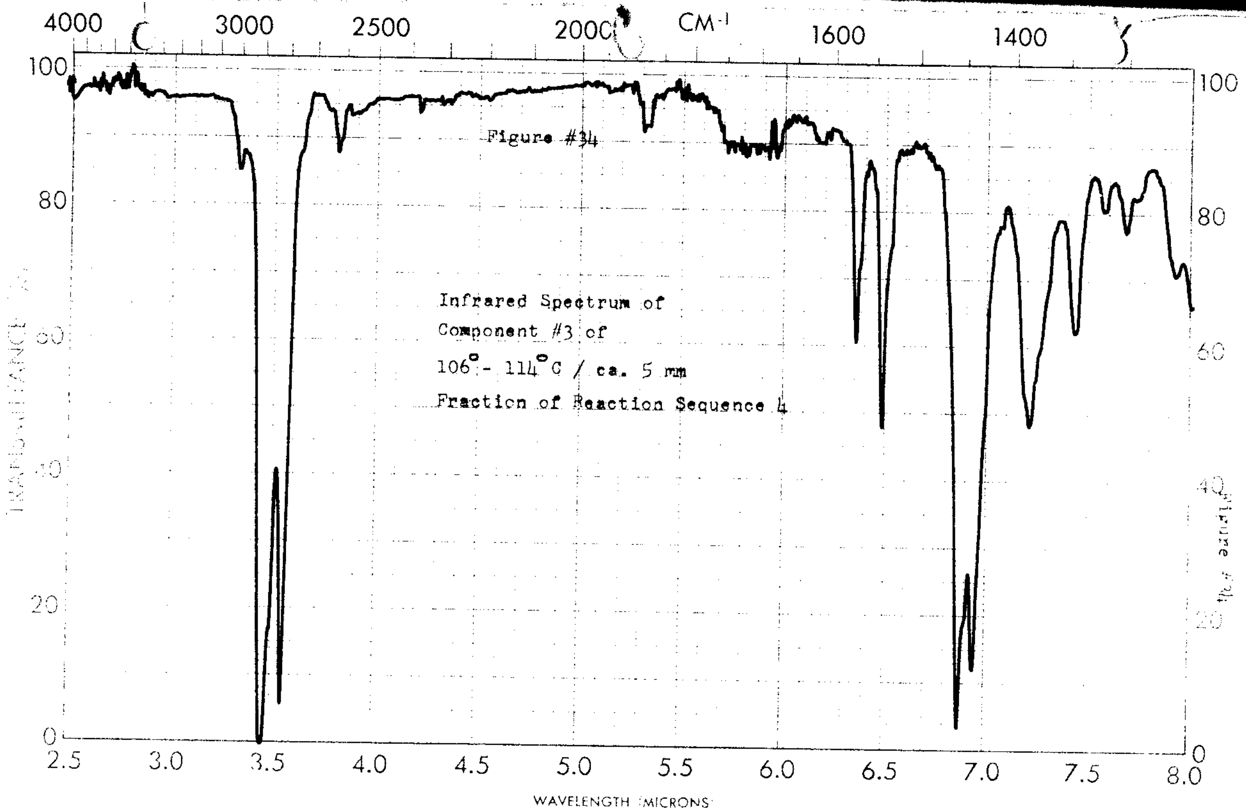


Figure #33

Figure #34



Infrared Spectrum of
Component #3 of
106° - 114° C / ca. 5 mm
Fraction of Reaction Sequence 4

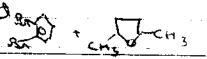
SAMPLE Sample 270 fraction #4
ORIGIN
SOLVENT

CURVE NO.
CONC. film on NaCl disc - Neat
CELL PATH
REFERENCE

SCAN SPEED F
SLIT N

OPERATOR AJD
DATE 8/30/76

REMARKS Read



PART NO. 237-1030

PERKIN-ELMER

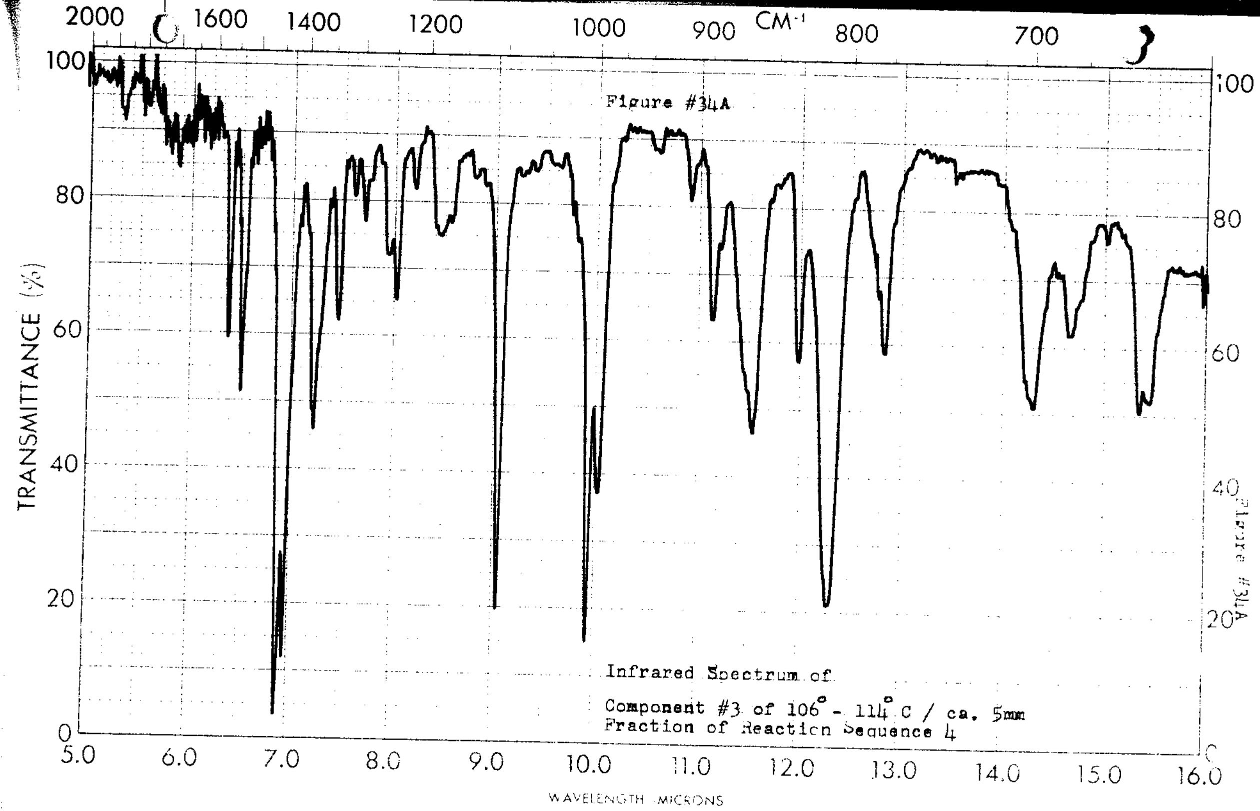


Figure #34A

Infrared Spectrum of

Component #3 of 106° - 114° C / ca. 5mm
Fraction of Reaction Sequence 4

Figure #34A

SAMPLE Sample 22D fraction
#4
ORIGIN
SOLVENT
CURVE NO.
CONC. film on NaCl disc-Neat
CELL PATH
REFERENCE
SCAN SPEED F
SLIT N
REMARKS
OPERATOR ajd
DATE 8/30/76

PART NO. 237-1031

PERKIN-ELMER

Figure #35

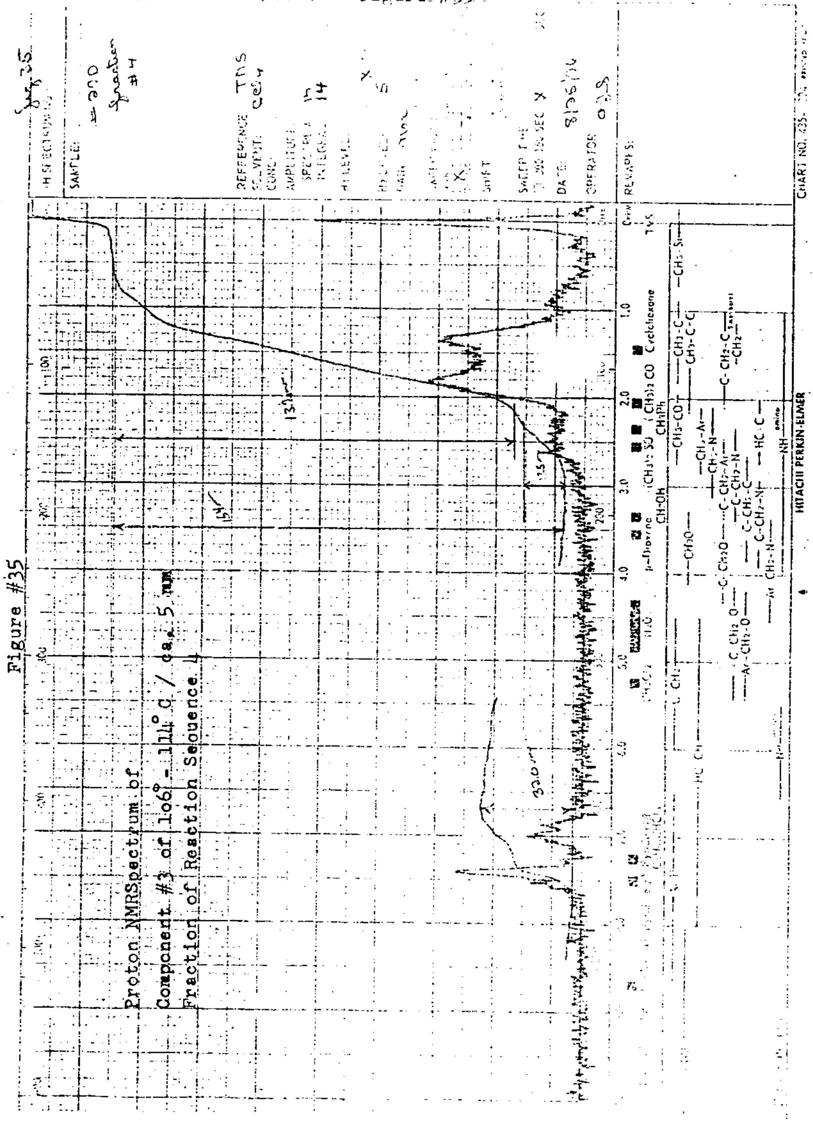
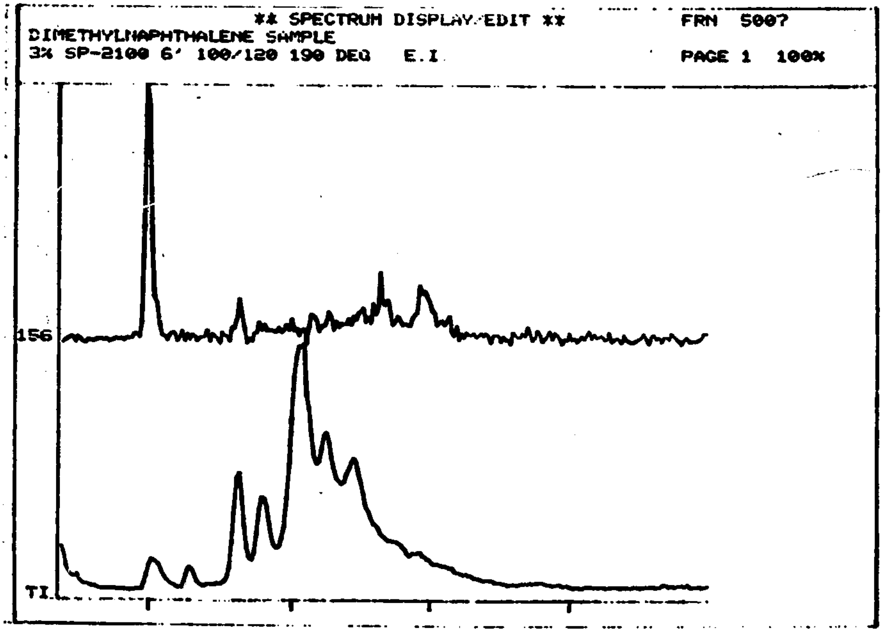


Figure #35

Proton NMRSpectrum of Component #3 of 106° - 114° C / ca. 5 mm Fraction of Reaction Sequence 4

Figure #36A

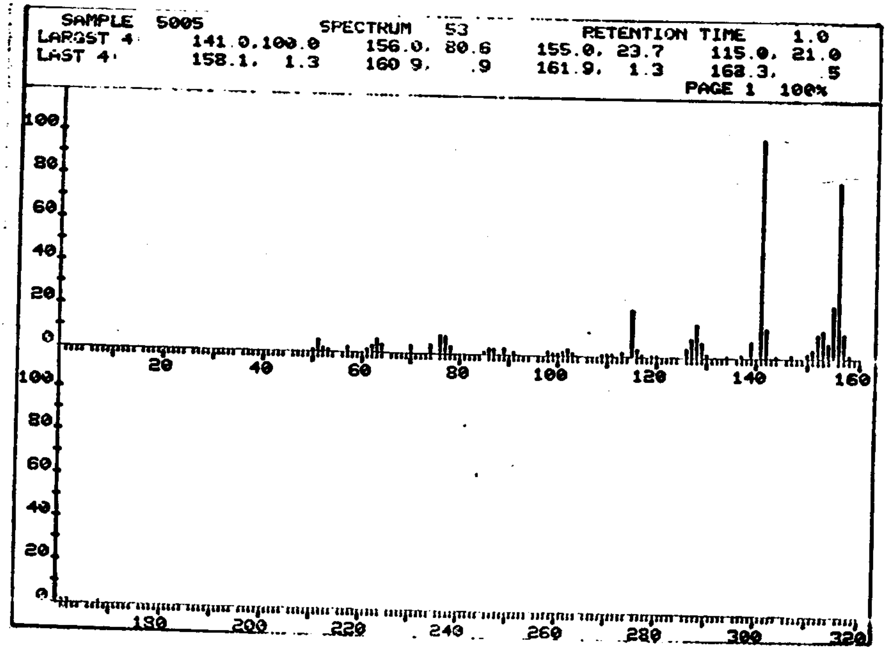
GC - Mass Spectrum of
Aromatization Product
Reaction Sequence 8



** SPECTRUM DISPLAY/EDIT **   FRN 5007
DIMETHYLNAPHTHALENE SAMPLE
3% SP-2100 6' 100/120 190 DEG   E.I.   PAGE 1 100%

Figure #36B

GC - Mass Spectrum Cont'd.



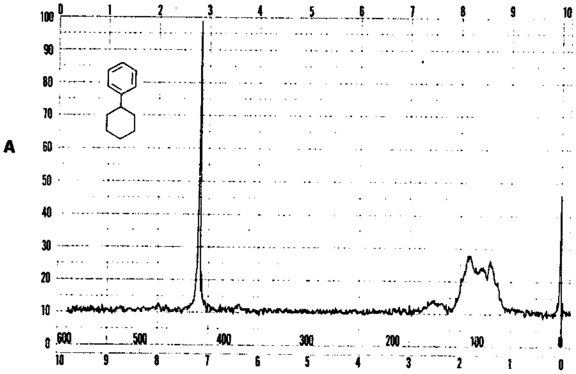
```
SAMPLE  5005          SPECTRUM   53              RETENTION TIME    1.0
LARGST 4     141.0,100.0     156.0, 80.6     155.0, 23.7     115.0, 21.0
LAST 4       158.1,   1.3    160 9,    .9    161.9,  1.3     162.3,    .5
                                                             PAGE 1  100%
```

Figure #37

Proton NMR Spectrum of

Cyclohexylbenzene

C10,480-9
Cyclohexylbenzene, 98%
$C_6H_5C_6H_{11}$ M.W. 160.26 m.p. 5-6°
b.p. 239-240° n_D^{20} 1.5258 d 0.95 Beil. 5,503
IR 422E



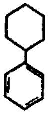
CONTRIBUTED BY
GULF OIL CANADA LIMITED, SHERIDAN PARK, ONTARIO, CANADA.

PHENYLCYCLOHEXANE

Figure #38

FORMULA $C12.H16$
M. WT. 160

INSTRUMENT CEC21-103C
INLET SYSTEM MICROTEK
INLET TEMP. 315 C
SOURCE TEMP. 250 C
ELECTRON VOLTAGE 70 EV



M/E	R I	M/E	R I	M/E	R I	M/E	R I
13.0	0.08	58.5	0.11	84.0	0.09	120.0	0.27
15.0	2.37	59.0	0.08	85.0	0.29	121.0	0.04
25.0	0.14	59.5	0.05	86.0	0.77	125.0	0.10
25.5	0.05	60.0	0.05	87.0	1.09	126.0	0.36
26.0	1.69	61.0	0.24	88.0	0.48	127.0	1.78
27.0	12.83	62.0	1.33	89.0	4.16	128.0	4.09
28.0	2.56	63.0	5.27	90.0	1.55	129.0	4.25
29.0	6.06	63.5	0.30	91.0 —	74.19	130.0	2.14
30.0	0.19	64.0	2.20	92.0	23.08	131.0	9.10
31.0	0.08	64.5	0.41	93.0	1.97	132.0	2.57
37.0	0.38	65.0	8.83	94.0	0.15	133.0	0.31
38.0	1.30	66.0	1.01	95.0	0.11	139.0	0.17
39.0	16.15	67.0	5.71	96.0	0.06	140.0	0.06
40.0	1.52	68.0	2.05	97.0	0.11	141.0	0.40
41.0	13.79	69.0	5.08	98.0	0.40	142.0	0.19
42.0	0.79	69.5	0.15	99.0	0.23	143.0	0.29
43.0	0.71	70.0	0.57	100.0	0.13	144.0	0.10
44.0	0.27	70.5	0.32	101.0	0.80	145.0	1.05
45.0	0.08	71.0	0.54	102.0	5.04	146.0	0.15
49.0	0.19	71.5	0.13	103.0	14.27	149.0	0.04
50.0	4.05	72.0	0.08	104.0 —	100.00	150.0	0.04
51.0	11.39	72.5	0.06	105.0	15.90	151.0	0.11
52.0	3.51	73.0	0.42	106.0	1.24	152.0	0.29
52.5	0.05	74.0	3.30	107.0	0.13	153.0	0.27
53.0	4.37	75.0	3.09	109.0	0.08	154.0	0.59
54.0	3.25	76.0	3.13	110.0	0.09	155.0	0.13
54.5	0.08	77.0	16.53	111.0	0.08	156.0	0.06
55.0	3.56	78.0	16.57	114.0	1.01	157.0	0.08
56.0	0.60	79.0	4.28	115.0	17.89	158.0	0.29
56.5	0.08	80.0	0.57	116.0	7.29	159.0	0.96
57.0	0.52	81.0	1.86	117.0 —	90.17	160.0 P	69.83
57.5	0.79	82.0	4.57	118.0	16.11	161.0	9.30
58.0	0.46	83.0	0.65	119.0	1.72	162.0	0.57

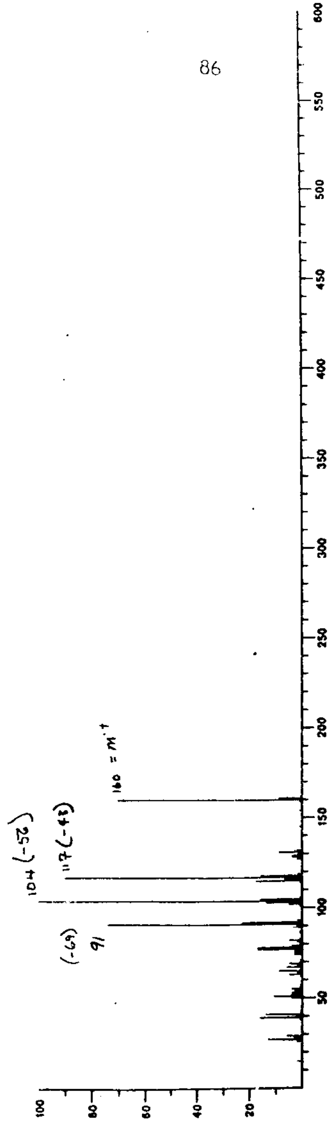
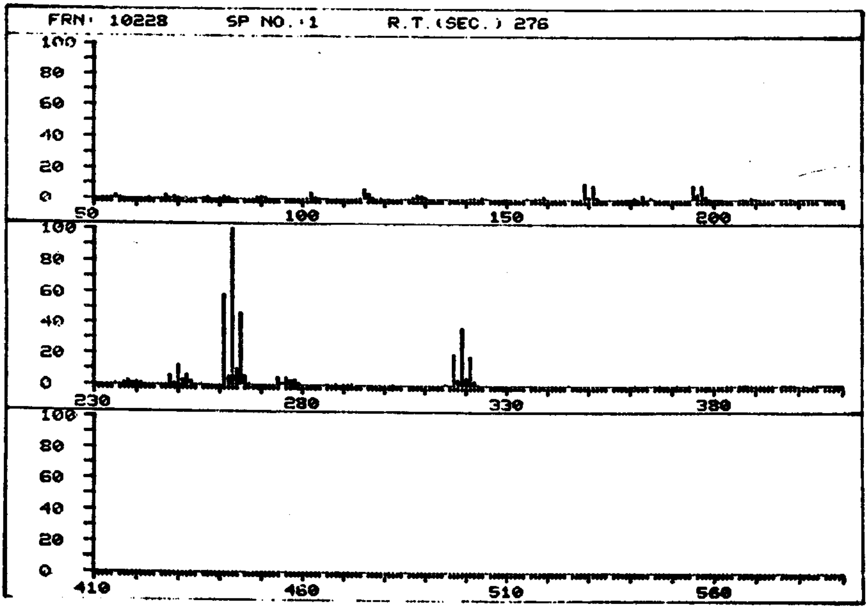


Figure #39

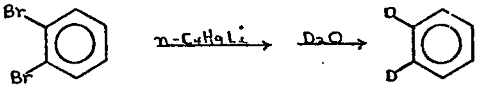
Mass Spectrum of Component #3 of

106° - 114° C / ca. 5mm

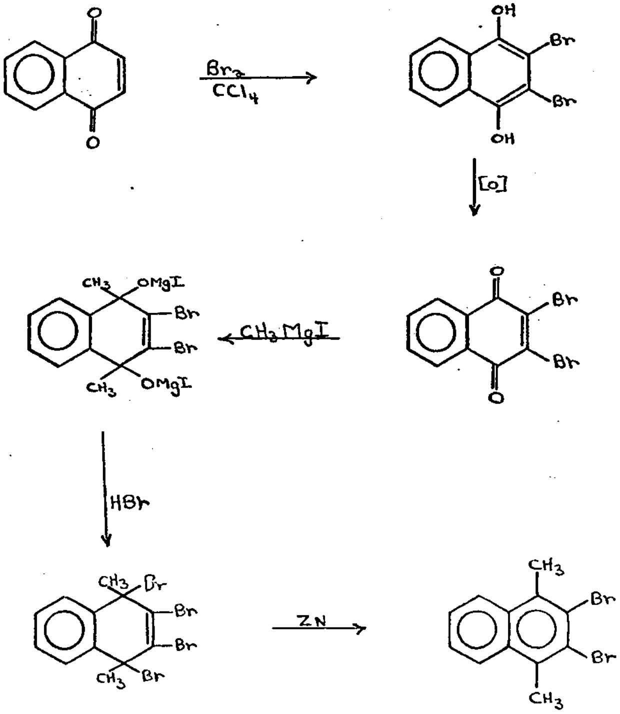
Fraction of Reaction Sequence 4



List of Reaction Sequences

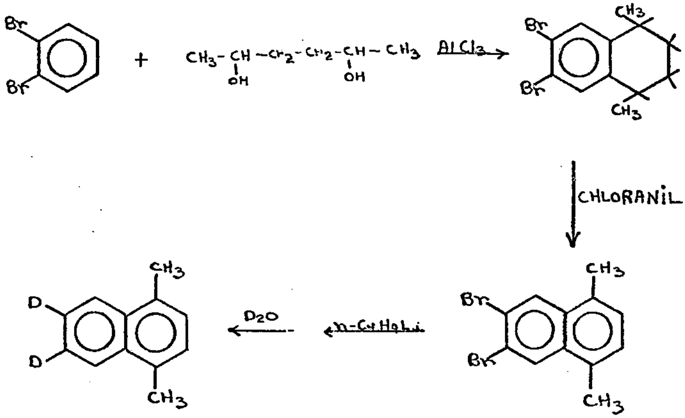


(1)



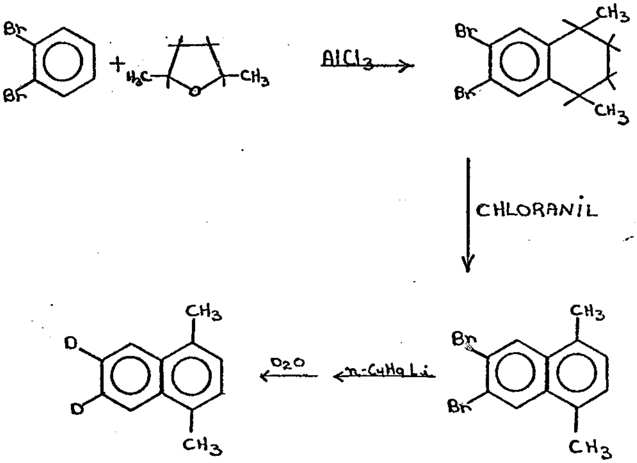
(2)

(2')


Br
Br
+
CH3-CH-CH2-CH2-CH-CH3
OH
OH
AlCl3
Br
Br
CH3
CH3
CHLORANIL
CH3
Br
Br
CH3
n-C4H9Li
D2O
CH3
D
D
CH3

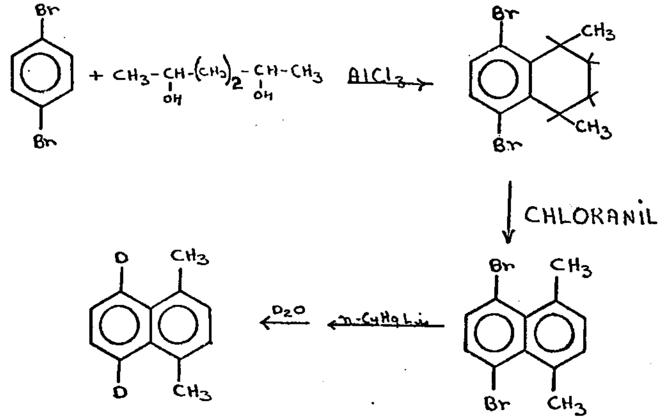
(3)

II


Br
Br
+
H3C
O
CH3
AlCl3
Br
Br
CH3
CH3
CHLORANIL
CH3
Br
Br
CH3
n-C4H9Li
D2O
CH3
D
D
CH3

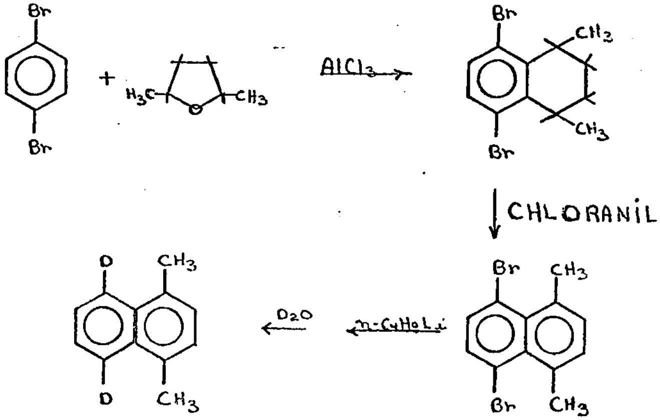
(4)

II


Br
Br
$+ CH_3-CH(OH)-(CH_2)_2-CH(OH)-CH_3$
AlCl3
CH3
CH3
Br
Br
CHLORANIL
Br
CH3
Br
CH3
n-C4H9Li
D2O
D
CH3
D
CH3

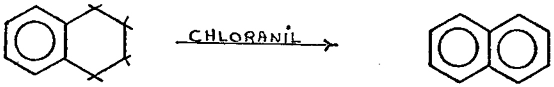
(5)

III

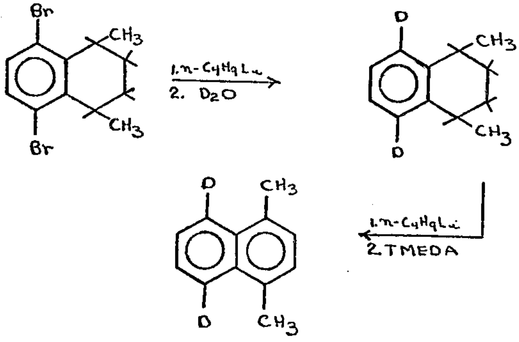

Br
Br
+
H3C
CH3
O
AlCl3
Br
CH3
CH3
Br
CHLORANIL
Br
CH3
Br
CH3
n-C4H9Li
D2O
D
CH3
D
CH3

(6)

III


CHLORANIL

(7)


Br
CH3
CH3
Br
1. n-C4H9Li
2. D2O
D
CH3
CH3
D
1. n-C4H9Li
2.TMEDA
D
CH3
D
CH3

(8)

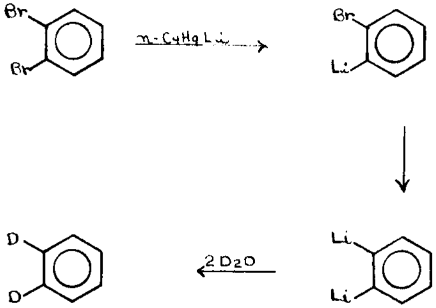
III

DISCUSSION

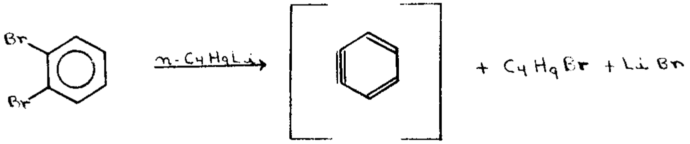
The synthetic procedures which were utilized in this research were aiming at precursors to symmetrically substituted dideuteriobenzo- [2,2]- paracyclophane. More specifically it was hoped to synthesize structures II, III and IV. Reaction sequence 1 represents a model reaction of a synthetic approach in which bromine is replaced by deuterium. Reaction sequence 2 represents a proposed synthetic approach by which it was hoped to obtain structure XII, a precursor of IV.A model reaction was attempted and will be discussed later. Equations 3,4,5 and 6 are the ones around which most of the work was centered. Reaction sequence 7 is a model reaction of a proposed method of aromatization utilizing chloranil. When the use of chloranil did not yield any satisfactory results in our aromatizations, reaction sequence 8(using tetramethylethylenediamine) was successfully used.

It was hoped that the technique for replacement of aromatic bromine by deuterium [7] would work for dibromodimethylnaphthalenes without severe complications. Replacement of two bromines by deuterium had been carried out previously by Martin[1] in satisfactory yield, but in that case, the two bromines were on two different rings.

Therefore, if the bromine for deuterium exchange is successful for two adjacent bromines on an aromatic ring, then this technique could be used for the bromine-deuterium exchange in our system. For this reason, o-dibromobenzene was used as a model case. The concept in bromine-deuterium exchange is the reaction of n-butyllithium with the aromatic bromine to give the lithio-aromatic, which would then react with D_2O to yield the deuterated aromatic. In the case of a dibromo-aromatic, the reaction is perhaps a two step process.

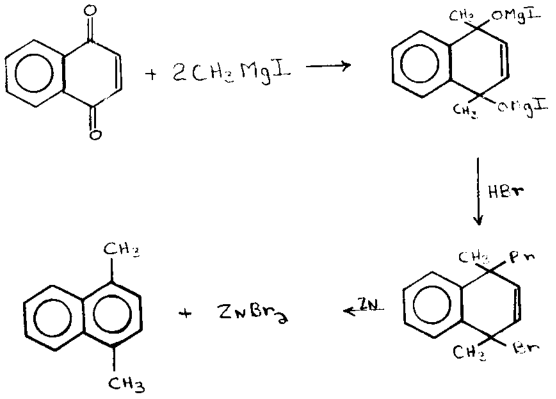


It was realized that this reaction might produce a very reactive benzyne intermediate.



The benzyne intermediate might also produce other products such as biphenylene. Other possible products of the reaction which should not be overlooked include monodeuteriobromobenzene, monodeuterio-n-butylbenzene and d_1-phenol. A gas chromatographic analysis of our reaction mixture suggested that trace amounts of o-dideuteriobenzene had been synthesized. However, a GC-mass spec(figure 1)analysis of the mixture showed that we had formed trace amounts of monodeuteriobenzene. A complete analysis of the other products formed has not been pursued since it appears that this reaction does not suit our synthetic needs. The yield of deuteriobenzenes by this reaction was far too small to consider this as a route to preparing a symmetrical dideuterio-1,4-dimethylnaphthalene.

An approach to the synthesis of structure XII that had been deemed possible was that of forming the 1,4-dimethyl derivative of tetrahydronaphthalene by Grignard addition[8] of methyl magnesium iodide to 1,4-Naphthoquinone. It was realized that this could alternately lead to 1,4 addition across an α,β- unsaturated carbonyl system, and perhaps this is indeed what happened, but it was hoped that significant yields of simple addition to the carbonyl groups might occur.

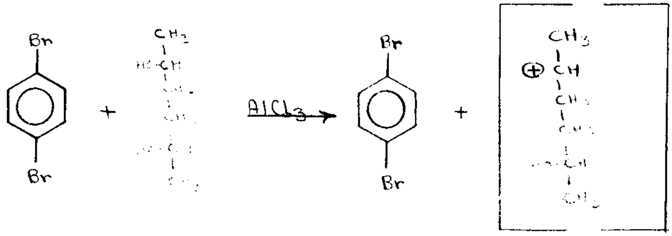


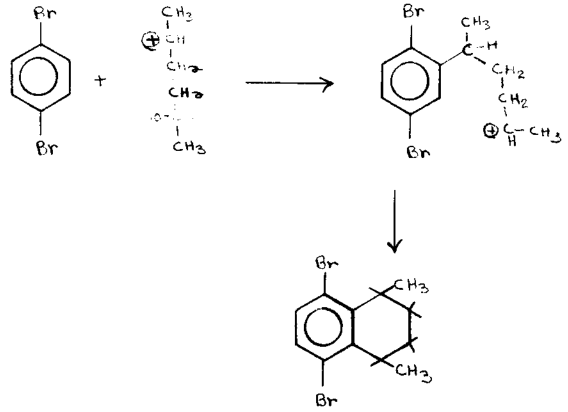
In spite of the apparent drawbacks, the addition was attempted as a fast, rather simple test. If this model reaction had proved successful, then reaction sequence 2 could have been used to try to obtain structure XII. Using standard 1,4-dimethylnaphthalene, a gas chromatographic analysis of the reaction mixture showed that the desired product (1,4-dimethylnaphthalene) had not been obtained. An investigation of the products formed was not completed because this reaction does not suit our synthetic needs.

Presuming that a dimethyltetralin would eventually be obtained, the method by which it was hoped to dehydrogenate the dimethyltetralin to a dimethylnaphthalene was investigated. As a model, commercial tetralin was treated with chloranil in a method analogous to that used for aromatization of other systems[11,12,13](reaction sequence 7). Analysis of the reaction mixture by gas chromatography showed that the tetralin to naphthalene conversion was 40% by this method.

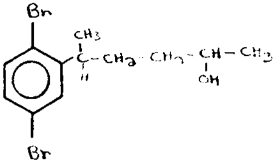
Friedel-Crafts alkylations and cyclizations of aromatic rings are well known. But no reference could be found to such a reaction on a dihalobenzene. In reaction sequences 3,4,5 and 6, attempts were made to synthesize structures II and III.

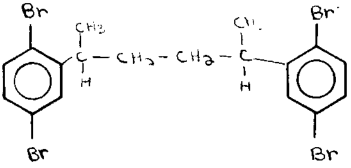
The first attempt at cyclization involved the reaction of p-dibromobenzene and 2,5-hexanediol[9] (reaction sequence 5). The reaction was catalyzed by Al Cl_3 and was carried out at room temperature in cyclohexane. Under these conditions, the reaction was expected to proceed as follows:



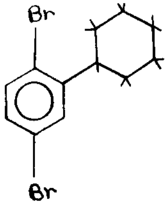


Other by-products expected from this reaction might be:



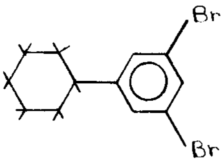


The reaction yielded three components, each of which was extensively analysed. It was found that our reaction resulted in various rearrangement products. Not only did an intramolecular rearrangement of the bromines occur, but also a startling rearrangement of the alkylating system may also have occurred. Rearrangement component #1 shows a mass spectrum (figure 12) with a parent peak at m/e 318 and a base peak at m/e 262. The mass spectrum of component #1 also exhibits the 2-bromine isotopic cluster. The infrared spectrum (figure 8-8A) of component #1 exhibits a small aromatic C-H stretch at 3.31 microns, aliphatic C-H stretch at 3.45 and 3.55 microns, aromatic C-C stretching bands at 6.40 microns and 6.50 microns, methylene scissoring bands at 6.88, 6.90 and 6.95 microns, and aromatic out of plane bending at 11.40 microns, 11.60 microns, 12.45 microns and 13.55 microns. The proton nuclear magnetic resonance spectrum (figure 10) features aromatic, benzylic and aliphatic hydrogen splitting in the ratio of 3-1-10. In fact, this NMR spectrum is very similar to that of phenylcyclohexane(figure 37). Both spectra exhibit the lack of any isolated methyl group or a methyl group split into a doublet by an adjacent hydrogen. The only difference between the two is in the aromatic region where both the splitting pattern and the integrated aromatic hydrogen count is different. Both of these differences are undoubtedly due to the two bromine substituents. By comparing the mass spectrum of component #1(figure 12) to the mass spectrum of phenylcyclohexane (figure 38) we can again see a striking similarity. The base peak in both spectra is at P-56, a loss of C_4H_8. This fragment seems to be quite characteristic of the breakdown pattern for the cyclohexane ring. Looking at the fingerprint region in the infrared spectrum(figures 8-8A), peaks are present at 11.60 microns(characteristic of one isolated hydrogen) and 12.45 microns(characteristic of two adjacent hydrogen).[15] Analysis of the proton NMR aromatic splitting patterns of dihalotoluenes [15] along with the data already presented identifies rearrangement component #1 as structure XIII, 1,4-dibromo-2-cyclohexylbenzene



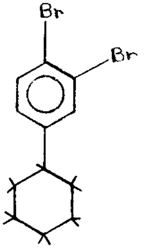
XIII

Rearrangement component #2 of reaction sequence 5 exhibits a mass spectrum(figure 13) similar to that of component #1 and phenylcyclohexane(figure 38). It shows the parent peak at m/e 318, the base peak at m/e 262(P-56) and the bromine isotopic cluster. The proton nuclear magnetic resonance spectrum(figure 11) is also very similar to that of phenylcyclohexane (figure 37). The infrared spectrum (figures 9-9A) contained aromatic C-H stretch at 3.30 microns, aliphatic C-H stretch at 3.45 and 3.55 microns, aromatic C-C stretching bands at 6.35 and 6.50 microns, methylene scissoring bands at 6.95 and 7.08 microns and aromatic out of plane bending at 11.80, 12.55 and 14.61 microns. The three peaks due to aromatic out of plane bending are characteristic of three isolated aromatic hydrogens.[15] A study of the NMR aromatic hydrogen splitting patterns of dihalotoluenes [17] along with the data already presented identifies rearrangement component #2 as 1,3-dibromo-5-cyclohexylbenzene, structure XIV.



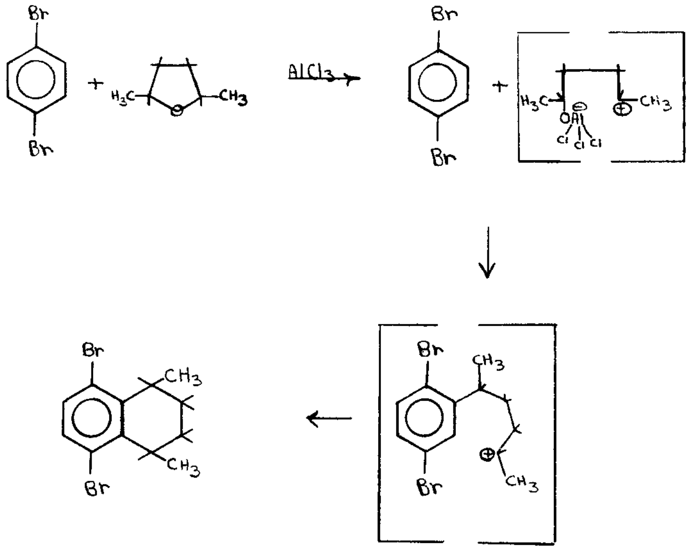
XIV

Rearrangement component #3 of reaction sequence 5 was collected in small amounts. It exhibits a mass spectrum(figure 15) similar to that of phenylcyclohexane(figure 38). The mass spectrum includes a parent peak at m/e 318, a base peak at m/e 262(P-56) and the two bromine isotopic cluster. The proton NMR spectrum(figure 14) is of poor quality due to the small amount of sample, but, nevertheless, the similarity to the proton NMR spectrum of phenylcyclohexane(figure 37) is evident. An infrared spectrum could not be obtained due to the small amount of sample, thus positive identification could not be made. But, based on the aromatic hydrogen NMR splitting pattern,[18] perhaps rearrangement component #3 is 1,2-dibromo-4-cyclohexylbenzene, structure XV.



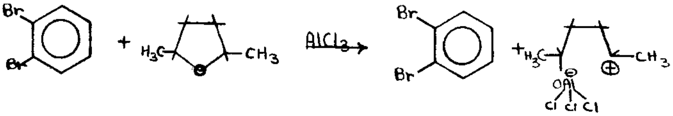
XV

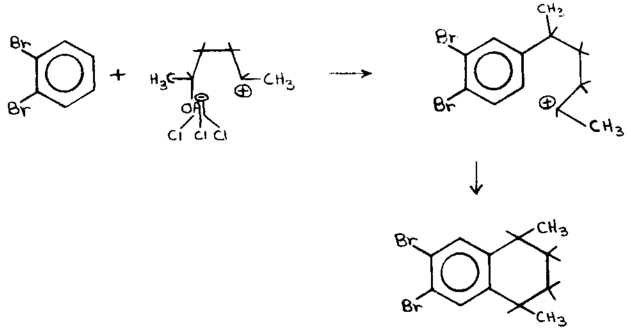
The second attempt at cyclization involved the reaction of p-dibromobenzene and 2,5-dimethyltetrahydrofuran as shown in reaction sequence 6. The reaction was catalyzed by Al Cl_3 and was carried out at room temperature in cyclohexane. Under these conditions, we expected the reaction to proceed as follows:



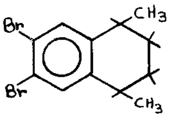
The reaction did not proceed as expected. The reaction yielded one major rearrangement component which was analytically studied. The mass spectrum (figure 24) showed a similarity to the spectra of the three components of reaction sequence 5 and that of phenylcyclohexane (figure 38) in that its parent peak is at m/e 318, its base peak is at m/e 262(P-56) and it exhibits the two bromine atom cluster. The proton NMR spectrum (figure 23) is also similar to that of the three components of reaction sequence 5 and phenylcyclohexane (figure 37). The infrared spectra(figures 22-22A) is identical to that of component #1 in reaction sequence 5. Based on this analytical data, the rearrangement component of reaction sequence 6 has been identified as 1,4-dibromo-2-cyclohexylbenzene, structure XIII.

Our third attempt at cyclization involved the reaction of o-dibromobenzene and 2,5-dimethyltetrahydrofuran as shown in reaction sequence 4. The reaction was catalyzed by Al Cl_3 and was carried out at room temperature in cyclohexane. Under these conditions, we expected the reaction to proceed as follows:

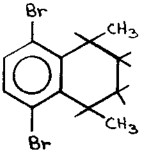




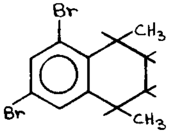
The reaction did not proceed as expected. Three rearrangement components of reaction sequence 4 were collected. An infrared spectrum (figures 28-28A) and a GC-mass spectrum (figures 29A, 29B, 29C,29D and 29E) were taken on component #1. Figure 29A shows that component #1 is a mixture. The mass spectra in figures 29D and 29E suggest that much of the mixture is again dibromocyclohexylbenzenes. The mass spectrum in figure 29C suggests a monobromo product which cannot be identified. The mass spectrum in figure 29B exhibits a dibromo compound with a parent peak at m/e 318 and a base peak at m/e 303 (P-15). Keeping in mind the fact that the mass spectrum of 1,4-dimethylnaphthalene (figure 36B) also exhibits a base peak at P-15, perhaps this material is one of the following dibromotetralins:



XVI



XVII



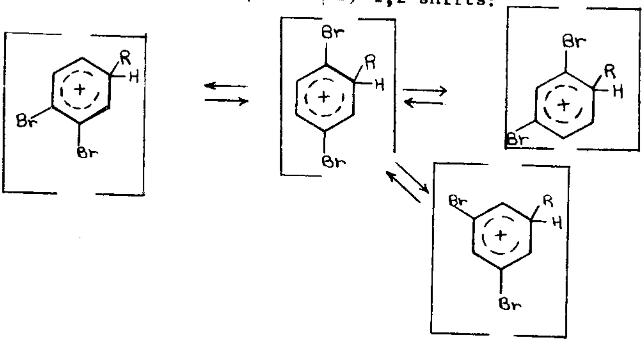
XVIII

Rearrangement component component #2 of reaction sequence 4 has an infrared spectrum (figures 30-30A), a proton NMR spectrum (figure 31) and a mass spectrum (figure 33) which are identical to rearrangement component #1 of reaction sequence 5 and the rearrangement component of reaction sequence 5. We also have a C^{13} nuclear magnetic resonance spectrum(figure 32) of component #2. Thus, component #2 of reaction sequence 4 has been identified as 1,4-dibromo-2-cyclohexylbenzene, structure XIII. Rearrangement component #3 of reaction sequence 4 has a mass spectrum(figure 39) which is very similar to all of the other dibromocyclohexylbenzenes. Its parent peak is at m/e 318, its base peak is at m/e 262(P-56) and it has the two bromine isotopic cluster. The proton NMR spectrum (figure 35) is again indicative of the dibromocyclohexylbenzenes. The infrared spectrum(figures 34-34A) has peaks at 11.55 microns (characteristic of one isolated hydrogen)[15] and 12.30 microns (characteristic of two adjacent hydrogens)[15] in the fingerprint region. Based on this data and a study of the splitting patterns of aromatic hydrogens in proton NMR spectra of dihalotoluenes,[18] component #3 of reaction sequence 4 has been identified as 1,2-dibromo-4-cyclohexylbenzene, structure XV.

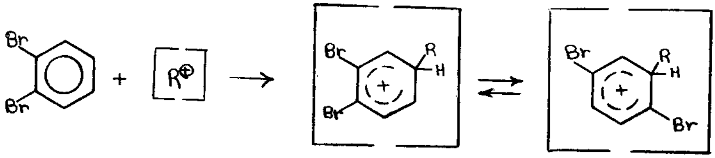
Reaction sequences 3,4,5 and 6 were not completed because the aromatization with chloranil failed. In an attempt to move quickly to the product(structures II or III) the impure reaction mixtures of reaction sequence 5 was treated with n-butyllithium, D_2O and tetramethylethylenediamine as shown in reaction sequence 8. The significant feature in the use of the alkyllithium-TMEDA complex for aromatization is the intermediacy of the dianions of polycyclic hydrocarbons which are generated through double proton extraction.[14] After subjecting the mixture of high boiling isomers which were obtained in reaction sequence 5 to the conditions shown in reaction sequence 8, a GC-mass spectrum(figures 36A and 36B) showed that some 1,4-dimethylnaphthalene(7% yield) had been formed. The 1,4-dimethyldideuterionaphthalene however was not made. It appears that our technique was poor, for although debromination occurred, replacement was mostly with hydrogen. This indicates early stage traces of water catalyzing decomposition of the aryl lithium intermediate. Nonetheless, in reaction sequence 8 debromination and then aromatizition was successful. The aromatization was carried out without any attempt to isolate the dimethyltetralin after debromination.

The result of reaction sequence 8 proves that our Friedel Crafts synthesis undoubtedly yielded some of the desired dibromo-1,4-dimethyl-1,2,3,4-tetrahydronaphthalene.

The rearrangement products that resulted from reaction sequences 4,5 and 6 were somewhat unexpected. Bromine rearrangements are not uncommon. There is evidence of bromine rearrangements in the presence of Al Cl_3, but our literature searching found this to be true only at elevated temperatures [19,20] (above 100°C). At no time did we approach this temperature, even with the heat of reaction. This suggests that either the alkylation intermediate or transition state causes rearrangement of the bromines or that once formed the alkyldihalobenzene itself undergoes rearrangement at low temperatures(30-35°C). The former seems a bit more likely. In the reaction where p-dibromobenzene was used as the starting material, the bromine rearrangement could be explained by 1,2 shifts:

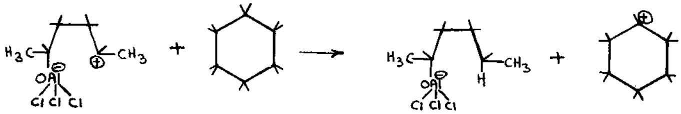


For o-dibromobenzene:



The puzzling appearance of the cyclohexyl substituent may be best explained by either of two approaches. First, it is possible that as little as two percent of cyclohexene impurity in cyclohexane would produce the observed products by Friedel-Crafts alkylation. However, an infrared spectrum of the solvent indicated no appreciable amount of olefin(by the absence of a C=C absorption at 6.08 microns and a cis-substituted C=C absorption at 14.50 microns). Secondly, in Al Cl_3 catalyzed reactions, it is apparently possible for hydride transfer to occur from solvent molecules to secondary or tertiary carbocations.[21]

In our case, the following might have occurred:



Then the cyclohexyl carbocation could alkylate the aromatic ring.

CONCLUSION

Fusion of a second ring onto dibromobenzene eventually led to the formation of some 1,4-dimethylnaphthalene. Deuteration by way of a dibromide was rather poor and it appears from our work that one should settle for specific monodeuteration rather than for symmetrical dideuterations of the 1,4-dimethylnaphthalene.

The Friedel-Crafts reactions that were attempted resulted in a number of isomeric products,namely various dibromocyclohexylbenzenes. These products were separated, characterized and identified.

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