6-1967

The formation of tertiary butyl phenyl ether by a diazonium salt decomposition

Allan Richard Bernstein

Union College - Schenectady, NY

Follow this and additional works at: https://digitalworks.union.edu/theses

Part of the Chemistry Commons

Recommended Citation

THE FORMATION OF TERTIARY BUTYL PHENYL ETHER

BY A DIAZONIUM SALT DECOMPOSITION

by

Allan Richard Bernstein *UC 1967*

Senior Thesis Submitted

in Partial Fulfillment

of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

JUNE 1967

This Thesis

Submitted by

Allan Richard Bernstein

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements

of the degree of Bachelor of Science with

a Major in Chemistry is approved by

William B. Martin, Jr

ACKNOWLEDGMENT

I would like to express my gratitude to Dr.
William B. Martin, Jr., whose invaluable advice and
constant guidance contributed greatly to the comple-
tion of the work presented herein.
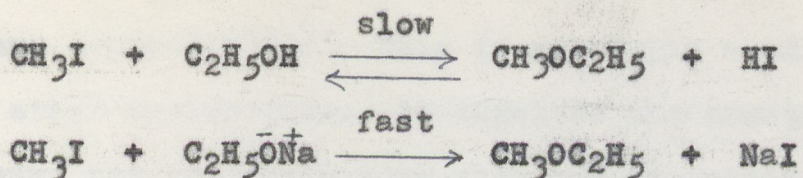
TABLE OF CONTENTS

LIST OF FIGURES AND ILLUSTRATIONS

I. INTRODUCTION.

Diaryl ethers have been prepared by various candidates for master's and bachelor's degrees at Union College in the past (1a,1b,1c). Ullmann reactions were involved, but with some variability in yields and some rather lengthy syntheses. More recently, decompositions of diazonium salts have been studied for preparation of aryl ethers. This might constitute a simpler or more efficient synthetic route.

An attempt was made to synthesize tertiary butyl phenyl ether by a diazonium salt decomposition. The reason for choosing this preparation method is that, although primary and secondary alkyl-aryl ethers are fairly simple to prepare in good yields by the Williamson synthesis, formation of tertiary alkyl-aryl ethers presents problems since the S_N1 type reactions with tertiary halides are slow, and reversible if hydrogen halide is formed and not removed.

One of the standard ways of preparing ethers is the Williamson synthesis (2). It involves the reaction of a primary halide, RX, with a metal alkoxide, $\overset{+}{Na}\overset{-}{OR'}$, to form the corresponding ether ROR'. The alkoxide is a powerful nucleophile that will readily enter into S_N2 type reactions. Whereas ethanol reacts very slowly with methyl iodide to give methyl ethyl ether, sodium ethoxide reacts quite rapidly.

$$CH_3I + C_2H_5OH \underset{fast}{\overset{slow}{\rightleftharpoons}} CH_3OC_2H_5 + HI$$

$$CH_3I + C_2H_5\overset{-}{O}\overset{+}{Na} \xrightarrow{fast} CH_3OC_2H_5 + NaI$$

Complications can occur, however; because with the increase of the nucleophilicity associated with the conversion of an alcohol to an alkoxide ion, there is an even greater increase in a competing elimination type reaction. The reaction of an alkyl halide with an alkoxide may be one of elimination to form an olefin rather than halide substitution leading to an ether, depending upon the temperature and the structure of the halide. For example, if we wished to prepare isopropyl methyl ether, better yields would be obtained if we were to use methyl iodide and sodium isopropoxide rather than isopropyl iodide and sodium methoxide because of the undesirable competition with an E2 type elimination with the latter reaction.

$$CH_3I + \overset{+}{Na}\overset{-}{O}C(CH_3)_2 \xrightarrow{S_N2} (CH_3)_2CHOCH_3 + NaI$$

$$(CH_3)_2CHI + \overset{+}{Na}\overset{-}{O}CH_3 \xrightarrow{E2} CH_3CH=CH_2 + CH_3OH + NaI$$
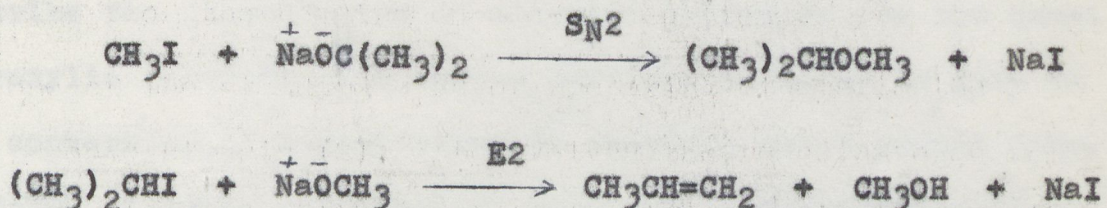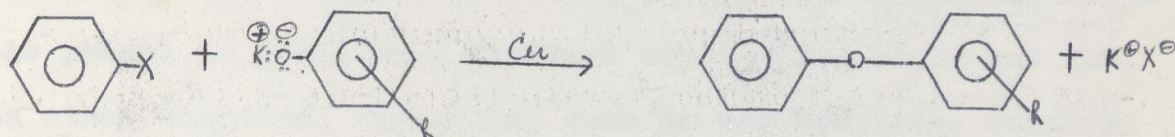
Therefore, the Williamson synthesis is best limited to reactions involving primary halides.

A second general method of preparing aromatic ethers is

the Ullmann synthesis (3). This is generally used to prepare diphenyl ether derivatives. It involves the treatment of halobenzenes and phenoxide ions with copper powder.
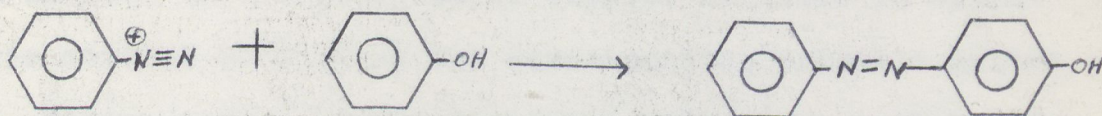

The halogen atom must be active, which is the reason why iodo benzene derivatives are commonly used.

An intensive search through the literature has revealed work already done in the preparation of tertiary butyl phenyl ether. Lawesson and Frisell (4) report the preparation of tertiary butyl phenyl ether in a 56% yield by reacting phenyl magnesium bromide with tertiary butyl phenyl peroxide. They also report its preparation with an 80 to 89% yield by the reaction of phenyl magnesium bromide with methyl tertiary butyl peroxy carbonate (5). Cram, Rickborn and Graham (6) describe the substitution of dimethyl sulfoxide for the usual hydroxylic solvents with sodium tertiary butoxide to give an 86% conversion of bromobenzene to tertiary butyl phenyl ether at 25°C. Another satisfactory approach is aroxylation of an olefinic double bond. Stroh, Seydel and Hahn have [7] treated phenol in ether at 10°C in the presence of dilute sulfuric acid with isobutylene to give an 80% yield of tertiary phenyl ether.

In 1965, Poccia (8) was able to synthesize diphenyl ether
in meager yields. Phenyl diazonium fluoroborate was dropped
into hot phenol at 80°C, inducing nitrogen evolution and
presumably creating a very active phenyl cation that attacked
the phenol to yield some diphenyl ether. The yield was low,
as other competing reactions, such as azo coupling, occurred
too:

$$\langle\bigcirc\rangle - \overset{\oplus}{N} \equiv N \quad + \quad \langle\bigcirc\rangle - OH \longrightarrow \langle\bigcirc\rangle - N = N - \langle\bigcirc\rangle - OH$$

This reaction led to the idea that the formation of an
ether might be promoted with the use of ultraviolet light.
Ultraviolet light would be used to irradiate the diazonium
salt and alcohol mixture, and one would look for an ether in
the products.

The proposed following reaction was investigated:

$$\langle\bigcirc\rangle - \overset{\oplus}{N} \equiv N \quad + (CH_3)_3 COH \xrightarrow[-N_2]{h\nu} \langle\bigcirc\rangle - O - C(CH_3)_3 + H^+$$
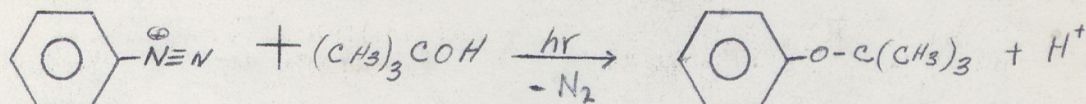
Still another approach was tried using a modification of
the Sandmeyer Reaction. The importance of copper as an
almost unique catalyst in the reactions of diazonium ions
is very interesting. Although many aspects of the behavior
of copper are still not clear, cuprous copper appears to

have the power to reduce diazonium ions and permit forma-
tion of aryl radicals (9). Copper metal seems to function
similarly, possibly because it always has some oxidized copper
on the surface (10).

A typical Sandmeyer reaction involves the nitrosation of
an aromatic amine to form an aromatic diazonium chloride
which in turn in the presence of cuprous chloride in hydro-
chloric acid at 60°C gives the corresponding aromatic halide
(11). Decomposition of the diazonium salt to an aryl halide
appears to involve the formation of aryl radicals by an
oxidation reduction sequence involving one electron transfers
in which copper acts first as a reducing and then as an
oxidizing agent (12).
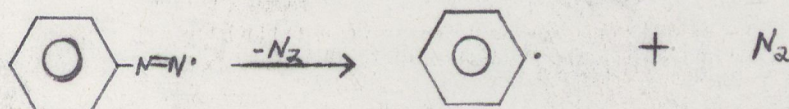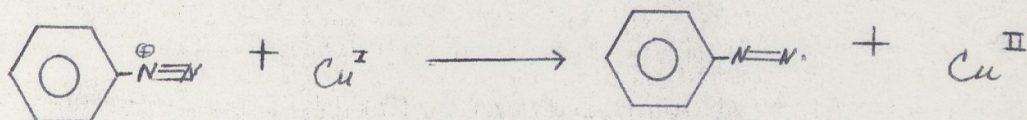
The role of copper in aiding formation of the halide
may involve either an intermediate carbonium ion or possibly
an organo-copper compound.

$$\langle\!\bigcirc\!\rangle\cdot + Cu^{I\!I} + Cl^- \longrightarrow \langle\!\bigcirc\!\rangle\overset{+}{-}CuCl \longrightarrow \langle\!\bigcirc\!\rangle-Cl + Cu^+$$
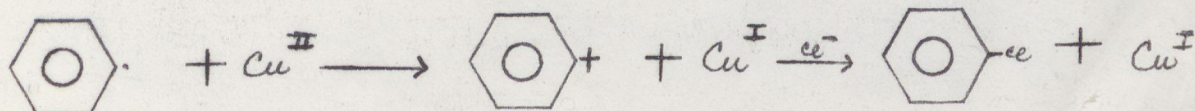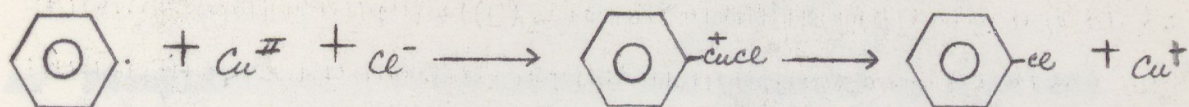
The following proposed reaction was tried on the assumption that the copper would aid in the formation of an intermediate cation.

$$\overset{+}{Na}\overset{-}{OC}(CH_3)_3 + CuCl \xrightarrow[\text{(in excess } C(CH_3)_3OH\text{)}]{} CuOC(CH_3)_3 + NaCl$$

$$\langle\!\bigcirc\!\rangle-\overset{+}{N}\!\equiv\!N\,\overset{-}{Cl} + CuOC(CH_3)_3 \longrightarrow \langle\!\bigcirc\!\rangle-OC(CH_3)_3 + CuCl + N_2$$
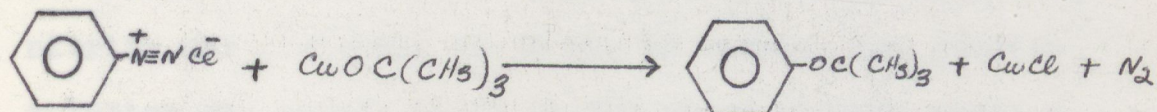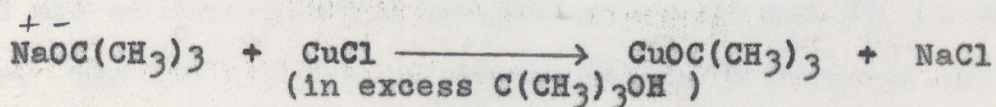
II. EXPERIMENTAL.

A. Phenyldiazonium fluoroborate was prepared by a method
identical to that given by Vogel (14) for the preparation
of p-methoxy-phenyldiazonium fluoroborate. However, aniline
was used instead of p-anisidine.

A quantity of 18.2 ml. (0.2 mole) of aniline was added
to 50 ml. of concentrated hydrochloric acid and 50 ml. of
water. The mixture was cooled to 3°C and a brownish salt
precipitated. A batch of 14.6 g. (1.72 mole) of sodium
nitrite was dissolved in 30 ml. of water. The nitrite
solution was slowly added to the above mixture until a
slight excess of nitrous acid was present as found by a
starch iodide paper test. The temperature of the reaction
was maintained below 5°C by the addition of ice. To the
diazonium salt , a chilled solution of 30.4 g. of sodium
fluoroborate in 60 ml. of water was added and the diazonium
salt precipitated out as a fluoroborate. The precipitate
was filtered, washed with 12 ml. of water, 6 ml. of methanol,
10 ml. of ether and dried overnight on filter paper. A
total of 23.2 g. of the diazonium salt was collected (60%
yield). Phenyldiazonium fluoroborate is stable and can be
kept for several days at room temperature.

The irradiation of the diazonium salt in tertiary butyl

alcohol was carried out in a quartz flask using ultraviolet
light generated from a mercury arc source.

Diagram of reaction apparatus:

STIRRER

QUARTZ FLASK

t BUTYL ALCOHOL
AND PHENYL-
DIAZONIUM
FLUOROBORATE

UV
SOURCE
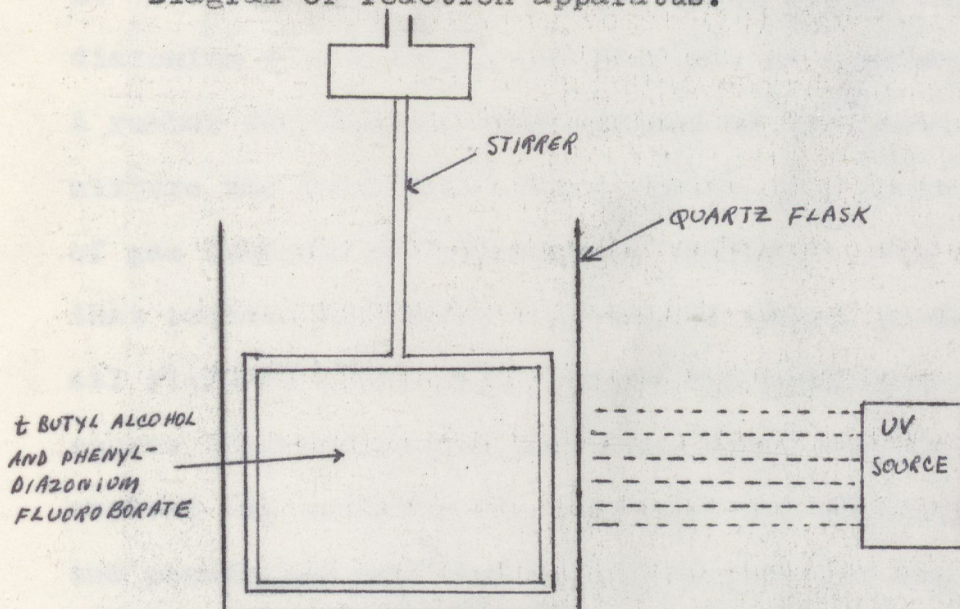
The first time the reaction was run there was no stirrer,
and 0.25 g. of phenyl diazonium fluoroborate was mixed with
20.0 ml. of the tertiary butyl alcohol. A delivery tube was
set up to measure the volume of gas evolved. This was necessary
not only to obtain a rough estimate of the yield, but to be
convinced as to whether the diazonium salt was actually
decomposing. The phenyldiazonium fluoroborate was insoluble.
It was to a small degree self-stirred by evolution of nitrogen
bubbles and by convection currents of the light heated solvent
and suspension. The steady, slow evolution of gas was observed,
but there was no displacement of water in the pneumatic trough
due to the probably poor seal between the cork and the quartz

flask. The reaction mixture slowly turned dark yellow with continued irradiation.

B. The reaction was run again using 9.6 g. of phenyl diazonium fluoroborate and 56.7 ml. of tertiary butyl alcohol. A rubber stopper was used instead of the previous cork. The mixture was irradiated for a period of 5 hours. The evolution of gas bubbles had practically ceased at this time. The gas that evolved displaced 21.6 ml. of water, giving a theoretical yield of about 18%. Due to the heat from the mercury arc source that warmed the reaction flask, part of the gas that evolved was probably the result of gas expansion. However, the percentage was high enough to indicate that the ultra-violet light had succeeded in decomposing part of the diazonium salt, since the solution temperature rose to no more than about 40°C.

The reaction mixture was washed first with water and then shaken three times with 25 ml. aliquots of benzene. The water eliminated fluoroborate ions, and hydrofluoric acid that were present. Two infra-red spectra (Fig. 1 & 2) were taken on the products of the benzene extraction after the removal of benzene.

C. The reaction was run again, this time stirring the reaction mixture so that as soon as the diazonium ion was re-

acted it would be swept away from the path of the ultraviolet light thereby reducing the chance for further photochemical reaction. A steady evolution of gas was observed and after five hours of irradiation, the mixture was washed with water and shaken three times with 25 ml. portions of benzene. The benzene was evaporated and an infrared spectrum taken. (Fig. 4) A cavity cell was used and the residue of the benzene extraction was dissolved in chloroform.

C. The catalytic agent cuprous chloride was prepared in the following manner (15). A batch of 10 g. of copper sulfate was added to 33 ml. of water and boiled to ensure the complete dissolution of the salt. Then 3.33g. of sodium chloride was added. Another solution of 2.33 g. of sodium bisulfite, 1.5 g. of sodium hydroxide, and 15 ml. of water was made up and added to the hot copper sulfate solution. A white precipitate of cuprous chloride formed which was allowed to cool in an ice bath and washed once with water by decantation.

A 0.92 g. piece of freshly cut sodium metal was reacted in an excess (30 ml.) of tertiary butyl alcohol. The reaction was extremely slow and the mixture was allowed to stand overnight, protected from the moisture of the air. The cuprous chloride was filtered, mixed with 50 ml. of tertiary
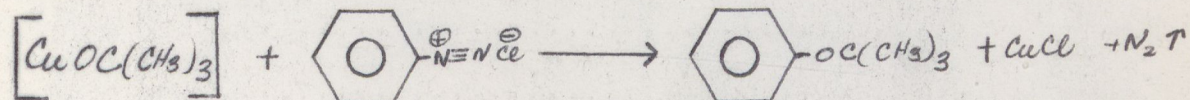
butyl alcohol, and added to the sodium tertiary butoxide.

$$(CH_3)_3\overset{-}{C}O\overset{+}{N}a \ + \ CuCl \longrightarrow \left[CuOC(CH_3)_3\right] \ + \ NaCl$$
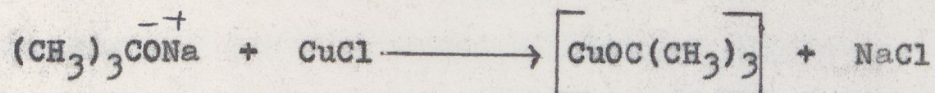
A light black precipitate formed instantly.

D. The following reaction was carried out using copper as
as catalytic agent.

$$\left[CuOC(CH_3)_3\right] \ + \ \langle O \rangle\text{-}\overset{\oplus}{N}\equiv\overset{\ominus}{N}\,\overset{\ominus}{Cl} \longrightarrow \langle O \rangle\text{-}OC(CH_3)_3 \ + CuCl \ +N_2\uparrow$$

A 5.6 g. (.04 mole) quantity of the diazonium salt was
reacted with approximately 0.04 moles of what may have been copper
tertiary butoxide. During the reaction there was a vigorous
evolution of nitrogen gas and it was necessary to add ice
in order to keep the reaction around 0°C. The copper seemed
to pass through a red transition complex eventually turning
to a dark reddish brown, which in time became black.

The mixture was shaken with ether in order to extract the
reaction products. The ether was washed successively three
times with 100 ml. portions of sodium hydroxide (eliminating
any traces of phenol), water, three times with 100 ml. portions
of hydrochloric acid, and finally with water again.

The ether was evaporated and a thin layer chromatogram was made on the residue. The adsorbent used was Camag's preparation of finely divided alumina containing plaster of paris as a binder. Four distinct substances were noted.

Solvent	R_f	
Benzene		(solvent: benzene)
1.	0.12	t-butyl phenyl ether (Martin)
2.	0.28	$R_f = 0.52$
3.	0.41	
4.	0.59	
Dioxane		
1.	0.63	

The liquid residue was allowed to coat the top of a column containing 100 cc. of alumina. The column was eluted with 200 ml. each of ligroin (30-60° boiling range), benzene, ether, and methanol. The first fraction that came off the column using ligroin was dark red in color. A nuclear magnetic resonance (Fig. 5) and an infrared spectrum were taken on the fairly impure substance.

The fraction was dissolved in chloroform and approximately 50 lambda of the solution was injected into the Perkin Elmer Model 154 Gas Chromatogram. The pressure of the helium was 10 psi. and the temperature maintained at 200°C using the two meter long R column. After one minute, the chloroform came off the column at an attenuation of 256.

After 31 minutes and 42 minutes two more peaks were recorded at an attenuation of 4. The helium was allowed to sweep through the column for another hour and no other peaks were recorded (Fig.7).

A nuclear magnetic resonance (Fig. 8) and an infrared spectrum (Fig. 9) were taken on the second fraction (dark brown) that came through the column using benzene.

The third fraction using ether as the eluting solvent was brown. An infrared spectrum (Fig. 9) was taken.

III. RESULTS AND DISCUSSION.

A. ULTRAVIOLET LIGHT

The infrared spectra (Fig. 1 & 2) of the products of the first reaction mixture (irradiation of diazonium salt in tertiary butyl alcohol) were compared with the infrared spectrum (Fig. 3) taken by Professor Martin who previously had synthesized tertiary butyl phenyl ether by dropping the diazonium salt into   hot tertiary butyl alcohol. The spectrum of Professor Martin's product matches almost peak for peak with that of the product (16) made by the reaction of phenol, isobutylene and phosphoric acid, a standard preparation for synthesizing tertiary butyl phenyl ether. The spectra that were obtained on the products of the irradiation of the phenyl diazonium fluoroborate in tertiary butanol did not show any similarities to those of authentic samples. The only functional group that definitely could be identified was the tertiary butyl group. A strong peak at 3.45μ. and a medium peak at 6.85μ. could be attributed to the presence of a tertiary butyl group. However, the 7.9 to 8.15 micron range did not indicate the existence of any arylalkyl ether linkage. The rest of the spectrum did not exhibit any absorption peaks which allowed structure assignment.

Since the desired product was not obtained, it was
postulated that the following coupling might have occurred.
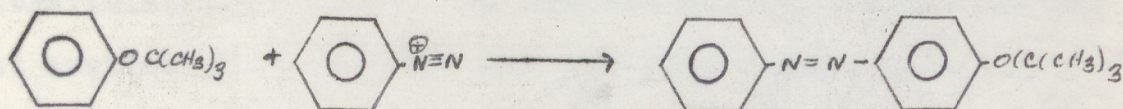
Bellamy (17) could not assign definite absorption
bands for -N=N- or $>$C-N= vibrations. However, Lüttke and
Kübler (18) made a study of azobenzene containing on N^{15}
atom. They showed that the sole difference between the
spectra of azobenzene with and without N^{15} lay in the posi-
tions of the bands at 1223 cm^{-1} and 813 cm^{-1} respectively.
They assigned these bands to $>$C-N= vibrations and did not
find evidence of a -N=N- bond. These frequencies were
checked and no absorption maxima were found in the spectra.

B. ULTRAVIOLET LIGHT

The reaction was run again, this time stirring the
reaction mixture so that as soon as the diazonium ion was
reduced it would be swept away from the path of the ultra-
violet light; thereby decreasing the probability of any
secondary photochemical reactions that might occur. The
infrared spectrum (Fig. 4) obtained was analogous to the first
two spectra obtained without stirring the reaction mixture.

At this point it was felt that the mercury arc lamp was inadaquate for further irradiation experiments since its ultraviolet light output was low and another source was not yet available. There was also the time consuming job of analyzing the reaction mixture, so still another approach was tried.

C. COPPER REACTIONS

When the cuprous chloride was allowed to react with the sodium tertiary butoxide, a light black precipitate formed which could have been caused by the simultaneous oxidation and reduction of the cuprous ion.

D. CUPROUS TERTIARY BUTOXIDE AND PHENYL DIAZONIUM CHLORIDE REACTION

During the reaction the copper in the solution passed through a red transition complex eventually turning a dark reddish brown which in time became black. This might have been caused again by the oxidation and reduction of the copper from the +1 state to the +2 and 0 oxidation states. The colors, however, suggest only +1 and 0 oxidation states.

The nuclear magnetic resonance spectrum (Fig. 5) on the first fraction that came through the column using ligroin (30-60° boiling range) showed two strong chemical shifts,

one at 7.45 ppm. and a singlet at 1.00 ppm. The 7.45 ppm.

chemical shift is probably a benzene absorption and the

singlet at 1.00 ppm. is attributed to a tertiary butyl

absorption. Comparison of this spectrum with known spectra

seems to confirm these suggestion. The infrared on the

first fraction (Fig. 6) was compared with the standard

infrared spectrum (Fig. 3) of tertiary butyl phenyl ether

and there was a matching, peak for peak of all the main

absorptions. Also present were many small absorptions

not found in the standard infrared spectrum. These were

attributed to the relative impurity of the author's prepara-

tion of tertiary butyl phenyl ether. and the need for

further purification of it.

At this stage, it was felt that it might be possible to

purify the substance using the Gas Chromatogram by insert-

ing cooled capillary tubes into the outlet of the instrument

and allowing the separate components to condense on the walls

of the capillary tubes as the various fraction came off the

hot column. The condensation was promoted by dropping ether

on the walls of the capillary tubes. As it turned out, no

effective separation was possible. Since the instrument was

operating at an extremely high temperature (200°C), any

solidified substance that was already on the walls of the

coils inside the instrument, was condensing on the walls of

the capillary tube along with the two components that were trying to be separated. Several times an attempt was made to clean the inner walls of the coils beyond the packed column by using an unpacked column and flushing the instrument successively with 0.2 cc. each of acetone, benzene, and toluene. However, the solvents would not condense even when the temperature was kept as low as $40^{\circ}C$.

The nuclear magnetic resonance spectrum (Fig.8) on the second fraction that came through the column using benzene shows strong resonances in the 7.3 to 7.5 ppm. range. It agreed completely with the known spectrum of biphenyl. The infrared spectrum (Fig. 9) of the second fraction agreed peak for peak with the known infrared spectrum of biphenyl.

An infrared spectrum (Fig. 10) on the third fraction has not yet been analyzed for its functional groups.

An estimated 20% yield of tertiary butyl phenyl ether has been calculated for this reaction from the areas measured under the peaks on the vapor phase chromatogram.

IV. SUMMARY AND CONCLUSIONS.

1. The use of ultraviolet light in the irradiation of phenyl diazonium fluoroborate and tertiary butyl alcohol appears to have produced a coupling reaction. The author feels, however, that if an ultraviolet light source of different frequencies were employed and if a homogeneous reaction mixture could be maintained with constant stirring, formation of tertiary butyl phenyl ether might be achieved.

2. The reaction of cuprous tertiary butoxide with phenyl diazonium chloride to form tertiary butyl phenyl ether appears to have been successful as verified by the nuclear magnetic resonance and infrared spectra obtained from the reaction product. An estimated 20% yield was calculated from the respective areas under the peaks on the vapor phase chromatogram. The yield is promising and the author feels that if the reaction were run at -30° C or even lower temperatures, the yield could be increased considerably. It would be interesting during the course of the reaction to check the far-infrared part of the spectrum of the reaction mixture to observe whether any copper in the +2 oxidation state is present, thereby

adding evidence to the propsed mechanism presented herein.

BIBLIOGRAPHY

(1a) Martin, R., Dielectric Constant Temperature Relationship in Some Chlorinated Phenyl Ethers, Union College Chem. Dept., Schenectady, N.Y., June 1958.

(1b) Schwab, F., Aryl Pseudohypochlorites - Some Reactions with Lewis Acids, Union College Chem. Dept., Schenectady, N.Y., May 1966.

(1c) Poccia, D., Synthesis and Absorption Spectra of 2,4,6-Trichlorodiphenyl Ether, Union College Chem. Dept., Schenectady, N. Y., May 1967.

(2) Roberts, J. D., and Caserio, M. C., Basic Principles of Organic Chemistry, W. A. Benjamin Inc., New York, 1964, pp. 386, 421.

(3) Horning, E. C., Organic Syntheses, John Wiley and Sons, Inc., New York, 1955, p. 339.

(4) Lawesson, S. O., and Yang, Nc C.; J. Am. Chem. Soc., 81, 4230-3, (1959).

(5) Lawesson, S. O., and Frisell, C.; Arkiv Kemi, 17, 393-400, (1961).

(6) Cram, D. J., Rickborn, B., Knox, G. R.; J. Am. Chem. Soc., 81, 6412-13, (1960).

(7) Bowman, R. S., Stevens, D. R., and Baldwin, W. E.; J. Am. Chem. Soc. 79, 87-92, (1957).

(8) Poccia, D., Synthesis and Absorption Spectra of 2,4,6-Trichlorodiphenyl Ether, Union College Chem. Dept., Schenectady, N. Y., May 1967.

(9) Roberts J. D., and Caserio, M. C., Basic Principles of Organic Chemistry, W. A. Benjamin Inc., New York, 1964, p. 890.

(10) Roberts, J. D., and Caserio, M. C., Basic Principles of Organic Chemistry, W. A. Benjamin Inc., New York, 1964, p. 891.

(11) Roberts, J. D., and Caserio, M. C., <u>Basic Principles of Organic Chemistry</u>, W. A. Benjamin Inc., New York, 1964, p. 841.

(12) Roberts, J. D., and Caserio, M. C., <u>Basic Principles of Organic Chemistry</u>, W. A. Benjamin Inc., New York, 1964, p. 841.

(14) Vogel, A. I., <u>A Textbook of Practical Organic Chemistry</u>, Spattiswoode, Ballantyne and Co. Ltd., London, 1961, p. 611.

(15) Fieser, L. F., Organic Experiments, D. C. Heath and Company, Boston, 1964, p. 237-8.

(16) Personal Communication with B. Adams at Schenectady Chemicals Incorporated.

(17) Bellamy, L. J., <u>The Infra-red Spectra of Complex Molecules</u>, John Wiley and Sons, Inc., New York, 1964, p. 229.

(18) Zollinger, H., <u>Azo and Diazo Chemistry</u>, Interscience Publishers Inc., New York (1961) p. 321.

FIGURE 1

FIGURE 2

Infrared spectrum chart. Frequency (CM⁻¹) axis labeled from 2000–10000 down to 650. Wavelength (Microns) axis from 1 to 15. Absorbance axis from 0.0 to 1.5.

Chart header information:
- SPECTRUM NO. Fig II
- SAMPLE SUSPECTED
- T-BUTYL PHENYL ETHER
- ORIGIN
- PURITY B. Koslow
- PHASE
- THICKNESS
- DATE 10/20/61
- OPERATOR BERN STEIN
- REMARKS
- PRISM N A Cℓ
- RESOLUTION
- RESPONSE
- GAIN
- SPEED
- SUPPRESSION
- SCALE
- THE PERKIN-ELMER CORP., NORWALK, CONN.
- NO. 021-6311

FIGURE 3a

-25a-

ABSORBANCE

WAVELENGTH (MICRONS)

SAMPLE Martin's (urine)
Suspected

ORIGIN
SOLVENT

CURVE NO. 1
CONC. Neat cell
CELL PATH
REFERENCE

SCAN SPEED F×S
SLIT N
REMARKS

OPERATOR Sim
DATE 9/20/66

PR 1129 (237-1028)

-25b-

FIGURE 3b

-26a-

FIGURE 4a

FIG. III

SAMPLE SUSPECTED T-BUTYL PHENYL ETHER (STIRRED REACTION)

ORIGIN

SOLVENT BENZENE

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED FAST

SLIT 25

REMARKS

OPERATOR BERNSTEIN

DATE 10/14/66

PERKIN ELMER

Figure 4b

-27b-

SAMPLE _suspected_ @ C-CH₃

ORIGIN

SOLVENT _benzene_

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED _fast_

SLIT _25_

REMARKS

OPERATOR _Berretter_

DATE _11/14/66_

PART NO. 237-1033   PERKIN-ELMER

FREQUENCY (CM⁻¹)

ABSORBANCE

FIGURE 5

-29a-

FIGURE 6

FIGURE 6b
-29b-

SAMPLE _____
_____
ORIGIN _____
SOLVENT _____

CURVE NO. _Na Cl_
CONC. _____
CELL PATH _____
REFERENCE _____

SCAN SPEED _____
SLIT _____
REMARKS _____

OPERATOR _Bemilon_
DATE _2/16/67_

PERKIN-ELMER

PART NO. 237-1033

FIGURE 7

FIGURE 7

FIGURE 8

-32a-

FIGURE 9a

FIGURE 9b

-32b-

SAMPLE _fraction no. 5_
from benzene
ORIGIN _____
SOLVENT _CHCl₃_

CURVE NO. _____
CONC. _____
CELL PATH _____
REFERENCE _____

SCAN SPEED _fast_ OPERATOR. _____
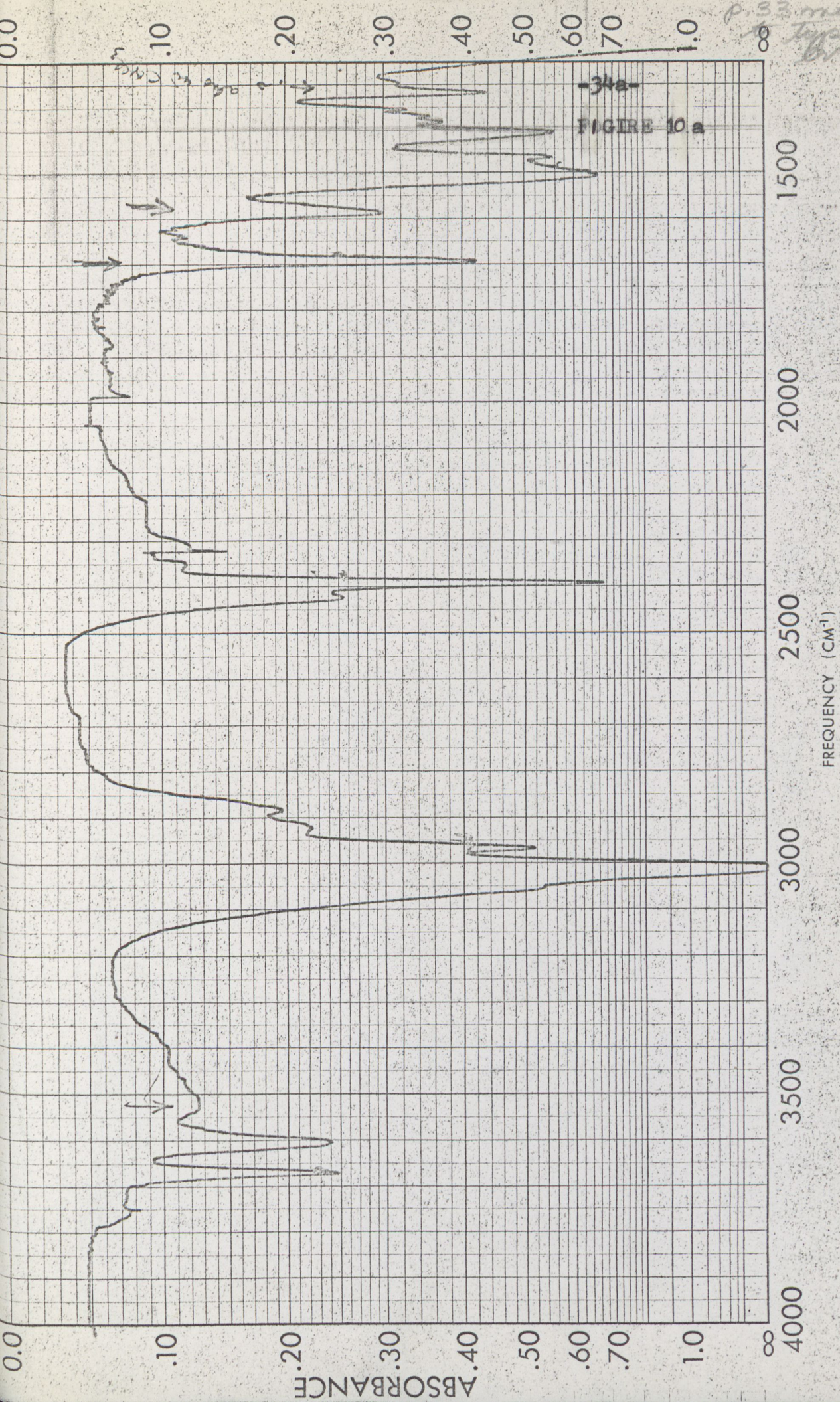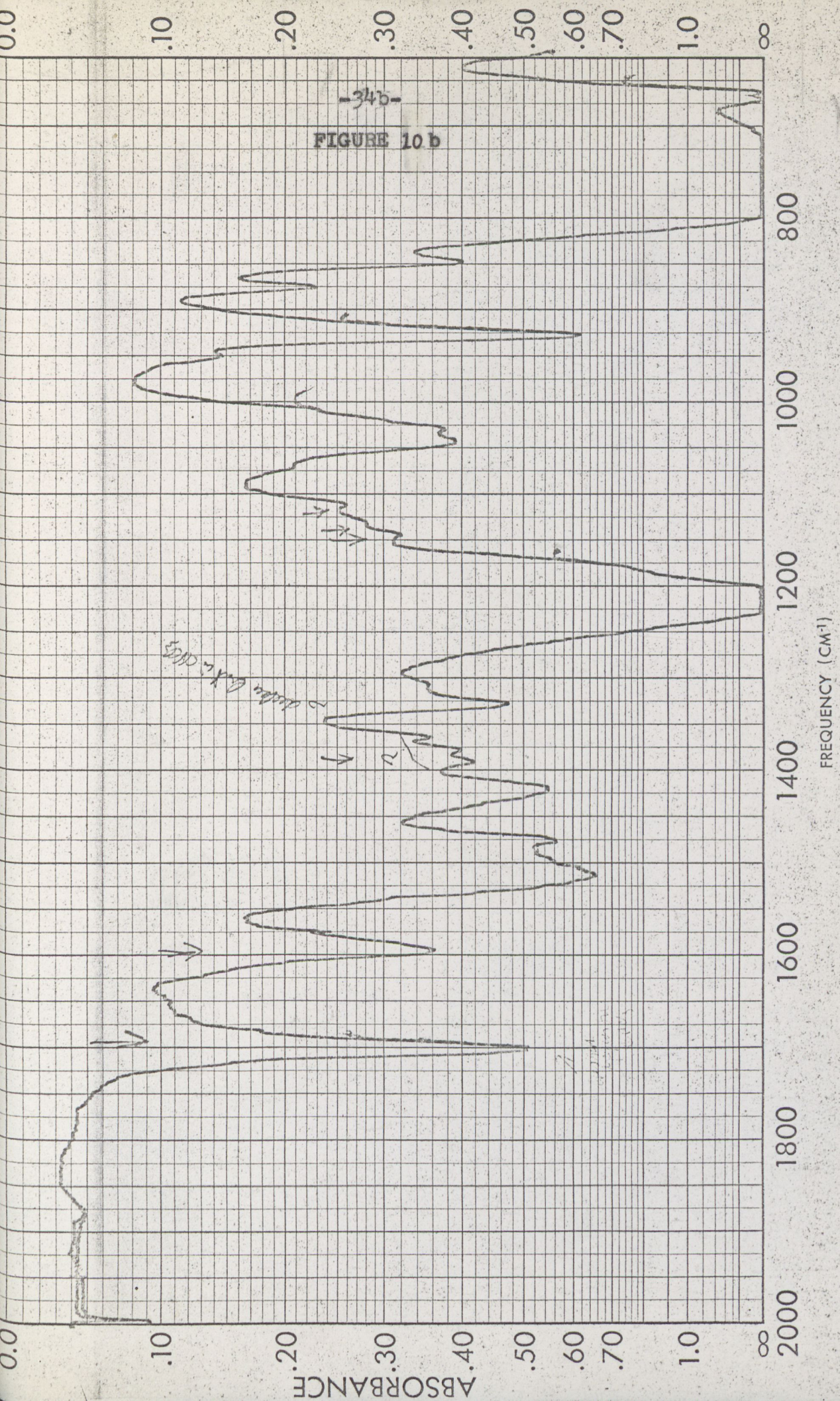SLIT _____ DATE _2/2/67_
REMARKS _____

PART NO. 237-1033   PERKIN-ELMER

-34a-

FIGURE 10a

SAMPLE _____

ORIGIN _____

SOLVENT _____

CURVE NO. _____
CONC. _____
CELL PATH _____
REFERENCE _____

SCAN SPEED _____
SLIT _____
REMARKS _____

OPERATOR _____
DATE _____

PERKIN - ELMER

FREQUENCY (CM⁻¹)

ABSORBANCE

PART NO. 237-1032 ®

FIGURE 10 b

-34b-

PART NO. 237-1033

PERKIN-ELMER

SAMPLE		OPERATOR
	SCAN SPEED	
	SLIT	DATE
ORIGIN	REMARKS	
SOLVENT $CHCl_3$		
	CURVE NO.	
	CONC.	
	CELL PATH	
	REFERENCE	

FREQUENCY (CM⁻¹)

ABSORBANCE