This is to certify that the

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"A Study of the Reduction and Fragmentation of Some Tertiary Carbinols When Condensed with Benzene in the Presence of Aluminum Chloride".

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Robert Verne Smith

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Ralph C. Huston
Major professor

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A STUDY OF THE REDUCTION AND FRAGMENTATION OF SOME TERTIARY CARBINOLS WHEN CONDENSED WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

by

ROBERT V. SMITH

A THESIS

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TABLE OF CONTENTS

INTRODUCTION

Extensive study has been made in the past on the alkylation of aromatic nuclei, particularly benzene and phenol, with tertiary alcohols in the presence of anhydrous aluminum chloride. The greater share of these investigations must be credited to Dr. R. C. Huston and coworkers of this laboratory. During these investigations it was observed (1) that there was a marked depressive influence on the condensing capability of alcohols in which there was an accumulation of alkyl groups on the carbon atom adjacent to the hydroxyl carbon. Subsequent studies by Huston and Awuapara (2), Huston and Barrett (3), Huston and Van Dyke (4), and Huston and Krantz (5), have resulted in the isolation of compounds which could be accounted for only by an apparent fragmentation or rearrangement and fragmentation of the alcohol during the reaction. These more recent investigations have led to the belief that fragmentation, rather than depressive influence of highly branched alcohols, accounts for the decreased yields of the expected alkyl benzenes.

In the work of Huston and Friedemann (6), Huston and Jackson (7), and Huston and Hughes (8), a saturated hydrocarbon fraction was isolated and identified as that corresponding to the alcohol condensed. No satisfactory

explanation was offered for this apparent reduction or "pulling out" of the oxygen of the alcohol.

It was the purpose of this investigation to study the fragmentation and reduction of all possible tertiary octanols, heptanols, hexanols, tertiary amyl and tertiary butyl alcohol, in which there are only primary alkyl groupings attached to the hydroxyl carbon, i.e., no alkyl substituents attached to carbon adjacent to the hydroxyl carbon.

HISTORICAL

The first attempt at using alcohols as agents for the alkylation of aromatic nuclei was reported by Nef (9) in 1897. He prepared diphenylmethane by condensing benzyl alcohol with benzene in the presence of anhydrous aluminum chloride. Repeating this work in 1916, Huston and Friedemann (10) reported other products formed during the reaction. These investigators (6) also condensed methylphenylcarbinol and ethylphenylcarbinol with benzene in the presence of anhydrous aluminum chloride and obtained in addition to the expected condensate, ethylbenzene and propylbenzene respectively, in approximately ten percent yields. The formation of these phenyl alkanes, apparently through reduction of the carbinol, was not satisfactorily explained. The optimum mole ratio of alcohol, benzene and aluminum chloride for the production of the main condensation product was also established by these investigators as one, five and one-half moles respectively. Increasing the amounts of aluminum chloride did not increase the yields. Less benzene and higher temperatures gave more by-products. Huston and Sager (11) showed that primary alcohols would not condense with benzene in the presence of anhydrous aluminum chloride using one-half mole of the condensing agent to one mole of the alcohol. Norris and

Sturgis (12) showed that only poor yields were obtained using large amounts of aluminum chloride at elevated temperatures. The latter also established that the reaction of alcohols and aromatic nuclei was a function of the quantity of aluminum chloride and temperature as Tzukervanik and Nazarova (13) had previously determined in regard to the condensation of secondary alcohols.

In 1933 Huston and Davis (14) found that from the condensation of triphenylcarbinol, triphenylmethane was obtained, rather than the expected tetraphenylmethane. This is another example of the apparent reduction of the carbinol to form the corresponding hydrocarbon. Huston and Goodemoot (15) have shown that, in general, alcohols alkylate aromatic nuclei in the presence of anhydrous aluminum chloride only when there is a strained carbon attached to the hydroxyl group. Huston, Fox and Binder (1) found that straight-chain carbinols, such as dimethyl-n-butylcarbinol, methylethyl-n-propylcarbinol and triethylcarbinol condense more readily than branched-chain carbinols. They explained that the latter have a larger tendency to form unsaturated compounds and tertiary alkyl chlorides.

It was first observed by Gustavson (16) only a year after the announcement of the Friedel-Crafts reaction that the tendency for rearrangement of alcohols in this reaction is primary > secondary > tertiary. He found that isopropylbenzene (cumene) was found by condensing

either n-propyl or isopropyl bromides with benzene in the presence of anhydrous aluminum chloride. This rearrangement phenomena was later corroborated by other workers (17, 18, 19). This isomerization of alcohols in the presence of aluminum chloride to the more stable secondary and tertiary alkyl groups is more pronounced with the lower molecular weight alcohols. However, as the carbinol increases in molecular weight and becomes highly branched, it tends to degrade or fragment into lower molecular weight compounds which can either condense with benzene, add hydrogen chloride or chloride anion, polymerize or be reduced. This was observed by Huston, Guile, Soulati and Wasson (20) in 1941. It was observed that when 2,4,4-trimethyl-2-pentanol and 2,3,3-trimethyl-2-pentanol were condensed with benzene low yields of the expected condensate were obtained. These investigators also showed that fragmentation was diminished at reduced temperatures. The yield of alkylbenzene and degradation is also a function of the amount of aluminum chloride used (1).

More recently other investigators (3, 4, 5) have shown demethylation and methyl migration to take place during the condensation of highly branched carbinols. For example, Huston and Barrett (3) have shown that the condensation of dimethyl-t-butyl carbinol produced t-amylbenzene and trimethyl styrene in addition to t-butyl benzene and the

expected heptylbenzene. The formation of the first two products could only be explained by demethylation, the formation of t-butyl benzene by fragmentation. Huston and Van Dyke (4) obtained methyl chloride, t-butyl and t-amyl benzene from the condensation of 2,2,3-trimethyl-3-pentanol which could only be explained by demethylation, methyl migration and fragmentation. Huston and Krantz (5) have shown that methyl group migration and fragmentation takes place in the condensation of 2,3,4-trimethyl-2-pentanol with benzene. They report the isolation of isobutane, t-butyl and t-amyl benzene with only a small amount of the octylbenzene formed. Although Awuapara (2) obtained nearly fifty percent yield of t-butylbenzene from the condensation of 2,3,4-trimethyl-3-pentanol in which a methyl radical must migrate, he obtained only very small yields of t-butyl and t-amyl benzenes from the condensation of 2,4-dimethyl-3-ethyl-3-pentanol since their formation necessitates the migration of an ethyl group.

Huston and Hughes (8) reported the isolation of sec-butyl benzene from the condensation of 3-phenyl-3-butanol with benzene. Also Jackson (7) isolated isopropyl benzene and sec-butyl benzene from the condensations of diphenylisopropyl carbinol and diphenyl sec-butyl carbinol respectively with phenol. They were first thought to result from the breakdown (with hydrogenation) of the condensation products under the influence of aluminum chloride. However, when p-hydroxytriphenylisopropylmethane was dissolved in ligroin

and treated with aluminum chloride, no isopropylbenzene could be isolated. Instead 1,1-diphenyl-2-methyl-1-propene was found along with phenol. They concluded from this that the sec-alkyl benzene was formed during the process of condensation and not by decomposition of the condensation product. The hydrogen donor was not determined.

THEORETICAL

The isolation of alkyl halide and alkene from the condensation of alcohol and benzene using anhydrous aluminum chloride as a catalyst strongly indicates that there is a close relationship between these three alkylating agents in the alkylation reaction.

It has been proposed that all of the three alkylating agents have a common ionic intermediate in the alkylation reaction, that the reaction with alcohols involves the formation of alkenes and/or alkyl halides as intermediates. Other intermediates which have been proposed are complexes of aluminum chloride with the alcohol and aromatic nuclei. Alkyl halides and alkenes require only catalytic amounts of aluminum chloride while alcohols require a larger amount due to the complex formed (12).

As to the reactivity of alcohols in the alkylation reaction the order is benzyl > tertiary > secondary > primary. This is shown by the fact that benzyl alcohol requires only traces of a weak catalyst such as zinc chloride while methyl alcohol requires a considerable quantity of a powerful catalyst such as aluminum chloride.

The assumption that the alkylation reaction between alcohol and benzene, using a dehydrating agent such as aluminum chloride, takes place by direct removal of water

does not explain the rearranged and lower molecular weight products obtained. On the basis of alkylation taking place from the formation of the alkyl halide as an intermediate, Tzukervanik (13) has proposed the following mechanism for tertiary alcohols.

$$t\text{-}C_5H_{11}OH + AlCl_3 \longrightarrow t\text{-}C_5H_{11}OAlCl_2 + HCl$$

$$t\text{-}C_5H_{11}OAlCl_2 \longrightarrow C_5H_{10} + AlCl_2OH$$

$$C_5H_{10} + HCl \longrightarrow t\text{-}C_5H_{11}Cl$$

$$t\text{-}C_5H_{11}Cl + C_6H_6 \xrightarrow{AlCl_3} t\text{-}C_5H_{11}C_6H_5 + HCl$$

The isolation of alkenes and alkyl halides has been offered as experimental evidence of the above type reactions. Evolution of HCl gas during the reaction was explained by the formation of the aluminum chloride-alcohol complex with subsequent elimination of the gas. He also proposed this type of mechanism for secondary alcohols, although he found no chlorides or alkenes as by-products. Norris and Sturgis (12) have proposed a similar mechanism. This mechanism, however, does not explain the rearranged products found by Kaye (22) from his work on the condensation of some secondary alcohols with benzene in the presence of anhydrous aluminum chloride. Complex formation of alcohols and aluminum chloride has been investigated by several workers (23, 24).

The formation of alkenes during the reaction has been used to propose a mechanism whereby rearrangement of the alkyl groups of certain primary and secondary

alcohols takes place. In connection with this, McKenna and Sowa (25) proposed a mechanism involving olefins as intermediates in order to help explain rearrangements during alkylation. Using boron trifluoride as a catalyst they have isolated small amounts of alkenes and their polymers from the products of the reaction.

$$R\text{-}CH_2\text{-}CH_2OH \xrightarrow{BF_3} R\text{-}CH{=}CH_2$$

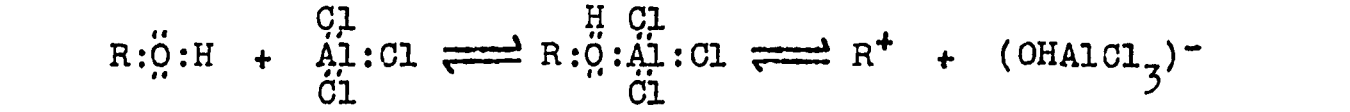
$$R\text{-}CH{=}CH_2 + C_6H_6 \longrightarrow RCH(C_6H_5)CH_3$$

Thus the condensation of a primary alcohol with benzene leads to a secondary alkyl benzene. Although this mechanism may account for the formation of alkenes, alkyl halides and rearranged products, it must be necessarily excluded in the case of both benzyl alcohol (6) and benzhydrol (10) in which intermediate olefin formation is impossible. Both of these alcohols are effective alkylating agents.

Several ionic mechanisms have been proposed by various workers in this field, all involving a catanoid attack on the aromatic nuclei. However, only the theory of Price (26) will be mentioned here. This theory involves an electrophilic attack on the alkylating agent, with subsequent formation of a carbonium ion. Wertyporoch and Firla (27) have demonstrated by conductance studies the formation of an ionic complex between aluminum chloride and alkyl halide.

$$R{:}\ddot{\underset{\ddot{}}{X}}{:} + \ddot{\underset{\ddot{Cl}}{\overset{Cl}{Al}}}{:}Cl \rightleftharpoons R^+ + (:X:\ddot{\underset{\ddot{Cl}}{\overset{Cl}{Al}}}{:}Cl)^-$$

Ulich and Heyne (28) have measured the equilibrium for the formation of certain of the catalyst-alkyl halide complexes postulated by Wertyporoch and in addition, found that the rate of alkylation was directly proportional to the concentration of this catalyst-alkyl halide complex. This type of complex can also be shown using oxygen containing compounds such as alcohols, ethers, esters, etc.

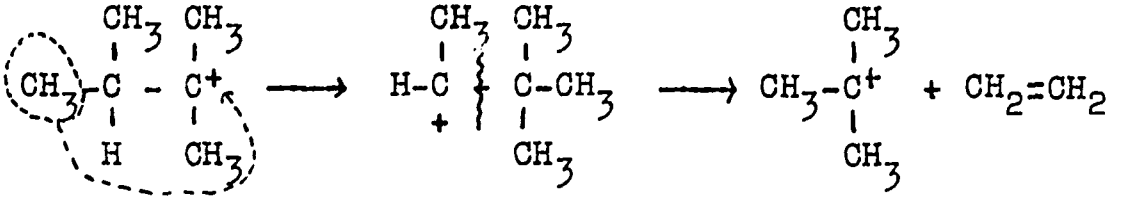


This again shows the formation of the electron deficient carbonium ion. The attack on the benzene ring then proceeds analogous to halogenation whereby the carbonium ion completes its octet by association with a pair of electrons from a double bond of the aromatic nucleus.

Ipatieff and Corson (29) have shown that the above equation is reversible by converting p-di-t-butylbenzene in benzene solution to t-butylbenzene in the presence of a catalyst. Although the above reaction is reversible, several investigators (30, 31, 32) have shown that catalysts will remove only tertiary alkyl groups unless vigorous catalysis with aluminum chloride is effected. This fact and the greater ease of alkylation with tertiary alkylating agents is undoubtedly due to the tenacity with which the R group will retain electrons it shares with the substituent group, halide, hydroxyl, etc. The order of electronegativity being primary) secondary) tertiary.

Where the R group of the alkylating agent is highly

branched the reaction becomes a little more complex as evidenced by the isolation of by-products such as lower molecular weight chlorides, isobutane, t-butyl benzene, etc. This, of course, strongly indicates a fragmentation and rearrangement reaction as indicated by the following example:



The shift of the methyl group to the positive carbon with subsequent scission of the carbon to carbon bond to form a low energy level tertiary grouping accounts for the isolation of tertiary butyl benzene and lower molecular weight chlorides. In some cases (4) the methyl group has become permanently detached with the formation of methyl chloride. The isolation of isobutane (5, 21) and not isobutene shows that reduction has taken place during the reaction.

The rearrangements encountered in these alkylation reactions, particularly where there is branching on the carbon adjacent to the hydroxyl carbon is, of course, in agreement with Whitmore's (33) views on molecular rearrangements.

EXPERIMENTAL - PART I

I. Preparation of Alcohols

All of the possible tertiary octanols, heptanols, and hexanols having only primary alkyl groups attached to hydroxyl carbon were selected for this study with the exception of 4-Ethyl-4-heptanol, 4-Methyl-4-heptanol, and 2,4,4-Trimethyl-2-pentanol which were previously studied. Tertiary amyl and tertiary butyl alcohols, which were also condensed in this work, were obtained directly from the stockroom. The alcohols prepared were properly identified by physical constants and, as a matter of interest, 3,5-Dinitrobenzoates were also successfully prepared and analyzed for nitrogen. Micro-Dumas method was used.

A. 2-Methyl-2-heptanol

B. 3-Methyl-3-heptanol

C. 3-Ethyl-3-hexanol

D. 2,4-Dimethyl-2-hexanol

E. 2,5-Dimethyl-2-hexanol

F. 2,4-Dimethyl-4-hexanol

G. 2-Methyl-2-hexanol

H. 3-Methyl-3-hexanol

J. 3-Ethyl-3-pentanol

K. 2,4-Dimethyl-2-pentanol

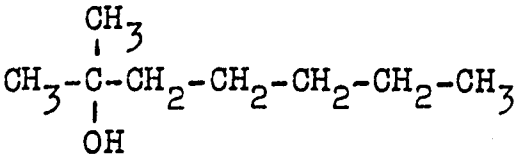
L. 2-Methyl-2-pentanol

M. 3-Methyl-3-pentanol

N. 2-Methyl-2-butanol

O. 2-Methyl-2-propanol

Part A. 2-Methyl-2-heptanol



As all of the alcohols were prepared by the addition of ester, ketone or acid to a Grignard reagent, only the detailed procedure for the preparation of the above alcohol will be given.

2-Methyl-2-heptanol was prepared by the addition of acetone to n-amyl magnesium bromide, followed by the hydrolysis of the resulting addition compound. The Grignard was prepared by placing 85 grams (3.5 moles) of magnesium turnings in a three liter, three necked, round bottom flask equipped with a glycerine sealed mechanical stirrer, reflux condenser, and dropping funnel. The condenser and dropping funnel were closed with calcium chloride filled drying tubes. The reaction was started by running into the flask, on top of the magnesium, about 5 ml of a 1:1 mixture of anhydrous ether and n-amyl bromide. The ether was dried over freshly cut sodium and the n-amyl bromide dried over anhydrous calcium chloride to remove water and alcohol, and distilled collecting that portion boiling between 127-131°C, and having a index of refraction of 1.4444 at 20°C. After allowing to stand from 3-5 minutes, six hundred ml of anhydrous ether was

added through the top of the condenser, the mechanical stirrer started, and the remainder of the n-amyl bromide-ether solution (528.5 g bromide; 3.5 moles) (600 ml ether) added at such a rate as to keep the reaction under control. External cooling with ice was used in order to increase the rate of addition. A total of 1200 ml of ether was used for the 3.5 mole run or 342 ml per mole of Grignard.

After the addition of the bromide was completed the reaction mixture was stirred for two hours and then allowed to stand overnight. The Grignard reagent was then titrated according to the method described by Gilman, Wilkenson, Fischel, and Meyers (34). The calculated amount of Grignard for an average run was 3.2 moles or an actual yield of 91.4%. On this basis 186 grams (3.2 moles) of acetone in anhydrous ether (400 ml per mole) was added at a rate of one drop per second. The acetone was dried over anhydrous potassium carbonate and distilled collecting that portion boiling between 55-57°C and having an index of refraction of 1.3591 at 20°C.

After the addition of the acetone was complete the mixture was stirred for two hours and then allowed to stand overnight.* The addition product was then hydrolized with ice and enough 1:1 sulfuric acid added to dissolve the

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* Although the author, in most cases, did not add benzene at this point, Bailey (35) found that by adding benzene, distilling off the ether, and refluxing at a higher temperature he was able to increase the yield of the alcohol as much as 17% in the case of 2-Methyl-3-ethyl-3-pentanol.

basic magnesium salts. The ether alcohol layer was separated from the water layer and the latter extracted with ether. The combined organic layers were washed with 10 percent sodium carbonate until basic to litmus, and then with distilled water, and dried over anhydrous sodium sulfate for twenty four hours. The ether was removed through a 60 x 1 cm Fenske type column packed with 1/16 inch glass helices. The alcohol was collected over a two degree range at reduced pressure.

Yield: 54%

BP_{17} : 63-65°C

n_D^{20} : 1.4235

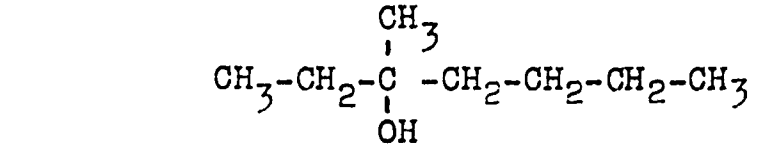
D_4^{20} : 0.8156

3,5-Dinitrobenzoate: M.P. 43-44°C

% N Calc. 8.63
Obs. 8.40

This alcohol was prepared by Whitmore and Williams (36) and the physical constants agree with their work in which they prepared the alcohol by the same method.

Part B. 3-Methyl-3-heptanol



This alcohol was prepared by the addition of methyl ethyl ketone to n-butyl magnesium bromide.

Yield: 68%

BP_{15} : 61-63°C

n_D^{20} : 1.4270

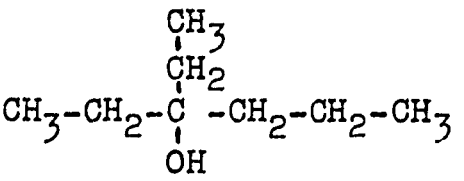
D_4^{20} : 0.8258

3,5-Dinitrobenzoate: M.P. 53-54°C

% N Calc. 8.63
Obs. 8.88

This alcohol was prepared by Whitmore and Badertscher (37) and Snyder (38) by the same method.

Part C. 3-Ethyl-3-hexanol



This alcohol was prepared by two different methods, both however, involving use of the Grignard reagent. The first method used was that of Huston and Bailey (35) in which one mole of n-butyric acid was added to three moles of ethyl magnesium bromide. The second method was that used by Clark and Riegel (39) in which diethyl ketone was added to propyl magnesium bromide. Although the second method produced slightly better yields the first method is more feasible costwise. The physical constants checked for each preparation.

Yield: 50% (using butyric acid)
58% (using diethyl ketone)

BP_{12} : 57-59°C

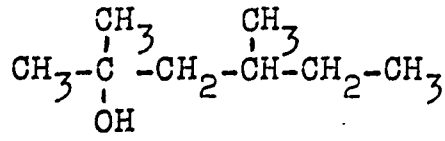
n_D^{20} : 1.4316

D_4^{20} : 0.8370

3,5-Dinitrobenzoate: M.P. 62-63°C

% N Calc. 8.63
Obs. 8.74

Part D. 2,4-Dimethyl-2-hexanol



This alcohol was prepared by two different methods. The first method used was that of Huston and Guile (20) in which acetone was added to active-amyl magnesium bromide. The second method involved the addition of carbon dioxide to active-amyl magnesium bromide and then the addition of methyl magnesium bromide to the acid complex. In the latter method the carbonation of the active-amyl magnesium bromide was accomplished according to the procedure given in Organic Synthesis (40) with slight modifications. The active-amyl magnesium bromide was prepared in a 5-liter, three-neck flask equipped with stirring motor, condenser and dropping funnel. For the carbonation the dropping funnel was replaced with a glass tube which extended 2 cm above the surface of the Grignard. To this tube was attached four safety bottles, two of which contained sulfuric acid. To these bottles was connected a tank of CO_2 gas. The reaction flask was cooled externally by solid carbon dioxide-ether to approximately $-12^{\circ}C$. The temperature rose to $0^{\circ}C$ during the addition of the carbon dioxide, which took approximately $5\frac{1}{2}$ hours for a three mole run. The addition was complete when the temperature dropped and the solution of the acid complex became dark and syrupy. The methyl

magnesium bromide was added directly to the acid complex with stirring. After this addition was complete the flask was fitted with a goose-neck tube and condenser, and the ether slowly distilled off until the temperature rose to 50-55°C. Then 1 liter of anhydrous benzene was added and the reaction mixture refluxed for four hours before hydrolysis. According to the work of Huston and Bailey (35) this procedure increased the yield of alcohol as much as 17% in one particular case already mentioned.

The physical constants of the alcohol are in agreement for both methods of preparation.

Yield: 24% (using acetone)
37% (using carbonation)

BP_{20} : 62-64°C

n_D^{20} : 1.4250

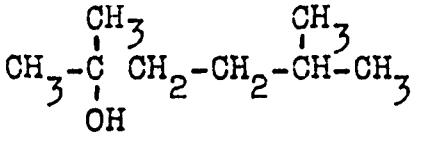
D_4^{20} : 0.8218

3,5-Dinitrobenzoate: M.P. 48.5-49°C

% N Calc. 8.63
Obs. 8.69

This alcohol was also prepared by Levene and Marker (41) using the ethyl ester of 3-methyl pentanoic acid and methyl magnesium iodide.

Part E. 2,5-Dimethyl-2-hexanol



This alcohol was prepared by Dr. Guile of this laboratory by the addition of acetone to isoamyl magnesium bromide.

BP_{748}: 151.6°C

n_D^{20} : 1.4210

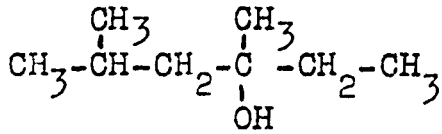
D_4^{20} : 0.8158

3,5-Dinitrobenzoate: M.P. 61-62°C

% N Calc. 8.63
Obs. 8.95

It was also prepared by Levene and Marker (40), using the ethyl ester of 4-methyl pentanoic acid and methyl magnesium iodide.

Part F. 2,4-Dimethyl-4-hexanol



This alcohol was prepared by two different methods. The first method employed by Levene and Marker (41) was the addition of acetone to isobutyl magnesium bromide. The second method was that employed by Clarke (42) in which methyl isobutyl ketone was added to ethyl magnesium bromide. This method gave much better yields and a purer product. Apparently when there is a choice of Grignard reagents, such as in the preparation of the above alcohol and others prepared for this problem, the more complex the Grignard reagent used, the poorer the yield of alcohol obtained. The theoretical aspect of this phenomena will be taken up under the discussion part of this thesis.

Yield: 21% (using acetone)

56% (using methyl ethyl ketone)

BP_{15} : 51.5-52°C

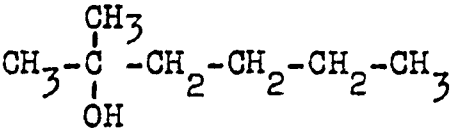
n_D^{20} : 1.4275

D_4^{20} : 0.8260

3,5-Dinitrobenzoate: M.P. 52-53°C

% N Calc. 8.63
Obs. 8.93

Part G. 2-Methyl-2-hexanol



This alcohol was prepared according to the method used by Whitmore and Church (43) and Whitmore and Badertscher (37) in which acetone was added to n-butyl magnesium bromide.

Yield: 67%

BP_{25} : 59-61°C

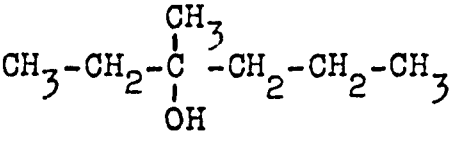
n_D^{20} : 1.4179

D_4^{20} : 0.8122

3,5-Dinitrobenzoate: M.P. 53-54°C

% N Calc. 9.02
Obs. 8.68

Part H. 3-Methyl-3-hexanol



This alcohol was prepared according to the method used by Whitmore and Badertscher (37) in which methyl ethyl ketone was added to ethyl magnesium bromide.

Yield: 54%

BP_{18} : 53-54°C

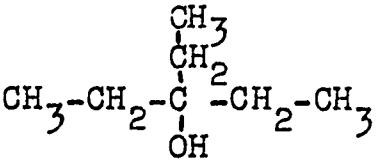
n_D^{20} : 1.4231

D_4^{20} : 0.8219

3,5-Dinitrobenzoate: M.P. 43-44°C

% N Calc. 9.02
Obs. 9.54

Part J. 3-Ethyl-3-pentanol



This alcohol was prepared according to the methods used by Moyer and Marvel (44) and Whitmore and Badertscher (37) in which diethyl carbonate was added to ethyl magnesium bromide.

Yield: 70%

BP_{52} : 72-73°C

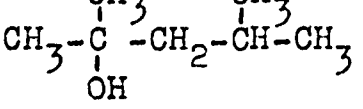
n_D^{20} : 1.4294

D_4^{20} : 0.8395

3,5-Dinitrobenzoate: M.P. 118-119°C

% N Calc. 9.02
Obs. 9.17

Part K. 2,4-Dimethyl-2-pentanol



This alcohol was prepared by the addition of methyl isobutyl ketone to methyl magnesium bromide. Edgar,

Calingaert and Marker (45) prepared the same alcohol by the addition of acetone to isobutyl magnesium bromide and obtained only a 30 percent yield. This is another example in which the choice of Grignard reagent has a great bearing on the yield and purity of the product obtained.

Yield: 89%

BP_{17} : 43°C

n_D^{20} : 1.4172

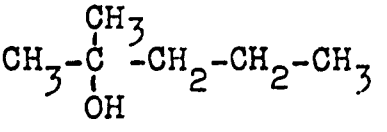
D_4^{20} : 0.8106

3,5-Dinitrobenzoate: M.P. 69-70°C

% N Calc. 9.02
Obs. 9.07

This alcohol was also prepared by de Graef (46).

Part L. 2-Methyl-2-pentanol



This alcohol was prepared by the method used by Huston and Hsieh (47) and Fox (48), in which acetone was added to n-propyl magnesium bromide.

Yield: 70.2%

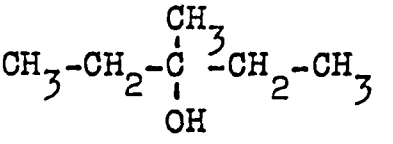
BP_{63} : 65-66°C

n_D^{20} : 1.4108

D_4^{20} : 0.8146

3,5-Dinitrobenzoate: M.P. Obs. 71-72°C
Lit. 71-72°C

Part M. 3-Methyl-3-pentanol



This alcohol was prepared by the method used by Huston and Hsieh (47) in which methyl ethyl ketone was added to ethyl magnesium bromide.

Yield: 70.4%

BP_{77} : 65-66°C

n_D^{20} : 1.4171

D_4^{20} : 0.8222

3,5-Dinitrobenzoate: M.P. Obs. 95.5-96.5°C
Lit. 95.5-96.5°C

Part N. 2-Methyl-2-butanol

This was obtained directly from the stockroom of a CP grade having physical constants which agreed with literature values.

Part O. 2-Methyl-2-propanol

This was also obtained directly from the stockroom of a CP grade having physical constants which agreed with literature values.

II. The Condensation Apparatus

The apparatus used for the condensation of the various alcohols was essentially the same as that devised by Van Dyke (4) in this laboratory with the exception of a few minor modifications. Figure 1 shows a diagram of the condensation apparatus with the important parts indicated by letter and listed below.

A. A three-neck, round bottom flask, the size varying with the amount of alcohol condensed.

B. Dropping funnel with inner sealed tube for equalizing the pressure in order to keep out moisture and forming an air tight system.

C. Mechanical stirrer consisting of an electric motor and a glycerine-rubber sealed glass rod stirrer.

D. Carbon dioxide generator system consisting of a vacuum bottle of concentrated sulfuric acid and a mercury safety valve to release gas pressure.

E. A sidearm delivery tube to which is attached a thermometer and reflux condenser.

F. Two way stop cock in order to bypass the ice-salt water cooled trap.

G. Ice-salt water cooled trap for condensing the vapors of the lower volatile liquids such as benzene and the alcohol.

H. Two way stop cock in order to bypass the solid carbon dioxide-acetone cooled trap leading to the nitrometer.

I. Solid carbon dioxide-acetone cooled trap to condense the highly volatile liquids not boiling lower than -80°C.

J. One way stop cock operated in conjunction with stop cocks F and H. This was closed when L was adjusted to bypass the trap.

K. Mercury trap to prevent back pressure due to the cooling down of the system towards the end of the reaction.

L. Safety bottle.

M. Gas nitrometer containing 50 percent CP potassium hydroxide for absorbing the carbon dioxide and hydrogen chloride. The nitrometer was of 300 ml. capacity with a diameter of 25 mm in the vertical sections and 10 mm in the curved section. Mercury was placed in the base to seal the potassium hydroxide solution from trap L.

N. Nitrometer leveling bulb consisting of a 250 ml. dropping funnel.

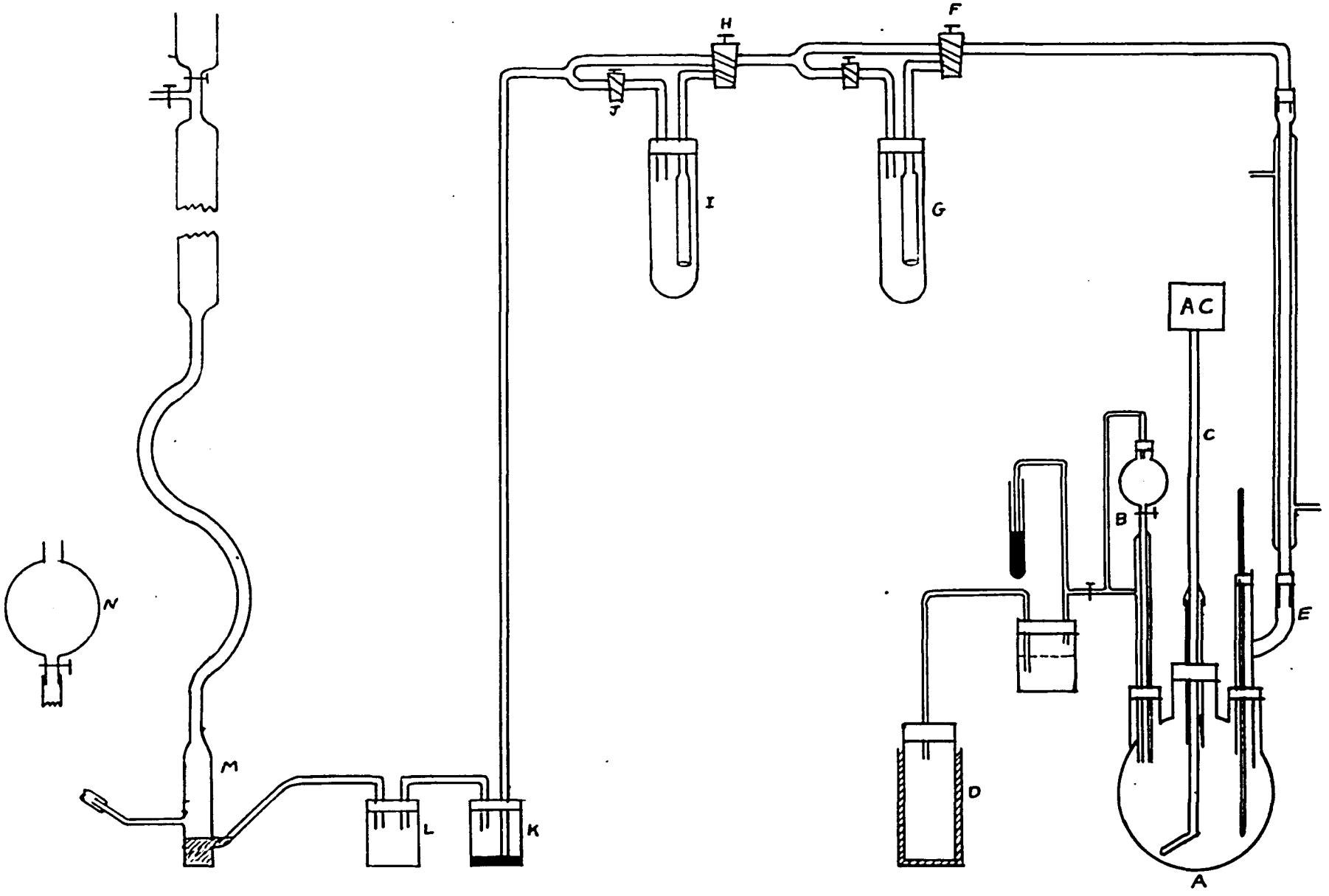


FIGURE 1

III. Condensation and Fractionation

The alcohols prepared as described were condensed with benzene in the presence of anhydrous aluminum chloride. The procedure used in regard to control of temperature, mole proportion and rate of addition of reactants was similar to that employed by several workers in this laboratory, studying this particular alkylation reaction. It was established by Huston and Friedmann (6) that the proportion of benzene to alcohol for obtaining maximum yields of alkyl benzene was approximately 5 moles to 1 respectively. The excess benzene not only acts as a diluent in this case but also minimizes disubstitution. The above molar ratio of benzene-alcohol was maintained for each condensation with the exception of 3-ethyl-3-pentanol in which a 1:1 mole ratio was used. The reason for this exception will be explained under Part J. It was also determined by the author (21) that the mole ratio of alcohol-aluminum chloride for obtaining maximum yields of alkyl benzene was 1:0.5 respectively. As the procedure for all condensations and fractionations was the same only one will be described in detail.

One hundred seventy nine and one-half grams (1.35 moles) of CP anhydrous aluminum chloride was placed in the reaction flask along with 1053 grams (13.5 moles) of anhydrous thiophene-free benzene. The benzene-aluminum chloride mixture was heated to reflux with stirring for activation purposes and was then allowed to cool to room

temperature. There was no noticeable color change at this point, however small amounts of gaseous hydrogen chloride were produced. After reaching room temperature the system was swept out with carbon dioxide until microbubbles appeared in the nitrometer. The carbon dioxide generator was then turned off and the alcohol (2,4-Dimethyl-2-pentanol in this case) (314 grams; 2.7 moles) added at such a rate as to keep the temperature of the reaction below 35°C. Gaseous evolution usually took place during the addition of the first one-third of the alcohol and back pressure was noticed after approximately one half of the alcohol was added. This back pressure was apparently due to the heat of the reaction subsiding and the cessation of the formation of any gaseous products. At the end of the addition of the alcohol the temperature dropped to around thirty degrees in most condensations. Stirring was continued for a period of two hours and then the reaction mix was allowed to stand for twenty-four hours before hydrolysis. At this time any gas collected in the nitrometer was transferred to gas burettes and tested for condensibility, burning and the supporting of combustion. The only gas which formed during any of the condensations was identified as isobutane and then only when such was formed by the fragmentation of the alcohol. The only volatile liquid condensed in the dry-ice acetone cooled trap was isobutane and this only when the configuration of the alcohol condensed

permitted fragmentation. The alcohol described in this condensation (2,4-Dimethyl-2-pentanol) did fragment and isobutane was found in the above mentioned trap. It was interesting to note that in each case where isobutane was produced it did so during the first one third addition of the alcohol. The isobutane was then fractionated many times by allowing it to come slowly to room temperature and pass into another receiver cooled by dry-ice acetone where it was recondensed. This procedure freed it from hydrogen chloride and any benzene which escaped the ice-salt water cooled trap.

The hydrolysis of the reaction complex was accomplished by the addition of small pieces of ice into the reaction flask, with stirring. The temperature usually rose sharply at this point and then subsided. Then 200 ml. of distilled water was added in 50 ml. portions. No acid was used in the hydrolysis, as the water was sufficient to dissolve the basic salts after considerable stirring. The organic layer was then separated from the aqueous layer, the latter extracted three times with 50 ml. portions of benzene, and the combined extracts plus the original organic layer were washed with 10% sodium carbonate and then distilled water, and then dried over anhydrous sodium sulfate. The color of the solutions of the various condensations, at this point, varied from light orange to dark greenish yellow, all having an opalescent tinge.

All initial distillations were carried out by a

60 x 1.8 cm column packed with 1/16 inch glass helices. The head on the column was designed for distillation under reduced pressure with a take off for permitting reflux. Thus it was possible to allow the vapors to come to equilibrium before a cut was made. The solvent in each case was distilled off at atmospheric pressure. During this period of the distillation a carbon dioxide-acetone cooled trap was connected between the head of the column and the vacuum safety flask. This was for the purpose of condensing any low boiling liquids which might have been dissolved in the solvent.

It was found in many cases by workers in this laboratory (4, 5), particularly with the highly branched carbinols, that it was necessary to remove the chloride fractions before distillation of the alkyl benzene fraction. The author had, in most cases, no apparent difficulty in this respect, i.e. chloride contamination, probably due to the nature of the alcohols condensed. In the one or two cases where it was necessary to remove the chloride contamination, this was accomplished by refluxing the alkyl benzene obtained from the initial fractionation with an equal volume of fifty percent alcoholic potassium hydroxide for a period of four to six hours. The organic layer was then separated from the water layer, washed several times with distilled water until neutral to litmus and then dried over anhydrous potassium carbonate. Upon distillation the alkyl benzene was found free from chloride. Occassionally the

higher fractions were also contaminated with unsaturated compounds. This unsaturation was removed by the addition of five percent bromine in carbon tetrachloride until color persisted, removal of excess bromine with ten percent sodium bisulfite, then washing with distilled water, and drying over anhydrous potassium carbonate.

Other columns used for further purification were of the same type except shorter in length or smaller in bore. These were of the sizes 20 x 1.0 cm packed with 1/32 inch glass helices; 30 x 1.8 cm packed with 1/16 inch glass helices; 92 x 0.8 cm packed with 1/32 inch glass helices.

Part A. The condensation of 2-Methyl-2-heptanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 2-Methylheptane

Eight to twelve grams of the saturated hydrocarbon per mole of alcohol condensed was isolated. It was contaminated to a small degree with the corresponding unsaturated hydrocarbon, as was to be expected. This was easily removed by shaking several times with small portions of cold concentrated sulfuric acid. As no derivative could be prepared it was identified by its physical constants, which are in close agreement with those reported in the literature (49).

Average Yield: 8.8%

BP_{743}: 115-116°C

n_D^{20} : 1.3962

D_4^{20} : 0.7001

M_R * : Calc. 39.16 Obs. 39.12

This hydrocarbon was also identified by means of its infra-red spectra which is shown in Fig. 2.

Fraction II. Chloride-Alcohol

Six to eight grams of this fraction collected per mole of alcohol condensed contained a mixture of octyl chloride and uncondensed alcohol and was not separated or purified. The odor was camphor-like, characteristic of tertiary alcohols, and gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 2-Methyl-2-phenylheptane

This fraction was the expected condensation product. The physical constants do not agree with those reported in the literature (20).

Average Yield: 27.4%

BP_1 : 69-70°C

n_D^{20} : 1.4910

D_4^{20} : 0.8702

M_R : Calc. 63.27 Obs. 63.16

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* Data for the calculation of molecular refraction was taken from Shriner and Fuson, "Identification of Organic Compounds".

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 37 grams per mole of alcohol condensed.

Part B. The condensation of 3-Methyl-3-heptanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 3-Methylheptane

Ten to twelve grams of the saturated hydrocarbon per mole of alcohol condensed were isolated. The same treatment for removal of traces of unsaturation was employed as with Fraction I, Part A. The physical constants were in close agreement with those reported in the literature (49).

Average Yield: 9.5%

BP_{749}: 117.5°C

n_D^{20} : 1.3980

D_4^{20} : 0.7055

M_R : Calc. 39.16 Obs. 39.14

This hydrocarbon was also identified by means of its infra-red spectra which is shown in Fig. 3.

Fraction II. Chloride - Alcohol

Eight to ten grams of this fraction collected per mole of alcohol condensed contained a mixture of octyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic

of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 3-Methyl-3-phenylheptane

This fraction was the expected condensation product. Its physical constants do not agree with those reported in the literature.(50).

Average Yield: 24.2%

BP_{14} : 111°C

n_D^{20} : 1.4955

D_4^{20} : 0.8778

M_R : Calc. 63.27 Obs. 63.12

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 27 grams per mole of alcohol condensed.

Part C. The condensation of 3-Ethyl-3-hexanol with benzene in the presence of anhydrous aluminum chloride.

This alcohol was condensed in previous work (21) and the hydrocarbon fraction was separated but not positively identified as 3-Ethyl heptane as its physical constants did not agree with those reported in the literature (49).

Fraction I. 3-Ethylhexane

Ten to twelve grams of this hydrocarbon per mole of

alcohol condensed were isolated. As its physical constants from several condensations agreed with each other but not with those reported in the literature, as mentioned above, a special column was built with the thought that Fraction I might possibly be composed of two or more isomers. This column was 98 x 0.8 cm in size and packed with 1/32 inch glass helices. Two separate fractions were collected upon distillation boiling two degrees apart. Infra-red spectra, Fig. 4, of the two fractions compared favorably with the spectra for 3-Ethylhexane showing them to be composed mainly of this hydrocarbon with apparently different degrees of impurity. The physical constants for the original fractions appear below.

Average Yield: 10-12%

BP_{746}: 115-116°C

n_D^{20} : 1.3980

D_4^{20} : 0.7052

M_R : Calc. 39.16 Obs. 39.02

Part D. The condensation of 2,4-Dimethyl-2-hexanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. Isobutane

This fraction was condensed in the carbon dioxide -

acetone cooled trap during the condensation. Repeated distillations freed the hydrocarbon of hydrogen chloride and benzene impurities and gave a constant boiling range. An Auschutz thermometer was used for recording its boiling temperature. The refractive index of the isobutane was taken on an ordinary Abbe type refractometer. Acetone cooled by solid carbon dioxide was forced back and forth through the prisms in such a manner as to keep the temperature as steady as possible at -25°C. Moisture was kept from the top and bottom prism surfaces by sealing in a piece of anhydrous calcium chloride with small plates of glass and ordinary stopcock grease. Several readings were taken and averaged.

Average Yield: 3.1%

BP : -10.2°C

n_D^{-25} : 1.3514

Fraction II. 2,4-Dimethylhexane

Five to seven grams of the saturated hydrocarbon per mole of alcohol condensed were isolated. Similar treatment for removal of traces of unsaturation was employed as with Fraction I, Part A. The physical constants are in close agreement with those reported in the literature (49).

Average Yield: 3.8%

BP_{745}: 109-109.5°C

n_D^{20} : 1.3970

D_4^{20} : 0.7012

M_R : Calc. 39.16 Obs. 39.08

This hydrocarbon was also identified by means of its infra-red spectra which is shown by Fig. 5.

Fraction III. Chloride - Alcohol

Six to eight grams of this fraction collected per mole of alcohol condensed contained a mixture of octyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction IV. 2-Methyl-2-phenylpropane

This fraction, like isobutane, resulted from the fragmentation of the alcohol during condensation. Its physical constants agreed with those reported in the literature (5). It was also identified by its acetamino derivative prepared according to the work of Ipatieff and Schmerling (52). Two ml. of the t-butylbenzene were placed in a test tube and 5 ml. of mixed acid (50% conc. HNO_3 - 50% conc. H_2SO_4) were slowly added to the alkyl benzene with shaking. After allowing to cool, the nitration product was poured on cracked ice, extracted with ether several times, washed with water and then the ether evaporated off. The residue was allowed to cool and then a few ml. of alcohol were added, 5 g of granulated tin and 5 ml. of conc. HCl, a few drops at a time with stirring.

This was allowed to stand for 30 minutes to insure complete reduction of the nitro compound. The amine-$SnCl_2$-HCl complex was then decanted from the excess tin and the amine released from the complex with 40% sodium hydroxide. The amine was then extracted with ether, the ether washed with 10% K_2CO_3. The ether was then evaporated from the amine, allowed to cool and then 2 ml. of acetic anhydride added. The acetamino derivative crystallized almost immediately. It was recrystallized several times with 40% alcohol. White pearly plates, M.P. 169°C.

Average Yield: 1.3%

BP_{738}: 169-170°C

BP_{18} : 56.5-57°C

n_D^{20} : 1.4918

D_4^{20} : 0.8656

M_R : Calc. 44.79 Obs. 44.94

Fraction V. 2,4-Dimethyl-2-phenylhexane

This fraction was the expected condensation product. Its physical constants agree with those reported in the literature (1).

Average Yield: 19.6%

BP_3 : 69-71°C

n_D^{20} : 1.4920

D_4^{20} : 0.8718

M_R : Calc. 63.27 Obs. 63.50

Fraction VI. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 38.8 grams per mole of alcohol condensed.

Part E. The condensation of 2,5-Dimethyl-2-hexanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 2,5-Dimethylhexane

Six to eight grams of the saturated hydrocarbon per mole of alcohol condensed were isolated. Similar treatment for removal of traces of unsaturation was employed as with Fraction I, Part A. The physical constants are in close agreement with those reported in the literature (49).

Average Yield: 5.7%

BP_{736}: 107-108°C

n_D^{20} : 1.3930

D_4^{20} : 0.6952

M_R : Calc. 39.16 Obs. 39.14

This hydrocarbon was also identified by means of its infra-red spectra which is shown in Fig. 6.

Fraction II. Chloride - Alcohol

Seven to nine grams of this fraction collected per mole of alcohol condensed contained a mixture of octyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of

tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 2,5-Dimethyl-2-phenylhexane

This fraction was the expected condensation product. Its physical constants do not agree with those reported in the literature (20).

Average Yield: 21.5%

BP_{16} : 106-108°C

n_D^{20} : 1.4910

D_4^{20} : 0.8697

M_R : Calc. 63.27 Obs. 63.19

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 24.6 grams per mole of alcohol condensed.

Part F. The condensation of 2,4-Dimethyl-4-hexanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. Isobutane

This fraction resulted from the fragmentation of the alcohol. It was collected and purified in the same manner as Fraction I, Part D.

Average Yield: 4.6%

BP_{737}: -10.1°C

n_D^{-25} : 1.3517

Fraction II. 2,4-Dimethylhexane

Three to five grams of the saturated hydrocarbon per mole of alcohol condensed were isolated. Similar treatment for removal of traces of unsaturation was employed as with Fraction I, Part A. The physical constants are in close agreement with those reported in the literature (49).

Average Yield: 3.9%

BP_{750}: 108.5-109°C

n_D^{20} : 1.3962

D_4^{20} : 0.7012

M_R : Calc. 39.16 Obs. 39.10

This hydrocarbon was also identified by means of its infra-red spectra which is shown in Fig. 7.

Fraction III. Chloride - Alcohol

Eight to ten grams of this fraction collected per mole of alcohol condensed contained a mixture of octyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction IV. 2-Methyl-2-phenylpropane

This fraction, like isobutane, resulted from the fragmentation of the alcohol during condensation. Its physical constants agreed with those reported in the literature (5). It was also identified by its acetamino derivative prepared according to the work of Ipatieff

and Schmerling (52) and given under Fraction IV, Part D. White pearly plates, M.P. 169°C.

Average Yield: 2.2%

BP_{744}: 168.5-169°C

BP_{15} : 52.5-53°C

n_D^{20} : 1.4918

D_4^{20} : 0.8660

M_R : Calc. 44.79 Obs. 44.94

Fraction V. 2,4-Dimethyl-4-phenylhexane

This fraction was the expected condensation product. Its physical constants agree with those reported in the literature (50).

Average Yield: 19.17%

BP_1 : 69.5-70°C

n_D^{20} : 1.4920

D_4^{20} : 0.8731

M_R : Calc. 63.27 Obs. 63.47

Fraction VI. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 77.2 grams per mole of alcohol condensed.

Part G. The condensation of 2-Methyl-2-hexanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 2-Methylhexane

The above hydrocarbon was not isolated in quantitative

amounts due to the fact that it was present in such a small amount as compared to the large excess of benzene. Although it boils approximately ten degrees above benzene it was not possible, with the still used, to separate enough for purification purposes. It was therefore necessary to fractionally freeze the hydrocarbon out by placing in the refrigerator in a beaker for one-half hour periods, decanting the liquid off each time until the concentrate would not freeze when placed in the freezing compartment. It was then treated with cold concentrated H_2SO_4 to remove traces of unsaturation, washed with ten percent Na_2CO_3, distilled water and then dried over anhydrous K_2CO_3. Fractional distillation gave four grams of the pure hydrocarbon from 2.3 moles of alcohol condensed. Its physical constants were in close agreement with those reported in the literature (49).

BP_{750} : 89.5°C

n_D^{20} : 1.3855

D_4^{20} : 0.6790

M_R : Calc. 34.53 Obs. 35.26

The hydrocarbon was also identified by means of its infra-red spectra which is shown in Fig. 8.

Fraction II. Chloride - Alcohol

Four to five grams of this fraction collected per mole of alcohol condensed contained a mixture of heptyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of

tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 2-Methyl-2-phenylhexane

This fraction was the expected condensation product. Its physical constants agree with those reported in the literature (1).

Average Yield: 31.3%

BP_{18} : 96-97°C

n_D^{20} : 1.4925

D_4^{20} : 0.8714

M_R : Calc. 58.65 Obs. 58.80

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 35.5 grams per mole of alcohol condensed.

Part H. The condensation of 3-Methyl-3-hexanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 3-Methylhexane

Four grams of the above hydrocarbon were isolated in the same manner as Fraction I, Part G, from 2.22 moles of alcohol condensed. Its physical constants were in close agreement with those reported in the literature (49).

BP_{733} : 89.5-90°C

n_D^{20} : 1.3895

D_4^{20} : 0.6890

M_R : Calc. 34.53 Obs. 34.86

The hydrocarbon was also identified by means of its infra-red spectra which is shown by Fig. 9.

Fraction II. Chloride - Alcohol

Six to eight grams of this fraction collected per mole of alcohol condensed contained a mixture of heptyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 3-Methyl-3-phenylhexane

This fraction was the expected condensation product. Its physical constants agree with those reported in the literature (1).

Average Yield: 30.0%

BP_{14} : 99-101°C

n_D^{20} : 1.4960

D_4^{20} : 0.8786

M_R : Calc. 58.65 Obs. 58.72

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 34.7 grams per mole of alcohol condensed.

Part J. The condensation of 3-Ethyl-3-pentanol with

benzene in the presence of anhydrous aluminum chloride.

Fraction I. 3-Ethylpentane

Three and one-half grams of the above hydrocarbon were isolated in the same manner as Fraction I, Part G from 1.63 moles of alcohol condensed. Its physical constants were in close agreement with those reported in the literature (49).

BP_{741} : 92.5-93°C

n_D^{20} : 1.3940

D_4^{20} : 0.6995

M_R : Calc. 34.53 Obs. 34.73

The hydrocarbon was also identified by means of its infra-red spectra which is shown by Fig. 10.

Fraction II. Chloride - Alcohol

Three to four grams of this fraction collected per mole of alcohol condensed contained a mixture of heptyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 3-Ethyl-3-phenylpentane

This fraction was the expected condensation product. Its physical constants agree with those reported in the literature (1).

Average Yield: 33.2%

BP_1 : 67-68°C

n_D^{20} : 1.4970

D_4^{20} : 0.8799

M_R : Calc. 58.65 Obs. 58.77

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 25.4 grams per mole of alcohol condensed.

Part K. The condensation of 2,4-Dimethyl-2-pentanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. Isobutane

This fraction resulted from the fragmentation of the alcohol. It was collected and purified in the same manner as Fraction I, Part D.

Average Yield: 2.2%

BP_{733}: -10.4°C

n_D^{-25} : 1.3516

Fraction II. 2,4-Dimethylpentane

The hydrocarbon could not be isolated as it boils at the same temperature as benzene.

Fraction III. Chloride - Alcohol

Five to six grams of this fraction collected contained a mixture of heptyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction IV. 2-Methyl-2-phenylpropane

This fraction like isobutane, resulted from the fragmentation of the alcohol during condensation. Its physical constants agreed with those reported in the literature (5). It was also identified by its acetamino derivative prepared according to the work of Ipatieff and Schmerling (52) and given under Fraction IV, Part D. White pearly plates, M.P. 168.5°C.

Average Yield: 2.8%

BP_{734}: 168-168.5°C

BP_{18} : 56.5-57°C

n_D^{20} : 1.4918

D_4^{20} : 0.8656

M_R : Calc. 44.79 Obs. 44.96

Fraction V. 2,4-Dimethyl-2-phenylpentane

This fraction was the expected condensation product. Its physical constants do not agree with those reported in the literature (1).

Average Yield: 22.2%

BP_{12} : 82.5-83°C

n_D^{20} : 1.4912

D_4^{20} : 0.8706

M_R : Calc. 58.65 Obs. 58.77

Fraction VI. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 44.4 grams per mole of alcohol condensed.

Part L. The condensation of 2-Methyl-2-pentanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 2-Methylpentane

Five to seven grams of the saturated hydrocarbon per mole of alcohol condensed were isolated. Similar treatment for removal of traces of unsaturation was employed as with Fraction I, Part A. The physical constants are in close agreement with those reported in the literature (49).

Average Yield: 7.0%

BP_{742}: 60-60.5°C

n_D^{20} : 1.3720

D_4^{20} : 0.6558

M_R : Calc. 29.91 Obs. 30.18

This hydrocarbon was also identified by means of its infra-red spectra which is shown by Fig. 11.

Fraction II. Chloride - Alcohol

Three to four grams of this fraction collected per mole of alcohol condensed contained a mixture of hexyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 2-Methyl-2-phenylpentane

This fraction was the expected condensation product. Its physical constants agree with those reported in the

literature (1).

Average Yield: 32.7%

BP_{14} : 84-85°C

n_D^{20} : 1.4945

D_4^{20} : 0.8725

M_R : Calc. 54.03 Obs. 54.05

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 21.2 grams per mole of alcohol condensed.

Part M. The condensation of 3-Methyl-3-pentanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 3-Methylpentane

Eight to nine grams of the saturated hydrocarbon per mole of alcohol condensed were isolated. Similar treatment for removal of traces of unsaturation was employed as with Fraction I, Part A. The physical constants are in close agreement with those reported in the literature (49).

Average Yield: 10.2%

BP_{18} : 83-84°C

n_D^{20} : 1.3780

D_4^{20} : 0.6655

M_R : Calc. 29.91 Obs. 30.00

This hydrocarbon was also identified by means of its infra-red spectra which is shown by Fig. 12.

Fraction II. Chloride - Alcohol

Three to four grams of this fraction collected per mole of alcohol condensed contained a mixture of hexyl chloride and uncondensed alcohol and was not separated or purified. Its odor was camphor-like, characteristic of tertiary alcohols, and it gave a heavy chloride test with 5 percent alcoholic silver nitrate.

Fraction III. 3-Methyl-3-phenylpentane

This fraction was the expected condensation product. Its physical constants agree with those reported in the literature (1).

Average Yield: 35.9%

BP_{18} : 83-84°C

n_D^{20} : 1.4960

D_4^{20} : 0.8785

M_R : Calc. 54.03 Obs. 53.91

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 19.5 grams per mole of alcohol condensed.

Part N. The condensation of 2-Methyl-2-butanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 2-Methylbutane (isopentane)

Three and one-half grams of this hydrocarbon were isolated from three moles of tertiary amyl alcohol. It

was purified by distillation during which it was passed through cold concentrated sulfuric acid to remove any unsaturation present. Its physical constants agreed with those reported in the literature (53).

Average Yield: 1.8%

BP_{742}: 26.5-28°C

n_D^{20} : 1.3552

D_4^{20} : 0.6197

M_R : Calc. 25.29 Obs. 25.32

Fraction II. Chloride - Alcohol

Two to three grams of this were isolated per mole of alcohol condensed. It was not separated or purified. It gave a heavy chloride test with 5 percent alcoholic cilver nitrate, and its odor was characteristic of that of the original alcohol.

Fraction III. 2-Methyl-2-phenylbutane

This was the expected condensation product. Its physical constants agree with those reported in the literature (5).

Average Yield: 40%

BP_{742}: 189-190°C

BP_{18} : 66.5-67°C

n_D^{20} : 1.4940

D_4^{20} : 0.8735

M_R : Calc. 49.40 Obs. 49.40

Fraction IV. Dark viscous residue

This fraction was that collected above the alkyl benzene and amounted to 27 grams from a three mole run. It undoubtedly consists of some di-tert-amybenzene and unsaturated polymeric material as it gave a positive test for unsaturation.

Part O. The condensation of 2-Methyl-2-propanol with benzene in the presence of anhydrous aluminum chloride.

Fraction I. 2-Methylpropane (isobutane)

Four grams of this hydrocarbon were isolated and purified in the same manner as Fraction I, Part D.

Average Yield: 2.22%

BP_{750}: -10.5°C

n_D^{-25} : 1.3516

Fraction II. Chloride - Alcohol

One to two grams of this fraction were isolated per mole of alcohol condensed. It was not separated or purified. It gave a heavy chloride test with 5 percent alcoholic silver nitrate, and its odor was characteristic of that of the original alcohol.

Fraction III. 2-Methyl-2-phenylpropane

This was the expected condensation product. Its physical constants agree with those reported in the literature (5).

Average Yield: 55%

BP_{744}: 168.5°C

BP_{18} : 56-57°C

n_D^{20} : 1.4918

D_4^{20} : 0.8656

M_R : Calc. 44.79 Obs. 44.94

Fraction IV. Not Identified

Yield: 3.5 grams

BP_{738}: 219.8°C

n_D^{20} : 1.4928

D_4^{20} : 0.8691

M.W. : 180

Dinitro derivative: M.P. 164-165°C

% N Calc. 10.37
Obs. 10.81

Oxidation: negative

Fraction V. 1,4-Di-tert-butylbenzene

Seven grams of the white crystalline solid were isolated from three moles of alcohol condensed. The hydrocarbon was recrystallized from 95% ethyl alcohol. White rhombic needles.

Yield: 1.2%

BP_{20} : 115-116°C

M.P. : 76°C

2,6-Dinitro-di-tert-butylbenzene: M.P. 191-192°C

Residue: 6 grams

EXPERIMENTAL - PART II

Preparation of Derivatives

3,5-Dinitrobenzoates of the Alcohols

The above derivatives were prepared according to the procedure as outlined in Cheronis and Entriken on the preparation of tertiary alcohol derivatives, except for slight modification. One-half gram of alcohol was placed in an eight inch test tube along with a large excess of 3,5-Dinitrobenzoyl chloride and dry pyridine. This was then placed on the steam bath for four to six hours, cooled to room temperature, then cooled in an ice bath. Five percent sulfuric acid was then added until the odor of pyridine was discharged and a faint odor of alcohol could be detected. The voluminous precipitate was then filtered, washed with water several times and then placed in a beaker. This precipitate was then treated with ten percent sodium carbonate to release the pyridine from its salt, filtered and the remaining precipitate recrystallized several times from ligroin.

Acetamino derivative of tert-Butylbenzene

The procedure for the preparation of the above derivative is outlined on p. 37.

Dinitro Alkylbenzenes

The above derivatives were prepared both with mixed

acid and fuming nitric acid Sp. Gr. 1.5 approx. The procedure using mixed acid was carried out at room temperature by allowing the reactants to stand for several hours. One-half gram of alkylbenzene was slowly added to a mixture of four c.c. of conc. sulfuric acid Sp. Gr. 1.84 and four c.c. of conc. nitric acid 70%, with shaking and cooling. This mixture was then allowed to stand for several hours, poured on ice, filtered, washed with distilled water and recrystallized several times from 95% ethyl alcohol.

The procedure using fuming nitric acid was carried out at 0°C. Twenty-five c.c. of fuming nitric acid were placed in a small Erlenmeyer flask and cooled to 0°C in an ice bath. The alkylbenzene was then added drop by drop with shaking. After addition was complete the reaction mix was then placed in the refrigerator for 24-48 hours at which time crystals were will formed. These crystals were then filtered after first pouring on cracked ice, washed with distilled water and recrystallized several times from 95% ethyl alcohol.

Identification of Fraction IV, Part O.

The physical constants for this fraction, p. 54, agree fairly well with those reported for p-t-butyl-isopropylbenzene (50). An attempt was thus made to prove its identity by means of its dinitro derivative as reported by Barbier (54). The dinitro derivative of Fraction IV was prepared using both mixed acid and fuming nitric as outlined above. Light yellow plates were formed which

melted at 164-165°C from both methods of preparation. Nitrogen analysis by micro Dumas method showed the presence of two nitro groups. This melting point does not agree with that reported in the literature (54), thus it was necessary to prepare p-tert-butyl-isopropylbenzene, nitrate it and check the melting point of the dinitro derivative. The hydrocarbon was prepared according to the procedure as outlined by Barbier (54) using isopropylbenzene (cumene), tert-butyl alcohol and concentrated sulfuric acid. This was then nitrated and its melting point determined as 212-214°C. In order to prove that the product was the para isomer, it was oxidized with boiling 20% nitric acid and the tert-butylbenzoic acid isolated. This acid melted at 164°C, which corresponds to that reported for p-tert-butylbenzoic acid (55).

From the calculation of Fraction IV's molecular weight by nitrogen analysis of its dinitro derivative it was thought that it might be the tert-butyl-ethylbenzene isomer. p-tert-Butyl-ethylbenzene was thus prepared and nitrated. Its dinitro derivative had a melting point of 94-95°C. Oxidation gave p-tert-butylbenzoic acid.

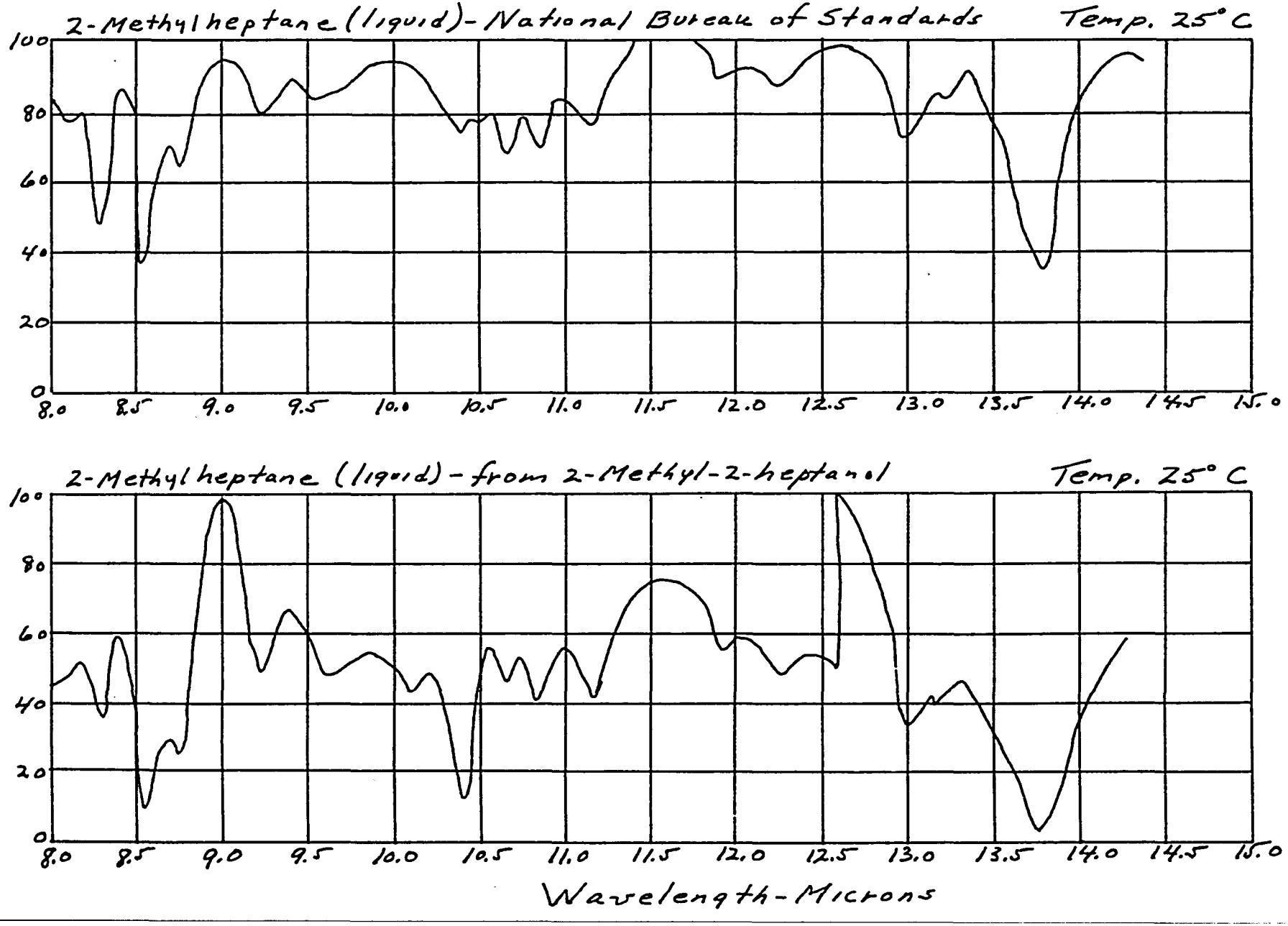
The next step in the identification of Fraction IV was its oxidation in order to determine the position of its alkyl groups on the ring. Oxidation using 20% boiling nitric acid failed. This might indicate that either Fraction IV was a mixture, of which a di-tert-butylbenzene isomer was predominant, or that it is an indan isomer formed by cyclization of an ortho dialkylbenzene through the

action of aluminum chloride. To eliminate the former thought, p-di-tert-butylbenzene was nitrated to check its melting point with that reported in the literature. The derivative melted at 190-191°C, which agreed with that reported by Boedtker (56).

From the foregoing results one is able to conclude that Fraction IV, Part O is an isomer whose molecular weight corresponds to $C_{12}H_{18}$, as calculated from its pure dinitro derivative, contains an aromatic nucleus which can be nitrated and possibly a carbocyclic ring which cannot be oxidized. This type of structure could be formed by elimination of methyl groups from the di-tert-butylbenzene isomer to form either ethyl or isopropyl-tert-butylbenzene or/and an indan isomer by cyclization. The formation of a gas collected in the nitrometer during the course of the reaction which would not condense but burned with a blue flame was evidence of the formation of methane.

Infrared Absorption Spectrogram

Figure 2.



Infrared Absorption Spectrogram

Figure 3.

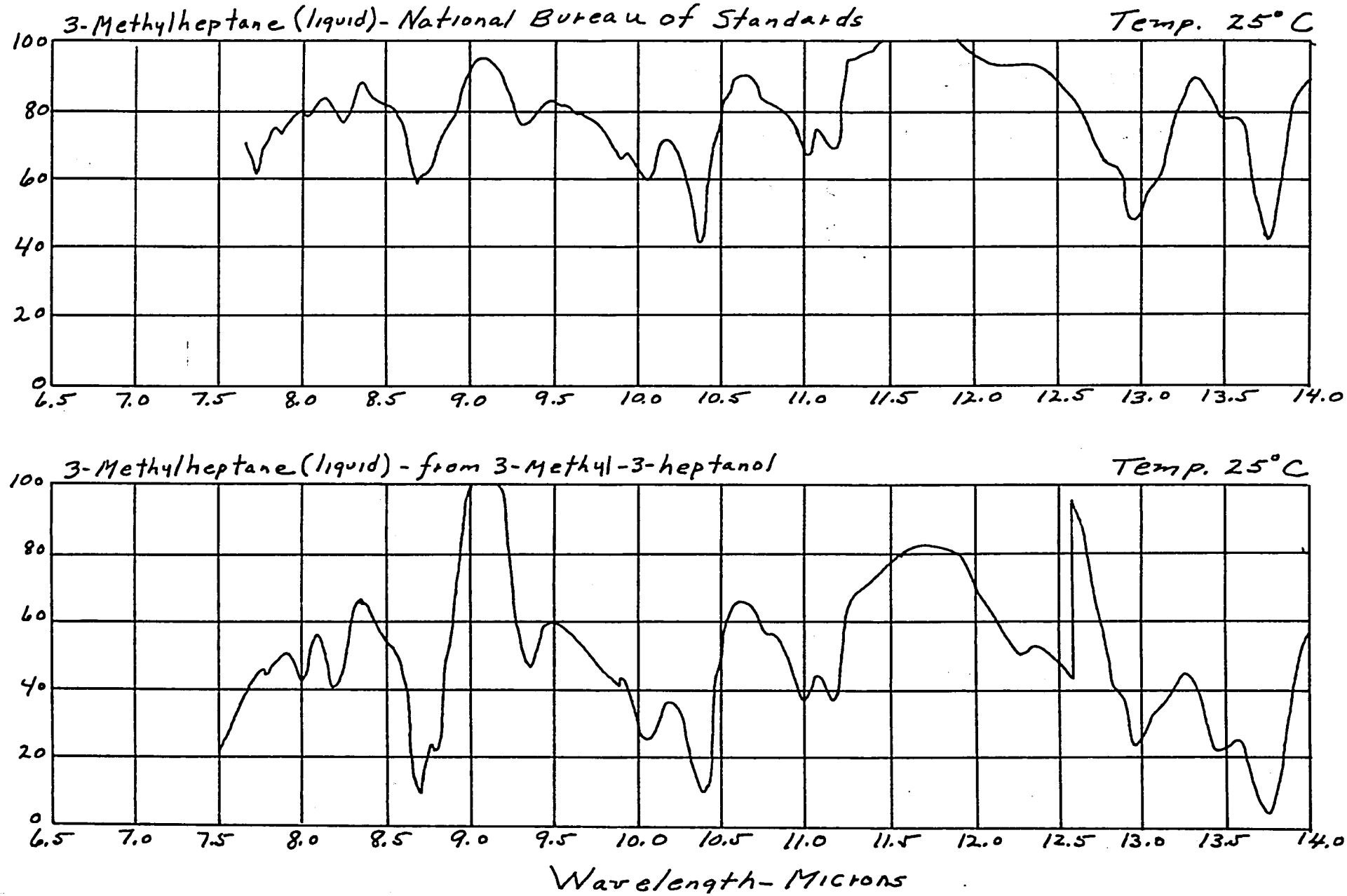


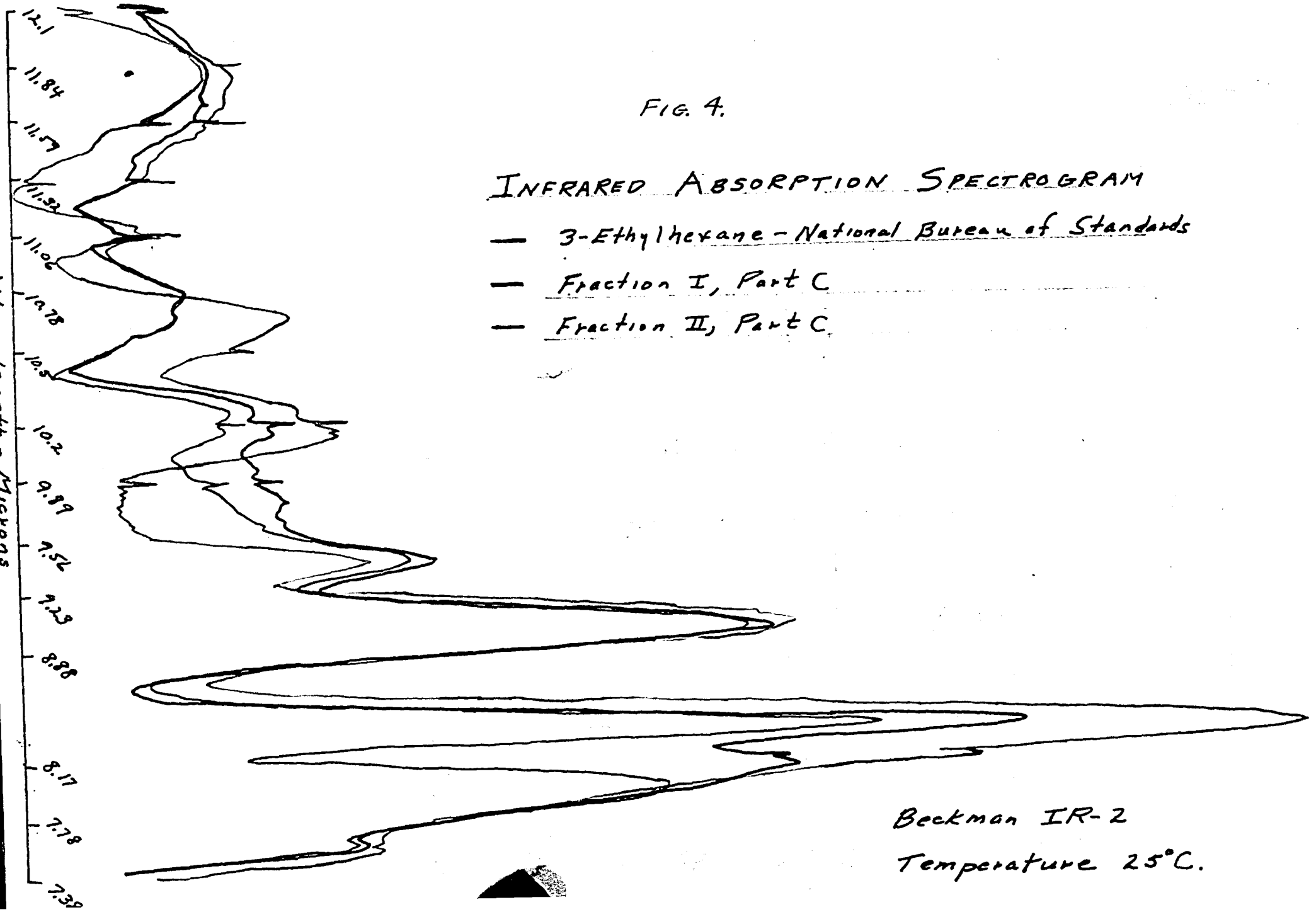
FIG. 4.

INFRARED ABSORPTION SPECTROGRAM

— 3-Ethylhexane - National Bureau of Standards

— Fraction I, Part C

— Fraction II, Part C

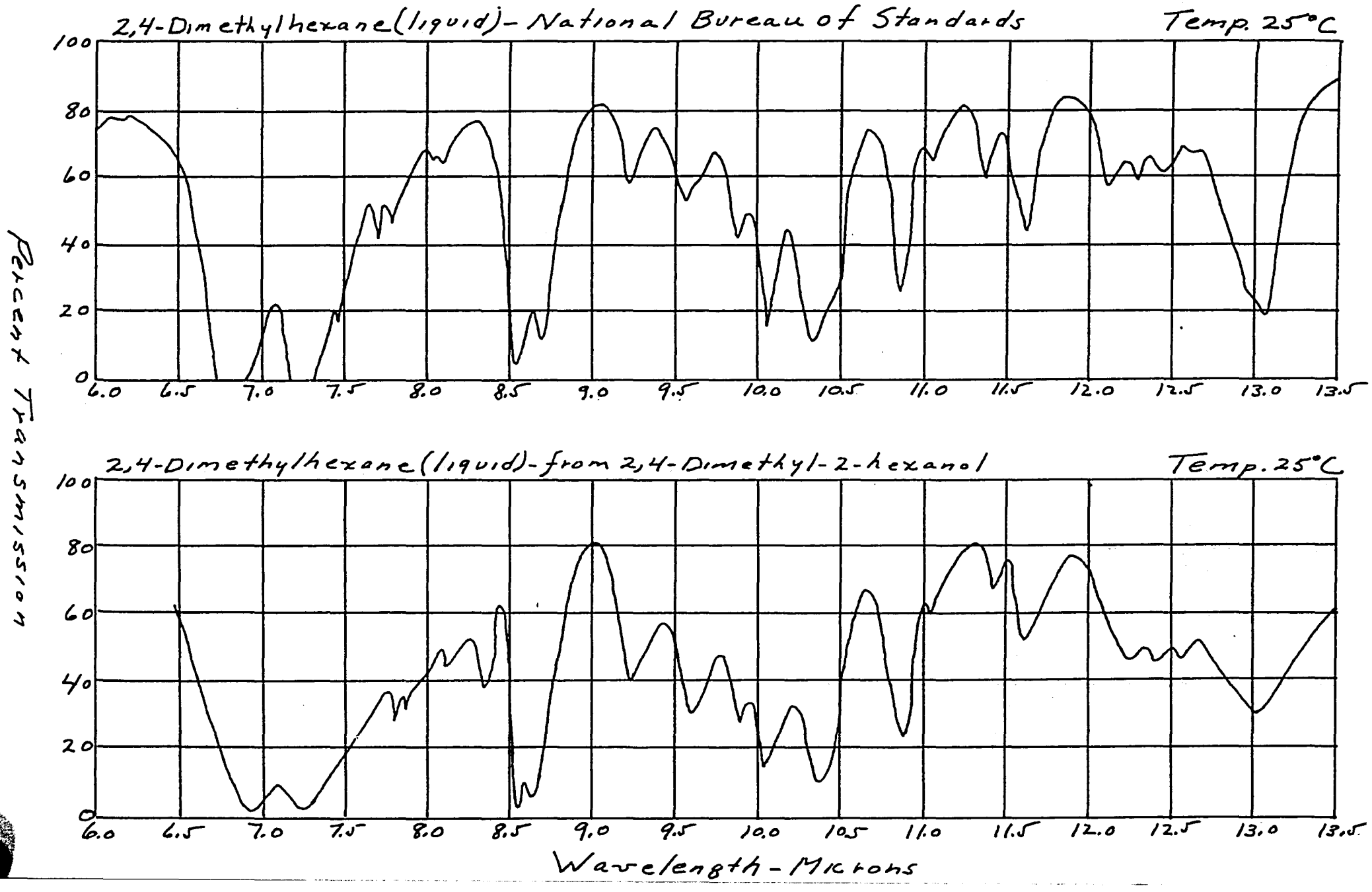


Beckman IR-2

Temperature 25°C.

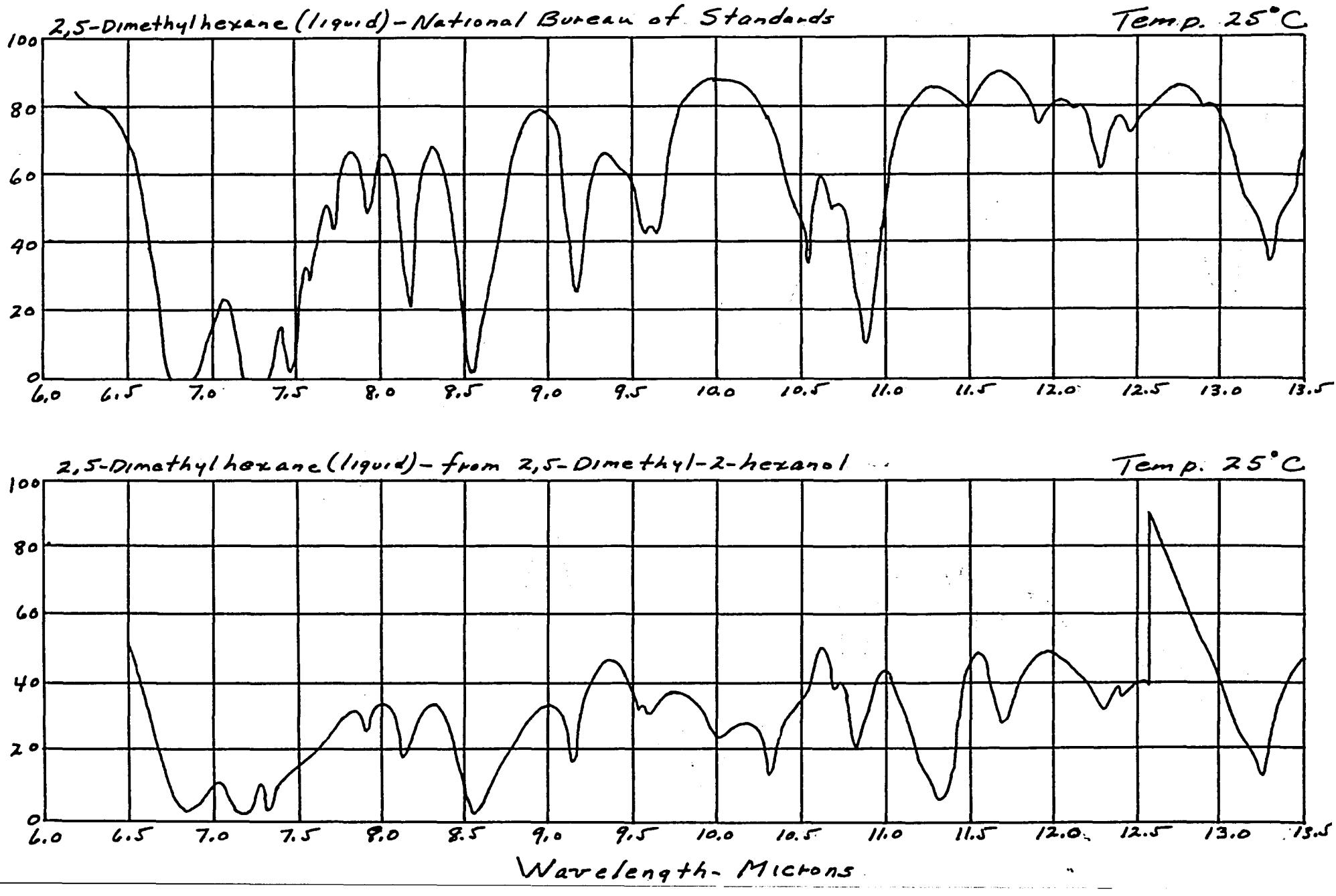
Infrared Absorption Spectrogram

Figure 5.



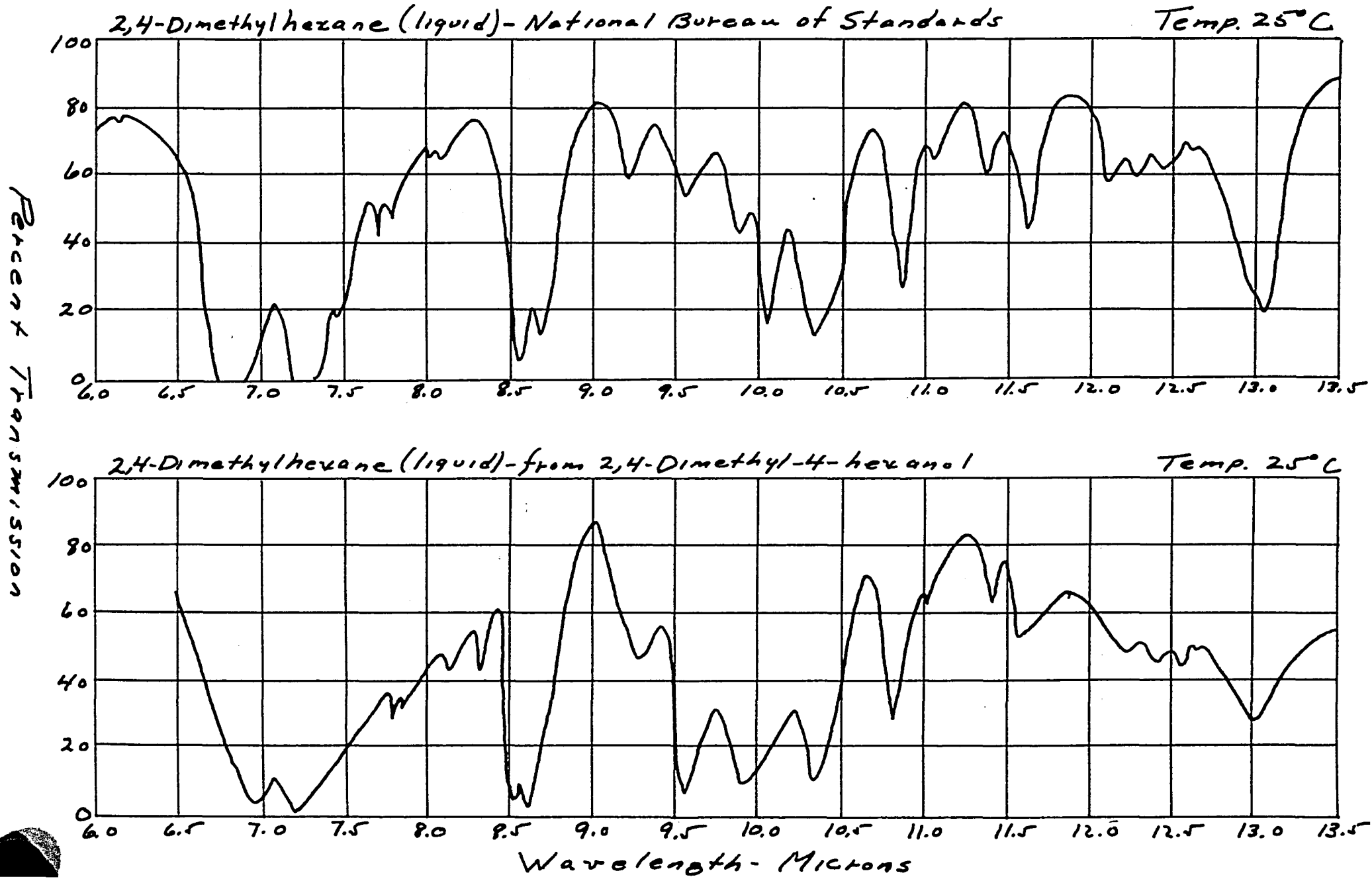
Infrared Absorption Spectrogram

Figure 6.



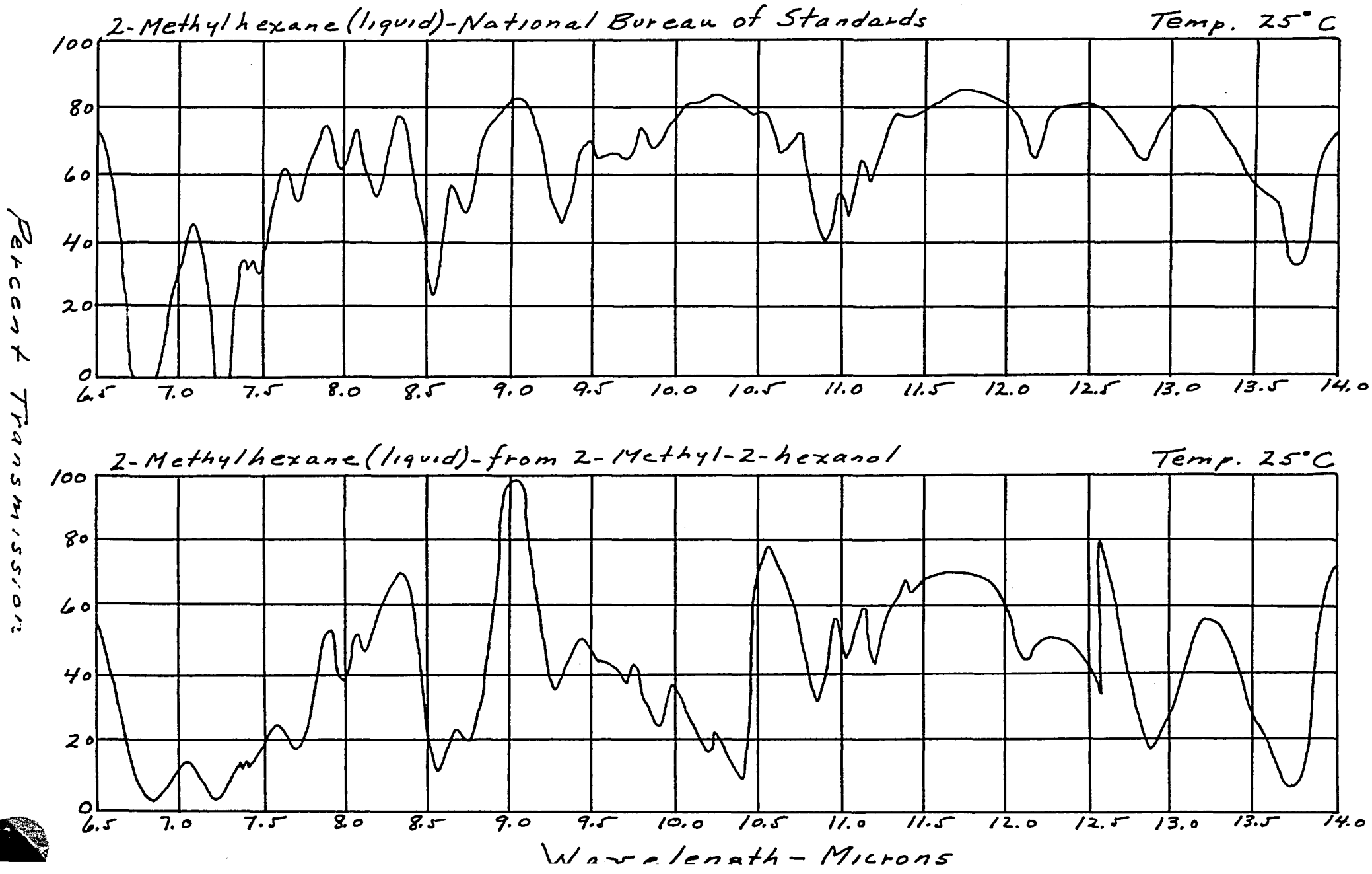
Infrared Absorption Spectrogram

Figure 7.



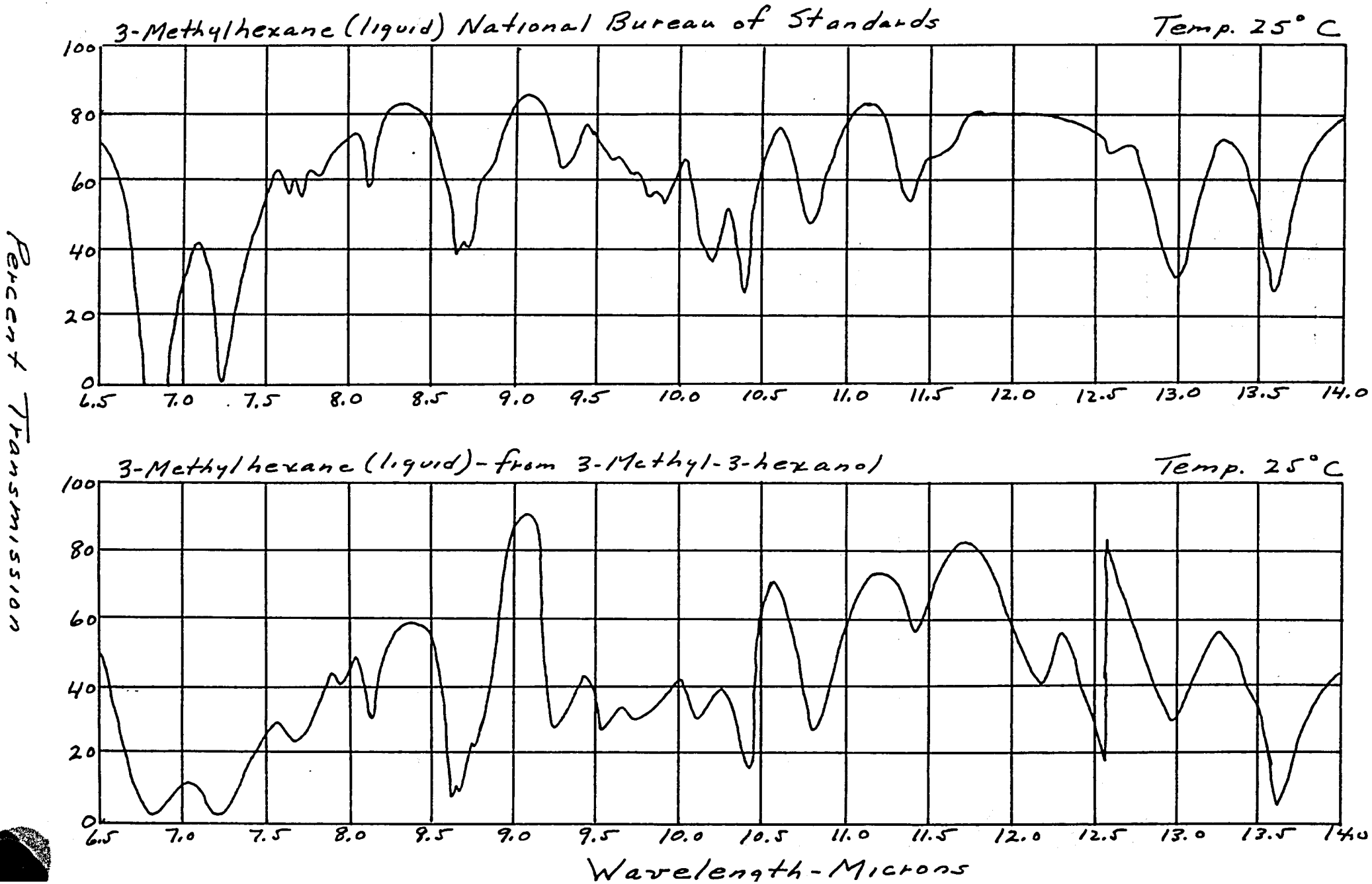
Infrared Absorption Spectrogram

Figure 8.



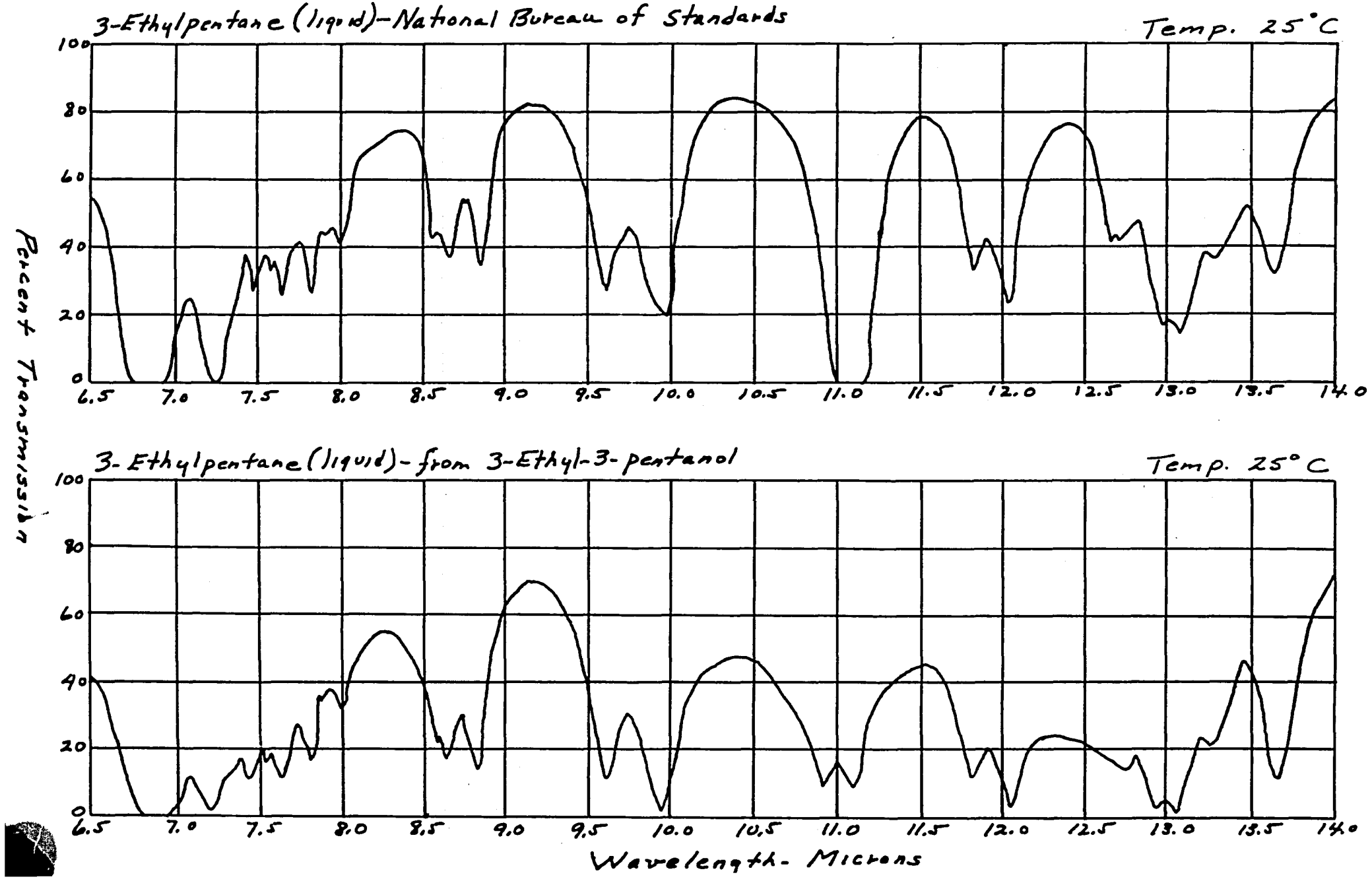
Infrared Absorption Spectrogram

Figure 9.



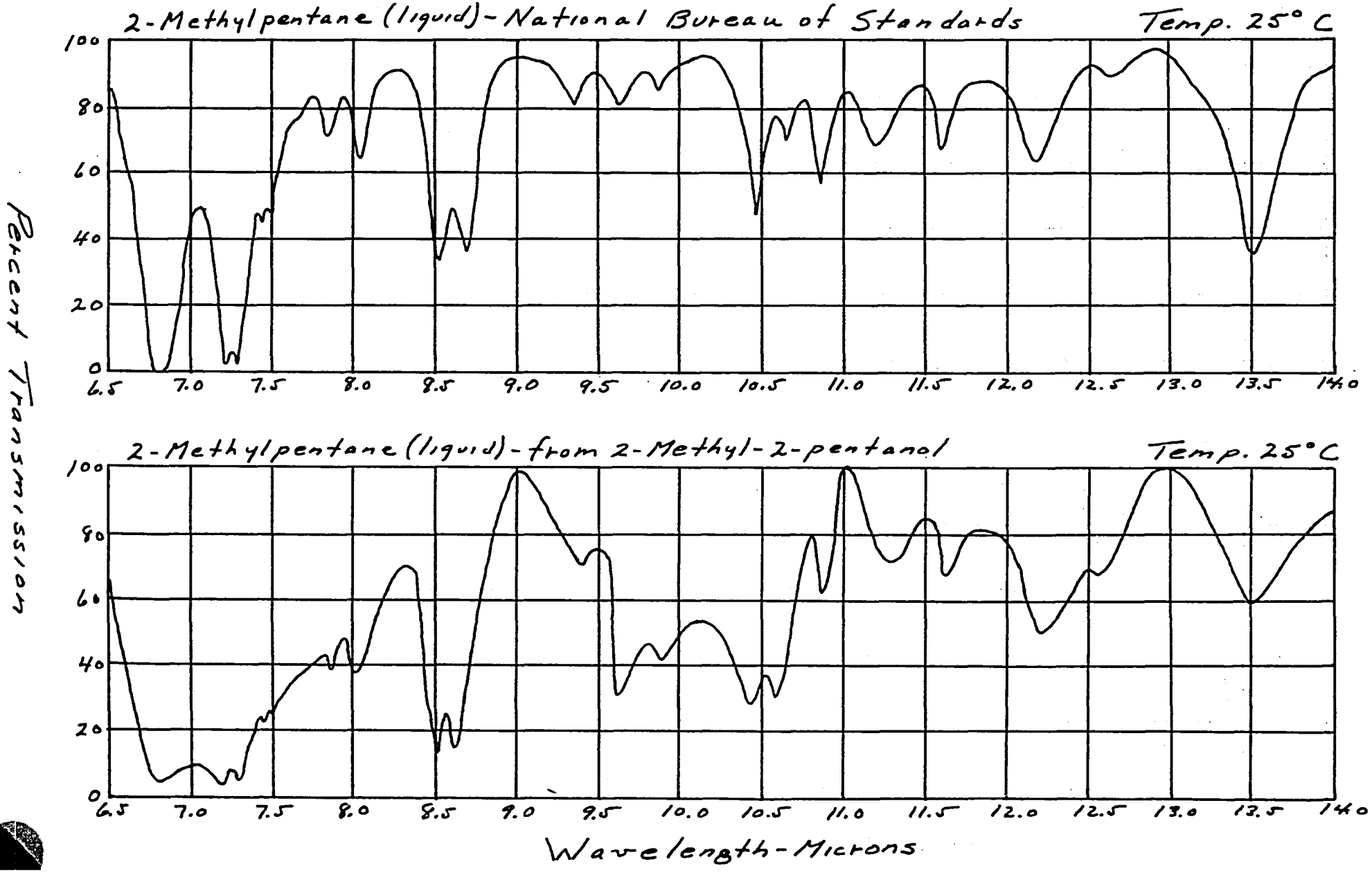
Infrared Absorption Spectrogram

Figure 10.



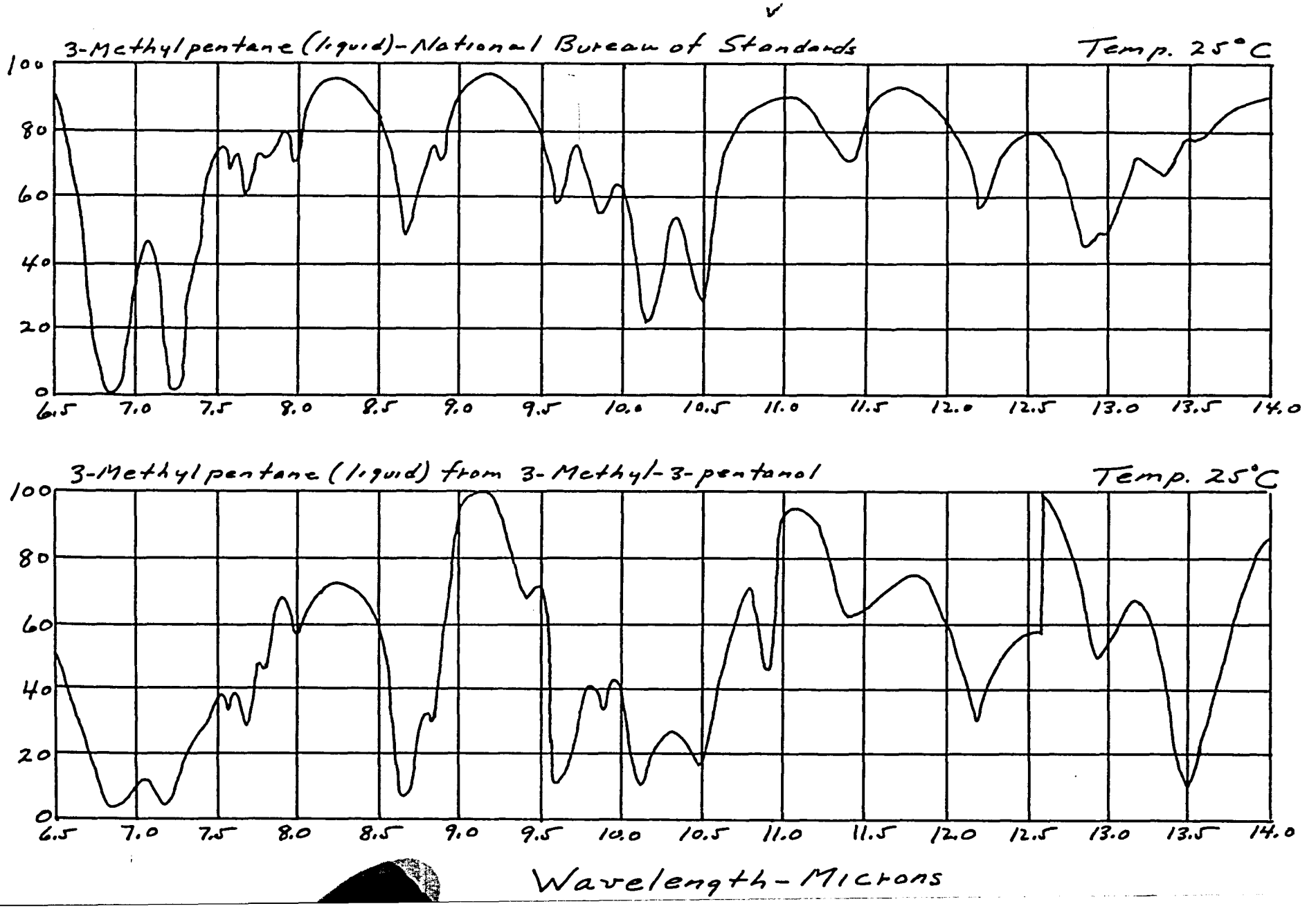
Infrared Absorption Spectrogram

Figure 11.



Infrared Absorption Spectrogram

Figure 12.



Alcohol Condensed	3,5-Dinitrobenzoate M.P. °C.	3,5-Dinitrobenzoate % N Calc.	% N Obs.	Moles Condensed	Moles $AlCl_3$ per Mole Alcohol	Isobutane
2-Methyl-2-heptanol	43-44	8.63	8.40	1.40	0.5	None
3-Methyl-3-heptanol	53-54	8.63	8.88	2.17	0.5	None
3-Ethyl-3-hexanol	62-63	8.63	8.74	0.73	0.5	None
2,4-Dimethyl-2-hexanol	48.5-49.5	8.63	8.69	1.94	0.5	3.1%
2,5-Dimethyl-2-hexanol	61-62	8.63	8.95	1.22	0.5	None
2,4-Dimethyl-4-hexanol	52-53	8.63	8.93	1.88	0.5	4.6%
2-Methyl-2-hexanol	53-54	9.02	8.98	2.3	0.5	None

Alkane Yield	tert-Butyl-benzene Yield	Alkyl Benzene Yield	Residue (above alkyl benzene) Yield
8.8%	None	27.4%	52g
9.5%	None	24.2%	60g
14.3%	None	25.1%	23.5g
3.8%	1.3%	19.6%	75.5g
5.7%	None	21.5%	30g
3.9%	2.2%	19.2%	77.2g
Not quantitative	None	31.3%	81.5g

Alcohol Condensed	3,5-Dinitrobenzoate M.P. °C.	3,5-Dinitrobenzoate % N Calc.	3,5-Dinitrobenzoate % N Obs.	Moles Condensed	Moles $AlCl_3$ per Mole Alcohol	Isobutane
3-Methyl-3-hexanol	43-44	9.02	9.54	2.22	0.5	None
3-Ethyl-3-pentanol	118-119	9.02	9.17	1.63	0.5	None
2,4-Dimethyl-2-pentanol	69-70	9.02	9.07	2.70	0.5	2.2%
2-Methyl-2-pentanol	71-72	In literature		2.0	0.5	None
3-Methyl-3-pentanol	95.5-96.5	In literature		2.0	0.5	None
2-Methyl-2-butanol	No derivative made			3.0	0.5	None
2-Methyl-2-propanol	No derivative made			3.0	0.5	2.22%

Alkane Yield	tert-Butyl-benzene Yield	Alkyl Benzene Yield	Residue (above alkyl benzene) Yield
Not Quantitative	None	30.0%	77g
Not Quantitative	None	33.2%	41.5g
Not isolated	2.8%	22.2%	120g
7%	None	32.7%	42.5g
10.2%	None	35.9%	39g
1.8%	None	40%	27g
2.22%	55%	55%	1.14% p-Di-tert-butylbenzene

DISCUSSION

In 1945, Dr. G. L. Goerner of this laboratory condensed 3-Ethyl-3-hexanol with benzene in the presence of anhydrous aluminum chloride and isolated a fraction which he tentatively identified as being a saturated aliphatic hydrocarbon formed apparently through the reduction of the alcohol. As the physical constants of this fraction did not agree with those reported in the literature (49) it was not definitely identified. This finding led to the problem of this thesis, and the author found through spectroscopic studies that the hydrocarbon fraction isolated from the above condensation consisted mainly of 3-Ethylhexane apparently contaminated with another isomer formed by action of the aluminum chloride.

During the preparation of the alcohols used in the condensations, the importance of selecting simple Grignard reagents, where more than one possibility exists, was brought out. For example, the preparation of 2,4-Dimethyl--4-hexanol may require either ethyl magnesium bromide or isobutyl magnesium bromide to react with methyl isobutyl ketone and methyl ethyl ketone respectively. When the former is used a yield of 70% is obtained whereas only a yield of 21% is obtained using the latter procedure. Another example is the preparation of 2,4-Dimethyl-2-pentanol from isobutyl magnesium bromide and acetone (45) giving a yield of 30%, whereas the author obtained an 89%

yield of the carbinol using methyl magnesium bromide and methyl isobutyl ketone. Apparently the structure of the ketone used is of little significance as to yield, as acetone was used in all of the following preparations.

2,4-Dimethyl-2-hexanol	act-amyl MgBr - Acetone	24%
2-Methyl-2-heptanol	n-amyl MgBr - Acetone	54%
2,4-Dimethyl-2-pentanol	iso-butyl MgBr - Acetone	30%
2-Methyl-2-pentanol	n-butyl MgBr - Acetone	67%

Also examples in which methyl ethyl ketone was employed are shown below.

2,4-Dimethyl-4-hexanol	iso-butyl MgBr-methyl ethyl ketone	21%
3-Methyl-3-heptanol	n-butyl MgBr-methyl ethyl ketone	68%

The theoretical significance of the above phenomena has been studied by several investigators among whom Noller (57) has shown that solutions of di-isobutyl magnesium, which were practically halogen free, reduced benzophenone to benzhydrol as well as the original Grignard reagent containing halogen. In connection with this, he has also shown that the Grignard reagent prepared from isobutyl bromide at a concentration of about 1.3 molar, exists to the extent of 75% in the form of diisobutyl magnesium. Noller and Hilmer (58) have also shown that the amount of this reduction increases with the increasing dialkyl magnesium content of the solution but is not proportional to the amount of dialkyl magnesium present. The dialkyl magnesium present in Grignard solutions appears to be influenced more by the structure than the molecular weight of the alkyl radical. Other competing side reactions are

pinacol formation, enolization, condensation and coupling, all apparently concerned with the structure of the alkyl group of the Grignard reagent.

Whitmore (33) has observed that catalysts such as aluminum chloride cause molecules to rearrange by methyl group migrations and in 1916 Boedtker and Halse (30) noticed rupture of the molecule with aluminum chloride as catalysts. Since this time Huston and co-workers have shown that whenever tertiary alcohols exhibiting methyl groups on the alpha carbon atom are condensed with benzene in the presence of aluminum chloride, methyl group migration takes place followed by fragmentation. Also in all highly branched alcohols one of the products of condensation is the low energy tertiary butylbenzene and more recently found (5) isobutane. In view of the above phenomena it was thought that alcohols selected for this problem should be all possible structures in which all alkyl groups attached to carbinol carbon are primary. This would minimize fragmentation allowing a better study of the reducing phenomena. Also it would show if branching on the alpha carbon atom was a prerequisite for fragmentation or if alcohols with branching on the β-carbon atom would fragment and if so, where, in relation to the positive carbon, formed by the electrophilic attack of the aluminum chloride on the alcohol. In consideration of the molecular structure of the non-branched alcohols condensed i.e., 2-Methyl-2-heptanol, it would

hardly be expected that any fragmentation or rearrangement would take place as they are all of a relatively low energy level, and the chance of weakening any bond by electron concentration would not be very great, as would be the case where branching exists on either or both the α - and β - carbon atoms. It was shown that branching on the γ - carbon atom is apparently too far removed from the electron deficient carbon to cause fragmentation.

The ionic mechanism of Price (26), as already discussed in the theoretical portion, has gained the most favor as a means whereby direct alkylation, methyl group migration and fragmentation can be satisfactorily explained. On the basis of his theory, the carbonium ion is formed by attack of the electrophilic agent, aluminum chloride, on alcohol, alkyl halide, olefin, or alkyl benzene. The electron deficient cation then receives its pair from the double bond of the benzene ring, analogous to halogenation in which the halogen cation completes its octet by association with a pair of electrons from the double bond of the aromatic nucleus. Showing the formation of the carbonium ion from the alcohol, the reaction proceeds in the following steps.

1. $(R)_3\,C:\ddot{O}:H \;+\; \begin{matrix}\ddot{Cl}\\ \ddot{Al}:Cl\\ \ddot{Cl}\end{matrix} \longrightarrow (R)_3\,C:\overset{H}{\ddot{O}}:\begin{matrix}\ddot{Cl}\\ \ddot{Al}:Cl\\ \ddot{Cl}\end{matrix}$

2. $(R)_3C:\overset{H}{\ddot{O}}:\begin{matrix}\ddot{Cl}\\ \ddot{Al}:Cl\\ \ddot{Cl}\end{matrix} \longrightarrow (R)_3C^{+} \;+\; Al(OH)Cl_3^{-}$

The carbonium ion is then able to stabilize itself in one of two ways: Either by association with a pair of electrons from the benzene ring with formation of alkyl benzene as shown in step 3,

3. $(R)_3C^+ + \bigcirc \longrightarrow (R)_3C: \begin{matrix} H \\ \bigcirc \\ H \end{matrix} \longrightarrow (R)_3C\bigcirc + H^+$

or by loss of a proton with formation of olefin which in turn may condense with benzene or add hydrogen chloride which in turn may condense. All of these apparent intermediates, except of course the cation, have been isolated from the reaction.

In the case of alcohols in which there is branching on the β-carbon atom the mechanism is a little more complex and compounds of lower molecular weight are isolated. The reaction may proceed in the following manner.

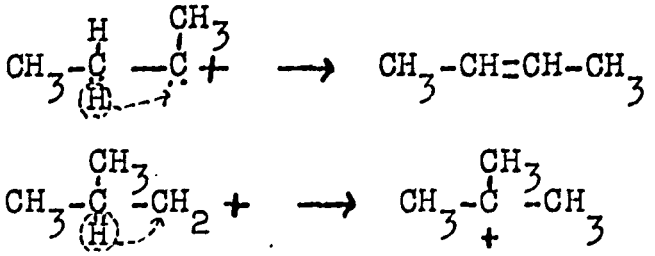
$$CH_3-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_3 + AlCl_3 \longrightarrow CH_3-CH_2-\overset{CH_3}{\overset{+}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_3 + Al(OH)Cl_3^-$$

$$CH_3-CH_2-\overset{CH_3}{\overset{+}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_3 \longrightarrow CH_3-CH_2-\overset{CH_3}{C}=CH-\overset{CH_3}{\underset{H}{C}}-CH_3 + HCl \longrightarrow \text{chloride}$$

$$\text{or } CH_3-CH_2-\overset{CH_3}{\overset{+}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_3 + C_6H_6 \longrightarrow CH_2-CH_2-\overset{CH_3}{\underset{C_6H_5}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_3 + H^+$$

The carbonium ion intermediate may take an alternative course in which a cission of carbon-carbon bond occurs.

$$CH_3-CH_2-\overset{CH_3}{\overset{+}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_3 \longrightarrow CH_3-CH_2-\overset{CH_3}{\overset{+}{C}}: + CH_3-\overset{CH_3}{\underset{H}{C}}-CH_2^+$$



The tertiary butyl cation may condense with benzene to form tert-Butylbenzene or be reduced to isobutane. The secondary cation undoubtedly stabilizes itself by olefin formation which in turn may polymerize to higher molecular weight unsaturates. Evidence of this was shown by Huston and Krantz (5).

It might be suspected that fragmentation would take place next to the cation in all cases, however, it has been shown in this work that cission takes place at that point which favors the direct formation of the tertiary butyl group. For example, the condensation of 2,4-Dimethyl-2-hexanol resulted in the isolation of isobutane and tert-butyl benzene and no isopentane and tert-amyl benzene which would be expected if the fragmentation took place adjacent to the cation. One might draw from this comparison that the relative energy differences between isobutane and isopentane are large enough so as to favor the formation of the former where the structure of the alcohol is such that either could be formed through fragmentation.

In the authors previous work (21) it was determined that a ratio of 1 mole of alcohol to 0.5 moles of aluminum chloride gave the maximum yield of the alkylbenzene. It

was interesting to note that in using a 1:1 mole ratio of alcohol-catalyst, the reduction seemed to be enhanced as was found in the case of 3-Methyl-3-heptanol. A 13.8% yield of the corresponding hydrocarbon was obtained as compared with 9.5% yield using a 1:0.5 mole ratio. However, in the former condensation, no separatable fraction of alkyl benzene could be obtained. In the case of 2,4-Dimethyl-4-hexanol, an 8.1% yield of isobutane and a 3.5% yield of the corresponding hydrocarbon were isolated when a 1:1 mole ratio of alcohol-catalyst was used as compared to 4.6% isobutane and 3.9% of the corresponding hydrocarbon were obtained using a 1:0.5 mole ratio. Again no separatable fraction of alkyl benzene could be obtained in the former case.

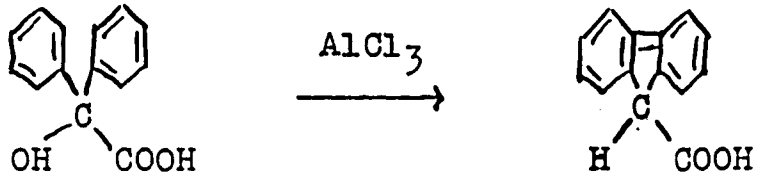
Many examples appear in the literature on the reduction of hydrogen acceptors in reactions which aluminum chloride is used as catalyst. Unfortunately these reactions occur over a wide range of conditions making it difficult to evaluate their results in order that they might be of help in explaining the reduction in the authors work. As was mentioned in the historical portion, evidence of reduction of alcohols during condensation with benzene and phenol has been reported by Huston and Hughes (8), Huston and Friedemann (6), Huston and Jackson (7). No explanation as to the source of hydrogen was advanced.

Various examples of reduction of compounds containing hydrogen acceptors confirm the evolution of hydrogen

effected by the action of aluminum chloride on aromatic compounds. The fate of the hydrogen evolved is definitely shown. Freund (59) found that when nitrobenzene is boiled with benzene and aluminum chloride there is formed, in addition to much resinous matter, an 8.5% yield of p-aminobiphenyl. Here the hydrogen is evolved by condensation of the benzenoid compound to a biphenyl derivative as well as the hydrogen produced during formation of the resinous mass.

Pummerer and Binopfl (60) demonstrated the dehydrogenating effect of aluminum chloride in benzene by conversion of azobenzene into p-aminobiphenyl in 70-80% yields. Pummerer and Prell (61) also showed that diarylhydroquinones are readily obtained by treatment of p-benzoquinone with aromatic hydrocarbons, phenols or phenol ethers in the presence of aluminum chloride.

Vorlander and Pritzscher (62) demonstrated that ring closure of benzilic acid occurs upon treatment with aluminum chloride.



Alexander, Jacoby and Fuson (63) found that reduction occurred in attempted reaction of 1,1-diaryl-2-acylethylenes with benzene and aluminum chloride. Instead of condensation only hydrogenation to the corresponding saturated diaryl-ketones occurred:

$$(Ar)_2C{:}CHCOR \xrightarrow[AlCl_3]{C_6H_6} (Ar)_2CH\text{-}CH_2COR$$

Although it was found that the reaction involved also replacement of the aryl group, the origin of the hydrogen was unknown.

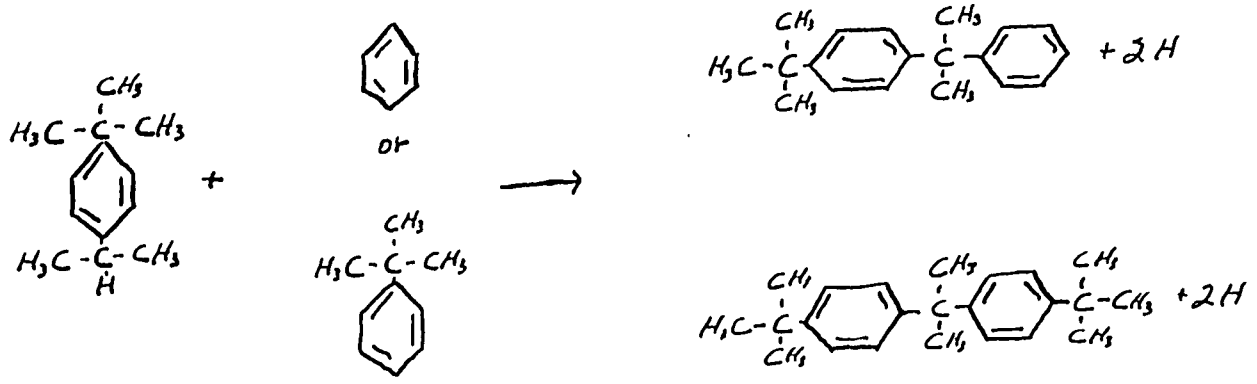
Nenitzescu and Isacescu (64) have noted the hydrogenation phenomena in the reaction of allyl chloride with benzene in the presence of aluminum chloride. The formation of an anthracene derivative in the condensation with evolution of hydrogen results in an anomolous course. Wispek and Zuber (65) claim that by varying the conditions, a fraction may be obtained, which consists primarily of n-propylbenzene. However, Nenitzescu and Isacescu state that the formation of n-propylbenzene is due to the use of aluminum chloride which has been "poisoned" by addition of water. Here the catalyst is so weakened that it effects dehydrogenation of a simultaneously formed dihydroanthracene, and a subsequent reduction of the primarily formed β-chloropropylbenzene is thereby obtained.

It is noteworthy that in many examples of aluminum chloride condensations in which reduction has been observed there has also been isolated a biphenyl type compound, anthracene derivative and/or much resinous mass. The formation of these compounds is accompanied by the formation of hydrogen. In addition to this, Nenitzescu (66) points out that in the action of aluminum chloride on saturated hydrocarbons, the electrons are bound so fast to carbon that the formation of a stable complex cannot be considered. It may,

however, cause an attraction of the electrons of carbon atoms whereby a reversible deformation of the electron shells occurs. This loosens one or more bonds so isomerization can occur. If acceptors for hydrogen are present reduction takes place. Halogen compounds have been shown to act as acceptors for the hydrogen evolved. Further, the saturated carbon chains themselves can also act as acceptors for the hydrogen by breakdown into lower molecular weight compounds. In addition to this, Nenitzescu points out that the hydrogen in the saturated hydrocarbons is strongly activated for which reason it is capable of all possible reductions of halogen. The aromatic hydrocarbons are in a middle position between saturated hydrocarbons and olefins. That is, they form no stable compounds, as do olefins, but their electron shells are considerably more deformed than those of saturated hydrocarbons, so that they are capable of the known reactions.

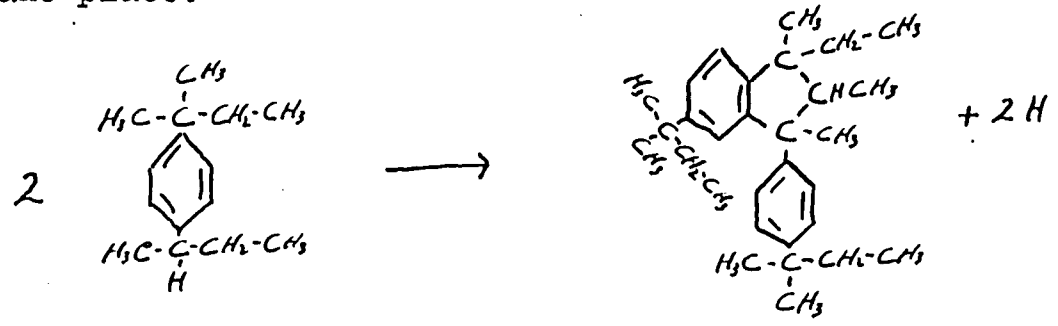
In the authors work it was hoped that a compound could be isolated from one of the reactions whose formation would necessarily result in the formation of hydrogen. This would account for one of the undoubtedly many sources of hydrogen during the condensation. Since it was suspected that methane was given off during all condensations it may be safe to assume that demethylation had taken place (67). It has been shown (6) that alkyl groups tend to split from the alpha carbon of alkylbenzenes and that this carbon has a tendency toward free radical formation (68). As already

described in Part II of the experimental a fraction was isolated between tert-butylbenzene and p-di-tert-butylbenzene in the tert-butyl alcohol condensation. If it is assumed that this compound was either p-tert-butyl-isopropylbenzene or p-tert-butyl-ethylbenzene these compounds could easily react, under the influence of aluminum chloride, with benzene or another molecule of tert-butylbenzene in the following manner.



The failure of Fraction IV, Part O to oxidize to a benzoic acid derivative cannot be explained.

If the alkyl portion is larger, then cyclization could take place.



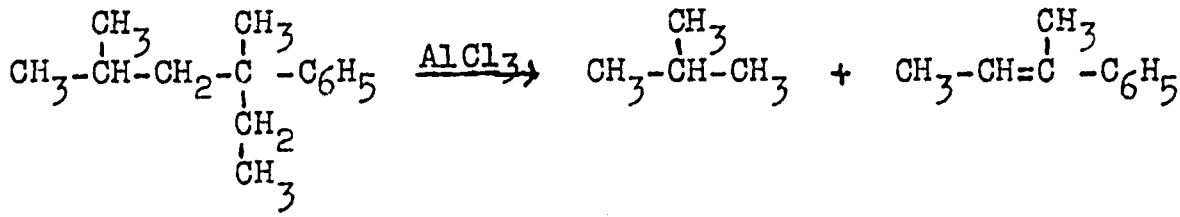
This type of reaction was shown by Pines, unpublished work, to take place when p-isobutyl toluene or p-sec-butyl toluene was reacted with 4-methylcyclohexene in the presence of either sulfuric acid or hydrogen fluoride at 0°C.

The 4-methylcyclohexene was reduced to methylcyclohexane to the extent of 60% or more. The fact that fractions isolated above the p-di-tert-butylbenzene contained predominantly aromatic groups, as shown by the refractive index and nitration, might further support the above theory.

If a cyclic indan structure is assumed for Fraction IV, Part O, this could only form by cyclization of an ortho dialkylbenzene.

Another main source of hydrogen is undoubtedly the large amount of resinous material formed, particularly with the condensation of the more highly branched and higher molecular weight alcohols. More reduction was found in these cases.

The formation of isobutane may be accounted for by the reduction of isobutyl cation, isobutene and/or tert-butyl chloride. It could also result from the direct cracking of the octylbenzene in the following manner:



To support the above assumption Huston and Barrett (3) found, in addition to isobutane, 2-methyl-3-phenyl-2-butene, 3,3-dimethyl-2-phenyl-1-butene, in the condensation of 2,3,-3-trimethyl-2-butanol with benzene and aluminum chloride.

In previous work (21), the author has shown that the presence of an aromatic nucleus is apparently necessary if

reduction is realized. n-Hexane was substituted for benzene in the reaction of 3-Ethyl-3-hexanol and aluminum chloride. Compounds isolated were the dehydration products of the alcohol and unreacted alcohol.

One is able only to postulate in what form the hydrogen acceptor is in during reduction. If one assumes that the formation of the olefin is necessary this would not explain the formation of triphenylmethane when triphenylcarbinol is condensed with benzene in the presence of aluminum chloride. If one assumes that the carbonium ion or complex is reduced, one must then postulate the formation of a hydrid ion.

It is more logical to assume that a necessary prerequisite in this reaction is the formation of the chloride which is in turn reduced by atomic hydrogen with the formation of the saturated hydrocarbon and hydrogen chloride. In connection with this, twelve grams of isobutane were isolated from a three mole condensation of tert-butyl chloride, benzene and aluminum chloride in comparison with only four and one-half grams isolated during the condensation of a similar run using tert-butyl alcohol. This observation would also tend to eliminate the probability that the reduction takes place through the formation of an aluminum tert-alkoxide.

SUMMARY

1. Fourteen tertiary alcohols having only primary alkyl groupings attached to carbinol carbon were prepared and condensed with benzene in the presence of anhydrous aluminum chloride.

2. Fragmentation was shown to take place only with those alcohols having branching on the beta carbon atom. Cission of the alkyl radical always took place at such a point as to favor direct formation of the isobutyl cation which was isolated in the form of isobutane and tert-butylbenzene. Branching on the gamma carbon is apparently too far removed from the positive carbon to effect fragmentation.

3. Reduction was shown to take place during condensation as evidenced by the isolation of the paraffin hydrocarbon corresponding to the structure of the alcohol condensed. Isobutane was also isolated in those cases where fragmentation of the alcohol occurred.

4. The paraffin hydrocarbons were identified by their physical constants and infra-red spectrograms. Tert-butylbenzene was identified by its acetamino derivative, isobutane by its boiling point and refractive index at -25°C, and p-di-tert-butylbenzene by its 2,6-dinitro derivative. 3,5-Dinitrobenzoates of the alcohols condensed were also prepared.

5. Possible mechanisms have been proposed for the fragmentation and reduction phenomena. It was shown in previous

work that the presence of an aromatic nucleus is necessary for reduction to take place under the conditions of the reaction. Reduction seemed to be enhanced considerably when tert-butyl chloride was substituted for tert-butyl alcohol.

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