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CONDENSATION OF THE BUTYL METHYL
ETHYL CARBINOLS WITH PHENOL IN
THE PRESENCE OF ALUMINUM CHLORIDE

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THESIS

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CONDENSATION OF THE BUTYL METHYL
ETHYL CARBINOLS WITH PHENOL IN
THE PRESENCE OF ALUMINUM CHLORIDE

A Thesis

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By

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TABLE OF CONTENTS

	Page
I. Introduction	1
II. Historical	1
III. Discussion	6
IV. Experimental	11
V. Tables of Results	
1. Physical constants of tert. octanols	19
2. Condensations of tert. octanols with phenol	21
3. Physical constants of p-tert. octyl phenols	22
4. Benzoyl esters	25
5. Alpha naphthyl urethanes	25
6. Phenyl urethanes	25
7. Para tert. octyl benzenes	30
8. Phy. constants of p-tert. octyl benzenes	31
9. Parachars and surface tensions	31
10. P-nitro-tert. octyl benzenes	32
11. P-amino-tert. octyl benzenes	32
VI. Summary	33
VII. Bibliography	35

INTRODUCTION

In the past, tertiary butyl, tertiary amyl, the tertiary hexyl, the tertiary heptyl, and some of the tertiary octyl phenols were prepared in this laboratory. ^{1,2,3} To further complete this investigation the following four butyl, methyl, ethyl carbinols; 3-methyl, heptanol-3; 3,4 dimethyl, hexanol-4; 2,4 dimethyl hexanol-4; 2,2,3 trimethyl pentanol-3 were prepared and condensed with phenol in the presence of AlCl_3 . Yields ranged from 21.1% to 81.5% of the para-tert. octyl phenol. The benzoyl esters, alpha naphthyl urethanes and phenylurethanes were prepared and analyzed. Three p-tert. octyl benzenes were prepared. The physical constants were obtained and the molecular volumes and parachors were experimentally determined.

HISTORICAL

In the year 1897 Nef (4) mentioned the condensation of benzyl alcohol and benzene in the presence of aluminum chloride, to form diphenylmethane. In 1916 Huston and Friedeman (5) condensed benzyl alcohol and benzene in the presence of aluminum chloride, with a 30% yield of diphenylmethane. They further reported that aromatic secondary alcohols such as benzhydrol, phenyl methyl and phenyl ethyl carbinols also reacted with benzene in the presence of aluminum chloride to give the corresponding hydrocarbons with good yields. Triphenylcarbinol reacts with benzene in the presence of aluminum chloride to give triphenylmethane and not tetraphenylmethane (6). In 1924 Huston (7) showed that anisole and phenetole acted like benzene in that they condense with benzyl alcohol to give the para substituted benzyl anisole and phenetole.

Huston and Sager (8) condensed allyl alcohol with benzene in the presence of aluminum chloride. The principal product was allyl benzene.



Huston and Wilsey (9) found 1,1 diphenyl-1-propene was the principal product from the reaction of 1,1 diphenyl ethyl carbinol with benzene, which was a dehydration reaction instead of a condensation.

Huston and Gootemott (10) showed that in condensation reactions with benzene in the presence of aluminum chloride the cycloalkyl carbinols show a progressive increase in activity as the number of carbon atoms of the ring is reduced from six to four, or as the strain on the carbonyl carbon is increased.

Likewise, Huston and Hradel (11) and Huston and Macomber (12) found that neither diaryl-alkyl carbinols nor dialkyl-aryl carbinols condensed with aluminum chloride. Instead, dehydration occurred.

Dimethyl-N-butyl carbinol, dimethyl iso-butyl carbinol, and dimethyl sec-butyl carbinol were successfully condensed with benzene to obtain the corresponding alkyl benzenes, but no yield was obtained by condensing dimethyl tert. butyl carbinol with benzene (13).

Huston and Hsieh (14) condensed aliphatic alcohols with phenol. The primary alcohols were found not to react at all; the secondary alcohols reacted with difficulty; and the tert. alcohols reacted very readily to form the corresponding alkyl benzenes.

Huston and Sculati (15) condensed dimethyl, amyl carbinols with benzene in the presence of aluminum chloride to the corresponding tert. octyl benzenes.

Huston and Fox (16) condensed tert. butyl and tert. amyl alcohols with benzene in the presence of aluminum chloride.

Summary

1. Unsaturated aliphatic primary alcohols, with the double bond adjacent to the hydroxyl carbon, condense with benzene.

2. Primary and secondary aromatic alcohols condense with benzene in the presence of aluminum chloride to form the corresponding benzene derivatives.

3. Dehydration of carbinols occurs to form the corresponding unsaturated hydrocarbon when aliphatic-aromatic alcohols react with benzene.

4. The primary aliphatic alcohols do not condense with benzene, The secondary aliphatic alcohols condense with difficulty. The tert. aliphatic alcohols react very readily to form corresponding alkyl benzenes.

CONDENSATION OF ALCOHOLS WITH PHENOL

In 1920 Huston (17) discovered that Benzyl Alcohol reacted with Phenol in the presence of Aluminum Chloride to give a good yield of p-Benzyl Phenol. Later Huston, Lewis and Grotemut (18) condensed methyl phenyl carbinol with phenol, (yield 33.0%) ethyl phenyl carbinol with Phenol, (yield 27.0%) and benzhydrol with Phenol, (yield 40.0%).

Huston, Swarthout and Wardell (19) benzylated o-cresol by condensing benzyl alcohol with o-cresol in the presence of Aluminum Chloride. The main product was 2-methyl 4-benzyl-phenol.

Huston and Lewis (20) condensed p-cresol and benzyl alcohol with Aluminum Chloride. A 35.0% yield of 2-benzyl, 4-methyl phenol and a 36.0% yield of 4-methyl 2,6, dibenzyl phenol were obtained.

Huston and Strickler (21) condensed phenyl propyl carbinol and a-chloro-butyl benzene with phenol to yield 4 (a-phenyl-butyl) Phenol.

Huston and Newmann (22) reported the condensation of allyl alcohol with Phenol.

Huston and Hsieh (23) found that ethyl alcohol, primary propyl and butyl alcohols did not condense with phenol in the presence of aluminum chloride. Iso-propyl alcohol reacted with Phenol, but the product was not identified. Sec. butyl alcohol did not react with phenol. The tert. aliphatic alcohols were found to condense readily with Phenol to give the para tert. alkyl phenols.

Huston and Jackson R.I. (24) condensed tert. butyl and tert. amyl alcohols with p-cresols in the presence of aluminum chloride.

Huston and Hedrick (25) condensed some tert. heptyl alcohols with Phenol, using a mixture of Zinc and Aluminum Chloride as a condensing agent. A small amount of o-tert. butyl phenol was found, and the principal product being the p-isomer.

DISCUSSION

Of the four tertiary octanols prepared, the secondary butyl methyl ethyl carbinol was not recorded in literature, but was prepared by M. F. Hunter (27). Physical constants of the n-butyl, methyl ethyl carbinol, iso-butyl methyl ethyl carbinol, and tert. butyl methyl ethyl carbinol checked with those recorded in literature.

Physical constants for sec. butyl methyl ethyl carbinol did not check well with M. F. Hunter's therefore the tertiary octanol was prepared in another manner. The first method was by adding methyl ethyl ketone to sec. butyl magnesium bromide, and hydrolyzing. The second method was by adding sec. butyl methyl ketone to ethyl magnesium bromide, and hydrolyzing. The constants of each tert. carbinol were determined with good checks, and the analysis for carbon and hydrogen also agreed, indicating the presence of the octanol.

The four tertiary octanols gave good yields when condensed with Phenol in the presence of aluminum chloride, (21.0%-81.3% yields. The 3 methyl, 3-p-hydroxyphenylheptane, and 2,2,3 trimethyl 3-p-hydroxyphenylpentane were prepared by J.E. Anderson (28) 1936.

These two p-tert. alkyl phenols were repeated, and 2,4 dimethyl 4-p-hydroxyphenylhexane, and 3,4,dimethyl-4-p-hydroxyphenylhexane were also prepared. Of these four the 2,2,3 trimethyl-3-p-hydroxyphenylpentane crystalized and was placed on a porous plate, and the melting point taken, M.P.= 61° which corresponded with the melting point given by J. E. Anderson,

M.P. = 57-58°. This product was further recrystallized eight times from pet. ether and the M.P. became constant on the electric plate at 112°. Later a portion of the phenol prepared in 1936 was recrystallized from pet ether, at first difficult to recrystallize and finally when more of the oil disappeared, the phenol recrystallized fairly well and the M.P. was increased to 108°-110° on an electric plate. The phenylurethane was prepared and recrystallized and a constant melting point obtained. The alpha naphthyl urethane could not be prepared as there was no alpha naphthyl iso cyanate on hand.

In the fractionation of the phenol-tertiary octanol condensations a little tert. octanol was received, then the temperature rose rapidly to the condensation product, and the last portion could not be identified. It was a hard polymerized product. In the case of the n-butyl methyl ethyl carbinol and phenol there was little polymerized product. The iso, and sec. butyl methyl ethyl carbinol with phenol gave between 2-6 gms. of the polymerized product. The tert. butyl methyl ethyl carbinol with phenol did not give any, but a high boiling fraction and more of the tert. octanol was received than the other three condensations. The alpha naphthal urethanes, phenyl urethanes, and the benzoyl esters were prepared for 2-methyl 3-p-hydroxyphenylheptane; 2,4 dimethyl-4-p-hydroxyphenylhexane, 3,4, dimethyl-4-p-hydroxyphenylhexane. The phenyl urethane was prepared from 2,2,3 trimethyl 3-p-hydroxyphenylpentane. The p-tert. octyl phenols and benzoyl esters were analyzed for carbon and hydrogen. The phenyl

urethane and alpha naphthyl urethanes were analyzed for nitrogen. The 2,2,3 trimethyl 3-p-hydroxyphenylpentane was not prepared until late and sufficient time was not available to analyze this compound for carbon and hydrogen.

The para positions of the four tert. octyl groups were determined through syntheses. The tert. butyl methyl ethyl p-hydroxyphenylmethane, and the n-butyl methyl ethyl p-hydroxyphenylmethane had been prepared (28), and their structure proven. In this work the four tert. octyl phenols were prepared, and the structure of n-butyl methyl ethyl-p-hydroxyphenylmethane, iso-butyl methyl ethyl-p-hydroxyphenyl methane, and sec. butyl methyl ethyl para-hydroxyphenyl methane were proven by synthesis. First the three p-tert. octyl benzenes were prepared and then nitrated according to Malherbe's method (29) to get the p-nitro tert. octylbenzenes. The para position of the nitro group was determined by oxidation of the tert. octyl group with dilute nitric acid (1.20), in a sealed tube heated to 130° for several hours in a carius combustion furnace, to p-nitro benzoic acid, M.P. = 250°. The p-nitro tert. octylbenzenes were reduced to the p-amino compounds by means of tin and hydrochloric acid. The three p-tert. octyl phenols thus synthesized were proven to be identical with the phenylurethanes of the phenols from the direct condensations.

A small portion of the three para tert. octyl benzenes were taken, and the physical constants were determined. Density, refractive indices, surface tension, parachor, and molecular volume. The parachors and molecular volumes of these three para

tert. octyl benzenes checked well with the calculated parachar and molecular volumes.

Analysis of the fractions from the benzene-octanol condensation showed in all cases first a low but not constant fraction, which when heated with KOH then acidified, and treated with AgNO_3 , showed a large precipitate of silver halide, the probable compound would be the chloride of the original octanol. This fraction was found just below the boiling point of the corresponding tert. octanol, and in each case from 5-10 CC of the original octanol was recovered. In one condensation of benzene and sec. butyl methyl ethyl carbinol, the temperature was held at 15°C and the recovered tert. octanol was over 30%. When the benzene condensations were carried out at the higher temperatures $25^\circ - 32^\circ$, a better yield of condensation product was obtained and the percentage of unreacted octanol was decreased but more high boiling material came over which was not identified. The high boiling fraction was not a constant boiling liquid. When the temperature was kept low there was little high boiling material and more of the original octanol recovered and more of this unidentified halide. This probably was the chloride of the corresponding octanol, due to the lower boiling point, and halogen content.

The four tert. butyl methyl ethyl carbinols condensed with phenol to give the para-tert. octyl phenols. The n-butyl methyl ethyl p-hydroxy-phenylmethane was the highest yield. (81.5%) The iso-butyl methyl ethyl-p-hydroxyphenyl methane was the next

highest yield (62.0%). The sec. butyl methyl ethyl-p-hydroxyphenyl methane was the third highest yield (40.0% and the tert. butyl methyl ethyl-p-hydroxyphenyl methane was the lowest. (21.1% yield).

The yields of the four p-tert. octyl phenols corresponded with the amount of branching in the side chains. The n-butyl methyl ethyl carbinol reacted very well with phenol. The iso-butyl methyl ethyl carbinol gave a somewhat lower yield of the p-tert. octyl phenol. The sec. butyl ethyl methyl carbinol gave a lower yield than the iso-butyl ethyl methyl carbinol with phenol. The tert. butyl methyl ethyl carbinol with the most branching gave the lowest yield when condensed with phenol.

EXPERIMENTAL

MATERIALS

Normal butyl bromide, iso butyl bromide, and sec. butyl bromide were prepared by treating the corresponding alcohols with HBr (48%) and concentrated sulfuric acid.

Methyl ethyl ketone was a C.P. grade, and dried completely before using.

Magnesium (turnings) prepared for Grignard reactions was used.

The phenol was distilled before using.

The benzene was C.P. thiophene-free.

The aluminum chloride was of excellent commercial grade.

Acetone was distilled and dried before using.

The reagent used for esters, alpha naphthyl isocyanate, phenyl isocyanate, and benzoyl chloride were of the Eastman Kodak variety.

PREPARATION OF THE FOUR TERTIARY OCTANOLS

Of the four possible butyl, methyl, ethyl, carbinols three are recorded in literature with their physical constants. The secondary butyl, methyl, ethyl carbinol is not recorded, but has been prepared by M. F. Hunter (27) "Senior Thesis". Physical constants given by Hunter did not check well with the ones prepared in this thesis, so the sec. butyl, methyl, ethyl carbinol was prepared by two different methods, and the result of these two preparations check well. The two methods are as follows:

Methyl, ethyl sec. butyl carbinol was prepared by Whitmore's modification of the grignard reaction. (30) In a five liter, three necked, round-bottom flask, fitted with an efficient stirrer, reflex condenser and dropping funnel, and placed first a few small crystals of Iodine and then 98 grams (4 moles) of fresh, dry Magnesium turnings. The bottom of the flask is heated with a small flame until the Iodine commences to vaporize, and is then allowed to cool while the sec. butyl bromide is being weighted out. 30 c.c. of a 50% mixture of the sec. butyl bromide and di-ethyl ether is added to the dry magnesium turnings. If the reaction does not start, the bottom of the flask is heated with warm water, and the reaction then starts rapidly. After the reaction had progressed for a minute, 200 c.c. of dry di-ethyl ether (dried over sodium) is added directly to the reaction mixture. The remaining portion of the 4 moles of halide, and 500 c.c. of ether is placed into a dropping funnel, and added with stirring, one drop per second. The mixture is then allowed to reflux during the halide-ether add-

ition, with no external heating being applied, and occasionally cooled with cold water. The stirring is continued for four hours after the addition of the ether-halide solution, and let stand over night.

To the sec. butyl magnesium bromide is added a solution of four moles of pure, dry methyl ethyl ketone in an equal volume of anhydrous ether. The remaining procedure is similar to that stated above for the preparation of the grignard reagent.

The magnesium complex is decomposed in a four liter erlenmeyer flask with ice and hydrochloric acid, by the addition of small portions of the magnesium complex to the ice in the erlenmeyer flask, and finally neutralized with hydrochloric acid. The hydrolyzed product is extracted three times with ether. The ether extract is then further neutralized with a sodium carbonate solution and then dried over anhydrous sodium sulfate. The alcohol is obtained by fractional distillation at reduced pressure after the ether has been boiled off on the steam bath. The yield was (400%) and the constants are B.P. = $153^{\circ}/741.0\text{mm}$; 60-61/14mm. $D^{25} = .8348$; $N_D^{24} = 1.4338$; 40-41/3mm.

Hunter (1) gave the following physical constants for sec. butyl methyl ethyl carbinol:

$D^{24} = .8431$	$N^{24} = 1.3820$	B.P. 42-44 / 5 mm.
$D^{24} = .8421$	$N^{24} = 1.3800$	
$D^{24} = .8439$	$N^{24} = 1.3880$	

The second method of preparing the sec. butyl methyl ethyl carbinol is: a two liter, three neck flask was fitted with an efficient stirrer, dropping funnel, and reflux condenser. One mole of magnesium turnings were placed into the flask, and three crystals of Iodine vaporized and let cool. The sec. butyl bromide was mixed with an equal quantity of anhydrous di-ethyl ether, about 25 c.c., of the halide ether solution was let drop into the magnesium turnings and the reaction started as in the other preparation. When the halide-ether solution was all added drop by drop the grignard reagent was let stand over night. The next day acetyl chloride was not added to the grignard as in the usual procedure but the sec. butyl magnesium grignard was added to the (1 mole) of acetyl chloride. After the sec. butyl magnesium bromide was added drop by drop the reaction was again let stand, hydrolyzed, acidified, and washed thoroughly with sodium carbonate solution. Dried with anhydrous sodium sulfate, the sec. butyl methyl ketone was distilled at 118 C.

In the meantime ethyl magnesium bromide was prepared as was the sec. butyl magnesium bromide, the sec. butyl methyl ketone was added to the ethyl magnesium bromide and let stand and the product hydrolyzed as before. The tertiary octanol was distilled under a reduced pressure, and the yield from the ketone was 61%. The physical constants for this sec. butyl methyl ethyl carbinol are: B.P. - 152 / 740 mm. 59/14mm. 40/2.5mm.

D_{25}^{25} - .8345

n_D^{25} - 1.4332

ANALYSIS:-

Calculated: C - 73.84%; H - 13.84%

Found: C - 73.72%; H - 13.67%

The physical constants for the sec. butyl methyl ethyl carbinol checked well with the physical constants obtained when the sec. butyl methyl ethyl carbinol was prepared from the ethyl methyl ketone and sec. butyl magnesium bromide, but disagreed with Hunter's to some extent.

The normal butyl methyl ethyl carbinol, iso-butyl methyl ethyl carbinol, and sec. butyl methyl ethyl carbinol were all made by the same procedure (30). The tertiary butyl ethyl methyl carbinol was prepared by first making Pinacol Hydrate (31), rearrangement of Pinacol Hydrate of Pinacolone, and the addition of an ethyl magnesium bromide grignard to the Pinacolone, the procedure is described below.

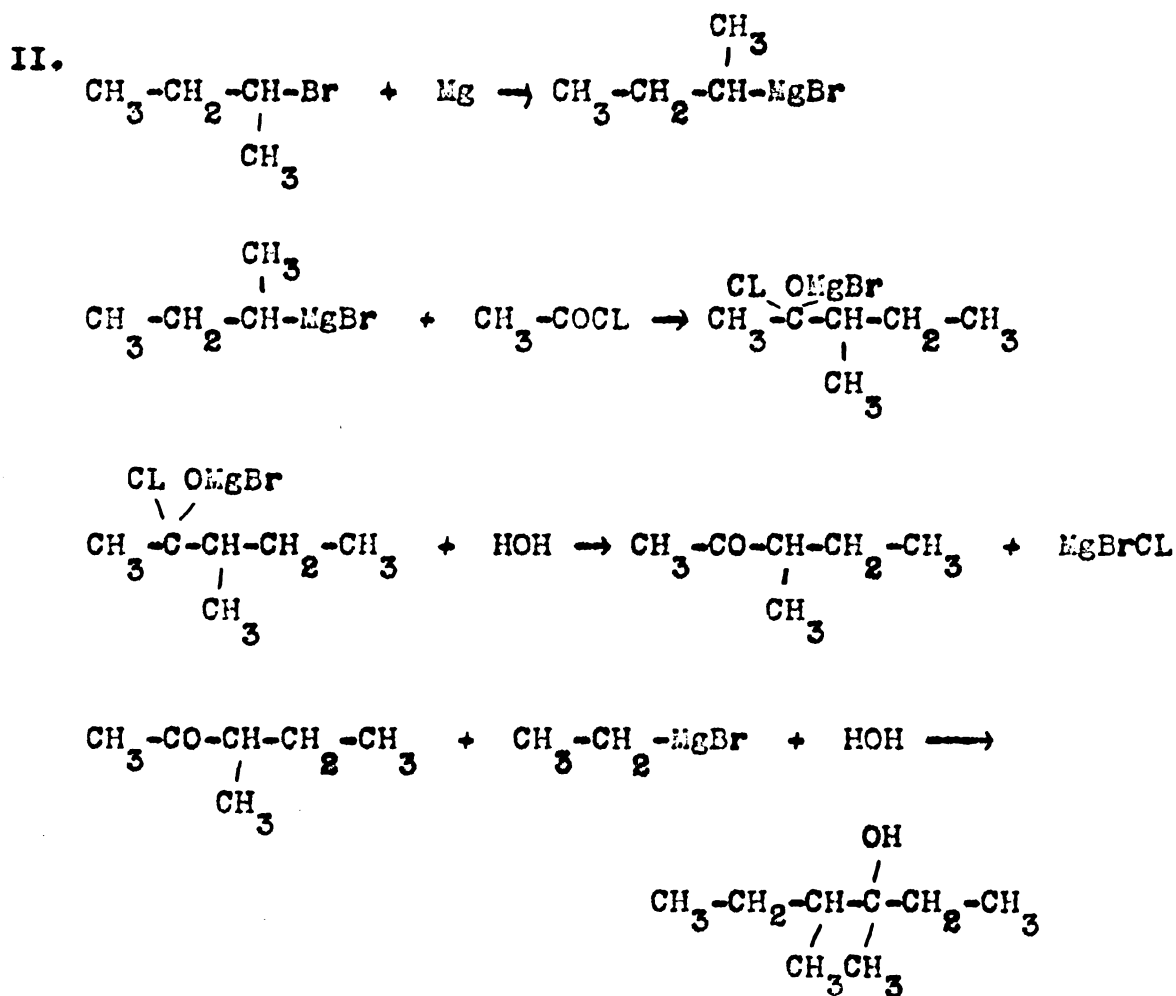
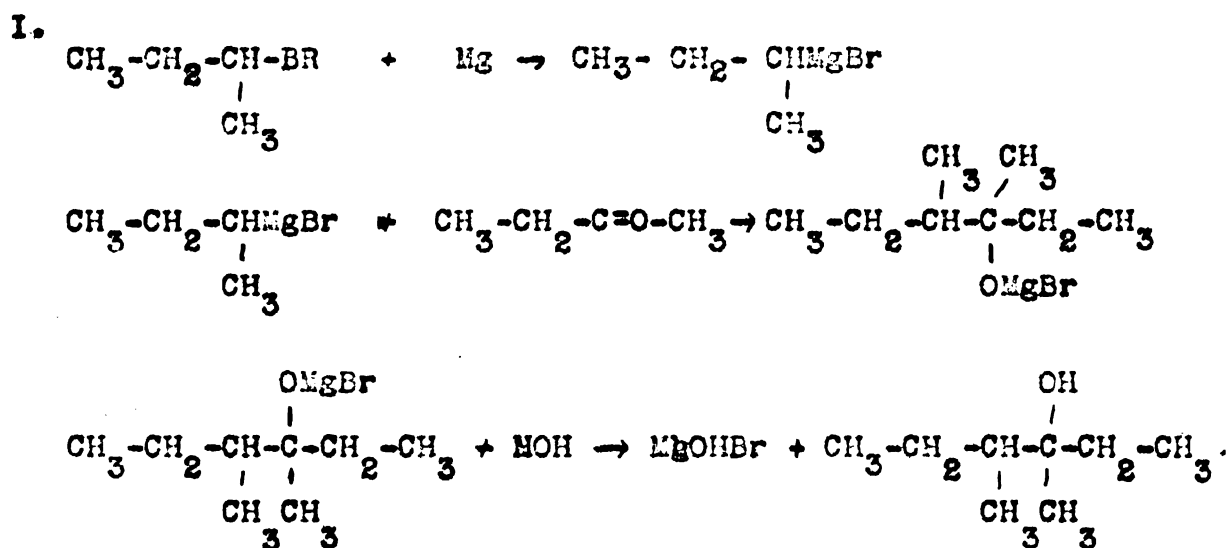
In a 5 liter round bottom flask fitted with a stopper holding a separatory funnel and a reflux condenser with a wide bore (.5in) closed at the top with a calcium chloride tube, are placed 80 gms. of magnesium turnings and 800 c.c. of dry benzene. Through the dropping funnel is added a solution of 90 gms. of mercuric chloride in 400 gms of acetone (dry) carefully at first, then faster as the reaction starts. Sometimes the reaction does not start until after a quantity of acetone has been added, in this case it proceeds very rapidly and the flask must be cooled. When all the 50% solution of acetone and benzene are added the reaction slows down and the flask is heated on a water bath till no further reaction is evident. During this time the magnesium pinacolate swells until it fills the flask about three-quarters full. The flask is removed from the condenser

and shaken until the reaction mass is well broken up. Through the separatory funnel is then added 200 c.c. of water and the reaction mixture is heated another hour, with occasional shaking of the flask. The reaction mixture is cooled to about 50° and filtered. The solid is returned to the flask and heated with a fresh 500 c.c. portion of benzene to dissolve any remaining pinacol. The original filtrate, and the second portion of benzene, after it is filtered from the magnesium hydroxide, are mixed and distilled to one-half the original volume in order to remove the acetone, the remaining benzene solution is treated with 300 c.c. of water and cooled to 10-15°. The pinacol hydrate separates and after about 30 minutes it is collected on a suction filter and washed with benzene, the pinacol hydrate is air-dried at room temperature (47% yield) M.P. - 46 - 47°.

Rearrangement: Pinacol hydrate to pinacolone in a two liter round bottom flask, fitted with a stopper carrying a dropping funnel and a connection to a condenser set for distillation are placed 750 gms. of 6 N sulfuric acid and 250 gms pinacol hydrate. The mixture is then distilled until the upper layer of distillate ceases to increase in volume (15-20 minutes). The pinacolone layer in the distillate is separated from the water and the water is returned to the reaction flask. First 60 c.c. of concentrated H_2SO_4 is added to the water and then a second 250 gms portion of pinacol hydrate is used.

The combined pinacolone fraction is dried over calcium chloride, filtered and fractionally distilled. The pinacolone comes over at 103°-107°.

The pinacolone is then added with an equal portion of dry di-ethyl ether to ethyl magnesium bromide in a 3 liter 3 neck flask fitted with a stirrer, reflux condenser and dropping funnel. This is added a drop per sec. and let stand over night, hydrolyzed, neutralized and fractionated under a reduced pressure. B.P. - 58 / 18 mm. yield - 53%. ✓

EQUATIONS:

PHYSICAL CONSTANTS OF TERTIARY OCTANOLS

Physical Constants Recorded in Literature

Phys. Const.	N-butyl methyl ethyl Carbinol	Iso-butyl methyl ethyl carbinol	Sec. butyl methyl ethyl carbinol	Tert. butyl methyl ethyl carbinol
B.P.	158°/745 mm.	151-153°/750 mm.	_____	149° - 152°/760 mm.
D	D ₄ ⁰ - 0.8446	D ₁₅ - . 8300	_____	_____
N _D	N _D ¹⁹ - 1.42735	N _D ¹⁹ - 1.4266	_____	_____
% Yield	65.0%	_____	_____	_____

Physical Constants Used

B.P.	158°/742.0 mm.	150°/743.5 mm.	150-152°/740.0mm.	148°-149°/742.7 mm.
B.P.	69° -70°/19 mm.	60°-62°/16 mm.	59°-61°/14 mm.	58°-59°/18 mm.
D	D ₂₄ - .8230 ✓	D ₁₆ - .8295	D ₂₆ - .8345 ✓	_____ ✓
N _D	N _D ³² - 1.4270	N _D ²⁰ - 1.4280	N _D ²⁴ - 1.4334 ✓	_____ ✓
% Yield	69.3%	59.0%	39.0%	59.1%

FIG. 1

CONDENSATION OF TERTIARY OCTANOLS WITH PHENOL:

The N-butyl methyl ethyl carbinol, iso-butyl methyl ethyl carbinol, sec. butyl methyl ethyl carbinol, and tert. butyl methyl ethyl carbinol were prepared and condensed with phenol in the presence of Aluminum Chloride. A typical run is described here.

Thirty-two and one-half grams (.25M) of sec. butyl methyl ethyl carbinol and 23.5 grams (.25M) of phenol were treated with 80 C.C. of petroleum ether in a 500 C.C. three necked flask, fitted with a stirrer and reflux condensor which carried a thermometer reaching to the alcohol phenol mixture, and a bent tube for the outlet of the HCl gas evolved. Then 17 gms. (.125M) of AlCl_3 was added to the mixture at such a rate so that the temperature was kept at about 30° centigrade. The flask was cooled with ice water when necessary. After the addition of AlCl_3 , the ice water was removed and the stirring continued for four (4) hours. After the flask was allowed to stand overnight its contents assumed a dark reddish color and was treated with ice and hydrochloric acid. The hydrolyzed product was then extracted four (4) times with ether and dried. The ether was removed by distillation, and the residue fractionated. The first fraction collected was phenol, B.P. = 72°/7 mm. Then the temperature rose rapidly to 143°-144°/5 mm; which was the p-tert. octyl phenol. (27.4 gms or 43.0% yield). See table

The results of the remaining condensations are listed on table 2 with the percentage yields. The physical constants and analysis are tabulated on table 3.

CONDENSATIONS OF TERTIARY OCTANOLS WITH PHENOL

Tert. Oct.	Grams	Phenol	Pet. ether	AlCl ₃	Product	Grams	Yield
N-butyl methyl ethyl carbinol	32.5	47.0g.	80. cc.	17. g	3-methyl, 3-p-hydroxy- phenylheptane	41.5	81.5%
N-butyl methyl ethyl Carbinol	32.5	47.0g	80. cc.	17. g	3-methyl, 3-p-hydroxy- phenylheptane	38.5	78.0%
Iso-butyl methyl ethyl carbinol	32.5	47.0g	80. cc.	17. g	2,4-dimethyl, 4-p-hy- droxyphenylhexane	29.0	60.3%
Iso-butyl methyl ethyl Carbinol	32.5	47.0g	80. cc.	17. g	2,4-dimethyl, 4-p-hy- droxyphenylhexane	31.0	62.0%
Sec. butyl methyl ethyl carbinol	32.5	47.0g	80. cc.	17. g	3,4-dimethyl, 4-p-hy- droxyphenylhexane	19.0	39.5%
Sec. butyl methyl ethyl carbinol	32.5	47.0g	80. cc.	17. g	3,4-dimethyl, 4-p-hy- droxyphenylhexane	20.7	40.3%
Tert. butyl methyl ethyl carbinol	22.4	47.0g	80. cc.	17. g	2,2, 3-trimethyl, 3-p-hydroxyphenyl- pentane	7.50	21.1%

Fig. 2

PHYSICAL CONSTANTS OF p-TERT. OCTYL PHENOLS:

Tert. Octanol Phenol	D ^{24°}	N _D ^{24°}	B.P.	Analysis
3-methyl, 3-p-hydroxy-phenylheptane	0.9503	1.5148	128°-130°/3 mm. 146°/7 mm. 293.6 at 755	Calcu.: C - 81.55%; H - 10.68% Found : C - 81.38%; H - 10.78%
2,4-dimethyl, 4-p-hydroxyphenylhexane	0.9538	1.5140	142°-144°/7 mm. 125°/3 mm. 259 at 725	Calcu.: C - 81.55%; H - 10.68% Found : C - 81.47%; H - 10.73%
3,4-dimethyl, 4-p-hydroxyphenylhexane	0.9714	1.5230	142°-143°/5 mm. 142 at 725	Calcu.: C - 81.55%; H - 10.68% Found : C - 81.41%; H - 10.57%
2,2,3-trimethyl 3-p-hydroxyphenylpentane	—	—	M.P. - 112°	Calcu.: C - 81.55%; H - 10.68% Found : C - —; H - —

Fig. 3

PREPARATION OF DERIVATIVES

Esters:

The Benzoyl esters were prepared by the Pyridine method (32). A typical run is described here.

One and one half cc. of benzoyl chloride is added to a mixture of 1.6 gms. of sec. butyl methyl ethyl-p-hydroxyphenylmethane dissolved in 8 cc. pyridine in a 225 cc. flask carrying a reflux condensor. The flask was heated with a free flame until the mixture boiled. After heating for two hours in the hood, the flask was cooled and then filled with water. The ester was separated from the aqueous layer, and extracted with ether twice. The ether extract was washed successively with dilute sulfuric acid, water, dilute sodium bicarbonate, and again with water. The ether was then boiled off on the steam bath. The remaining ester was then placed into a 25 cc. distilling flask. Distilled under reduced pressure. When the low boiling materials were distilled off, and the temperature rose above $160^{\circ}/6$ mm. the distillation was stopped, and the remaining ester that was in the flask upon cooling immediately crystallized, and was recrystallized from Petroleum ether or ethyl alcohol. The results are given in Fig. (4).

URETHANES

The Alpha naphthyl and phenyl urethanes were prepared (33). About 1 gm. of Alpha naphthyl isocyanate was added to 1 gm. of the p-tert. octyl phenol in a 50 cc. erlenmeyer flask. Then four or five crystals of anhydrous potassium carbonate were added to the mixture and a calcium chloride tube was

immediately inserted. The flask was heated on the steam bath with shaking for ten minutes. After cooling, the solid impure urethane was dissolved in boiling ligroin. In case the di-naphthyl urea was formed, it would be insoluble in ligroin. The hot ligroin was filtered through a warm suction filter and crystallized. The crystals then were recrystallized from alcohol until the melting point did not increase. The alpha-naphthyl urethanes of the three p-tertiary octyl phenols were easily crystallized, and the results are given in Fig. (4).

The phenyl urethanes were prepared from the four p-tert. octyl phenols in the same manner, using phenyl isocyanate in place of alpha naphthyl isocyanate. CAUTION: The phenyl isocyanate is very poisonous and should be handled carefully. The phenyl urethanes crystallized well, and the results are found in Fig. (4).

ANALYSIS:

The Benzoyl esters were analyzed for Carbon and Hydrogen by Fisher's Modification of the Liebig Combustion method (34). The results are tabulated in Fig. (4).

The Alpha naphthylurethanes, and the phenyl urethanes were analyzed for Nitrogen content. Allen's Micro Kjeldahl apparatus and modification of the Pregl method were used. (35) and (36). The results are listed in Fig. (4).

BENZOYL ESTERS OF P-TERT. OCTYL PHENOLS

Octyl phenol

Analysis:

3 methyl, 3-p-hydroxy-phenylheptane	M.P. -122°	Calc.: C-81.29%; H-8.39% Found.: C-81.13%; H-8.23%
2,4-dimethyl, 4-p-hydroxyphenylhexane	M.P. -123°	Calc.: C-81.29%; H-8.39% Found.: C-81.18%; H-8.31%
3,4-dimethyl, 4-p-hydroxyphenylhexane	M.P. -125°	Calc.: C-81.29%; H-8.39% Found.: C-81.23%; H-8.29%

ALPHA NAPHTHYL URETHANES

3-methyl, 3-p-hydroxy-phenylheptane	M.P. - 94°	Calculated: N - 3.72% Found : N - 3.58%
2,4-dimethyl, 4-p-hydroxyphenylhexane	M.P. - 90°	Calculated: N - 3.72% Found : N - 3.67%
3,4-dimethyl, 4-p-hydroxyphenylhexane	M.P. - 129°	Calculated: N - 3.72% Found : N - 3.51%

PHENYL URETHANES

3-methyl, 3-p-hydroxy-phenylheptane	M.P. - 104°	Calculated: N - 4.32% Found: N - 4.28%
2,4-dimethyl, 4-p-hydroxyphenylhexane	M.P. - 94°	Calculated: N - 4.32% Found: N - 4.21%
3,4-dimethyl, 4-p-hydroxyphenylhexane	M.P. - 119°	Calculated: N - 4.32% Found: N - 4.18%
2,2,3-trimethyl, 3-p-hydroxyphenylpentane	M.P. - 134°	Calculated: N - 4.32% Found: N - <u>4.18%</u>

Fig. 4

PROOF OF STRUCTURE

The structure of methyl ethyl N-butyl p-hydroxyphenylmethane was proven by preparing the p-tertiary octyl benzene, then nitrating the tert. octyl benzene. The position of the Octyl group was proven by the Carius oxidation of the nitro tert. octylbenzene to p-nitrobenzoic acid. The p-nitro tert. octyl benzene was then reduced to the p-amino tert. octyl benzene, and the p-amino tert. Octyl benzene was diazotized and hydrolyzed to the p-tert. Octyl phenol. This p-tert. Octyl phenol was then treated with Phenyl Isocyanate and the resulting urethanes showed a similar melting point. Analysis and mixed melting point showed it to be the same urethane as derived directly from the methyl ethyl N-butyl Carbinol and phenol in the presence of Aluminum Chloride.

PREPARATION OF THE TERT. OCTYL BENZENES

The tert. octyl benzene were prepared by the Huston Aluminum Chloride Condensation Method (37). A typical run is described here.

A 500 ml. three-necked flask was fitted with an efficient stirrer, a dropping funnel and a condenser. A thermometer was introduced into the flask from the condenser and was suspended from the latter with a copper wire. A drying tube was placed at the top of the condenser. The benzene was introduced into the flask, and the stirrer started. The (.25 mole) of AlCl_3 was added to the benzene. The carbinol was then added drop by drop so as to keep the temperature below 30° . The stirring was

continued for four (4) hours after the addition of the Carbinol. The mixture was then allowed to stand from forty-eight to ninety six hours; then decomposed with ice and hydrochloric acid. The benzene layer was separated and the aqueous portion extracted several times with ether. A little HCl was added in extracting with ether, to break up the water-ether emulsion that formed. The combined ether and benzene extracts were washed with dilute sodium carbonate solution to remove any remaining HCl. The mixture was dried and the ether distilled off, and the remainder was fractionally distilled.

NITRATION OF THE P-TERT OCTYL BENZENES

The nitration of the Octyl benzene was carried out by an adoption of Malherbe's procedure (29). An equal weight of the hydrocarbon was added slowly to fuming nitric acid (Sp.Gr. -1.51) in a 250 cc. flask. After the first violent reaction is completed the mixture was shaken vigorously and allowed to remain in a water bath at 90° for one hour, being shaken from time to time. Water was poured into the flask, the product was separated, washed with sodium carbonate solution, dried with anhydrous calcium chloride and distilled under reduced pressure. The product foamed during distillation and in the case of the Sec. butyl methyl ethyl phenylmethane the nitro compound decomposed very easily upon heating. In the case of the Iso-butyl methyl ethyl p-nitro phenyl methane was not so easily decomposed as the Sec. butyl methyl ethyl p-nitro

phenylmethane. The N-butyl methyl ethyl p-nitro phenylmethane did not show decomposition upon distillation. The results and analysis are tabulated on Fig. (7).

REDUCTION OF P-NITRO TERT. OCTYL BENZENE

Reduction was carried out by means of tin and concentrated HCl. A typical run is as follows. (38)

Thirty grams of tin are put into a 500 cc. round bottom flask fitted with an air condenser, and a mechanical stirrer. 100 cc. of concentrated HCl is added and then 20 grams of p-nitro tert. octyl benzene. The mixture is warmed under the hood. After two hours it is allowed to cool, treated with a large amount of water and made alkaline with NaOH. Then steam distilled from a 2 liter flask. The amino compounds coming over with the steam is salted out, separated, dried with crushed, solid KOH and distilled under pressure.

OXIDATION OF P-NITRO TERT. OCTYL BENZENE

The oxidation was adapted from Malherbe's method (29). One gram of the Octyl nitro compound and 20 cc. of dilute nitric acid (1.20 or 6 N.) were sealed in a carius tube, and heated at 130° in the carius combustion furnace. After 3 days yellow-white crystals appeared in the tube. The tube was cold when opened. The contents were poured into a 400 cc. beaker of H₂O. The crystals were suction filtered and freed from some unchanged nitro compound by washing with a little cooled ether. Then were further recrystallized M.P. 235° to 238°. Mixed M.P. with p-nitro benzoic acid showed no depression in the melting point.

PHENOL FROM P-AMINO TERT. OCTYL BENZENE

A typical diazation is as follows (39).

18 grams of p-amino tert. octyl benzene are treated with 10 cc. of concentrated H_2SO_4 in 60 cc. of water. The solid salt formed is suspended in 300 cc. of water. After cooling in an ice bath at 0° , 7.6 grams of sodium nitrite in 32 cc. of water is added drop by drop to the stirred suspension from a dropping funnel with a capillary tube attached to the stem. Starch Iodine paper is used to determine when enough sodium nitrite has been added. The diazotization mixture is acid throughout the reaction.

The diazotized solution is warmed on the steam bath and then steam distilled. The p-tert. octyl phenol was a liquid as the original one. The Alpha naphthylurethane was prepared, as this was the most convenient to prepare. A mixed melting point of this urethane showed no depression with the original phenol from the tert. octanol with phenol in the presence of AlCl_3 . The compound was colorless, M.P. $\approx 94^\circ$.

CONDENSATION OF TERT. OCTANOLS WITH BENZENE

<u>Tert. Octanol</u>	<u>Benzene</u>	<u>AlCl₃</u>	<u>Product</u>	<u>Gms.</u>	<u>Yield</u>
N-butyl methyl ethyl carbinol	97.0 g.	17.0	3-methyl, 3-phenylheptane	29.0	61.4%
N-butyl methyl ethyl carbinol	97.0 g.	17.0	3-methyl, 3-phenylheptane	26.0	57.6%
N-butyl methyl ethyl carbinol	97.0 g.	17.0	3-methyl, 3-phenylheptane	28.2	60.3%
Iso-butyl methyl ethyl carbinol	97.0 g.	17.0	2,4-dimethyl 4-phenylhexane	14.5	31.0%
Iso-butyl methyl ethyl carbinol	97.0 g.	17.0	2,4-dimethyl 4-phenylhexane	12.0	28.4%
Iso-butyl methyl ethyl carbinol	97.0 g.	17.0	2,4-dimethyl 4-phenylhexane	11.2	25.7%
Iso-butyl methyl ethyl carbinol	97.0 g.	17.0	2,4-dimethyl 4-phenylhexane	12.6	29.2%
Sec. butyl methyl ethyl carbinol	97.0 g.	17.0	3,4-dimethyl 4-phenylhexane	6.5	15.4%
Sec. butyl methyl ethyl carbinol	97.0 g.	17.0	3,4-dimethyl 4-phenylhexane	7.5	17.2%
Sec. butyl methyl ethyl carbinol	97.0 g.	17.0	3,4-dimethyl 4-phenylhexane	8.4	18.9%
Sec. butyl methyl ethyl carbinol	97.0 g.	17.0	3,4-dimethyl 4-phenylhexane	8.0	18.3%

Fig. 5

PHYSICAL CONSTANTS OF PARA TERT. OCTYL BENZENES

<u>Para Tert. Octyl Benzene</u>	<u>B. P.</u>	<u>N</u> ^{20°}	<u>D</u> ^{20°}	<u>Surface Tension</u>
3-methyl, 3-phenylheptane	120°-121°/17 mm.	1.4932	0.8738	31.95
2,4-dimethyl 4-phenylhexane	114°-116°/10 mm.	1.4898 ⁹¹⁸	0.8750 ¹⁵⁴	31.27
3,4-dimethyl 4-phenylhexane	111°-114°/10 mm.	1.4919 ²	0.8757	31.05

PARACHORS, SURFACE TENSION AND MOLECULAR VOLUME

<u>Para tert. Octyl Benzene</u>	<u>Surface Tension</u>	<u>Molecular Volume</u> <u>Calc.</u>	<u>Found</u>	<u>Parachors</u> <u>Calc.</u>	<u>Found</u>
3-methyl, 3-phenylheptane	31.95	220.76	218.53	516.43	516.24
2,4-dimethyl 4-phenylhexane	31.27	220.76	218.23	513.43	513.42
3,4-dimethyl 4-phenylhexane	31.05	220.76	218.12	513.43	510.31 ²

Fig. 6

PARA NITRO TERT. OCTYL BENZENES

3-methyl, 3-p-nitro phenylheptane	B.P.-145°-147°/3mm.	Calcu: N = 5.89%
	171°-173°/11mm.	Found: N = 5.72%
2,4-dimethyl, 4-p-nitro phenylhexane	B.P.-162°-163°/9mm.	Calcu: N = 5.83%
		Found: N = 5.81%
3,4-dimethyl, 4-p-nitro phenylhexane	B.P.-159°-60°/9mm.	Calcu: N = 5.89%
		Found: N = _____

PARA AMINO TERT. OCTYL BENZENES

3-methyl, 3-p-amino phenylheptane	B.P.-129°-130°/3mm.	Calcu: N = 6.82%
		Found: N = 6.74%
2,4 dimethyl, 3-p-amino phenylhexane	B.P.-130°-131°/3mm.	Calcu: N = 6.82%
		Found: N = 6.67%
3,4 dimethyl, 3-p-amino phenylhexane	B.P.-134°-136°/3mm.	Calcu: N = 6.82%
		Found: N = _____

FIG. 7

SUMMARY

(1) Sec. butyl methyl ethyl carbinol was not reported in literature and was prepared by two methods, the physical constants determined and analysis for carbon and hydrogen determined.

(2) The four butyl methyl ethyl carbinols were condensed with phenol in the presence of aluminum chloride to give good yields of 3-methyl, 3-p-hydroxyphenylheptane, 2,4 dimethyl, 4-p-hydroxyphenylhexane, 3,4-dimethyl, 4-p-hydroxyphenylhexane, and 2,2,3-trimethyl, 3-p-hydroxyphenylpentane.

The structures of 3-methyl, 3-p-hydroxyphenylheptane; 2,4 dimethyl, 4-p-hydroxyphenylhexane and 3,4 dimethyl, 4-p-hydroxyphenylhexane were proven by syntheses.

(3) The benzoyl esters, alpha naphthyl urethanes and phenyl urethanes were prepared from 3-methyl 3-p-hydroxyphenylheptane; 2,4 dimethyl, 4-p-hydroxyphenyl hexane, and 3,4 dimethyl, 4-p-hydroxyphenylhexane, and 3,4 dimethyl, 4-p-hydroxyphenylhexane and all derivatives were solids.

(4) The benzoyl esters were analyzed for carbon and hydrogen. The alpha naphthyl urethanes and phenyl urethanes were analyzed for nitrogen.

(5) N-butyl methyl ethyl carbinol, iso-butyl methyl ethyl carbinols and sec. butyl methyl ethyl carbinols were condensed with Benzene in the presence of Aluminum Chloride to give the corresponding tert. octyl benzenes.

(6) Only the phenyl urethane was prepared from the 2,²~~3~~,3 trimethyl-2-p-hydroxyphenylpentane.³

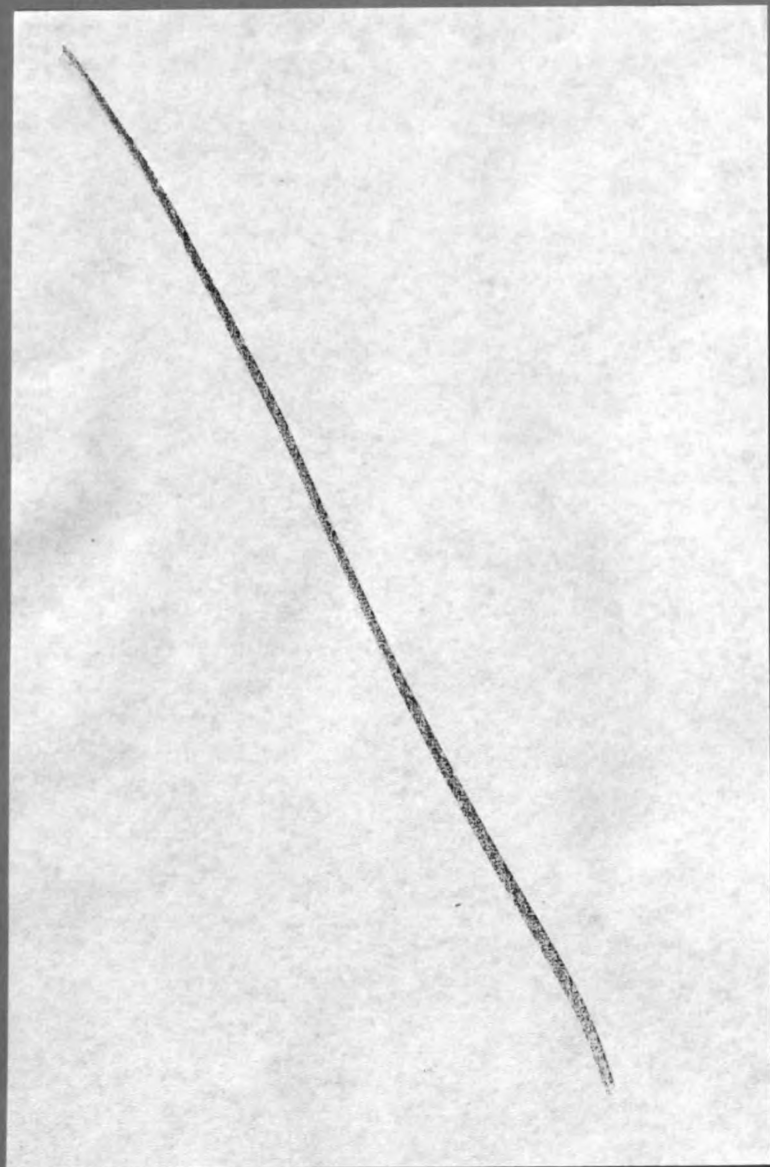
(7) The physical constants of the three p-tert. octyl benzenes were determined. The calculated parachors and calculated molecular volume checked with that determined experimentally.

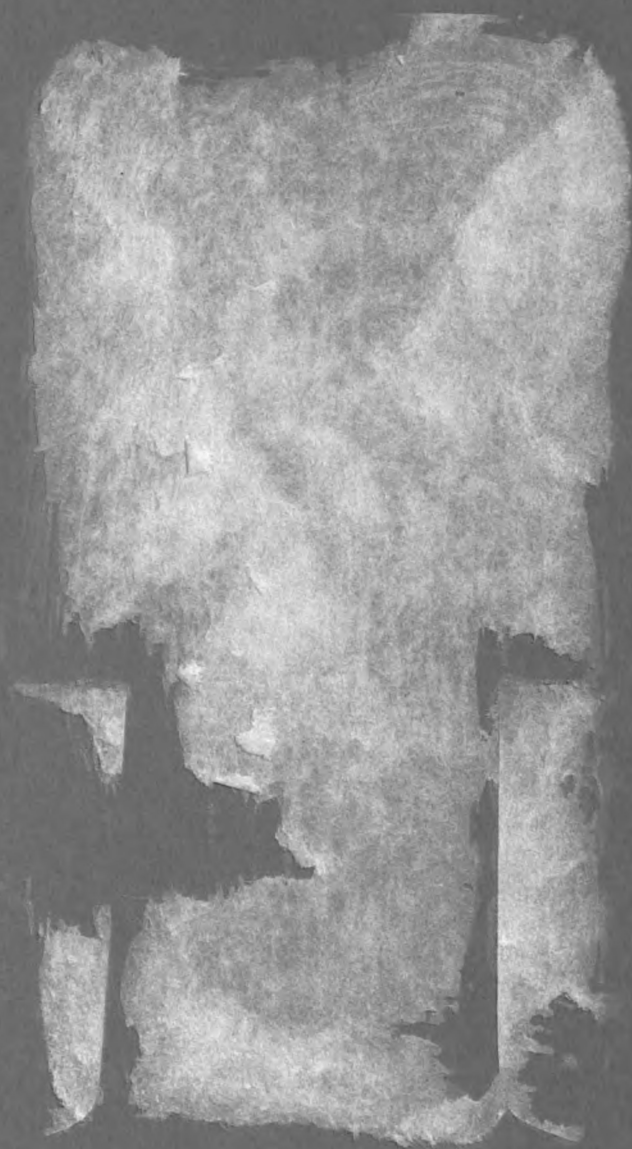
(8) The p-nitro tert. octyl benzenes, and p-amino tert. octyl benzenes were analyzed for carbon and hydrogen. *mixture*

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