THE CONDENSATION OF DIETHYL N-PROPYL CARBINOL AND DIETHYL ISOPROPYL CARBINOL WITH PHENOL IN THE PRESENCE OF ALUMINUM CHLORIDE

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INTRODUCTION

In the year 1916 Huston and Friedman (1) discovered that aromatic alcohols condense with aromatic hydrocarbons in the presence of aluminum chloride as a catalyst.

In the year 1936 Huston and Hsieh (3) discovered that some simple tertiary aliphatic alcohols condense with phenol in the presence of aluminum chloride. Since that time Huston and coworkers have condensed a number of tertiary aliphatic alcohols with phenol.

In order to further this investigation, diethyl normalpropylcarbinol and diethylisopropylcarbinol were condensed with phenol.

HISTORICAL

There are a number of methods by which phenols may be alkylated. Since this work is concerned only with the condensations of phenol in the presence of aluminum chloride, only this type of condensation will be discussed. However, it should be mentioned that in 1884 Auer (4) obtained alkyl phenols from simple aliphatic alcohols and phenol, with a mixture of zinc chloride and zinc.

In 1897 Nef (5) reported the formation of diphenyl methane from benzyl alcohol and benzene with aluminum chloride as a catalyst. Huston and Friedman (2) repeated his work with a 30 % yield. They continued this work and condensed mixed aliphatic aromatic secondary alcohols and aromatic secondary alcohols with benzene.

In 1924 Huston (6) extended the reaction of benzyl alcohol using phenol, anisole, and phenitole. 45, 45, and 50 percent yields respectively were obtained. In 1926 Huston and Sager (7) attempted to condense a number of primary alcohols with benzene and were successful only with allyl alcohol. Huston and Neumann (8) then condensed allyl alcohol with phenol.

Later Huston (9) and co-workers reported the condensation of benzhydrol, methylphenyl and ethylphenyl carbinols with phenol giving good yields. Benzhydrol gave a much higher yield of condensation product. Due to the fact that benzhydrol has two alpha carbons which are on unsaturated benzene rings, this gave additional information as to the effect of unsaturation of the alpha carbon atom on condensations.

Huston and Wilsey (10), and Huston and Hradel (11) attempted to condense several diaryl-alkyl alcohols and dialkyl-aryl alcohols with benzene, with no success. Only dehydration of the alcohol occurred.

Huston and Hsieh (3) opened a new field, with the condensation of saturated aliphatic secondary and tertiary alcohols with phenol and benzene or their homologs. They obtained cumene by the condensation of isopropyl alcohol with benzene in the presence of aluminum chloride. They discovered that under the conditions used, primary alcohols do not condense either with benzene or phenol, secondary alcohols condense with benzene, and tertiary alcohols condense with phenol. Huston and Fox (12) condensed the tertiary alcohols which had already been condensed by Huston and Hsieh (3) with phenol, with benzene. Tzukervanik (13) condensed simple secondary and tertiary alcohols with benzene and tolulene, but explained the condensations by a different mechanism. The condensation reactions of the tertiary alcohols were extended to the tertiary heptyl alcohols. These alcohols were condensed with phenol and benzene by Huston and Hedrick (14), and Huston and Binder (15) respectively.

Very recently Huston and Guile (16) extended this investigation to the tertiary octyl alcohols. They were successful in condensing the eight dimethyl amyl carbinols with phenol.

Huston and Breining (17) condensed diethyl isopropyl carbinol and diethyl normalpropyl carbinol with benzene. This present work deals with the condensation of these two alcohols with phenol, with aluminum chloride as a catalyst.

THEORETICAL

It has been shown by Huston and co-workers that in every case in which there is condensation between an alcohol and an aromatic hydrocarbon, the alpha carbon atom of that alcohol must be under strain. This strain causes the bond between the carbon and oxygen of the hydroxyl group to be relatively unstable. There are three main types of alcohols which fall into this classification:

1. Aromatic alcohols in which the alpha carbon atom is a member of a ring
2. Allyl alcohols
3. Tertiary alcohols

Secondary alcohols are under some strain and might belong to the third group. In allyl and benzyl alcohols there are two groups attached to the carbinol carbon, each of which has a strong attraction for the electron pair between the carbon and oxygen. In tertiary and secondary aliphatic alcohols, the alkyl groups have a relatively small attraction for that electron pair allowing the pair to shift close to the oxygen, thus giving the OH group a tendency to split off.

Three mechanisms have been proposed for condensations between tertiary aliphatic alcohols and aromatic hydrocarbons:

1. Alkyl halide formation plus Friedel-Craft reaction.
2. Alkene formation plus condensation.
3. Ether formation plus rearrangement.

The net result is that the hydroxyl group splits off of the alcohol and a hydrogen splits off of the aromatic compound with the formation of water. These mechanisms attempt to explain how the net result is accomplished.

Alkyl Halide Formation Plus Friedel-Crafts Reaction: This was the scheme outlined by Tzukervanik and Nazarova (13). They observed that after the first phase of the condensation, there were present all the components of the Friedel-Craft reaction. They proposed that the reaction proceeds in several steps:

1. Aluminum chloride plus tertiary alcohol gives an aluminate plus HCl.
2. $AlCl_2OH$ splits from the alcohol giving an olefin.
3. Olefin plus HCl gives an alkyl halide.
4. Alkyl halide plus aromatic compound gives alkyl-aryl compound plus HCl.

It seems unlikely that this is the proper mechanism. It appears illogical that the hydrogen of a tertiary OH group can be replaced by the aluminate radical. Hedrick (14) proved that any HCl given off couldn't be used to form an alkyl halide. He added a tertiary alcohol to some aluminum chloride in an inert solvent and there was instantaneous evolution of hydrogen chloride. If HCl were evolved, it would not be available for alkyl halide formation.

Alkene Formation Plus Condensation: This idea was offered by McKenna and Sowa (18) for the alkylation of benzene with boron trifluoride as a catalyst. Evidence of this reaction is shown by the fact that normal and secondary alcohols give identical products as do iso and tertiary alcohols. McGreal (19) and Niederal suggested a like mechanism for condensation with the use of zinc chloride. There is evidence against such a mechanism in the case of aluminum chloride. However, it is true that olefins do condense with aromatic hydrocarbons in the presence of aluminum chloride. A much higher temperature was used with the hydrocarbon condensations as well as a different catalyst. Consequently, contrary to the work of Huston and Sagar (7), they were able to condense primary alcohols and benzene.

Ether Formation Plus Rearrangement:

Smith (20) has shown that a number of alkyl ethers will rearrange into alkyl phenols. Rearrangement may be effected by equal molecular amounts of aluminum chloride. However, there is a great deal of evidence which indicates that this is not the mechanism of condensation. Tertiary alcohols may be condensed with compounds which have no possibility of intermediate ether formation such as benzene, anisole, and phenetole.

No mechanism yet reported has been very satisfactory. It is possible that the reactions proceed through an intermediate addition compound of aluminum chloride, alcohol, and phenol, followed by rearrangement.

EXPERIMENTAL

Materials

1. N-butyric acid. This was obtained from Eastman's. (B.P. 161-163° C)
2. Isobutyric acid. Eastman's (B.P. 153.5-155° C)
3. Ethyl bromide. Eastman's (B.P. 38-40° C)
4. Chloracetic acid. Eastman Practical
5. Ethyl alcohol. Obtained from the stockroom, 95 %.
6. N-butyrlchloride was prepared from n-butyric acid and phosphorous trichloride. (B.P. 99-101° C)
7. Iso-butyrylchloride was prepared from isobutyric acid and phosphorous trichloride. (B.P. 90-92° C)
8. Phosphorous trichloride. Obtained from Eastman.
10. This was redistilled, using a one-degree fraction.
11. Aluminum Chloride. Merck's Reagent anhydrous resublimed.
12. Magnesium turnings. These were especially prepared for Grignard reactions and were dried in a desiccator over calcium chloride.
13. Benzene. Thiophene free C.P. This was dried over freshly cut sodium.
14. Anhydrous ether for Grignard reactions which was dried over freshly cut sodium.
15. Petroleum ether. B. P. 30-65° C. Dried over freshly cut sodium.

16. Diethyl n-propyl carbinol. This alcohol was prepared in three ways:

   1. Ethyl butyrate reacting with two moles of ethyl magnesium bromide.
   2. N-butyryl chloride reaction with two moles of ethyl magnesium bromide.
   3. Chloracetyl chloride reacting with three moles of ethyl magnesium bromide.

17. Diethyl isopropyl carbinol. This was prepared from isobutyryl chloride and two moles of ethyl magnesium bromide.

The Preparation of the Alcohols

A. The Preparation of the Grignard Reagent.

The only Grignard reagent used was ethyl magnesium bromide. The usual Whitmore procedure (21 and 22) was modified somewhat. Less ether was used and a faster rate of addition employed.

In a three liter three-necked flask fitted with an efficient glycerine sealed stirrer, reflux condenser, and dropping funnel are placed four moles of magnesium turnings (98 grams). Thirty cc. of a mixture of four moles of ethyl bromide and two volumes of anhydrous ether are added directly to the turnings. After the reaction has started and progressed for a few minutes, 200 cc. of ether is added directly to the dry magnesium. The remaining halide ether solution is then added with stirring at such a rate that the ether refluxes about one drop per second. After about one-half of the halide solution has been added, the solution in the flask may become warmer than the reflux temperature of ether due to the formation of the Grignard reagent. Under these circumstances, a little external cooling may be used. After the halide-ether mixture has been added, the solution is stirred for four more hours and let stand overnight.

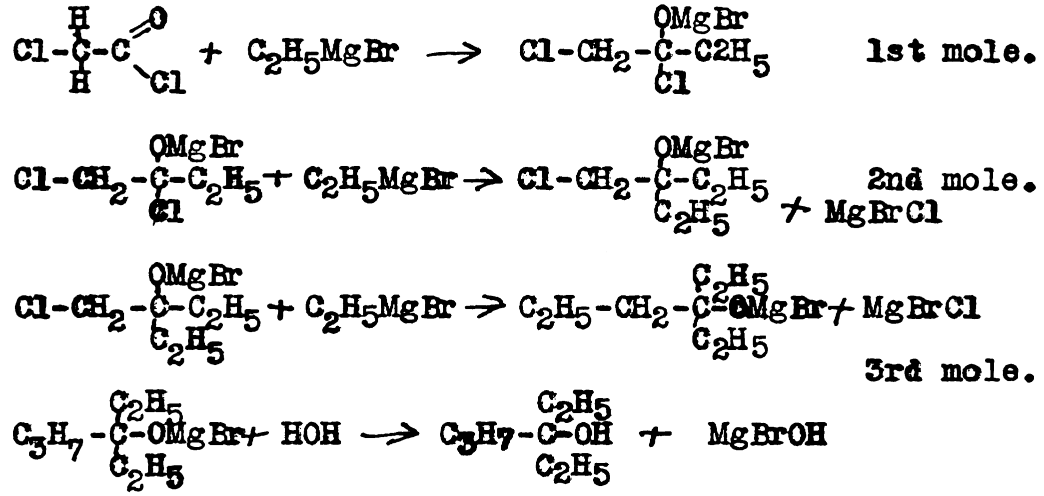
After the solution has stood overnight, the proper amount of the ester or acid halide is diluted with two volumes of anhydrous ether. This solution is added at the rate of one drop per second until all of the solution has been added. The formation of the addition complex is instantaneous and therefore it may be hydrolyzed immediately. It is decomposed by pouring on ice. The precipitated magnesium compounds are dissolved by adding 10 % HCl until the solution is clear. The ether layer is separated and the water layer is extracted several times with ether. The ether solutions are combined and are washed with dilute sodium carbonate solution. They are then dried over anhydrous sodium sulfate.

The ether is evaporated off and the alcohol distilled under vacuum.

B. The Preparation of Diethyl N-Propyl Carbinol

Diethyl n-propyl carbinol was first prepared by Masson (25) from ethyl butyrate and ethyl magnesium bromide. It was later prepared by Clarke and Riegel (23) from diethyl ketone and n-propyl magnesium bromide. It was prepared by Whitmore (24) by the Grignard-ester synthesis, and Breining prepared it from normal butyryl chloride and ethyl magnesium bromide. The author prepared this alcohol by both the ester and acid chloride synthesis with yields between 62 and 70 percent in each case. Jackson (Kedzie Chemistry Laboratory) suggested that an attempt be made to make this alcohol using one mole of chloracetyl chloride and three moles of ethyl magnesium bromide.

Equations for this reaction:



$$(1)\quad Cl-\overset{H}{\underset{H}{C}}-C\overset{\nearrow O}{\searrow Cl} + C_2H_5MgBr \rightarrow Cl-CH_2-\overset{OMgBr}{\underset{Cl}{C}}-C2H_5 \qquad \text{1st mole.}$$

$$(2)\quad Cl-CH_2-\overset{OMgBr}{\underset{Cl}{C}}-C_2H_5 + C_2H_5MgBr \rightarrow Cl-CH_2-\overset{OMgBr}{\underset{C_2H_5}{C}}-C_2H_5 + MgBrCl \qquad \text{2nd mole.}$$

$$(3)\quad Cl-CH_2-\overset{OMgBr}{\underset{C_2H_5}{C}}-C_2H_5 + C_2H_5MgBr \rightarrow C_2H_5-CH_2-\overset{C_2H_5}{\underset{C_2H_5}{C}}-OMgBr + MgBrCl \qquad \text{3rd mole.}$$

$$(4)\quad C_3H_7-\overset{C_2H_5}{\underset{C_2H_5}{C}}-OMgBr + HOH \rightarrow C_3H_7-\overset{C_2H_5}{\underset{C_2H_5}{C}}-OH + MgBrOH$$

72 and 77 percent yields were obtained by this method. The only modification of the above Grignard procedure was that after the addition of the chloracetyl chloride to the Grignard reagent, the ether was evaporated off and the reaction mixture was let stand on the steam bath for twenty-four hours in order to insure the hydrocarbon type of synthesis on the alpha carbon atom.

C. The Preparation of Diethyl Isopropyl Carbinol

Breining prepared this alcohol from isobutyryl chloride and two moles of ethyl magnesium bromide. This was the method by which this alcohol was prepared, and the procedure used was the same as the above procedure for the preparation. of diethyl n-propyl carbinol.

Diethyl n-propyl carbinol boiled at 55.56°C at 8 mm. pressure, or 157-157.8°C at 744.5 mm. pressure. Diethyl isopropyl carbinol boiled at 33-35°C at 8 mm. pressure or at 157-158°C at 742 mm.

Condensations With Phenol

The following procedure for the condensing of the above alcohols with phenol has been found to be very satisfactory for the past and present workers in this laboratory.

A 500 cc. round-bottomed three-necked flask was fitted with a condenser, mechanical glycerine sealed stirrer, and stopper fitted with a thermometer. Thirty-two grams (0.25 mole) of octyl alcohol and 47 grams (0.5 mole) of phenol, dissolved in 200 cc. of petroleum ether were placed in the flask. Seventeen grams (0.125 mole) of aluminum chloride were added to the flask over the course of an hour. The temperature was controlled between 25 and 30° C by immersing the flask in cold water. The condenser was protected from the moisture of the air by a calcium chloride tube. HCl was given off during the course of the reaction. After standing overnight, the mixture was poured into ice and concentrated HCl. The two layers were separated. The water layer was extracted three times with ether and this extract combined with the ether layer. The combined extract was dried over anhydrous sodium sulfate and the ether removed at ordinary pressure.

The residue was fractionated with a Claisen flask having a 12 to 18 inch column. Three main fractions were obtained in this fractionation. The fractionation was carried out with a pressure from 2 to 7 mm. The first fraction below 65° C consisted mainly of unreacted alcohol and its decomposition products. The next fraction up to 100° C was chiefly phenol. The fraction 100-130° C was mainly the octyl phenol and was refractionated several times in order to obtain a product which distilled over a narrow range.

The average yield of the condensation product of diethyl n-propyl carbinol and phenol was 36 %. The average yield of the condensation product of isopropyl carbinol and phenol was 54 %.

Derivatives

A. Benzoyl Esters

Benzoyl esters of both alkyl phenols were prepared. The procedure used is that of Shriner and Fuson (26). Three grams of the alkyl phenol were dissolved in 4 cc. of pyridine and 3 cc. of benzoyl chloride were added. After the initial reaction, the mixture was refluxed over a low flame for one hour and then poured on ice. The material was extracted with ether. The pyridine was removed by washing with dilute sulfuric acid and then the excess acid was removed by washing with sodium carbonate solution. The ether was removed and the ester distilled under reduced pressure. After standing in the refrigerator, the ester crystallized out. The oil was removed on a porous plate, and the ester was recrystallized from petroleum ether and from ethyl alcohol until it had a constant melting point. Data on these esters are found in table II.

B. Alpha-naphthylurethanes

These were prepared in the method described by Wertel (16). One gram of the tertiary octyl phenol was placed in a test tube and 1.5 cc. of alpha-naphthyl isocyanate was added, the reaction being catalyzed by two drops of dilute anhydrous ether solution of trimethylamine. The tube was fitted with a calcium chloride tube. The reaction was heated on a steam bath for a half an hour and cooled. The solidified contents were extracted with 60 cc. of boiling ligroin (B.P. 80-120° C) and filtered. Upon cooling the urethane crystallized out. It was recrystallized from petroleum ether until a constant melting point was obtained. Data on these urethanes are given in Table III.

Proof of Structure

The proof of structure of these phenols was carried out in a manner similiar to that described by Guile (16) and Hedrick (14). The first step in this procedure was the preparation of the corresponding alkyl benzene. Both of these alkyl benzenes were prepared by Breining (17). Data on this are given in Table IV. The second step was the preparation of the para nitro alkyl benzene. The third step was the oxidation of the above nitro compound to para nitro benzoic acid in order to prove that it was substituted in the para position. The fourth step was the reduction of the nitro compound to the corresponding amino compound. The fifth step was the diazotization of this amine and hydrolysis to the corresponding phenol.

A. Preparation of the Alkyl Benzenes

The procedure for the preparation of the alkyl benzenes is very similiar to that for the preparation of the alkyl phenols. Both Breining and Guile (17 and 16) give a detailed procedure for these condensations.

B. Nitration of the Tertiary Octyl Benzenes

Malherbe's (27) procedure was used. The hydrocarbon was treated with an equal weight of fuming nitric acid and cooled during the addition. After the reaction had subsided, the mixture was warmed to 90° C on a steam bath for an hour. It was then poured on ice and extracted with ether three times. This extract was dried over calcium chloride and after the removal of the ether, was fractionally distilled under reduced pressure. Data on these compounds are given in Table V.

C. Oxidation of the Para Nitro Tertiary Alkyl Benzenes

Malherbe's (27) method was used for this oxidation. The purpose was to establish the position of the tertiary alkyl group on the benzene ring. One gram of the nitro compound and 20 cc. of 6 N nitric acid were placed in a Carius tube, sealed and heated in a Carius furnace at 130° C until a large number of crystals had formed in the tube. From three to eight days were required. The crystals were removed from the tube. They were washed with hot petroleum ether to remove oily materials and then recrystallized several times from alcohol. In both cases the crystals melted 238-240° C and there was no lowering of the melting point when mixed melting points were taken with para nitro benzoic acid. This indicated that the alkyl group was para to the hydroxyl group in the original compound.

D. Reduction of the Para Nitro Tertiary Alkyl Benzenes

Thirty grams of tin were placed ina liter Erlenmeyer flask. About 15 grams of p-nitro tertiary alkyl benzene were added and 100 cc. of concentrated HCl. The mixture was heated on the steam bath. If there still was an oily layer on top of the liquid after the tin had been digested, more tin an HCl were added. After addition of 200-300 cc. of water, the mixture was made alkaline with 40 percent sodium hydroxide. The alkaline solution was steam distilled. The distillate was extracted with ether and the ether solution was dried with solid potassium hydroxide. After removal of the ether, the solution was fractionally distilled in a small modified Claisen flask. Data on these amines are found in Table VI.

E. Phenols From the Para Amino Tertiary Alkyl Benzenes

The procedure used was that given by Guile (16). The amine was treated with concentrated sulfuric acid, 5 cc. in 10 cc. of water, for each 2 grams of amine. The solid amine salt was suspended in ten times the volume of water. The solution was cooled to 5^{o} C and an equivalent amount of 25 percent sodium nitrite solution calculated to react with the amine, was added over a five hour period. Stirring was continued for two hours and the solution was warmed on the steam bath for an hour. The reaction mixture was steam distilled. The phenol was extracted from the distillate with ether, and the extract dried over anhydrous sodium sulfate. The pure alkyl phenol was obtained by fractional distillation under reduced pressure.

Benzoyl esters and alphanaphthyl urethanes were made of the two above phenols. In each case the melting points of the derivatives were the same as that of the corresponding derivative of the phenol made by condensation of the tertiary alcohol with phenol in the presence of aluminum chloride. There were no melting point depressions when mixed melting points were taken. This indicated that the alkyl phenols synthesized by the two different methods were identical.

Tables of Physical Constants

Table I. Alkyl Phenols

	Diethyl n-propyl p-hydroxy phenyl methane	Diethyl isopropyl p-hydroxy phenyl methane
Melting Point °C	(liquid)	33.5-34
Boiling Point: °C		
Atmospheric Pres.	265, 741 mm.	260, 741 mm.
Reduced Pressure	134-137, 6 mm.	110-112, 2 mm.
Refractive Index $N_D^{14.5^\circ C}$	1.5212	(solid)
Surface Tension 27°C	36.62	(solid)
Specific Gravity $\frac{20^\circ}{20^\circ}$	.9561	(solid)
Percent Carbon*	81.60	81.42
Percent Hydrogen*	10.92	10.69

* Calculated for $C_{14}H_{22}O$, C = 81.49 H = 10.75

Table II. Alkyl Benzenes

Alkyl Benzene	Average Yield	Boiling Point
Diethyl n-propyl phenyl methane	46 %	90-93°C, 6 mm.
Diethyl isopropyl phenyl methane	42 %	70-71°C, 3 mm.

Table III. Para Nitro Alkyl Benzenes

Substance	Boiling Point °C	Analysis: % N*
Dithyl n-propyl p-nitro phenyl methane	125-130, 3 mm.	6.07
Diethyl isopropyl p-nitro phenyl methane	130-135, 6 mm.	5.97

* Calculated for $C_{14}H_{21}O_2N$, N = 5.95

Table IV. Para Amino Tertiary Octyl Benzenes

Substance	Boiling Point °C	Analysis: % N*
Diethyl n-propyl p-amino phenyl methane	120-125, 3 mm.	6.80
Diethyl isopropyl p-amino phenyl methane	125-130, 6 mm.	6.75

* Calculated for $C_{14}H_{23}N$, N = 6.82

Table V. Benzoyl Esters

Benzoyl Ester of	Melting Point °C	Analysis*	
		% C	% H
Diethyl n-propyl p-hydroxy phenyl methane	40-40.5	81.18	8.42
Diethyl isopropyl p-hydroxy phenyl methane	38.2-38.6	81.06	8.64

* Calculated for $C_{21}H_{26}O_2$, C = 81.24 H= 8.44

Table VI. Alpha Naphthyl Urethanes

Alpha Naphthyl Urethane of	M. P. °C	Analysis: % N*
Diethyl n-propyl p-hydroxy phenyl methane	106.7-107	3.66
Diethyl isopropyl p-hydroxy phenyl methane	1.28-128.5	3.68

* Calculated for $C_{26}H_{29}O_2N$, N = 3.73

SUMMARY

1. The tertiary octyl alcohols, diethyl n-propyl carbinol and diethyl isopropyl carbinol, have been condensed with phenol in the presence of aluminum chloride to yield p-tertiary octyl phenols.

2. The benzoyl esters and alpha naphthyl urethanes of these two phenols have been prepared.

3. The structures have been established by synthesizing them in a different way.

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