CONDENSATION OF SOME ALKYL PHENYL CARBINOLS WITH PHENOL IN THE PRESENCE OF ALUMINUM CHLORIDE

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By

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INTRODUCTION

Although previous workers in this laboratory have condensed alkyl phenyl carbinols with phenol, the study of these condensations was still incomplete.

The ortho alkylphenol was reported only in the condensation of propyl phenyl carbinol with phenol. Its formation may be expected in all condensations of this type. For this reason it was considered desirable to continue the study of the condensation of alkyl phenyl carbinols with phenol. Methyl through amyl phenyl carbinols were prepared, and condensed with phenol in the presence of aluminum chloride.

HISTORICAL

A complete review of the literature dealing with the alkylation of aromatic compounds would be needless repetition. Many previous papers have furnished brief and fairly complete surveys (1), (2), and (3). An extensive survey on the role of aluminum chloride in organic chemistry has been made by Thomas (4).

Since this work is a study of the condensation of alkyl phenyl carbinols with phenol in the presence of aluminum chloride, only those researches dealing with this subject will be summarized.

Earlier workers in this laboratory who condensed alcohols with phenol, used two methods. Huston and Hsieh (20) devised a procedure where the alcohol and phenol were dissolved in petroleum ether, and the aluminum chloride was added in portions. Esterdahl (21) modified the procedure of Huston and Hsieh by using no solvent to condense some secondary alcohols with phenol. Breiter (22) used this method to condense octyl alcohols with phenol. The second procedure developed by Huston and Hedrick (23) consisted of suspending the aluminum chloride in petroleum ether and adding a solution of phenol and carbinol in petroleum ether dropwise from a dropping funnel.

Aromatic alcohols had not been condensed with aromatic compounds in the presence of aluminum chloride until Huston and Friedmann (24) began their investigations in 1916. Later, they extended their experiment (25) to secondary alcohols with benzene and aluminum chloride using methyl phenyl carbinol, ethyl phenyl carbinol and benzhydrol, obtaining diphenylmethane, diphenylpropane

and triphenylmethane respectively. The temperature and amounts of reagents were varied to find conditions for the greatest yield. In preparing 1,1-diphenylethane they obtained the best yield (65%) by keeping the temperature below 10°C and using one half of a molecular equivalent of methyl phenyl carbinol and five moles of benzene. Under these conditions they also obtained a 40% yield of 1,1-diphenylpropane. Huston and Friedmann (Loc.cit.) report that an excess of aluminum chloride tends to eliminate a phenyl or an alkyl radical from the product especially if the temperature is not kept low.

Alkylation of phenol by means of methyl and ethylphenyl carbinols was reported by Huston, Lewis, and Grotemut (5) in 1927. They obtained 33-35% p-hydroxy-1,1-diphenylethane, and 27-30% p-hydroxy-1,1-diphenylpropane from the two carbinols. Proof that the entering group takes the para position on phenol was obtained by oxidising the methyl ether to p-methoxybenzophenone.

In 1926 Bartlett (6), working in this laboratory condensed butyl phenyl carbinol with phenol. He obtained a 33% yield of p-hydroxy-1,1-diphenylpentane, but it was not pure enough to recrystallise or form a derivative. He made no mention of the ortho isomer.

Huston and Strickler (7) condensed propyl phenyl carbinol with phenol in 1927 to obtain 20% p-hydroxy-1,1-diphenylbutane and 6% o-hydroxy-1,1-diphenylbutane. Up to this time the preparation of the ortho alkylphenol had not been reported. They also

prepared the ortho isomer by Claisen's (8) method of ring alkylation, as additional evidence of its formation.

Thus, a study of the alkylation of phenol with alkyl phenyl carbinols, initiated by Huston and co-workers included the first four alkyl phenyl carbinols with the publication of Huston and Strickler in 1933.

EXPERIMENTAL

I Preparation of Aromatic- Aliphatic Carbinols

Amyl phenyl carbinol can be conveniently prepared by the addition of a Grignard reagent to benzaldehyde the best results are obtained when heat is not applied (9) and particularly by controlling the relative proportion of the reactants. In studying ethyl phenyl carbinol, Meisenheimer (10) found that the best results could be obtained when the Grignard reagent and the benzaldehyde were in the proportion 3:2, otherwise large quantities of benzyl alcohol and high boiling by-products are obtained.

The preparation of amyl phenyl carbinol will be described in detail, the other carbinols were prepared by the same method. See Table I for data.

Preparation of Amyl Phenyl Carbinol

The reaction was carried out in a 5 liter three-neck flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel. The condenser and dropping funnel were fitted with calcium chloride tubes filled with a calcium chloride-soda lime mixture to protect the reaction mixture from moisture and carbon dioxide.

Into the dry flask was placed 6.4 moles (153.6 g.) magnesium turnings with 500 ml. anhydrous ether. To start the reaction 25 ml. of an amyl bromide (B.P. 128-129 /740mm., n_D^{20} 1.444) was added. The remainder of the 6 moles (941g.) of amyl bromide mixed with one liter of anhydrous ether, was added dropwise when it was evident that the reaction had started. The mixture was stirred

for two hours after addition of the bromide then allowed to stand overnight.

The Grignard reagent was analyzed by Gilman's (11) method in which an aliquot was hydrolysed with standard acid, and back titrated with standard base. Starting with 6 moles amyl bromide, 5.7 moles (95%) Grignard reagent was obtained.

The Grignard reagent was packed in ice and 3.8 moles (402.8g.) freshly redistilled benzaldehyde (B.P. 174-178°C./743 mm.) in one liter anhydrous ether was added dropwise. After addition was complete the mixture was stirred for two hours and allowed to stand overnight. After hydrolysis with ice and dilute hydrochloric acid, the organic layer was separated. The water layer was extracted four times with 150 ml. ether. The ether extracts were combined, washed with 10% sodium bicarbonate then water and dried over anhydrous sodium sulphate. The ether was removed (distilled) at atmospheric pressure and the residue fractionated at reduced pressure.

After three distillations, 473.5g. 70% amyl phenyl carbinol was obtained, boiling at 128-131°C./6mm.

COMPOUND	EXPERIMENTAL			LITERATURE		
	Boiling Point	n_D^{20} Refractive Index	$Sp.G._4^{20}$	Boiling Point	Refractive Index	Sp.G.
Methyl Phenyl Carbinol	93-94°/11mm.	1.5210	1.006	94°/12mm. (13)	n_D^{20} 1.5211 (17)	$Sp.G._4^{15}$ 1.008 (14)
Ethyl Phenyl Carbinol	82-83°/4mm. 70 /1mm.	1.5220	1.001	93°/4mm (16) 105-8°/10mm. (17)	n_D^{20} 1.5208 (16)	$Sp.G._4^{20}$ .9967 (15)
Propyl Phenyl Carbinol	89-91°/4mm.	1.5198	.988	94-96°/6mm. (7)	$n_D^{13.7}$ 1.51914 (18)	$Sp.G._4^{24}$ .980 (19)
Butyl Phenyl Carbinol	97-98°/1mm.	1.5090	.960	115°/6mm. (16)	n_D^{20} 1.5078 (16)	$Sp.G._4^{24}$ .966 (19)
Amyl Phenyl Carbinol	108°/1mm. 128-131°/6mm.	1.5060	.950	128°/5mm. (16)	n_D^{20} 1.5105 (16)	

ALKYL PHENYL CARBINOLS

TABLE I

II Aluminum Chloride Condensations

To ascertain which method would give better yields in condensing secondary aliphatic-aromatic alcohols with phenol, two condensations were carried out. One mole of butyl phenyl carbinol was condensed with phenol according to the method of Huston and Hsieh (20). The carbinol and phenol were dissolved in anhydrous petroleum ether, and the aluminum chloride added in portions. The result was (86.18g.) 36% crude alkylphenol, boiling at 155-166°C. /1mm. A second condensation was carried out using the method of Huston and Hedrick (23). The aluminum chloride was suspended in anhydrous petroleum ether and a mixture of phenol and carbinol in petroleum ether added dropwise. One mole of butyl phenyl carbinol by this method produced only (56.96g.) 24% crude alkylphenol, boiling at 155-166°C./1 mm. The temperature during the condensations was not allowed to rise above 30°C.

To determine the effect of temperature on the yield of alkylphenol, two condensations were carried out. One-fourth mole of methyl phenyl carbinol was condensed with one-fourth mole phenol using one-eighth mole aluminum chloride according to the procedure of Huston, Lewis and Grotemut (5) modified by using anhydrous petroleum ether as a solvent. When the temperature was kept below 40° C. during addition of the aluminum chloride (20.45 g.) 41% p-hydroxy-1,1-diphenylethane was produced. A second condensation was carried out under similar conditions but the temperature during

addition of the aluminum chloride was not allowed to exceed 10°C., the yield of p-hydroxy-1,1-diphenylethane increased to (22.58g.) 46%.

To determine the effect of low temperature on the condensation of longer chain carbinols, one-half mole butyl phenyl carbinol was condensed with .6 mole phenol using .25 mole aluminum chloride and petroleum ether. The temperature was held under 10°C. Under these conditions phenol crystallized on the side of the flask and the reaction mixture remained yellow. After eight hours at 10°C. the reaction mixture was allowed to warm up to room temperature and stirred for four hours. The characteristic deep red addition product was formed and a 36% yield of alkylphenol resulted. This is evidence that a longer carbon chain alcohol, requires a higher temperature for condensation.

A - Condensation of Methyl Phenyl Carbinol With Phenol

A one liter three-neck flask was fitted with a mercury sealed mechanical stirrer, condenser containing a thermometer and an addition tube for introduction of the anhydrous aluminum chloride from a shaker. The following reagents were introduced into the flask: .41 mole (50 g.) methyl phenyl carbinol, .50 mole (47.50 g.) phenol and 400 ml. anhydrous petroleum ether. The anhydrous aluminum chloride was added in small portions over a period of two hours while the temperature was held below 10° C. using an ice bath. A pink color was first produced, then as the color deepened to an orange, gaseous hydrogen chloride was given off and a gummy addition

product formed. The mixture was stirred for eight hours and then allowed to stand twelve hours before hydrolysis with ice and dilute hydrochloric acid. The organic layer was separated, and the water layer extracted three times with 50ml. of ether. The ether extracts were combined and washed with 10% sodium bicarbonate to remove the acid and then water to remove the base.

The ether extract was dried over anhydrous sodium sulphate. The ether was distilled off at atmospheric pressure and the residue fractionated at reduced pressure using a 10 in. heated Vigreux column.

The following fractions were obtained:

	up to 83°C./18mm.	7.10 g. phenol discarded
(1)	75 - 93°C./1mm.	20.22 g. phenol and carbinol
(2)	131 - 150°C./1mm.	43.30 g. alkyl phenol
(3)	148 - 150°C./1mm.	5.16 g. alkyl phenol
(4)	Residue	11.42 g.

Fraction (2) partially solidified, fraction (3) solidified immediately. Fraction (2) on redistillation crystallised giving 41.22 g. boiling at 148-150°C./1mm. This gives a total yield of (46.45 g.) 57% p-hydroxy-1,1-diphenylethane. The solid was recrystallised from petroleum ether to a constant melting point, forming needles melting at 57-57.5°C. Huston, Lewis and Gretemut (5) prepared p-hydroxy-1,1-diphenylethane, obtained 33-35% yield and report a melting point of 57-58°C. and a boiling point of 168-170°C./5mm. The ortho substitution product was expected but not formed in

quantities sufficient for isolation.

B - Condensation of Ethyl Phenyl Carbinol With Phenol

The condensation was carried out using the same procedure as in the condensation of methyl phenyl carbinol with phenol, except that the temperature of the reaction mixture was held under 15°C. when the aluminum chloride was added. The reagents were as follows:

.75 mole (102 g.) ethyl phenyl carbinol

.875 mole (82.3 g.) phenol

.750 ml. anhydrous petroleum ether

.375 mole (50.0 g.) aluminum chloride

The first addition of aluminum chloride produced a yellow color which changed to orange then to blue. Gaseous hydrogen chloride was given off and the color remained purple, after two-thirds of the aluminum chloride had been added. The following fractions were obtained from the first distillation:

(1) up to 83°C./18mm.	17.36 g. phenol
(2) 65-90°C./4mm.	10.84 g. phenol and carbinol
(3) 133-170°C./6mm.	12.77 g.
(4) 170-175°C./6mm.	66.24 g.
(5) Residue	53.75 g.

Fractions (3) and (4) were redistilled giving the following fractions:

(1) 145-147°C./1mm.	2.82 g.	n_D^{20}1.5828
(2) 147-154°C./1mm.	2.48 g.	n_D^{20}1.5858
(3) 154-157°C./1mm.	36.83 g.	n_D^{20}1.5864
(4) 157°C./1mm.	25.48 g.	
(5) Residue	12.53 g.	

Fraction (1) was undoubtedly the ortho substituted phenol but it is formed in such a small amount it is impractical to work with. Fraction (2) was a mixture of ortho and para substituted phenol. Fractions (3) and (4) solidified, they were the main product, p-hydroxy-1,1-diphenylpropane. The overall yield of ortho and para substituted phenol was (67.61 g.) 43% with (2.82 g.) 2% o-hydroxy-1,1-diphenylpropane and (62.31 g.) 39% p-hydroxy-1,1-diphenylpropane.

The solid was recrystallised from ligroin to a constant melting point of 66-67°C., forming very fine crystals having a powdery appearance. The benzoyl derivative formed rectangular crystals melting at 67°C.

Huston, Lewis and Grotemut (5) prepared p-hydroxy-1,1-diphenylpropane, obtained a 27-30% yield and report a boiling point of 175-177°C./6mm. and a melting point of 64.5°C. The benzoyl derivative melted at 67°C.

C - Condensation of Propyl Phenyl Carbinol With Phenol

The condensation was carried out using a procedure similar to previous condensations, but the temperature of the reaction mixture was not allowed to rise above 25°C. The following reagents were used:

.60 mole (81.2 g.) propyl phenyl carbinol

.72 mole (67.68 g.) phenol

500 ml. anhydrous petroleum ether

.30 mole (40.00 g.) aluminum chloride

The first addition of aluminum chloride produced a pink color which turned to purple on addition of more aluminum chloride. Gaseous hydrogen chloride was given off and the usual gummy red-purple addition product was formed.

The following fractions were obtained from the first distillation:

(1) up to 83°C./18mm.	(75.72 g.)	ether & phenol
(2) 60-89°C./1mm.	(25.04 g.)	phenol & carbinol
(3) 97-148°C./1mm.	(15.57 g.)	
(4) 148-151°C./1mm.	(22.47 g.)	
(5) 151-159°C./1mm.	(32.12 g.)	
(6) Residue	(28.67 g.)	

Fractions (3) (4) and (5) were refractionated several times. The ortho and para substituted phenols were difficult to separate by distillation because of the ease with which they superheat. The following fractions were finally obtained:

(1) 149-151°C./1mm.	(13.75 g.)	n_D^{20} 1.5830
(2) 151-157°C./1mm.	(4.38 g.)	n_D^{20} 1.5800
(3) 157-159°C./1mm.	(32.48 g.)	n_D^{20} 1.5770

Fraction (1) was o-hydroxy-1,1-diphenylbutane, fraction (2) a mixture of the ortho and para substituted phenol and fraction

(3) p-hydroxy-1,1-diphenylbutane. This last fraction solidified on cooling. The overall yield of alkylated phenol was (50.61 g.) 37% with (13.75 g.) 10% o-hydroxy-1,1-diphenylbutane and (22.48 g.) 24% p-hydroxy-1,1-diphenylbutane.

The solid para substituted phenol was recrystallised from petroleum ether to a constant melting point of 46-47°C. The benzoyl derivative forms long rectangular crystals melting at 70-71°C.

Huston and Strickler (7) prepared o-hydroxy-1,1-dephenylbutane by two methods. They obtained a 6% yield using aluminum chloride and a 12-13% yield by the Claisen rearrangement of the ether. They report a boiling point of 144-146°C./6mm. Huston and Strickler (Loc.cit.) also prepared p-hydroxy-1,1-diphenylbutane. They obtained a yield of 20% and report the boiling point as 154-156°C./6mm. and the melting point as 49-50°C. The benzoyl derivative melted at 70-71°C.

D - Condensation of Butyl Phenyl Carbinol With Phenol

The first condensation was carried out in the usual manner, the temperature being held under 30°C. during addition of aluminum chloride. The following reagents were used:

1.0 mole (164 g.) butyl phenyl carbinol

1.2 mole (112.8 g.) phenol

1000 ml. anhydrous petroleum ether

.5 mole (66.6 g.) aluminum chloride

The first addition of aluminum chloride produced a violet color which deepened on addition of more aluminum chloride to a

red-violet. Gaseous hydrogen chloride was liberated and the usual gummy-red addition product formed. The following fractions were obtained for the first fractionation:

(1) 60-85°C./18mm.	34.58 g.	phenol
(2) 74-86°C./1mm.	17.75 g.	phenol & carbinol
(3) 125-133°C./1mm.	8.15 g.	
(4) 150-180°C./1mm.	96.08 g.	
(5) 180-200°C./1mm.	13.58 g.	
(6) Residue	68.33 g.	

Fractions (1) and (2) were discarded after several distillations the following fractions were obtained.

(1) 155-157°C./1mm.	16.65 g.
(2) 158-162°C./1mm.	12.06 g.
(3) 163-165°C./1mm.	20.32 g.
(4) 165-166°C./1mm.	37.15 g.

Fraction (1) was o-hydroxy-1,1-diphenylpentane, fractions (2) and (3) a mixture of ortho and para substituted phenol, and fraction (4) p-hydroxy-1,1-diphenylpentane. The para alkylphenol solidified on standing. The overall yield of alkylphenol was (86.18 g.) 36%, with (16.65 g.) 7% pure o-hydroxy-1,1-diphenylpentane and (37.15 g.) 15% pure p-hydroxy-1,1-diphenylpentane.

A second condensation was carried out using the method of Huston and Hedrick (23). The apparatus was the same as in previous condensations except that a dropping funnel was substituted for the aluminum chloride addition tube. One-half mole (66.6 g.) aluminum

chloride was suspended in 700 ml. anhydrous petroleum ether in a two-liter three-neck flask. A mixture of 1.2 mole (112.8 g.) phenol, 1 mole (164 g.) butyl phenyl carbinol and 200 ml. anhydrous petroleum ether was added dropwise over a period of 6 hours. After one hour a yellow solid adhered to the sides of the flask, and gaseous hydrogen chloride was evolved. Twenty minutes later the color deepened to a red-violet. The mixture was stirred 4 hours after the addition was complete, and allowed to stand 10 hours before hydrolysis. Fractions obtained from the first distillation are as follows:

(1) 60-85°C./18 mm.	29.56 g.	phenol
(2) 80-90°C./1mm.	17.30 g.	phenol & carbinol
(3) 145-175°C./1mm.	64.54 g.	
(4) 180-230°C./1mm.	12.86 g.	
(5) Residue	53.60 g.	

Fractions (1) and (2) were discarded and the others redistilled several times. The following fractions were isolated:

(1) 155-158°C./1mm.	11.82 g.
(2) 159-162°C./1mm.	3.67 g.
(3) 161-163°C./1mm.	28.27 g.
(4) 163-166°C./1mm.	7.97 g.

Fraction (1) was o-hydroxy-1,1-diphenylpentane, Fraction (2) a mixture of ortho and para substituted phenols, and fraction (3) and (4) p-hydroxy-1,1-diphenylpentane. Fractions (3) and (4)

solidified on standing. The overall yield of alkylphenol was (56.96 g.) 24% with (11.82 g.) 5% pure o-hydroxy-1,1-diphenylpentane and (36.24 g.) 15% pure para isomer.

The corresponding fractions of alkylphenol from the two condensations of butyl phenyl carbinol and phenol were combined and redistilled in an attempt to separate the ortho and para alkylphenols more completely. The following fractions were obtained from two moles of carbinol:

(1) 155-157°C./1mm.	52.25 g.	n_D^{20} 1.5685
(2) 157-164°C./1mm.	5.72 g.	n_D^{20} 1.5665
(3) 164-166°C./1mm.	86.16 g.	(solid)

From two moles of the carbinol, the two methods of preparation gave an overall yield of alkyl phenol of (144.13 g.) 30% with fraction (1) (52.25 g.) 10% o-hydroxy-1,1-diphenylpentane and fraction (3) (86.16 g.) 20% p-hydroxy-1,1-diphenylpentane. The solid para isomer was recrystallised from petroleum ether forming fine needles melting at 35-36°C.

Bartlett (6) condensed butyl phenyl carbinol with phenol in this laboratory in 1926. He reported a boiling point of 170-171°C./5mm. for p-hydroxy-1,1-diphenylpentane but no melting point, and did not identify the ortho isomer.

Since o-hydroxy-1,1-diphenylpentane has not been reported in the literature, a carbon hydrogen analysis was carried out with the following results:

Sample I .004783g CO_2, .014794 H_2O, .003510

Sample II .005276g CO_2, .016414 H_2O, .003916

Calculated for C_{17} H_{20} O C, 84.94% H, 8.39%

Sample I found C, 84.75% H, 8.21%

Sample II found C, 84.85% H, 8.31%

E - Condensation of Amyl Phenyl Carbinol with Phenol

This condensation was carried out under conditions identical with the first condensation of butyl phenyl carbinol, the temperature was held under 30°C. while the aluminum chloride was added over a period of two hours. The reagents used were as follows:

1 mole (178g.) amyl phenyl carbinol

1.2 mole (112.8 g.) phenol

1000 ml. anhydrous petroleum ether

.5 mole (66.6g.) aluminum chloride.

The fractions isolated from the first distillation were as follows:

(1) up to 85°C./18mm. 56.73g. some ether & phenol

(2) 74-105°C./1mm. 11.20 g. carbinol

(3) 106-172°C./1mm. 35.74 g.

(4) 172-173°C./1mm. 21.82 g.

(5) 173-175°C./1mm. 61.20 g.

(6) 175-230°C./1mm. 66.94 g.

(7) Residue 2.30 g.

Fractions (1) and (2) were discarded, the others were redistilled several times resulting in the following fractions:

(1)	115-166°C./1mm.	5.38g.	
(2)	166-171°C./1mm.	9.05g.	
(3)	171-173°C./1mm.	39.23g.	n_D^{20} 1.5600
(4)	178-178°C./1mm.	64.38g.	n_D^{20} 1.5604
(5)	178-183°C./1mm.	9.84g.	
(6)	Residue	52.3g.	

One mole of carbinol gave an overall yield of (103.61g.) 41% substituted phenol (fraction 3 and 4), with fraction (3) representing (39.23g.) 15% o-hydroxy-1,1-diphenylhexane and fraction (4) representing (64.38g.) 25% p-hydroxy-1,1-diphenylhexane. The para isomer solidified in the ice box but remains an oil at room temperature. It would not crystallize from petroleum ether or hexane like similar compounds, but formed a crystalline α-naphthylurethane like other para substituted phenols.

Neither ortho nor para hydroxy-1,1-diphenylhexane has been reported in the literature, carbon-hydrogen analysis were carried out as fellows:

o-hydroxy-1,1-diphenylhexane

Sample I	.004736g.	CO_2, .014693	H_2O, .003595
Sample II	.004332g.	CO_2, .01345	H_2O, .003303
Sample I found		C, 84.61%	H, 8.56%
Sample II found		C, 84.58%	H, 8.52%

p-hydroxy-1,1-diphenylhexane

Sample I	.003478g.	CO_2, .010830g.	H_2O, .002778
Sample II	.003393g.	CO_2, .010586g.	H_2O, .002666

Sample I found	C, 84.92%	H, 8.92%
Sample II found	C, 85.09%	H, 8.79%
Calculated for $C_{18}H_{22}O$	C, 84.98%	H, 8.72%

COMPOUND	Boiling Point and Melting Point	n_D^{20}	Sp.G. $\frac{20}{4}$	% Yield
p-Hydroxy-1,1-diphenylethane	M.P. 57-57.5° B.P. 148-150°/1mm.			57%
p-Hydroxy-1,1-diphenylpropane	B.P. 154-157°/1mm. M.P. 66-67°	1.5864		39%
o-Hydroxy-1,1-diphenylpropane	B.P. 145-147°/1mm.	1.5828		2%
p-Hydroxy-1,1-diphenylbutane	M.P. 46-47° B.P. 157-159°/1mm.	1.5770		24%
o-Hydroxy-1,1-diphenylbutane	B.P. 149-151°/1mm.	1.5830	1.072	10%
p-Hydroxy-1,1-diphenylpentane	M.P. 35-36° B.P. 164-166°/1mm.			20%
o-Hydroxy-1,1-diphenylpentane	B.P. 155-157°/1mm.	1.5685	1.037	10%
o-Hydroxy-1,1-diphenylpentane (Claisen Rearrangement)	B.P. 155-157°/1mm.	1.5682	1.037	9%
p-Hydroxy-1,1-diphenylhexane	B.P. 176-178°/1mm.	1.5604	1.001	25%
o-Hydroxy-1,1-diphenylhexane	B.P. 171-173°/1mm.	1.5600	1.001	15%
o-Hydroxy-1,1-diphenylhexane (Claisen rearrangement)	B.P. 171-173°/1mm.	1.5607	1.001	7.5%

ALKYL PHENOLS
TABLE II

EXPERIMENTAL

III Claisen Rearrangement

A. Preparation of o-Hydroxy-1,1-diphenylpentane

In order to determine the characteristic difference between the ortho and para substituted phenols, the ortho compound was prepared by Claisen's method of ring alkylation. (8) He shows that ortho alkylation of phenols result when sodium phenolate is heated with certain alkyl halides in a non-dissociating medium.

Preparation of α-Chloroamylbenzene

This compound was prepared by the method of Kharash and Kleiman (26). Dry hydrogen chloride was bubbled thru .5 mole (82g.) of butyl phenyl carbinol, a water layer formed after the second hour, hydrogen chloride was bubbled thru for one hour more and the mixture was allowed to stand overnight at -10°C. The water layer was separated, and the α-chloroamylbenzene washed with water and dried over a anhydrous calcium chloride to remove water and unreacted carbinol. The α-chloroamylbenzene was used in the following condensation without further purification.

Condensation of α-Chloroamylbenzene and Sodium Phenolate

In a 500 ml. three-neck flask fitted with a condenser and thermometer, .42 mole (9.70g.) finely chopped sodium was suspended in 150 ml. of anhydrous toluene. Then .45 mole (42.3g.) phenol was added, after a few minutes a vigorous reaction took place which gradually diminished. The mixture was refluxed at 120°C. for 3 hours until all the sodium reacted, then cooled and the

chloroamylbenzene added. The resulting mixture was refluxed for thirty-two hours. Then it was cooled and washed with water. The mixture was distilled to 120°C. to remove water and toluene. The residue was dissolved in 250 ml. of Claisen's (27) alcoholic potassium hydroxide solution and extracted four times with 50 ml. petroleum ether. Vavon and Zakaria (28) recommend that petroleum ether be used for the extraction of the ether and that excess alkali be employed. The remainder was acidified with dilute hydrochloric acid and extracted four times with 50 ml. of diethyl ether. Both ether extracts were washed with water, dried over anhydrous sodium sulphate and the solvent removed by distillation.

Isolation of o-hydroxy-1,1-diphenylpentane

The diethyl ether extract was distilled using a 10 inch Vigreux column, resulting in the following fractions:

(1)	up to 70°C./1mm.	(3.85g.) phenol
(2)	70-110°C./1mm.	(6.30g.) some phenol
(3)	132-150°C./1mm.	(14.68g.)
(4)	Residue	(46.83g.)

Most of fraction (3) distilled at 154-155°C./1mm., it was redistilled giving (10.82g.) 9% o-hydroxy-1,1-diphenylpentane boiling at 155-157°C./1mm., n_D^{20} 1.5682, Sp. G.$_4^{20}$ 1.037. These constants check with those obtained when the same compound was prepared using aluminum chloride.

A carbon-hydrogen determination was carried out on this sample of o-hydroxy-1,1-diphenylpentane with the following results:

Sample I	.005625g.	CO_2, .017467	H_2O, .004093
Sample II	.004972g.	CO_2, .105476	H_2O, .003662
Sample I found		C, 84.69%	H, 8.14%
Sample II found		C, 84.87%	H, 8.24%
Calculated for $C_{17}H_{22}O$		C, 84.94%	H, 8.39%

Isolation of 1-Phenyl-1-pentene and Phenyl Amylphenyl Ether

The petroleum ether extract of the alcoholic KOH solution was distilled giving the following fractions:

(1) 70-86°C./1mm. 7.86g.

(2) 90-130°C./1mm. 6.43g.

(3) 137-142°C./1mm. 24.04g.

(4) Residue 8.58g.

Fractions (1) and (2) gave a positive Baeyer test for unsaturation, they were redistilled several times giving 10.02g. 1-phenyl-1-pentene boiling at 85-86°C./5mm., n_D^{20} 1.5310, Sp.G.$_4^{20}$ .8901. Prevost and Kaujat (29) report n_D^{17} 1.5318, Sp.G. $_4^{20}$ .8924.

Fraction (3) was redistilled several times giving (15.67g.) 13.5% phenyl amylphenyl ether boiling 132-134°C./1mm, n_D^{20} 1.5446, Sp.G. $_4^{20}$ .9983.

Phenyl amylphenyl ether has not been reported in the literature. A carbon-hydrogen analysis was carried out with the following result:

Sample I	.004291g.	CO_2, .013356g.	H_2O, .003616
Sample II	.003659g.	CO_2, .011369g.	H_2O, .003034
Sample I found		C, 84.89%	H, 8.426%
Sample II found		C, 84.74%	H, 8.29%
Calculated for	$C_{17}H_{20}O$	C, 84.94%	H, 8.39%

B. Preparation of o-Hydroxy-1,1-diphenylhexane

This compound was prepared by the same method as o-hydroxy-1, 1-diphenylpentane. The amounts of reagents used were as follows:

.54 mole (97.11g.) amyl phenyl carbinol

.5 mole (11.5g.) sodium

.6 mole (56.4g.) phenol

150 ml. anhydrous toluene

The following fractions were obtained from the diethyl ether extract:

(1) 55-61°C./.5mm. (4.53g.) most phenol

(2) 157-169°C./1mm. (2.31g.)

(3) 167-172°C./1mm. (11.88 g.)

(4) Residue 19.39g.

Fraction (2) and (3) were redistilled several times giving (9.74g.) 7.5% o-hydroxy-1,1-diphenylhexane boiling at 171-173°C. /1mm., n_D^{20} 1.5607. The index of refraction of the same compound prepared using aluminum chloride was n_D^{20} 1.5600.

A combustion was carried out on this fraction with the following results:

Sample I	.005137g.	CO_2, .015910	H_2O, .003935
Sample II	.001280g.	CO_2, .004003	H_2O, .001008
Sample I found		C, 84.47%	H, 8.57%
Sample II found		C, 85.29%	H, 8.81%
Calculated for $C_{18}H_{22}O$		C, 84.98%	H, 8.72%

Isolation of 1-Phenyl-1-hexene and Phenyl Hexlphenyl Ether

The petroleum ether extract of the alcoholic potassium hydroxide solution on distillation gave the following fractions:

(1) 81-96°C./1mm. (23.19g.)

(2) 77-122°C./1mm. (5.20g.)

(3) 144-147°C./1mm. (20.22g.)

(4) Residue 13.93g.

Fraction (1) was redistilled several times giving 9.85 g. of 1 phenyl-1-hexene boiling at 97-98°C./4mm. The index of refraction was carefully determined as n_D^{20} 1.5254, Sp.G.$_4^{20}$ .8874. Marvel (30) and co-workers report n_D^{25} 1.5377, D_o^{25} .9455.

To obtain further evidence of the formation of 1-phenyl-1-hexene, the compound was oxidised with permanganate by the method of Shriner and Fuson. Benzoic acid, with a melting point of 121-122°C. was isolated. The aqueous residue was extracted with ether to remove the valeric acid. The ether extract was dried over anhydrous sodium sulphate and the ether removed. The amide of valeric acid was formed by refluxing the acid with thionyl chloride, and then pouring the reaction mixture on cold concentrated ammonia. The solid formed was filtered off and the ammonia solution extracted with chloroform. The chloroform solution was concentrated and the amide of valeric acid crystallised. After recrystallisation from chloroform it melted at 106°C. Shriner and Fuson (31) report the melting point of the amide of valeric acid as 106°C.

Fraction (3) from above was redistilled giving (14.83g.) 10%

phenyl hexylphenyl ether boiling at 154-155°C./2mm. n_D^{20} 1.5388, Sp.G. $\frac{20}{4}$ .9866.

A carbon-hydrogen determination was carried out on the ether with the following results:

Sample I	.004304g.	CO_2, .013354	H_2O, .003276
Sample II	.003257g.	CO_2, .010119	H_2O, .002524
Sample I found		C, 84.62%	H, 8.517%
Sample II found		C, 84.73%	H, 8.673%
Calculated for $C_{18}H_{22}O$		C, 84.98%	H, 8.722%

CLAISEN REARRANGEMENT

TABLE III

	Yield from .5 mole Carbinol	Boiling Point	n_D^{20}	Sp.G. $\frac{20}{4}$
o-Hydroxy-1,1-diphenylpentane	10.82g. (9%)	155-157°C./1mm.	1.5682	1.037
1-Phenyl-1-pentene	10.02g.	85-86°C./5mm.	1.5310	.8901
Phenyl Amylphenyl Ether	15.67g.(13.5%)	132-134°C./1mm.	1.5446	.9983
o-Hydroxy-1,1-diphenylhexane	9.74g.(7.5%)	171-173°C./1mm.	1.5607	1.001
1-Phenyl-1-hexene	9.85g.	97-98°C./4mm.	1.5254	.8874
Phenyl Hexylphenyl Ether	14.83g.(10%)	154-155°C./2mm.	1.5388	.9866

EXPERIMENTAL

IV DERIVATIVES

The α-naphthylurethan, 3,5 dinitrobenzoate (32) and benzoate (33) were prepared from o-hydroxy-1,1-diphenylpentane in an attempt to obtain a crystalline derivative for the ortho substituted phenols, but all three derivatives remained as oils.

The α-naphthylurethan derivatives were prepared from the para substituted phenols according to the method of French and Wirtel (34) and analyzed for nitrogen.

To one gram of alkylphenol was added one milliliter of α-naphthyl isocyanate. A few drops of an ether solution of trimethylamine were added to catalyze the reaction. The reaction mixture was protected from moisture by a calcium chloride tube, and warmed on a steam bath for an hour, then two milliliters of water were added to remove the excess α-naphthyl isocyanate. On cooling, it solidified. The solid was extracted several times with boiling ligroin, in twenty milliliter portions, and the insoluble material filtered off. The α-naphthylurethan crystallized as small white plates, and was recrystallized from ligroin to constant melting point.

Analysis

The α-naphthylurethans were analyzed for nitrogen by the semi-micro Kjeldahl method (35). Ten to thirty milligram samples were used and the ammonia evolved was absorbed in excess .01 N hydrochloric acid, the excess acid was back titrated with .01 N sodium hydroxide.

α-NAPHTHYLURETHANS

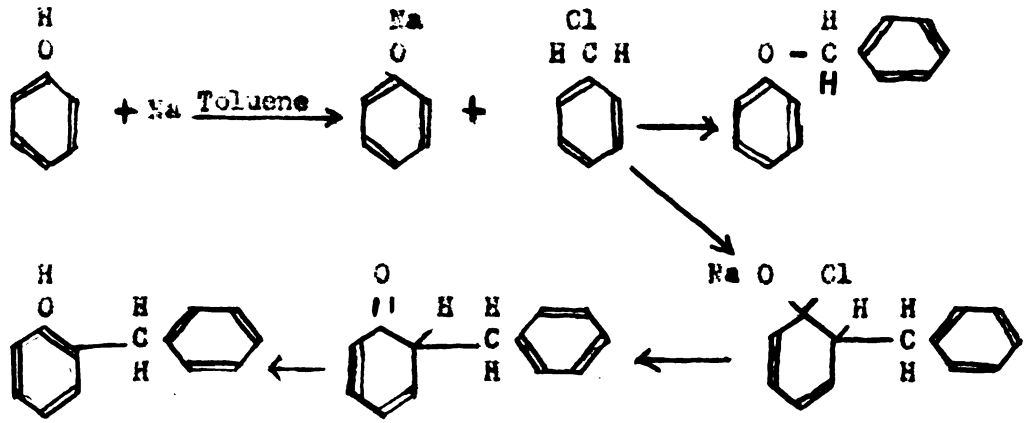
TABLE IV

p-Hydroxy-1,1-diphenyl-	Melting Point	Calculated % N	Experimental % N
Ethane	114-114.5°C.	3.77	3.76
			3.80
Propane	142-142.5°C.	3.64	3.63
			3.61
Butane	134-135°C.	3.51	3.58
			3.57
Pentane	108-109°C.	3.39	3.42
			3.37
Hexane	104-104.5°C.	3.28	3.21
			3.19

I Claisen Rearrangements

In 1923 Claisen (36) published work on the carbon alkylation of phenols in the ring. He found that both oxygen and carbon alkylation of phenols took place, when alkyl halides and socium derivatives of monohydric phenols were reacted. When a dissociating medium such as methyl or ethyl alcohol was used oxygen alkylation of phenol was favored, while in a non-dissociating medium such as benzene or toluene more of the carbon alkylation is produced. Claisen further noted that the unsaturated alkyls affect the carbon alkylation to a greater extent than do saturated alkyls. The tendency toward carbon alkylation is still further increased if alkyl phenols are used.

The formation of ortho substituted phenols has been explained according to the mechanism proposed by Claisen and co-workers (8) for the formation of a benzyl phenol.



The simplest course of the reaction would result in the formation of the ether. But when the reaction is carried out in a non-dis-

sociating medium (toluene) the ortho substituted phenol is also formed, this may be accounted for by assuming that the benzyl chloride adds to the phenol in the manner shown, sodium chloride then splits off leaving a compound of quinoid structure which enolizes forming the ortho substituted phenol.

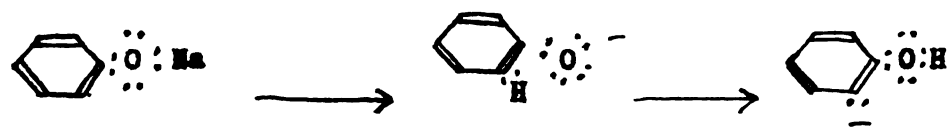
In 1926, Von Auwers, Wegner, and Bahr (37) attempted to explain the ring alkylation noted in connection with the Claisen rearrangement. They advanced three hypotheses:

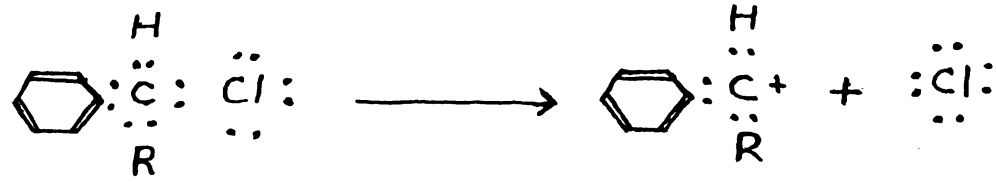
(1) The formation of addition products and subsequent splitting off of salt as indicated by Claisen.

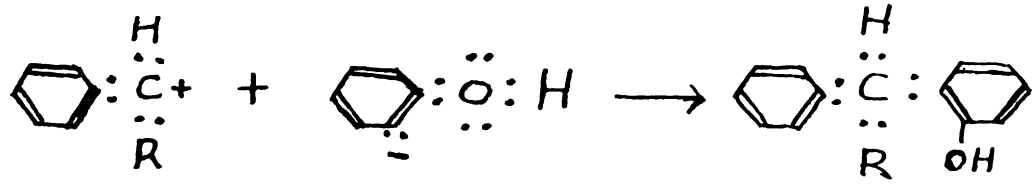
(2) Initial oxygen alkylation, followed by rearrangement of the molecule to carbon alkylation.

(3) The separation of the metal and halogen as a metalic halide, leaving a free alkyl radical and a free enol radical, the two radicals then combine to form the alkylated phenol.

The first hypothesis agrees with Claisen. Tarbell (38) in more recent work agrees with the second theory of initial oxygen alkylation. The third theory seems most reasonable. The formation of the free enol radical would require a proton shift, as shown in the following series of reactions.

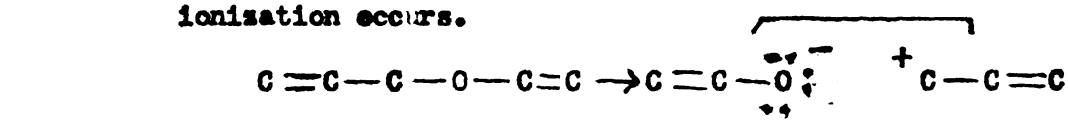




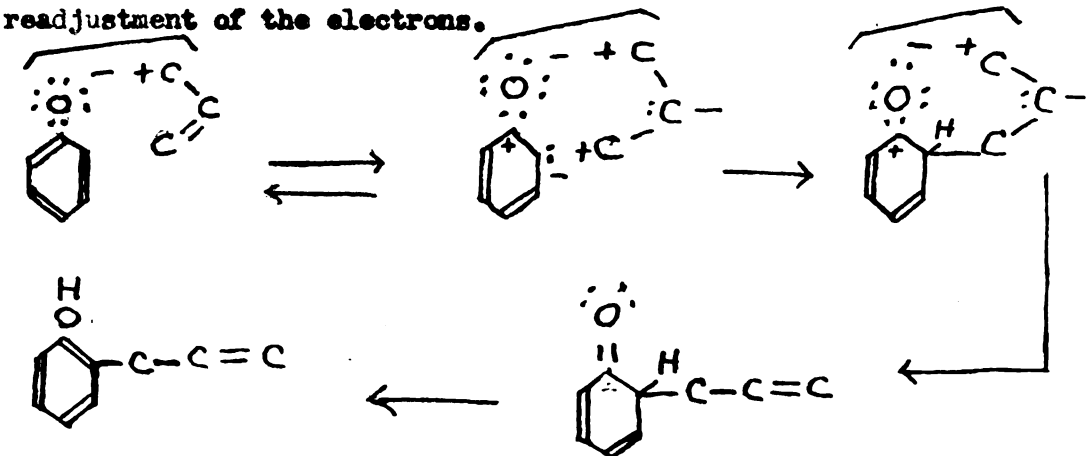


This mechanism will be used as the basis to explain the mechanism of Claisen's method of ring alkylation.

Tarbell (38) studied the thermal rearrangement of allyl phenyl ethers. He supports the cyclic electronic mechanism proposed by Hurd, and Pollack (12). They assume that the initial effect of heat on the system alters the position of the electron pair which binds the allyl group to the oxygen, so that a semi-ionization occurs.



This effect combined with the spatial proximity of the atoms at the end of the system, brings about a temporary ring closure and readjustment of the electrons.

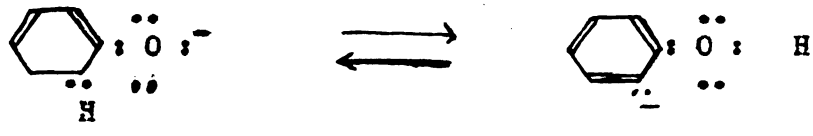


This mechanism is only satisfactory for compounds where the alkyl group is unsaturated. The semi-ionic positive carbon seeks to satisfy its electron deficiency by appropriating electrons from the neighboring double bond.

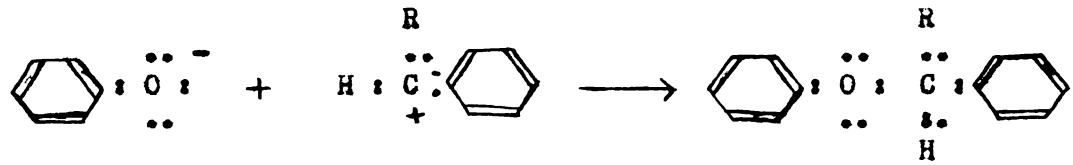
Claisen showed the effect of the medium in which the reaction occurred by reacting allyl bromide with sodium phenolate in alcohol, obtaining 90% of the ether, while a non-dissociating medium like benzene or toluene gave only 30% ether and 70% allylphenol.

Most of the work concerning alkyl phenyl ethers and alkylphenols has been a study of the rearrangement of the ether, no effort has been made to analyze the effect of a non-dissociating medium on the reaction. The most generally accepted views consider ether formation as the first step with subsequent rearrangement to an alkyl phenol in a dissociating medium. Also direct carbon alkylation is considered to take place in a non-dissociating medium. These theories are not completely satisfactory because they fail to explain the effect of the medium on carbon and oxygen alkylation.

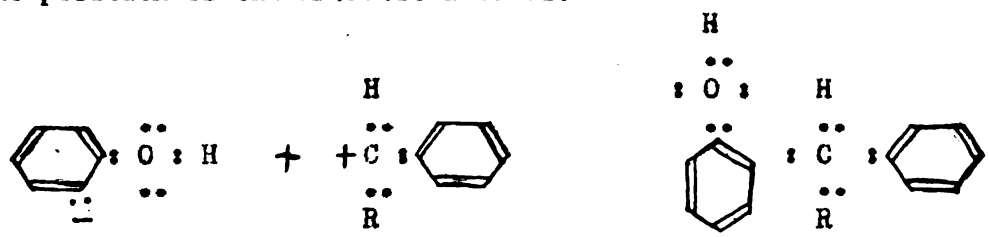
A more plausible reaction mechanism involves the formation of a carbonium ion from the halide and a carbanion from the sodium phenolate. The carbanion exists in equilibrium of two forms due to a proton shift.



A dissociating medium (alcohol) favors ether formation by union of the carbonium ion with the ether form of the carbanion. The proton shift of the carbanion is inhibited by the polarity of its environment.



A non-dissociating medium (toluene or benzene) favors phenol formation by union of the carbonium ion with the phenol form of the carbanion. A proton shift of the carbanion activates the ortho position of the aromatic nucleus.



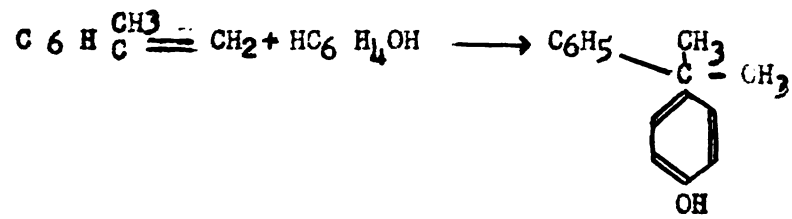
This mechanism explains the fact of ether and phenol formation in both media. It also explains why phenol formation is favored in a non-dissociating medium, and ether formation is favored in a dissociating medium.

The thermal rearrangement of the ether with or without solvent as reported by Tarbell can be explained by a shift of the equilibrium of the carbanion from the ether form to the phenol form under the influence of heat. Since the rearrangement is exothermic (38), a conversion to the lower energy level would be expected.

II Aluminum Chloride Condensations

Several theories have been proposed in attempting to explain the mechanism of alkylation of aromatic nuclei with alcohols in the presence of a dehydrating catalyst as aluminum chloride. No one theory seems to be completely satisfactory. These theories have been thoroughly discussed by previous workers in this laboratory and will be only mentioned here.

Huston and co-workers had observed in their early investigations that aluminum chloride favored condensation only when the alpha carbon atom of the alcohol was double bonded or the member of a benzene ring. Further evidence of this theory is presented in the condensations under consideration in this paper. Welsh and Drake (39) in condensing dimethyl phenyl carbinol, and methyl diphenyl carbinol with phenol at 100°C. using .5 mole phenol per mole carbinol, report the formation of an olefin from the carbinol. They propose a mechanism whereby the aromatic compound is added to the olefin.



This type mechanism could not be postulated where the alcohol is incapable of dehydration to an olefin (benzyl alcohol). No olefins were isolated in the condensation of secondary alkyl phenyl carbinols with phenol, it is doubtful that the condensation proceeds by this mechanism.

Tsukervanik and Nasarova (40) condensed phenols with secondary alcohols using excess aluminum chloride and high temperature. They isolated small amounts of dialkylphenyl ethers and alkylphenyl ethers, and proposed a mechanism with ethers as intermediates.

$$ROH + AlCl_3 \longrightarrow HCl + AlCl_2(OR)$$

$$C_6H_5OH + AlCl_3 \longrightarrow HCl + C_6H_5OAlCl_2$$

$$AlCl_2(OR) + C_6H_5OAlCl_2 \xrightarrow{HCl} C_6H_5OR + AlCl_3 + AlCl_2OH$$

The alkyl ether is converted to the dialkyl ether by alkylation or rearrangement (41).

$$C_6H_5OR + ROH + AlCl_3 \longrightarrow RC_6H_4OR + AlCl_2OH + HCl$$

$$2\ C_6H_5OR \xrightarrow{AlCl_3} RC_6H_4OR + C_6H_5OH$$

The alkylphenol may form under conditions of excess aluminum chloride at high temperature by either of the following methods:

$$RC_6H_4OR + HCl \longrightarrow RC_6H_4OH + RCl$$

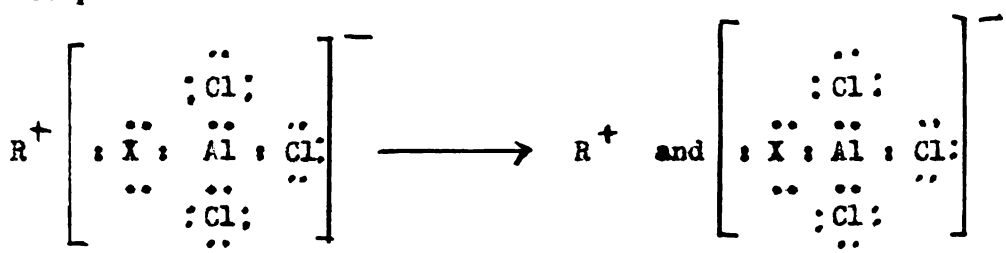
$$RC_6H_4OR + C_6H_5OH \longrightarrow 2\ RC_6H_4OH$$

This mechanism is questionable as it does not explain the rearrangements obtained when some secondary alcohols are condensed with benzene. Also Huston and co-workers in condensing alkyl phenyl carbinols with phenol have not isolated any of the intermediate ether.

Work carried out in this laboratory by Evart (1) in 1936 led to the proposal that addition compounds of aluminum chloride, the alcohol, and phenol are first formed.

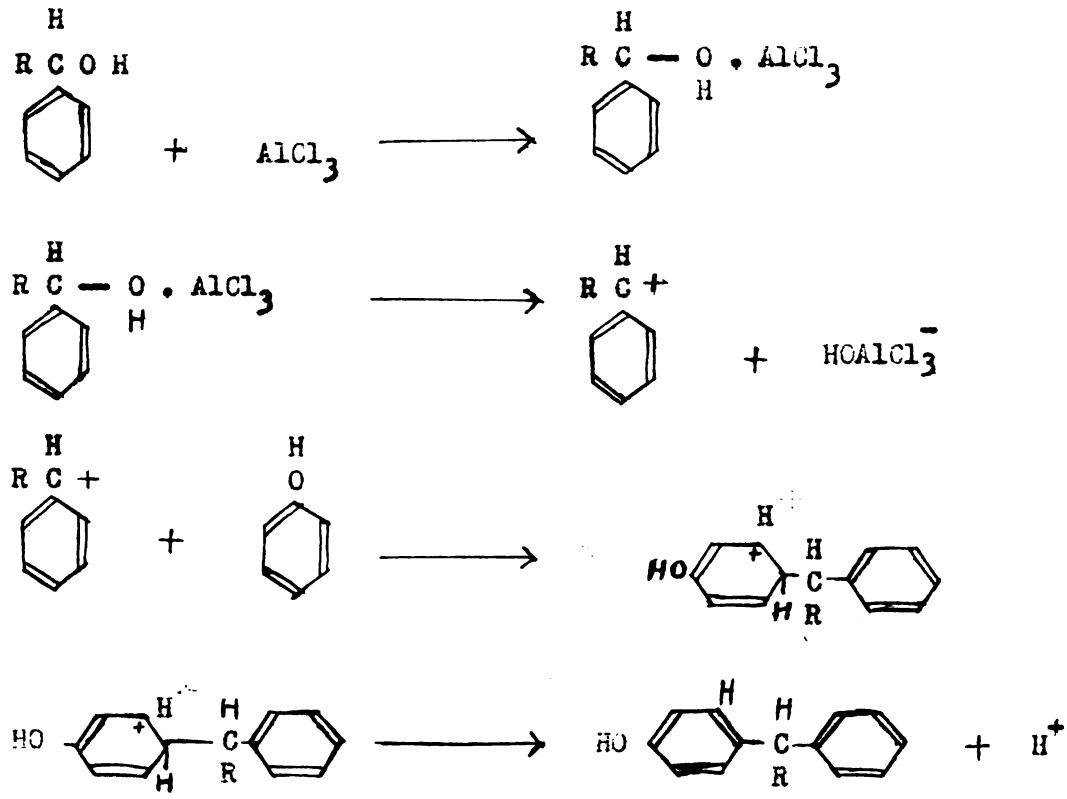
This complex molecule being unstable, rearranges to a more stable configuration by splitting out aluminum chloride and water to yield alkylphenol.

An ionic type of mechanism has been suggested by Price (42) for the alkylation of benzene. The formation of an ionic complex between aluminum chloride and an alkyl halide has been demonstrated by Weryforoch and Firla (43). In this complex the carbon-hologen bond is weakened, and the compound dissociates into an electron deficient carbonium ion and a negatively charged aluminum complex:



The electron deficient carbonium ion (R) completes its octet by association with a pair of electrons from a double bond of the aromatic nucleus. The alkyl benzene is formed by the loss of a proton. Based on the work of Huston and Awuapara (44) Barrett (45) and Van Dyke (3), a mechanism was proposed in which an initial reaction between aluminum chloride and the alcohol yielded a complex molecule which decomposed to produce an alkyl cation or carbonium ion. This mechanism satisfactorily explains the rearrangement of branched alkyl groups as well as the isolation of low molecular weight alkyl benzenes (22).

Applied to the alcohols under consideration, the mechanism proposed above would lead to the following series of reactions.



DISCUSSION

Apparently the chain length of the carbinol has some affect in determining the relative amounts of ortho and para substitution of phenol. In all the condensations under consideration the total yield of ortho and para alkylphenols varied from 57-30% yet the amount of ortho substituted phenol varied inversely from zero to 15% (See Table II), as the chain length increased

The melting point of the para alkylphenols varies with the carbon chain length. p-hydroxy-1,1-diphenylethane melts at 57°C. while p-hydroxy-1,1-diphenylpropane melts at 66°C., a maximum. The next two homologs melt lower, with p-hydroxy-1,1-diphenylhexane remaining liquid at room temperature. The α-naphthylurethans show the same variation in melting point with the maximum melting point at the same compound.

The two ortho substituted phenols obtained from the aluminum chloride condensation that have not been reported in the literature were indentified by preparing the same compounds by the Claisen rearrangement of the ether, and comparing their physical constants. Carbon-hydrogen analysis were also carried out as additional proof.

In the preparation of ortho substituted phenols by the Claisen rearrangement, a phenyl alkene was isolated from the reaction mixture. Strickler (7) reports the formation of 1-phenyl-1-butene from α-chlorobutylbenzene. The phenyl alkene corresponds to the chloride and was probably formed by elimination of HCl under conditions of the reaction.

The para isomers were identified by comparison of their physical constants with those obtained by earlier workers in this laboratory. Additional proof was obtained by preparation and analysis of the α naphthylurethans of the para compounds. The new compound p-hydroxy-1,1-diphenylhexane was analyzed for carbon hydrogen.

SUMMARY

1. Methyl phenyl carbinol thru amyl phenyl carbinol were condensed with phenol in the presence of aluminum chloride.
2. The expected normal alkyl phenols were isolated from each condensation.
3. The yield of para alkyl phenol decreased from 57% for p-hydroxy-1,1-diphenylethane to ~~30~~ 20% for p-hydroxy-1,1-diphenylpentane, and then increased to ~~40~~ 25% for p-hydroxy-1,1-diphenylhexane. The yield of ortho alkylphenol varied from zero for o-hydroxy-1,1-diphenylethane to 15% for o-hydroxy-1,1-diphenylhexane.
4. The following new compounds were prepared and analyzed; o-hydroxy-1,1-diphenylpentane, phenyl amylphenyl ether, o-hydroxy-1,1-diphenyl hexane, and p-hydroxy-1,1-diphenyl hexane.

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