CONDENSATIONS OF ORTHO- AND PARA CHLOROPHENOLS WITH TERTIARY AMYL AND BUTYL ALCOHOLS IN THE PRESENCE OF $AlCl_3$

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A THESIS

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HISTORICAL

Sulfuric acid, phosphorous pentoxide, zinc chloride, hydrochloric acid, sulfuric and acetic acids, absolute alcohol, stannic chloride, and acetic acid are the reagents commonly used to bring about the condensation of aromatic alcohols with aromatic compounds to form derivatives of di- or triphenylmethane.

Anhydrous aluminum chloride has been used in organic chemistry as a dehydrating agent by Merz and Wieth (1); Wass (2); Frankforter and Kritchensky (3); Frankforter and Kolcatinur (4); and others.

The type of condensation described in this paper is a modification of the well known Friedel-Craft's reaction. By this reaction the introduction of an alkyl or acyl group by means of the corresponding halide and aluminum chloride is accomplished:

$$C_6H_6 + C_2H_5Br \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HBr$$

In this reaction the hydrogen halide is split off.

Although anhydrous aluminum chloride had been used as a dehydrating agent to quite some extent in organic chemistry the work of Huston and co-workers was the first concerning the dehydrating action on aromatic alcohols and aromatic compounds in the presence of that agent. In 1916 Huston and Friedmann (5) reported a 30% yield of diphenylmethane from the reaction of benzyl alcohol and benzene in the presence of aluminum chloride. They reported later (6) that secondary aromatic alcohols such as phenylmethyl and phenylethyl carbinols react with benzene in the presence of aluminum chloride to give the corresponding hydrocarbons in good yield.

Huston (7) reported that benzyl alcohol reacts with phenol in the presence of aluminum chloride to give a good yield of p-benzylphenol according to the equation:

$$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH + H_2O$$

Later Huston and co-workers (8) reported that aromatic secondary alcohols such as benzhydrol, phenylmethyl, phenylethyl and phenyl n-propyl carbinols react with phenol inthe presence of aluminum chloride to give the corresponding para substituted phenols.

In 1934 Huston and Goodemoot (9) reported the condensations of some cyclo alkyl carbinols with benzene in the presence of aluminum chloride.

In 1926 Huston and Sager (10) reported that saturated aliphatic alcohols do not condense with benzene. They found that unsaturated alcohols, such as allyl alcohol, willcondense with benzene. However, in 1936 Huston and Hsieh (11) reported that aliphatic primary alcohols do not condense with phenol or benzene inthe presence of aluminum chloride. Alphatic secondary and tertiary alcohols condense with benzene to give the corresponding alkylbenzenes. Aliphatic tertiary alcohols condense with phenol to give good yields of p-tertiary-alkyl phenols.

In 1933 Klarmcinn, Shternow and Gates (13) reported the preparation of para tertiary amyl o-chlorophenol by the ether rearrangement. The boiling point was reported as 105-110° at 2mm.

EXPERIMENTAL

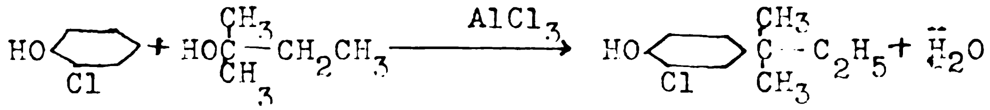
Tertiary amyl and tertiary butyl alcohols and p-chlorophenol were obtained from the Eastman Kodak Co. The o-chlorophenol was prepared according to the method of Huston and Neeley (12). The anhydrous aluminum chloride was of good grade.

(1) CONDENSATION OF TERTIARY AMYL ALCOHOL WITH O-CHLOROPHENOL

Twenty-six grams (.2 mole) of o-chlorophenol and eighteen grams (.2 mole) of tert-amyl alcohol were suspended in 100cc. of petroleum ether in a 500cc. three neck flask fitted with a mercury-sealed stirrer, a reflux condenser and a thermometer. Twenty-six grams (.2 mole) of anhydrous aluminum chloride were added slowly to the mixture so that the temperature did not rise above 30°C. Stirring was continued three to four hours after all the aluminum chloride had been added. After standing over night the mixture, dark red in color, was treated with 100g. of ice and 100cc. conc. HCl to effect hydrolysis. The ether-water mixture was separated and the water layer was washed three times with ethyl ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue was fractionated. All fractionations were carried out at 5mm. pressure. The first fraction 50-80° was discarded since it contained ether and unreacted reagents. The second fraction was collected from 80-100°. The residue was a dark gummy mass. The fraction was purified by repeated fractionation until the boiling point was constant at 91-92°C.

The second fraction was then subjected to distillation at atmospheric pressure in a distilling flask. The final product boiled at 255-256.5° at 736mm.

The equation of the reaction is as follows:



The mole equivalents of the alcohol, chlorophenol and aluminum chloride were varied, however, the best yields were obtained when equal mole equivalents of the three substances were used.

PROOF OF STRUCTURE OF P-TERT.AMYL O-CHLOROPHENOL

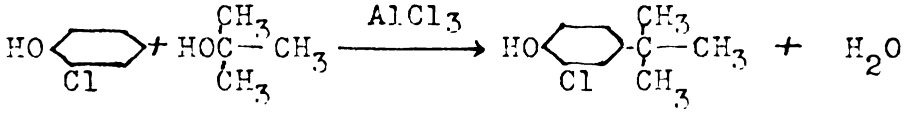
Five tenths mole of p-tert. amyl phenol, prepared by the method of Huston and Hsieh (11), was suspended in chloroform in a 500cc three neck flask and chlorinated at room temperature until the theoretical amount of chlorine had been taken up. The contents of the flask were stirred mechanically during the chlorination. The chloroform was evaporated off and the resulting oil was purified by distillation at atmospheric pressure. The purified oil boiled at 254-255° at 734mm.

As further proof of structure both products, obtained by condensation and chlorination, were treated with diphenyl carbamine chloride to form the diphenyl urethane derivatives. Both of the resulting urethanes had a melting point of 116-117°. Both were analyzed for chlorine content. The calculated percentage is 9.01. The actual amount as determined by the Parr bomb method was 9.03% in the case of the product and 9.09% for the proof.

(2) CONDENSATION OF TERTIARY BUTYL ALCOHOL WITH O-CHLOROPHENOL

The condensation was carried out using the same procedure as that outlined for #1. The method of purification was also the same. The resulting oil boiled at 241-242.5° at 743mm pressure.

The equation of the reaction is as follows:



PROOF OF STRUCTURE OF P-TERT.BUTYL O-CHLOROPHENOL

18 grams of p-tert.amyl phenol were chlorinated in the same manner as #1. The resulting oil boiled at 240-241.5° under 742mm pressure.

The diphenyl urethane derivatives were prepared from both the products of condensation and chlorination. Each of the resulting derivatives melted at 142-143°. The calculated chlorine percentage is 9.35. The percentage found was 9.34 for the derivative of the product obtained by condensation, and 9.42 for the product obtained by chlorination.

The halogen percentage of the products of condensation was determined by the Carius method.

The p-tertiary-alkyl products are hygroscopic and take up water very rapidly.

(3) CONDENSATION OF TERTIARY AMYL AND BUTYL ALCOHOLS WITH P-CHLOROPHENOL

These condensations were carried out using the same procedure as given under #1. After the final fractions were purified by fractionation and distillation they solidified and were recrystallized from petroleum ether. The crystals obtained from all of these condensations melted at 37°. The melting point of p-chlorophenol given in the literature is 37°. The Parr Bomb determination of the halogen content of the crystals showed that they were p-chlorophenol.

Table 1.

CONDENSATIONS OF TERTIARY ALCOHOLS WITH O-CHLOROPHENOL

Reactants in Moles

	Alcohol	Phenol	$AlCl_3$	Product	B.P. °C	Yield
Tert-amyl alcohol	.6	.6	.6	p-tert-amyl o-chlorophenol	255-256.5° 736mm	37%
Tert-butyl alcohol	.6	.6	.6	p-tert-butyl o-chlorophenol	241-242.5° 743mm	24%

CONDENSATIONS OF TERTIARY ALCOHOLS WITH P-CHLOROPHENOL

Tertiary alcohols do not condense with p-chlorophenol.

CONSTANTS

Compound	B.P. °C	Chlorine% Calc.	Chlorine% Found
P-tertiary-amyl o-chlorophenol	255-256.5°/736mm	17.85	17.43
P-tertiary-butyl o-chlorophenol	241-242.5°/743mm	19.23	18.51

Table 2.

DERIVATIVES OF P-TERTIARY-ALKYL O-CHLOROPHENOLS

	Diphenyl Urethanes		
		Chlorine%	
Compound	M.P. °C	Calc.	Found
P-tertiary-amyl o-chlorophenol	116-117°	9.01	9.03
P-tertiary-butyl o-chlorophenol	142-143°	9.35	9.34
	Nitro Derivatives		
P-tertiary-amyl o-chlorophenol	108-109°	14.58	15.20
P-tertiary-butyl o-chlorophenol	114-115°	15.45	15.70

SUMMARY

1. Tertiary amyl and butyl alcohols condense with o-chlorophenol in the presence of aluminum chloride to give good yields of p-tertiary-alkyl o-chlorophenols.

2. Tertiary alkyl alcohols do not condense with p-chlorophenols in the presence of aluminum chloride.

3. Diphenyl urethane and nitro derivatives of the p-tertiary-alkyl o-chlorophenols were prepared.

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(5) Huston and Friedmann, *Ibid.*, 38, 2527, (1916).

(6) Huston and Friedmann, *Ibid.*, 40, 785, (1918).

(7) Huston, Ibid., 46, 2775, (1924).

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