CONDENSATION OF PHENOL AND ALLYL ALCOHOL IN THE PRESENCE OF ALUMINUM CHLORIDE

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CONDENSATION OF PHENOL AND ALLYL ALCOHOL IN THE PRESENCE OF ALUMINUM CHLORIDE

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by

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HISTORICAL DATA

As an historical background for this thesis the author has not included the history of condensation reactions brought about by such catalysts as $ZnCl_2$, $MgCl_2$, H_2SO_4, P_2O_5, PCl_5, $AlCl_3$, etc. The history of such condensations has been amply covered by former workers in this laboratory, for example, G. Warren, W. Lewis, B. Fayerweather, and M. Ballard. The writer feels that since this material is already available in good form, it would be better to give a survey of the research that has been done on such compounds that have a direct bearing on the problem investigated. In this survey will be included the allyl, propenyl and iso-propenyl derivatives of phenol and anisole that were considered as possible constituents of the reaction mixture. In all cases the phenolic fractions were converted into their methyl ethers, as the literature supplies much more data on the allyl, propenyl, and iso-propenyl derivatives of anisole than it does of phenol.

ALLYL PHENYL ETHER

Allyl phenyl ether, $C_6H_5OCH_2CH{:}CH_2$, was first prepared by Claisen and Eisleb (Ann. 401, 21;1915; Ann. 418, 78;1918). A mixture of phenol, allyl bromide, potassium carbonate and acetone were boiled for eight hours on a water bath under a reflux condenser.

The yield was very good. Purification must be carried out under diminished pressure because of a rearrangement which will take place on the application of too much heat.

Allyl phenyl ether is described as an oil with a rather pleasant

odor. It has a sp. gr. of .986 at 20°C; boiling at 191.7°C (corr), 85°C at 19 mm. It cannot be crystallized even on extreme cooling.

o-ALLYL PHENOL

o-Allyl Phenol (o-Chavicol, 1-hydroxy 2-allyl benzene) was first encountered by Claisen (Ann. 401, 73:1913) on decomposing 3-allyl salicylic acid by means of heat.

It is best obtained by the general method discovered by Claisen (Ann. 418, 78:1918) for the conversion of the allyl ethers of phenols into their corresponding o-allyl phenols.

Allyl phenyl ether was boiled under an air condenser until the temperature no longer rose (about six hours). The gradual rise in temperature from about 190°C to 220°C was due to a remarkable rearrangement, somewhat analogous to that taking place when alkyl anilines, in the form of salts, are heated to high temperatures. The allyl group wandered to the o-position in the benzene ring.

o-allyl phenol is an oily substance with a guaiacol-like odor, boiling at 109-110°C under a pressure of 22 mm., and solidifying in a freezing mixture to a mass of crystals melting at -6°C. It reduces $KMnO_4$ in an aqueous solution and produces a blue to greenish brown color with $FeCl_3$. The yield of o-allyl phenol is almost quantitative when prepared as described above.

p-ALLYL PHENOL

p-Allyl Phenol (Chavicol, 1-hydroxy 4-allyl benzene) was first isolated by Eykman from the fresh leaves of the Betel Nut tree as found in Java (B. 22, 2736; 23, 859;1890). It has also been found in oil of bay. According to all available information it has never been synthesized. Chavicol is a colorless, highly odorous liquid having the following properties according to Eykman:- B. P. 237°C, D_{18} 1.033, Refractive Index 1.5441. It produces an intense blue color with a solution of ferric chloride. As proof of structure and composition, the following was given: molecular weight and analysis determinations checked with the calculated values for $C_9H_{10}O$. The methyl ether was prepared by means of potassium hydroxide and methyl iodide. It is reported by Eykman as having a B. P. of 226°C and produced on oxidation with potassium permanganate in hot or cold solution, an acid with a melting point of 177-178°C. On titration, this acid proved to have an equivalent weight equal to that of anisic acid (p-methoxy benzoic acid) and answered to the description of this acid both as to chemical and physical properties.

o-ANOL

o-Anol (o-propenyl phenol, 1-hydroxy 2-propenyl benzene) was prepared by Pauly and Buttlar (Ann. 383, 280;1911) from Salicylic aldehyde and ethyl magnesium iodide in a diethyl ether solution. A compound, possibly $(C_9H_{10}O)_2$, of high boiling point was reported as forming along with the propenyl phenol. Pauly and Buttlar described it as a pale yellow, viscid oil, giving a yellow red color with concentrated sulfuric acid and dissolving in sodium hydroxide.

o-Anol crystallises in silky needles from ligroin, has a melting point of 54.8°C and boiling point of 229-231°C. The odor and taste are similar to those of phenol.

o-Anol may also be conveniently prepared by heating on an oil bath o-allyl phenol with three times its volume of methyl alcoholic potassium hydroxide for a period of two hours.

p-ANOL

p-Anol (p-propenyl phenol, 1-hydroxy 4-propenyl benzene): $CH_3CH{:}CHC_6H_4OH$.

Ladenburg (A. Spl. 8,88) prepared this compound by heating ten parts of anethol and eight parts of alcoholic potassium hydroxide for a period of twenty-four hours at a temperature of 200-230°C.

It crystallises in leafs, melting at 93°C and boiling at 250°C. On standing in the light it acquires the color of a brownish oil.

It is also reported prepared by Behal and Tiffeneau (Bl. (4), 5, 303) from p-hydroxy benzadehyde and three molecular weights of ethyl magnesium bromide.

o-ISOPROPENYL PHENOL

o-Isoprepenyl Phenol (2-hydroxy 1-isopropenyl Benzol): $CH_2C(CH_3)\ C_6H_4OH$. Behal and Tieffeneau (Bl. (4), 5, 315) report the preparation of this compound from the methyl ester of salicylic acid and three molecular weights of methyl magnesium iodide.

It is also reported prepared from 2. 1'dioxy-1-isopropyl benzol by distillation at atmospheric pressure. (Hoering and Baum, D. R. P. 208, 886; C. 1909 I, 1522).

It is reported as a colorless liquid having an odor resembling thymol; boiling point of 204°C. at 760 mm., and 83°C at 18 mm. It is somewhat soluble in water and polymerises easily on standing.

Neiderl, Smith and McGreal (J. Am. Chem. Soc. 53, 3390;1931; ibid 55, 284;1933) report the preparation of o-isopropenyl phenol by condensing allyl alcohol and phenol in the presence of sulphuric acid.

METHYL ETHER OF p-ALLYL PHENOL

Methyl Ether of p-Allyl Phenol (Methyl chavicol, estragol, isoanethol, p-allyl aniscle, p-methoxy allyl benzene); $CH_2:CHCH_2C_6H_4OCH_3$

This compound has been found to be a constituent of many essential oils such as tarragon, anise bark, bay, fennell, estragon, and terpentine.

Eykman (B. 22, 2743) reports the preparation of this compound from p-allyl phenol by heating with methyl iodide in an alcoholic solution of methyl alcohol.

Tiffeneau (C. r. 139, 482) reports that it may be prepared by treating 4-methoxy phenyl magnesium bromide in an ether solution with allyl bromide.

Ekyman reports this compound as having a boiling point of 226°C; however, the more recent workers report boiling points of 215-216°C, 214-218°C, and 212°C.

By heating, for twenty-four hours with three to four volumes of a saturated solution of alcoholic potassium hydroxide, it was changed into anethol (p-propenyl aniscle). (Grimaux, Bl. 3, 11, 54; Eykman, B. 23, 869; Tiffeneau, C. r. 139, 482).

Upon oxidation with potassium permanganate in a cold acetic acid solution there was produced 4-methoxy phenyl acetic acid and anisic acid. (Eykman, B. 22, 2744; Bertram and Walbaum, Ar. 235, 183)

It was not reduced by sodium and alcohol. (Klages, B. 32, 1439)

ANETHOL

Anethol (isoestragol, 1-methoxy 4-propenyl benzene, p-propenyl anisole): $CH_3CH{:}CHC_6H_4OCH_3$ is the principal constituent of anise, staranise, and fennell oils and has been reported present in these oils by many investigators. It was first carefully studied by Cahours (Ann. chem. phys. (3), 2, 274; 14, 489).

It has been synthesized in several ways. Grimaux (Bl. (3), 11, 35), Eykman (B. 23, 859) report that by boiling p-allyl anisole with alcoholic potassium hydroxide it was converted into anethol. Hell and A. Hoffman (B. 58, 1680) report that anethol may be prepared by the distillation of ethyl (4-methoxy phenyl) carbinol with sulphuric acid. Behal and Tiffeneau (C. r. 132, 563; Bl. (4) 3, 304) report its preparation from anisic aldehyde and ethyl magnesium iodide by heating the mixture on a water bath.

Anethol is described as an oil with a pleasant odor of anise, crystallising in plates from alcohol, which melt at 21.1°C, and boiling at 233°C at 751.1 mm.

On bromination it produced first a dibromide melting at 67°C (Hell and Garttner J. f. prakt. Chem. II, 52, (1895) 198) and also a mono Brom anethol dibromide melting at 107-108°C.

On fusion with potassium hydroxide, anethol formed p-propenyl phenol together with some p-hydroxy benzoic acid. (Ladenburg and Leverkus, Ann. Chem. Supl. Bd., 8, 88, and 141, 260).

Anethol upon oxidation with potassium permanganate, as well as potassium dichromate, yielded as its oxidation product p-methoxy benzoic acid (Anisic acid). (Rossel, A. 151, 28; Carelli, G. 20, 693).

Much additional information was obtained on this much studied substance; however, since it had no direct bearing on the investigation being conducted it is not included here.

METHYL ETHER OF o-ISOPROPENYL PHENOL

Methyl Ether of o-Isopropenyl Phenol (1-methoxy 2-isopropenyl benzene): $CH_2:C(CH_3)C_6H_4OCH_3$. Behal and Tiffeneau (Bl., 3, 515) report the preparation of this compound by the methylation of o-isopropenyl phenol using dimethylsulphate in an alkaline potassium hydroxide solution. It is also reported by the same investigators as being prepared from the methyl ester of o-methyoxy benzoic acid and three molecular weights of methyl magnesium iodide. (C. r. 139, 140; Bl. 4, 3, 515). They report it as a colorless liquid boiling at 198-199°C. Upon oxidation with potassium permanganate in the cold there is produced 2-methoxy acetophenone (C. R. 141, 596). The same workers report that upon reduction with sodium and alcohol o-isopropyl anisole is formed. (Bl., 3, 516; C. r. 141, 597).

METHYL ETHER OF p-ISOPROPENYL PHENOL

Methyl Ether of p-Isopropenyl Phenol (4-methoxy 1-isopropenyl benzene, p-isopropenyl anisole): $CH_2:C(CH_3)C_6H_4OCH_3$.

Behal and Tiffeneau report (C. r. 132, 561; 139, 140; Bl. 4, 3, 517) obtaining this compound as a dimer by heating on a water bath the ethyl ester of anisic acid and two molecular weights of methyl magnesium iodide. The monomer was obtained by the distillation of the dimer at atmospheric pressure. The monomer formed crystals with an odor resembling anethol and estragol, melting at 52°C. and boiling at 220-222°C. (Klages, B. 37, 3995; B.,T., C. r. 132, 561). It was insoluble in water and soluble in ethyl alcohol.

On oxidation with potassium permanganate in the cold it produced 4-methoxy acetophenone (B., T., C. r. 141, 597; Bl. 4, 3, 518).

Upon reduction with sodium and ethyl alcohol, p-isopropyl anisole resulted. The dimer mentioned above is reported by Behal and Tiffeneau (C. r. 132, 561; Bl. 4, 3, 520) to form odorless crystals, melting at 58°C and boiling at 210-215°C, 15 mm. It was depolymerized by distilling ordinary pressure. It did not add bromine or decolorize potassium permanganate in the cold.

STATEMENT OF THE PROBLEM

To determine if phenol and allyl alcohol can be condensed by means of aluminum chloride. To examine the condensation mixture for the presence of para allyl phenol.

EXPERIMENTAL DATA

PART I

Preparation of Allyl Phenyl Ether: $C_6H_5OCH_2CH:CH_2$

As preliminary work, allyl phenyl ether and o-allyl phenol were prepared. It was felt these compounds might be obtained from the condensation mixture of phenol and allyl alcohol.

Allyl phenyl ether was prepared using the method described by Claisen. (Ann. 401, 21; 1913).

Molar quantities of phenol, allyl bromide, and potassium carbonate together with 150 grams of acetone were heated for eight hours on the water bath under a reflux condenser. Potassium bromide settled out and the reaction mixture became a thick paste. On cooling the mixture was treated with water and extracted with petroleum ether. After washing the ethereal extract with sodium hydroxide and water, it was dried over potassium carbonate and distilled in vacuo. Yield was 120 grams; boiling at 77°C under a pressure of 10 mm. 89% of theoretical.

Preparation of o-Allyl Phenol

This compound was prepared using the method described by Claisen and Eisleb (Ann. 401, 21; 1913; 418, 78; 1918).

75 grams of allyl phenyl ether were boiled under an air condenser until there was no further rise in the boiling point. This required about six hours, the boiling point rising from 191°C to 220°C. This rise in the boiling point was due to the rearrangement of the allyl phenyl ether (B. P. 191°C) into o-allyl phenol (B. P. 221°C).

The rearranged product, after cooling, was dissolved in 20% aqueous sodium hydroxide and extracted with petroleum ether to remove any unchanged allyl phenyl ether and small amounts of alpha methyl coumarane which may have formed. The o-allyl phenol was liberated from the alkaline solution by acidification with sulphuric acid, taken up with diethyl ether, and dried over sodium sulphate. After concentrating the ethereal extract it was distilled in vacuo and produced an oil boiling at 92-93°C at 10 mm. Yield 68 grams, 91% of theoretical. It possessed all of the properties described by Claisen.

PART II

The Aluminum Chloride Condensation. (Huston's Method)

Materials and Quantities Used.

188 g. phenol	(2 moles)
39 g. allyl alcohol	(2/3 mole)
44 g. aluminum chloride	(1/3 mole)
250 cc petroleum ether	

The freshly distilled phenol was dissolved in the petroleum ether contained in a three necked flask equipped with a mechanical stirrer, a reflux condenser, and a cork stopper equipped with a thermometer. The latter served as a means of following the temperature of the reaction mixture, and by removing it, the materials could be conveniently added.

After thoroughly mixing, the allyl alcohol was added, followed by the aluminum chloride which was added in small amounts over a period of one hour. During the addition of the aluminum chloride, hydrochloric acid gas was liberated in a generous amount and the reaction mixture became a dark red in color. During the condensation the temperature never varied from 50 to 55°C. After the final addition of the aluminum chloride the mixture was stirred for about one hour and then let stand over night.

The aluminum chloride complex molecule was then decomposed by using a mixture of 150 g. of ice and 40 cc. of concentrated hydrochloric acid. The resulting mixture was extracted with sulphuric ether.

After drying the ether extract with anhydrous sodium sulphate, it was concentrated and on distillation produced the following:

B. P. Range	Pressure	Approximate Composition
Up to 85	743 mm.	ether
85 - 110	743 mm.	allyl alcohol
70 - 80	19-20 mm.	phenol
80 - 160	19-20 mm.	condensed product
160 - 240	20 mm.	condensed product
240 - (residue)		

From the fraction 70-80, upon redistillation, there was obtained 109 g. of pure phenol; 78 g. having taken part in the reaction.

Analysis of Fraction 80-160 at 19-20 mm.

This fraction included the boiling points of allyl phenyl ether, o-allyl phenol, and p-allyl phenol. It was dissolved in an excess of Claisen's alcoholic potassium hydroxide which rendered the phenolic compounds soluble. The mixture was then extracted with petroleum ether. During this extraction great care was taken to keep the mixture cool as it is a common thing for allyl derivatives to change into propenyl derivatives when heated in the presences of alkali.

The petroleum ether extract produced, on concentration and distillation, 5 g. of an alkali insoluble material boiling at 80-85° at 12 mm. This was assumed to be allyl phenyl ether. It will be considered later in this paper.

The alkaline Claisen solution, on acidification with hydrochloric acid and extraction with sulphuric ether, produced 5 g. of an oily

liquid distilling at 108-115° at 16 mm. The higher boiling point fraction was too small to be of any consequence.

Fraction 160-240°, which was by far the largest of the fractions, produced 50 g. of a straw-colored, viscid, semi-solid material that distilled for the most part at 208-216° at 6 mm.

The final fractionations produced the following:

B. P. Range	Pressure	Composition	Weight
70 - 80	19-20 mm.	Phenol	109 g.
80 - 85	12 mm.	Alk. insol. portion	3 g.
108 - 115	16 mm.	Condensed product	3 g.
115 - 208	16 mm.	Of no consequence	
208 - 210	6 mm.	Condensed product	26 g.
210 - 216	6 mm.	Condensed product	3 g.
216 -		Tarry residue	15 g.

A total eight condensations were carried out with similar procedure and results. The various fractions were combined and analysed as described on the following pages.

EFFECT OF TEMPERATURE

The condensation was repeated to note the effect of temperature on the amounts of the various fractions. The condensation was carried out in a freezing mixture of water, ice, and salt. A temperature between 0 and 5°C was maintained during the time of addition of the aluminum chloride. The reaction proceeded as usual, yielding the final fractions as follows:

B. P. Range	Pressure	Assumed Composition	Weight
80-100°C	15-16 mm.	Phenol	118 g.
105-115°C	4- 6 mm.	Condensed Prod.	4 g.
205-210°C	4- 6 mm.	Condensed Prod.	15.5 g.
210-216°C	4- 6 mm.	Condensed Prod.	2.5 g.
216-	4- 6 mm.	Tar	10.0 g.

The foregoing data gives evidence that the reduced temperature decreases the amount of the high boiling point fraction as well as the amount of tar. It increases the amount of fraction 105-115°C. From the amount of phenol recovered it follows that the reduced temperature decreases the total amount of condensation.

ANALYSIS OF THE ETHEREAL FRACTION

From the several condensations there was obtained, by extraction with Claisen's alcoholic potassium hydroxide, a total of 20.8 g. of an oily product with a boiling point of 80-83°C at 12 mm.; 68°C at 7-8 mm.; insoluble in dilute alkali; soluble in sulphuric and petroleum ethers. It was assumed that the fraction under consideration was allyl phenyl ether since it answered fairly well to the description of that compound. Boiling points of allyl phenyl ether given in the literature are; 85°C at 19 mm.; 191.7°C at 760 mm. (The boiling point of the product in question was not determined at atmospheric pressure because of its rearrangement into o-allyl phenol at that temperature).

In attempting to confirm the assumption the following procedure was carried out:

Ten grams of the supposed ether were boiled under an air condenser for a period of six hours in an attempt to bring about its rearrangement into o-allyl phenol. (Claisen, Ann. 418, 78; 1918). The initial boiling point was 191°C. During the remaining refluxing period it failed to rise further. (During the rearrangement of allyl phenyl ether into o-allyl phenol there is always a marked rise in the boiling point, from 191°C, the boiling point of the ether, to 220°C, the boiling point of o-allyl phenol. (Claisen, Ann. 418, 78; this present thesis, page).

The reaction mixture, after treatment with alcoholic potassium hydroxide, was extracted with petroleum ether to remove traces of unchanged ether. From the petroleum ether there was obtained 9.5 g.

of the unchanged ether, B. P. 196-198°C. The alkaline solution on acidification and extraction with sulphuric ether failed to yield anything of any consequence, yet the rearrangement of the allyl ether of phenol into the o- substitution product is practically quantitative according to the literature and to the work done by the author. This gave evidence of an incorrect assumption.

The rearrangement was attempted again, using 20 g. of the ether and refluxing the mixture for a period of twenty-four hours. The boiling point failed to rise appreciably and practically all of the alkali in soluble material was recovered. It boiled sharply at 196-197°C and did not possess the odor of allyl phenyl ether as prepared by Claisen's method (Ann. 401, 21;1913).

Allyl phenyl ether is not an isolatable product in the condensation mixture of allyl alcohol and phenol by means of aluminum chloride.

This investigator expects to examine further this ethereal fraction, assuming it to be alpha methyl coumarane which is known to be one of the by-products produced in the rearrangement of allyl phenyl ether. Possibly the presence of aluminum chloride influenced the changing of the allyl ether into alpha methyl coumarane.

It is reported in the literature that o-allyl phenol changes readily into alpha methyl coumarane by boiling in the presence of dry pyridine hydrochloride. (Cf. Ger. pat. 279,864).

ANALYSIS OF FRACTION 105-115° at 16 mm.

From the several condensations there was obtained a total of 25 grams of this fraction. Distillation at atmospheric pressure produced 15 grams of an almost colorless oil distilling at 235-237°. B. P. of p-allyl phenol 237°. (Eykman; Ber. d. Chem. Ger. 22, 2756).

This phenolic substance possessed the following properties which check with those given by p-allyl phenol by Eykman as above; Soluble in dilute alkali, blue color with aqueous ferric chloride, cinnamon-like odor.

Preparation of the Methyl Ether

Fifteen grams of the supposed p-allyl phenol were dissolved in a slight excess of 20% potassium hydroxide, and with agitation, 15 g. of dimethyl sulphate were added over a period of one hour. A temperature below fifty degrees was maintained. The reaction mixture was heated on a water bath for thirty minutes to remove the excess dimethyl sulphate. After being made alkaline, with sodium hydroxide, the mixture was extracted with petroleum ether.

Distillation of the ether extract produced the two fractions;

200-224	3 g.
224-230	9 g.

Fraction 224-230 was considered as the methyl ether of p-allyl phenol (B. P. given by Eykman, 226°C).

Six grams of the methyl ether, B. P. 224-230°, were oxidised by using neutral potassium permanganate and warming on a water bath for one hour. The oxidation was not very vigorous although there was a rapid discoloration of the permanganate. The oxidation product, after being recrystallised five times from hot water, was a white, needlelike compound with a melting point of 181.5 - 182°. That given for anisic acid is 184°.

These results check with the data given by Eykman (Ber. d. Chem. Ges. 22, 2736) for the proof of structure for p-allyl phenol.

Bertram and Walbaum (Arch. d. Pharm. 235, 177;1897) report that by careful oxidation of methyl chavicol in the cold, using potassium permanganate para methoxy phenyl, acetic acid resulted (M. P. 85-86 C)

Using the method of Bertram and Walbaum, the remainder of the methyl ether (3 grams) was shaken with two grams of potassium permanganate in 200 cc. of water, and 2 cc. of acetic acid. During the oxidation a temperature below five degrees was maintained. The reaction mixture after being made alkaline with sodium carbonate was filtered. The filtrate after being made acid with sulphuric acid was extracted with ether several times. The ether extract failed to produce anything of consequence. The oxidation was not repeated as the supply of the material was exhausted. Bertram and Walbaum report using 20 grams of the material in an oxidation.

On the basis of information furnished by Eykman and the above-discussed data, the conclusion is reached, that p-allyl phenol is produced in a small amount by condensing allyl alcohol and phenol in the presence of aluminum chloride. There is every evidence of para substitution.

ANALYSIS OF FRACTION 208-210° at 6 mm.

This was by far the largest of the fractions obtained. From the several condensations approximately 175 grams of this material was obtained.

It possessed the following properties:

(a) Soluble in dilute alkali, reprecipitated by hydrochloric acid.

(b) Straw-colored, very viscous liquid, acquiring a brownish color on standing.

(c) Bluish-brown color with aqueous ferric chloride.

(d) Absorbed bromine in chloroform solution without the liberation of hydrobromic acid.

(e) Gave a negative test for halogens.

(f) Failed to crystallise from ether, alcohol, benzene, toluene, xylene, etc. It did, however, form a whitish amorphous powder by the evaporation of a benzene solution over a period of several days.

A search of the literature revealed no allyl, propenyl, or iso-propenyl derivative of phenol that answered to this description, especially with respect to the boiling point.

Combustion Analysis.

Wt. of Sample	% C	% H	% O
.226 g.	79.3	7.25	13.55 (calc)
.231 g.	78.76	6.98	14.23 "
Average	79.03	7.11	13.95
Calc. for $C_9H_{10}O$	80.5	7.46	11.9

Although the agreement of experimental and calculated data is not a close one, it is at least an indication that the substance in

question, since it is not one of the allyl, propenyl, or isopropenyl derivatives of phenol reported in the literature, is a polymer of one or more of the afore-mentioned compounds.

Several investigators have reported that in the synthesis of at least some of the above-mentioned compounds there was a marked tendency toward polymerisation, and in some cases the product was actually obtained as a polymer. Eykman, however, in his original article does not mention any polymerising tendency of p-allyl phenol.

(See Pauly and Buttlar, Ann. 383, 280;1911
Behal and Tiffeneau, Bull. Soc. Chem. 4, 3, 515;1908
Meiderl Smith McGreal, J. Chem. Soc. 55, 3390;1931)

In the light of the reports by previous investigators, it was assumed that the substance in question was a polymerised product.

Molecular weight determinations by the boiling point method gave the following results:

Solvent, benzene.

Grams Solvent	Grams Substance	Observed Elevation	Molecular Weight found
12.64	.518	.272	402
12.64	1.2796	.68	398

Calculated for $C_9H_{10}O$, 134;

The molecular weight found is approximately three times that of the monomer. Therefore the conclusion is that the substance in question is a trimer.

(The author is indebted to A. H. Neeley for this molecular weight determination).

On standing, in a solution of benzene, which was allowed to evaporate spontaneously over a period of several weeks, the polymerized product formed a white amorphous powder that melted to a semi-viscous liquid over a temperature range of 148-155°. On cooling from a hot mixture of xylene and water it formed white, fluffy, somewhat needlelike crystals at the junction of the two immiscible liquids. This semi-crystalline substance melted over a temperature range of 145-155°.

DEPOLYMERIZATION

In all cases where compounds of the type being considered were obtained as polymers, the monomers were secured by distillation at atmospheric pressure.

One hundred and fifty grams of the polymer were distilled at atmospheric pressure. During the distillation considerable decomposition took place. The distillate weighing about 110 grams was a mobile, straw-colored liquid, distilling over the wide range of 190-240°. It was found to be soluble in alkali, gave an unsaturation test with bromine, and produced a muddy blue color with aqueous ferric chloride.

After several refractionations were accomplished using a fifteen-inch fractionating column the following fractions were obtained:

Up to 195	8 g.
195-200	10 g.
200-210	60 g.
210-220	15 g.
220-240	12 g.
240- residue (tar)	7 g.

Niederl reports (J. Amer. Chem. Soc. 55, 3390; 1931) the preparation of o-iso-propenyl phenol by condensing phenol and allyl alcohol in the presence of sulphuric acid. It was obtained as a polymer which was depolymerized by distillation at atmospheric pressure. It was felt at the time that the large fraction 200-210 might possibly be o-isopropenyl phenol on account of its boiling point, 203-206 (Behal and Tiffeneau Bull. Soc. Chem. 3,515;1908). No other allyl, propenyl, or sio-propenyl derivative of phenol has a reported boiling point within ten degrees. No reaction mechanism, similar to the one given by Niederl for the formation of o-iso-propenyl phenol, could be worked out on the basis of aluminum chloride as the condensing agent.

The fraction 200-210 was carefully fractionated and the fraction 202-206 collected. Yield, 48 grams.

The methyl ether was prepared by using dimethyl sulphate as described on page 18, of this thesis.

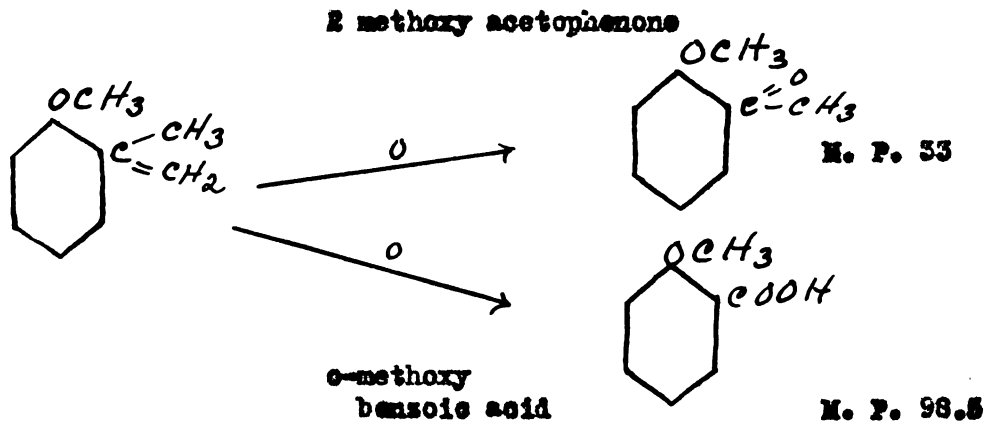
Fractionation of the methylated product produced the following:

B. P. Range	Pressure	Weight
175 - 195	745 mm.	4 g.
195 - 200	745 mm.	35 g.
200 - 210	745 mm.	6 g.

The boiling point given for iso-propenyl anisole is 198-199. The large fraction 195-200 was an indication of the presence of iso-propenyl anisole.

Behal and Tiffeneau (C. r. 141, 596) report that on oxidation with potassium permanganate in the cold, o-iso-propenyl anisole produces 2-methoxy acetophenone M. P. 33.

Ten grams of the methyl ether were mixed with 7 grams of potassium permanganate dissolved in 250 cc. of water. On standing over night there was considerable discoloration of the permanganate. After filtering, the filtrate on being acidified liberated a white flaky precipitate. After being recrystallized from hot water six times there was obtained a white, monoclinic crystalline compound (M. P. 183.6). o-iso-propenyl anisole should yield on oxidation;



The crystalline product was soluble in dilute sodium hydroxide and reprecipitated by hydrochloric acid. Its melting point corresponded to that of anisic acid. (p-methoxy benzoic acid M. P. 184°).

The oxidation was repeated with similar results, once as just described and again by heating the reaction mixture in a water bath for two hours. The variation in temperature had no effect on the final result.

Equivalent Weight Determination;

There was evidence that the oxidation product was anisic acid.

Tritation Data:

.1175 g. were dissolved in 50 cc. of water and 50 cc. of ethyl alcohol in a volumetric flask. Three 25 cc. portions were titrated using .1005 N. sodium hydroxide and phenolthalein as an indicator.

Sample	I	II	III
cc. NaOH	1.95	1.95	2.00
Equivalent Weight	150.7	150.7	153.8

Calculated for Anisic acid ($C_8H_8O_3$) 152
Found (Average) 151.7

The product obtained by oxidising the fraction in question must be anisic acid because of (a) its melting point, (b) its likeness to anisic acid, (c) equivalent weight determination.

o-iso-propenyl phenol is not a constituent of the condensation mixture of phenol and allyl alcohol. This is positive proof of para substitution in this aluminum chloride condensation, a fact which extends the scope of Huston's Method in synthesising organic compounds.

ANALYSIS OF FRACTIONS 210-220° and 220-240°

B. J. Eykman (Ber. d. Chem. Ges. 22, 2756;1889) reports that the methyl ether of p-allyl phenol has a boiling point of 226°C. This, however, does not agree with data furnished by recent workers.

Grimaux reports (Bull. Soc. Chem (Paris) 3, 11, 35) the preparation of Estragol by repeated fractionation of Oil of Estragon. He gives a boiling point of 215-216°C (corr.). Estragol was proved to be the same as methyl chavicol. In 1892, some two years before the work of Grimaux

on estragol, Schimmel and Co. (Bericht d. Chem. Ges. 1892, 17) found that the chief constituent of oil of estragon was methyl chavicol, and later their chemists, Bertram and Walbaum (Arch. d. Pharm. 235, 177:1897) estimated the amount of this substance in oil of estragon to be 67.8%. On oxidation this substance produced the same oxidation products as those reported by Eykman, namely, para-methoxyphenylacetic acid and anisic acid. It seems highly probable that methyl chavicol and estragol are identical. This assumption received confirmation by the report of Hell and Gaab, (Ber. d. Chem. Ges., 29, 344) who found that methyl chavicol from estragon oil (isosmethol, they called it) gave a monobrom dibromide $C_6H_3Br(OCH_3)\ CH_2CHBrCH_2Br$ when treated with bromine in an ether solution. On oxidation it yielded a ketone having the formula $C_6H_3Br(OCH_3)\ COCHBrCH_2Br$.

Orndorff, Terrasse and Morton (Am. Chem. Journ. 19, 845) report the preparation of methyl chavicol from oil of estragon purchased from Fritzsche Bros. They report it as having a boiling point of 210-212°C (uncorr.). When heated with an alcoholic solution of caustic potash they report a rearrangement into anethol (p-propenyl anisole). They also report the preperation of anisic acid by oxidation, using the method given by Ladenburg and Fritz (Ann. Chem. (Liebig), 141, 248). On bromination in an ether solution they found that it readily absorbed one molecule of bromine; however, it was impossible to isolate the dibromide. Hydrobromic acid was liberated after the addition of one mole of bromine. The reaction mixture produced the tri-bromide compound described by Hell and Gaab (Ber. d. Chem. Ges. 29, 244).

On the assumption that the boiling points reported by the more recent workers are correct and that Eykman had made an error in his reported boiling points, the following procedure was followed:

The fractions 210-220 and 220-240 were combined and the methyl ether prepared by using the method described on page 18, of this thesis. The methyl ether was carefully fractionated and the fraction 210-216 collected, 50 grams of the phenolic fractions, on methylation and fractionation, yielded the following.

Up to 210	5 g.
210 - 216	28 g.
216 - 224	4 g.
224 - 230	7 g.
230 - 235	2 g.

235 - residue, of no consequence.

Fifteen grams of the fraction 210-216 were heated for a period of thirty hours with three times its volume of saturated methyl alcoholic potassium hydroxide. This treatment is reported to cause an allyl group to change into the isomeric propenyl group. When methyl chavicol is treated in this way it is changed into its isomer anethol (para propenyl anisole).

After the period of heating, the mixture was diluted with water, extracted with petroleum ether, dried over sodium sulphate, and then distilled with the following fractions:

210 - 217	12 g.
217 - 228	1.5 g.

This gave evidence that no shifting of the double bond had occurred, for if it had the resulting product, anethol, would have distilled at 233-234.

A second attempt was made to rearrange the the methyl ether in question but with no success.

Hell and Gaab (Ber. d. Chem. Ges. 29, 544:1896) report that by bromination it was impossible to isolate the dibromide of methyl chavicol, but they did succeed in obtaining a mono brom methyl chavicol dibromide melting at 68.4°C.

Five grams of the methyl ether B. P. 210-216 were dissolved in 25 cc. of chloroform and after cooling in an ice mixture, two moles of bromine were added in a solution of chloroform from a dropping funnel. At first the color of the bromine disappeared at once without the liberation of hydrogen bromide,. After about one half the bromine had been added, hydrogen bromide was liberated in a large amount.

After standing over night, the mixture was taken up with petroleum ether, dried over calcium chloride, concentrated and distilled in vacuo, yielding a light straw-colored oil distilling at 140-145°C at 18-20 mm. The oil failed to crystallise from petroleum ether, and would not solidify in a freezing mixture of ice and salt or at the temperature of solid carbon dioxide.

Several distillations followed by intense cooling failed to bring about the solidification of the oil.

The bromination was repeated and the resulting oil failed to solidify or crystallise.

A sample of oil of estragon, obtained from Fritzche Bros., was carefully fractionated by using a fractionating column and the fraction 212-216 collected. This fraction according to Walbaum and Bertram (Arch. d. Pharm. 235, 177;1897), Orndorff, Terrasse and Morton (Am. Chem. Journ. 19, 845), is methyl chavicol or estragol. This fraction had more of a terpene odor than did methyl ether of the corresponding fraction collected by depolymerization of the condensation product.

Eight grams of oil of estragol, obtained by the above mentioned distillation, were divided into two portions and brominated in a chloroform solution. To one portion was added one mole of bromine and to the other two moles. On distillation in vacuo the former decomposed. The latter failed to crystallize from the several solvents tried and would not solidify in a freezing mixture. According to the literature (Hell and Gaab, Ber. d. Chem. Ges. 29, 344) methyl chavicol obtained from oil of estragon formed on bromination a mono brom methyl chavicol dibromide, which crystallized from petroleum ether and melted at 62.4°C. Further attempts are being made to bring about the crystallization of the brominated product. It was the intention to use the crystallized bromide in seeding the brominated condensation product.

OXIDATION OF METHYL ETHER 224-230°C

This ether resembled somewhat the methyl ether obtained from the phenolic fraction 235-237°C from the original condensation mixture.

Seven grams of this ether fraction were heated on a water bath for two hours together with 200 cc. of water and 5 grams of potassium permanganate. Oxidation was indicated by the change in color of the permanganate. The oxidation mixture failed to yield anything of consequence.

SUMMARY

The results of the work outlined in this thesis may be summarized as follows:

Allyl alcohol and phenol condensed in the presence of aluminum chloride.

The condensation mixture produced the following:

(a) An alkali insoluble portion which could not be identified as allyl phenyl ether. This material is still unidentified.

(b) A phenolic fraction which if we accept the data and proof of structure as furnished by Kykman is para allyl phenol.

(c) A polymer which by analysis and molecular weight determinations proved to be a trimer of the molecular formula $C_9H_{10}O$.

Depolymerization was effected by distillation at atmospheric pressure. The depolymerized product has not been definitely identified, but does contain a para substituted phenol.

By oxidation there is definite proof of para substitution.

The investigation of this condensation is to be continued.