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CONDENSATION OF ALLYL ALCOHOL WITH BENZENE
IN THE PRESENCE OF ALUMINIUM CHLORIDE

THESIS FOR DEGREE OF M. S.

DEWITT DUNN SAGER

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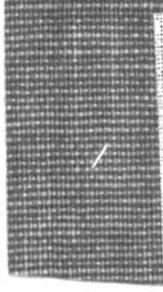
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THESIS

Submitted to the Faculty of Michigan State
College in Partial Fulfillment of the
requirements for the degree of Master of
Science.

BY

DeWitt Dunn Sager

1925

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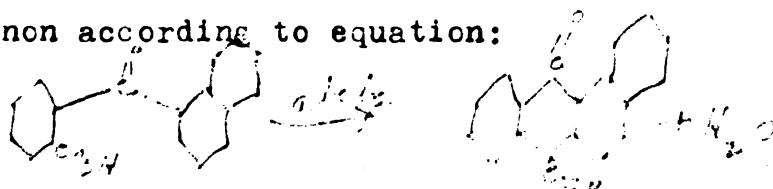
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I. Review of Previous Work.

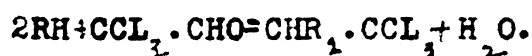
1. Aluminium chloride as a dehydrating agent in organic chemistry.

Aluminium chloride has been used as a dehydrating agent in organic chemistry by a considerable number of investigators: Waas (1882) (1) prepared di and tri phenylethane by the action of aluminium chloride on dichlorethyl oxide and benzene. The course of the reaction was experimentally shown to be as follows: the aluminium chloride first converts the dichlorethyl oxide into mono chloraldehyde, which, reacting with benzene, forms first mono chlorodiphenylethane and finally triphenylethane. Merz and Weith (1881) (2) prepared diphenylether by the action of aluminium chloride on phenol. Graebe (1901) (3) prepared aniline in small quantities by the action of hydroxylamine on benzene in the presence of aluminium or ferric chloride, but not in the presence of zinc chloride. By the same method Toluene gave a mixture of p-toluidine with a little o-toluidine, o-xylene gave a relatively good yield of 4-amino-1:2 xylene; m-xylene gave 4-amino-1:3-xylene, and p-xylene gave a small amount of 2-amino-1:4xylene. Mesitylene was partially converted into mesidine. Naphthalene gave a small yield of α - and β naphthylamine. Jaubert (1901) (4) similarly prepared the hydrochloride of the amine by using hydroxylamine hydrochloride. The yield however was low. Scholl & Seer (1912) (5) succeeded in uniting aromatic nuclei, especially in case of aromatic ketones eg. 1 part (1) naphthylphenylketon-2-carboxylic acid with 3 parts of aluminium chloride and heated for 2 hours at 130 gave 1-2

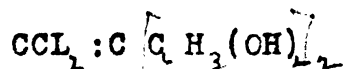
benzanthra chinon according to equation:



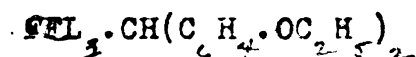
G. B. Frankforter & W. Kritchevsky (1914) (6) state that the applicability of aluminium chloride as dihydro-
 ting agent appears to be almost as universal as that of
 sulphuric acid, and they have employed it in preparing
 condensation products of the aliphatic, benzine, naphtho-
 lene and anthracene series, not only with chloral, but also
 with chloral hydrate and bromal. Benzine, toluene and
 xylene produced with chloral the same condensation products
 as are obtained by means of other condensation agents,
 formed according to the equation:



Pentane and chloral react very violently: the product is a
 mixture of substances which is being investigated, but is
 evidently produced by dihydrotin. Benzyl alcohol, chloral,
 and aluminium chloride at ordinary temperatures produces
 benzaldehyde and a mixture of two or more chlorinated
 unidentified substances. Resorcinal and chloral in cold
 carbon disulfide were converted by aluminium chloride into
 dichloro as doesoreylethylene,



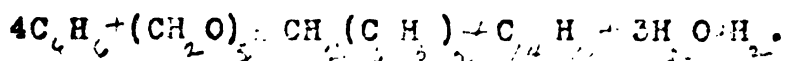
Phenetole, chloral, & aluminium chloride gave trichloro-
 diphenethl ethene,



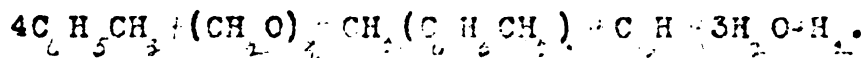
Phenetole, bromal, and aluminium chloride give the similiar
 tribromo compound.

Frankforter & Kokatnur (1914) (7) prepared diphenyl-
 methane and anthracene by the action of aluminium chloride
 of benzine and trioxymethylene. They represented

the above reaction by the following equation:



The reaction between toluene and trioxymethylene in presence of aluminium chloride was similar, producing benzene in small amounts and also ditallylmethane and dimethylantracene according to the equation:



O-xylene under similar conditions yielded a mixture of substances from which was isolated; benzene, possibly some toluene, dixylylmethane ($C_{12}H_{10}$) and tetsamethylantracene. Mesitylene treated in the same way gave; tetramethylantracene, benzene, toluene, x-yylene, dimesitylmethane and durene.

Frankforter & Kritchevsky (1915) (8) extended their researches to the more complex aromatic derivatives and found that they condensed with chloral and bromal as well as the less complex compounds. A mixture of naphthalene and chloral when treated with aluminium chloride gave α-dinaphthyldichloroethylene ($C_{10}H_7 - CCl_2$) and β-dinaphthyldichloroethylene. It worked equally well with bromal giving dibromo compound instead of the dichloro. Anthracene treated in a similar manner gave dianthracene dichloroethylene, when the mixture was suspended in petroleic ether. When suspended in benzene or carbon disulphide it gave 9, 10-anthracenedichloroethylene. Phenanthrene gave similar compounds. Phenanthrene, benzaldehyde in carbon disulfide gave diphenanthrene phenylmethane ($C_{14}H_9$)₂:CH.C₆H₅ and dibenzalmesotriphenanthrene ($C_{12}H_9$)₂:CH.C₆H₅.

Huston and Friedman (1916) (9) were first to use aluminium chloride as a condensing agent for aromatic

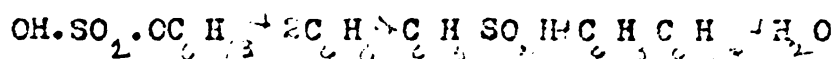
alcohols with aromatic compounds. They prepared diphenylmethane and anthracene from benzene and benzyl alcohol in presence of aluminium chloride. They found that the amounts of reagents used and the temperature at which the reaction took place greatly influenced the yield. The same authors (1918) (10) extended their experiments to secondary alcohols with benzene and aluminium chloride. They used methylphenyl carbinol, ethyl phenyl carbinol, and benzhydrol and obtained diphenylmethane, diphenyl propane and triphenylmethane respectively. In (1924) R. C. Huston (11) condensed benzyl alcohol with phenol by means of aluminium chloride to form benzyl phenol. He also condensed benzyl alcohol with anisol and phenetol and obtained the methyl and ethyl esters respectively of benzyl phenol.

2. Condensation of aliphatic alcohols with benzene.

Very little has been accomplished along the line of condensing aliphatic alcohols with benzene by any dehydrating agent. Goldschmidt (1882) (1) prepared homologues of benzene by the action of zinc chloride on mixtures of aliphatic alcohols and benzene at high temperatures. Thus benzene and isobutyl alcohol gave isobutyl benzene and the dibutyl benzene. Toluene and butyl alcohol gave methyl butyl benzene. Benzene and ethyl alcohol gave ethyl benzene. In the latter case the yield was small owing to the difficulties of manipulation.

A. Brochét and P. C. Boulenger (1893) (2) found that ethyl benzene and hexethyl benzene were formed when 1 part benzene was heated with 2 parts of ethyl alcohol and 4 parts sulphuric acid in a sealed tube at 175° - 200° for 3-4

hours. Similar results were obtained with n-propyl alcohol and also butyl alcohol. The mechanism of the reaction appears to be exhibited in the case of hexyl alcohol. Benzene sulphonic acid was formed and recognized by conversion into its calcium salt and phenol. The hydrogen hexylic sulphate first formed appears to react with benzene according to the equation:



The two references above are the only two I have been able to find of aliphatic alcohols, saturated or unsaturated, being condensed with benzene.

3. Allylation of benzene by other methods.

In reviewing the literature there seems to be considerable differences of opinion as to the properties of allyl benzene. This is probably due to the fact that the allyl benzene was prepared only in small quantities and not sufficiently purified. Also there has not been a clear distinction made between allyl benzene ($\text{C}_6\text{H}_5\text{CH}_2\text{-CH=CH}_2$) and propenyl benzene ($\text{C}_6\text{H}_5\text{CH=CH-CH}_2$).

Wagner and Tollens (1873) (1) attempted to make allyl benzene by heating at 60° a mixture of 48 parts of allyl bromide, 56 parts of brom benzene, 102 parts of benzene and 73 parts of sodium. They found that this yielded principally benzene and diallyl. Another experiment yielded diphenyl and a dark oil. From this data they considered it probable that allyl benzene was formed and its polymerization products were contained in the dark oil. C. Chojnacki (1873) (2) heated equal parts of benzene and allyl iodide or bromide with 1/5 part of powdered zinc at 100° under pressure. The

quantity of phenyl allyl was very small. It boiled at 155°.

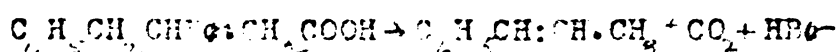
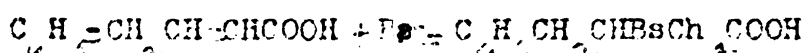
Analysis:	Calculated	Found.
C.	91.5	91.0 & 91.2
H.	8.5	7.8 & 8.3

He said that he wanted to extend his researches in order to assure himself of the constitution and properties of this hydrocarbon.

Rugheimer (1874) (3) prepared what he called allyl benzene ($C_6H_5-CH_2CH=CH_2$) by reducing cynamil alcohol with sodium amalgam. The allyl benzene as he prepared it boiled at 155°. The dibromderivative ($C_6H_5-CHBrCHBrCH_2$), made by direct union with bromine melted at 66.5°. Fittig (1874) (4) tried without success to prepare $C_6H_5CH_2-CH=CH_2$ from brombenzene and allyl iodide, also from brom benzene and allylbromide. He tried to prepare the same compound by heating brombenzene, allyl bromide, sodium and a little ether in a sealed cube but without success. He replaced the sodium in the preceding experiment with pulverized silver but obtained no results. B. Radziszewski (1874) (5) heated phenyl propane ($C_6H_5CH_2CH=CH_2$) to 150°-160° and found that it absorbed 1 molecule of bromine. He found that HBr was given off when the product was distilled and that the entire fraction came over between 165°-170° at 728 m.m. This fraction after three fractionations boiled at 164°-165° at 728 m.m. This on analysis proved to be $C_6H_5C_2H_3$. He found that it combined easily with bromine in a chloroform solution. The bromide separated upon standing. The bromide crystals melted at 65°-66°. This upon analysis gave the formula $C_6H_5C_2H_3Br_2$. R. Fittig (1874) (6) reviewed his unsuccessful attempts to

to prepare allyl benzene, $C_6H_5CH_2-CH=CH_2$. He appeared to doubt the correctness of Chojnacki's assertion that this hydrocarbon is formed when a mixture of brombenzene and allyl iodide was treated by Zincke's method.

In (1875) M. Eosivitz and B. Aranheim (7) attempted to prepare allyl benzene. They diluted, with ether, a mixture of vinyl bromide and benzyl chloride and treated the mixture with sodium. Crotonylene and dibenzyl were formed. They found that allyl cyanide and benzyl chloride do not react at a temperature of 200° . Binder (1877) (8) showed that hydrobromo or hydricdo cinnamic acid, when treated with bases, not only lost hydro bromic or hydricda acids, but also carbonic anhydride, chemically pure cinnamene being produced in considerable quantities. W. H. Perkin (1877) (9) applied the above principle to the hydro bromo derivatives of phenylcrotonic, phenyl angelic acids and others. He obtained allyl benzene (?) ($C_6H_5CH=CHCH_2$) from the phenyl crotonic acid according to the equations:



The allyl benzene (?) boiled at $174^\circ-175^\circ$ and had a sp. gr. .918. Its dibromide melted at 67° .

Analysis gave the following results:

	Theoretical	Found.
C.	91.52	91.25
H.	8.47	8.43

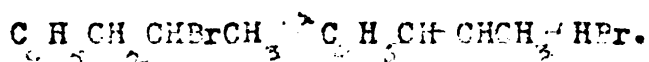
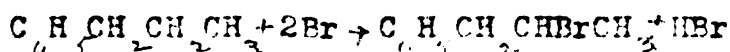
Triman (1878) (1.) prepared phenyl propylene along with *cinnamyl alcohol with 25 vols.* toluene by heating 10 vols. of fuming HI in a sealed tube at $180^\circ-200^\circ$ for 4-5 hours. The phenyl propylene boils at

165°. It was identified by its boiling point alone.

In (1884) Wagner (11) obtained allyl benzene (?) ($C_6H_5CH_2CH=CH_2$) by treating ethyl phenyl carbinol with HCl . This allyl benzene (?) boiled at $174^\circ-175^\circ$ and yielded a dibromide which melted at 66.5° . G. Frera (1885) (12) prepared the unsaturated hydro carbon $C_6H_5CH_2CH=CH_2$ by treating the monochloro propyl benzene with hot saturated alcoholic KOH . This boiled at $178^\circ-180^\circ$ and gave a dibromide which melted at 65° .

N. H. Ferkin, Jr. and J. Stenhouse (1891) (13) prepared allyl benzene (?) $C_6H_5[CH=CH-CH_2]$ by heating methyl phenyl hydroxypropionic acid. They gave the boiling point as $174^\circ-175^\circ$. They treated the hydro carbon with a calculated amount of bromine in a chloroform solution and allowed it to stand at ordinary temperatures. This gave them dibrompropyl benzene, which melted at 66.5° .

M. F. Genvresse (1893) (14) prepared allyl benzene (?) by heating 36 grams of propyl benzene up to 150° and adding 50 grams of bromine drop by drop. After all the bromine was added the heating was continued until no more HBr was given off. The resulting mixture was then distilled. The fraction boiling between $165^\circ-180^\circ$ was redistilled several times until finally it came over between $172^\circ-175^\circ$. This consisted mostly of allyl benzene (?) of which the dibromide melted at 65° . He gave the following equation for this reaction:



Senfter and Tafel (1894) (15) prepared propenyl-1'

benzene $C_6H_5CH=CH-CH_3$ from phenyl propyl trimethyl ammonium iodide. They warmed the iodide on a water bath with an excess of silver oxide and strong alkali. The resulting syrup was distilled on an oil bath until the residue was a dark pitchy mass. The distillate was treated with strong H_2SO_4 until an oil separated out which was extracted with ether. The ether solution was washed several times with dilute H_2SO_4 and then neutralized with K_2CO_3 . A fraction boiling between $174^{\circ}-176^{\circ}$ was obtained from the ether solution after several fractionations. It was analyzed for C_9H_{10} .

	Calculated.	Found.
C.	91.52	91.31
H.	8.47	8.51

Alfons Luib (1894) (16) prepared phenyl propylene $C_6H_5CH=CH_2$ by refluxing phenyl brombutyrix acid with 100 parts of water and then distilling with steam. The bromine derivative of this melted at $90^{\circ}-100^{\circ}$ (?). August Klages (1902) (17) prepared propenyl benzene. He reduced propionyl benzene with sodium and alcohol, according to the method worked out by Klages and Alledorff. He then took the resulting carbinal and formed the chloride which treated with pyridin under a reflux condenser. The hydrocarbon was dissolved with ether. The ether was washed with water and dried with sodium sulfate. The propenyl benzene was distilled over sodium and under reduced pressure. It boiled at 74° at 13 m.m., and had a sp. gr. .9083 $15^{\circ}/40^{\circ}$

	Calculated.	found.
Analysis C.	91.52	91.52
H.	8.47	8.42

C. Hell and H. Bauer (1903) (18) prepared 1-phenyl propene by treating ethyl phenyl carbinol with HCl , and then boiling with water free pyridin. The 1-phenyl propene boiled at 174-175 and formed a dibromide in chloroform solution with bromine. The dibromide melted at 66 . 2

August Klages (1903) (19) continuing his researches prepared allyl benzene (?) or propenyl benzene from phenyl ethyl carbinol. The carbinol was converted into the chloride. The chloride was treated with two mol. of pyridin under pressure at 125 . This caused the addition product of pyridine and the chloride to be completely decomposed. The propenyl benzene boiled at 72 -74 at 15 m.m. and had a sp. gr. of 9338, 14/4 . At ordinary temperature it boiled at 174 -175 . He found that the propenyl benzene was not easily reduced to n-propyl benzene. F. Kunekell and W. Dettmar (1903) (20) made the assumption that propenyl benzene is easily polymerized owing to the differences in boiling point and also differences in sp. gr. heretofore recorded. They added to 10 grs. of 2

chlor ~~3~~-brompropyl benzene, dissolved in 100 c.c. of ether, 10 grams of sodium. They heated this for 4 1/2 hours on a water bath under a reflux condenser. The ether solution was filtered off and washed with water and finally dried over calcium chloride. They obtained 4 grams of propenyl benzene that boiled at 65 -67 at 10 m.m. When they distilled this at ordinary pressure they obtained one drop at 165 -166 . Most of remainder came over at 167 -170 . After three distill- 2

ations they obtained three grams at 167 -170°, which had a specific gravity of .908 at 15°. The fraction at 167 -170° they called pure propyl benzene.

	Calculated	Found.
Analysis C	91.5%	91.4%
H	8.5%	8.9%

A. Klages (1903) (21) in replying to Kunckell (20) asserted that allyl benzene prepared by the two methods described by him in other papers possessed the following physical properties: Sp. gr. .9141 at 21/4°, N 1.5497 at 12°, B. Pt. 176 -178° at 754 m.m. He claimed this data agrees with Perkins (8) but not with Kunckell. Klages also claimed this was due to the presence of small amounts of ~~n~~-propyl benzene in Kunckell's preparation as to the presence of an isomeric hydro carbon. F. Kunckell (1903) (22) in reply to Klages (21) said that the n-propyl benzene was easily removed from his preparation by fractional distillation. He claimed also that his allyl benzene (?) gave a normal yield of the dibromide.

M. Tiffeneau (1904) (23) obtained allyl benzene $C_6H_5CH_2CH=CH_2$ by the action of allyl bromide on C_6H_5MgBr . It possessed the following physical data: B.Pt. 156 -157°, D -0.9012, N 1.5143. The allyl benzene was characterized by its transformation when boiled with alcoholic KOH, to propenyl benzene, $C_6H_5CH=CHCH_3$. The dibrom derivative of the latter melted at 70°. E. Chabloy (1907) (24) reduced cinuamyl alcohol by $NaNH_2$ at -80°. This reduction gave a small quantity of phenyl propylene (allyl benzene) which boiled at 165 -170°. The dibrom derivative melted at 67°.

H. Fmdl (1911) (25) in reviewing the preparation of propenyl benzene by the reduction of quaternary ~~clindanyl~~ ammonium salts with sodium amalyam considered the possibility of the material so prepared containing allyl benzene or propyl benzene. The preparation was divided into four equal parts and each of these decomposed by ozone. In no case was phenyl acetaldehyde or phenyl acetic acid obtained. All four parts gave benzaldehyde or benzoic acid. Hence allyl benzene was not present.

4. Preparation of chloropropyl benzene.

G. Errera (1) in order to determine the constitution of the chloropropyl benzene obtained by the action of chlorine on the boiling hydro carbon, prepared the three alcohols derivably from propyl benzene and converted them into their corresponding chloro derivations. Phenyl propyl alcohol $C_6H_5CH_2CH_2CH_2OH$, when heated in a sealed tube with concentrated hcl acid yielded the chloro derivative $C_6H_5CH_2CH_2CH_2Cl$. He described this compound as a pale yellow liquid which boiled at 219° . Methyl benzyl carbinol $C_6H_5CH_2CH(OH)CH_3$ when heated with hcl acid in a sealed tube yielded $C_6H_5CH_2CH(Cl)CH_3$ a yellowish liquid which boiled at $204-207^\circ$ with partial decomposition into allyl benzene. Ethyl phenyl carbinol $C_6H_5CH(OH)CH_2CH_3$ was converted by gaseous hcl , even at ordinary temperatures into $C_6H_5CH(Cl)CH_2CH_3$ a yellow liquid which boiled at $200-205^\circ$, but with considerable decomposition into "allyl benzene". The $C_6H_5CH(Cl)CH_2CH_3$ was distinguished from the other two by the readiness with which it reacted with silver acetate yielding the acetyl derivative boiling at 227° .

P. Genvresse (1893) (2) subjected the vapours of boiling propyl benzene to the action of a slow current of chlorine in a reflux apparatus, until a thermometer placed in the vapour indicated 200°. The product was a chloro-propyl benzene which boiled at 208°-210° with a slight decomposition. It did not attack the eyes and had a sp. gr. of 1.0687. When heated with a concentrated solution of K_2CO_3 in a sealed tube at 180°-200° for 2 days, allyl benzene and α -chloro propyl benzene boiling at 205°-206° was obtained. The latter resisted the action of K_2CO_3 but was converted into allyl benzene by KOH and yielded benzoic acid when boiled with alkaline $KMnO_4$.

E. Merck (1912) (3) prepared $C_6H_5CH_2CH_2CH_2Cl$, a colorless oil with a penetrating odor, B.Pt. 219-220° or 110° at 21 m.m. in a 98% yield by diazotizing γ chloro propyl aniline and then reducing with stannous chloride in alkaline solution.

J. Braun and E. Aust (1916) (4) prepared γ chloro propyl benzene, B.Pt. 110° at 20 m.m., but the action of phosphorus chloride on the platinum salt of methyl amino-propyl benzene.

II. Allylation of Benzene and Formation of γ -chloropropyl in the Presence of Aluminium Chloride.

In reviewing the literature one finds that there has been no attempt to allylate benzene by the condensation of benzene and allyl alcohol.

When a mixture of allyl alcohol and benzene was mechanically stirred during the addition of aluminium chloride it was found that the temperature rose and that hydrochloric acid fumes were copiously evolved. After the evolution of HCl gas had ceased the mixture was decomposed in finely cracked ice. The benzene portion was separated from the water portion and the latter extracted with ether. The ether, benzene and allyl alcohol were removed by distillation. The residue when fractionated yielded a distinct fraction from 157° - 159° at ordinary pressure, one at 90.5° - 92.5° at 18 m.m., and one at 148° - 153° at 18 m.m. The first of these fractions is allyl benzene and the second is γ -chloropropyl benzene, while the third is probably a mixture of the chloride and higher hydrocarbons. This will be proven in the experimental part of this thesis.

Experimental.

1. Method.

In all the condensations that were run: 1 mol (87 grs) allyl alcohol, five mols (585 grs.) benzene, and one half mol (99) aluminium chloride were used. The allyl alcohol was mixed with the benzene and cooled to the required temperature by placing an ice solution around it. The mixture was stirred mechanically. The aluminium chloride was added slowly so that the temperature would not rise. The addition of the

aluminium chloride took, in general, from two hours to two and one half hours. Hydrochloric acid fumes were copiously given off in all cases, starting shortly after the addition of the aluminium chloride. The mixture was stirred for eight-nine hours during which time it gradually took on a dark reddish brown color. The next morning, when the evolution of Hcl fumes had considerably slowed down, the mixture was decomposed in ice and a little Hcl acid. The benzene layer was separated from the water layer. The water portion was extracted three times with 200-250c.c. of ether each time. After the ether, benzene and allyl alcohol was removed the residue was fractionally distilled. Note(any variation from above method or peculiar phenomenon will be recorded with the condensation in which it occurs).

I. Temperature 10°-15°.

(A dark heavy solution settled to the bottom comprising about one half of the total volume.

Recovered 498 grams Benzene.

" 15 grams allyl alcohol.

160°-170° - 5 grams.

140°-150° at 18 m.m. 2 grams.

II. Temperature 10°-15°.

(same as I only II was decomposed after eight hours stirring).

Recovered 515 grams benzene.

" 40 grams allyl alcohol.

Very little tarry residue left after allyl alcohol was removed.

III. Temperature 20°-25°.

(No heavy layer separated out as in the two previous condensations).

Recovered 405 grams benzene

" 60 grams allyl alcohol.

160 -170 -----8 grs.

Up to 100 (mostly 90-100) at 18 m.,-----3 grs.

100 -140 at 18 m.m.-----1 1/2 grs.

140 -190 at 18 m.m.-----3 grs.

IV. Temperature 20 -25 .

160 -170 -----10 grs.

90 -100 at 18 m.m.-----8 grs.

100 -140 at 18 m.m.-----7 grs.

140 -170 at 18 m.m.-----5 grs.

V. Temperature 20 -25 .

160 -170 -----5 grs.

90 -100 at 18 m.m.-----4 grs.

100 -140 at 18 m.m.-----2 grs.

140 -190 at 18 m.m.-----2 grs.

The fractions boiling between 160 -170 were combined.

To this was added about 10 grams of distillate coming over a little below 160 making a total of 38 grams. This was fractionated into the following fractions: 150 -160 ,

160 -170 , 170 -180 . After a considerable number of fractionations (at least eight) the fractions between 160 -170 and 170 -180 , dissappeared. 29 grams came over at 150 -160 . The distillate boiling above 180 was put in the fraction boiling at 90 -100 at 18 m.m.

The fractions boiling at 90 -100 at 18 m.m. were combined. Those that boiled at 140 -190 were combined. This

gave:

90 -100 at 18 m.m. 15 grs.
 100 -140 " " " 10½ grs.
 140 -190 " " " 12 grs.

These were repeatedly fractionated until it was evident that the main fractions were 90 -100 at 18 m.m. and 140 -190 at 18 m.m. The fractions 100 -140 at 18 m.m. kept getting smaller. In order to reduce the 100 -140 fraction as much as possible we collected between 85 -105 (18 m.m.) and 135 -175 (18 m.m.). After a large number of fractionations (about twelve) we obtained the following results:

Up to 85 at 18 m.m.-----2 grs.
 85 -105 " " " -----15 grs.
 105 -135 " " " -----1½ grs.
 135 -175 " " " -----12 grs.
 Above 175 " " " (tarry residue 5-6 grs.

The fractions boiling at 85 -105 at 18 m.m. and 135 -175 at 18 m.m. obtained from the three preliminary condensations were fractionated twice and then were added above fractions.

The preceding condensations were run on allyl alcohol prepared by Eastman Co. The following condensations were run on allyl alcohol prepared by myself according to the method of Oliver Kamm and C. S. Taylor and checked by H. T. Clarke and E. R. Taylor.

VI. Temperature 20 -25 .

Recovered 545 grs. benzene.

" 27 grs. allyl alcohol.

Residue 19 grams.

VII. (Used 525 grams benzene) Temperature 20 - 5 .

Recovered 480 grs. benzene.

" 31 grs. allyl alcohol.

Residue 27 grams.

VIII. (Used: 120 grs. allyl alcohol.

807 grs. benzene.

138 grs. aluminium chloride).

Recovered 635 grs. benzene.

" 46 grs. allyl alcohol.

Residue 30 grs.

The residues from the above four condensations were combined giving 93 grams. They were run three following fractionations: 100 -135 , 135 -165 , up to 85 at 18 m.m., 85 -105 at 18 m.m., 105 -135 at 18 m.m., 135 -175 at 18 m.m. The first fractionation did not give a very good separation. Twelve grams of tarry residue remained. The second fraction gave a fair separation with two grams of residue. The third gave a good separation with only one gram of residue.

The three fractionations yielded:

100 -135 -----	12 grams.
135 -165 -----	36 grams.
165 ordinary pressure- 85 at 18 m.m.	1 gram.
85 -105 at 18 m.m.-----	7½ grams.
105 -135 at 18 m.m.-----	3½ grams.
135 -170 at 18 m.m.-----	17 grams.

The fraction 105 -135 at 18 m.m. was distilled a fourth time when only one half a gram came over under 100 at 18 m.m. The remainder came over 105 -135 at 18 m.m.

The fraction 135 -165 from all the condensations were combined and fractionated into the following fractions: 135 -156 , 156 -158 , 158 -161 , 161 -165 . After four fractionations the collection temperatures of fractions 156-158 , and 158 -161 were changed because they were the largest and maintained their volume. The temperatures 135 -157 , 157 -159 , 159 -161 , 161 -165 were used assuming the boiling point of the liquid to be 158 . After two fractionations this yielded:

135 -157 (mostl, 154 -157)-----	7 grams.
157 -159 (mostly 158)-----	37 grams.
159 -161 -----	none.
161 -165 -----	2 grams.

The boiling point of the liquid 157 -159 or most 158 , Bar. 746 m.m. indicated allyl benzene $C_6H_5CH_2CH=CH_2$. (M. Tiffeneau (1904) Comp. Rend. 139, 482).

The fractions boiling from 85 to 105 at 18 m.m. from all the condensation were combined and fractionated into the following fractions: 85 -90 , 90 -95 , 95 -100 , 100 -105 . After three fractionations it was apparent that the pure compound came over chiefly at 90.5 -92.5 . Hence the temperatures were changed to: 85 -90.5 , 90.5 -92.5 , 92.5 -95 , 95 -100 . Two distillations gave the following results:

85 -90.5 (18 m.m.) -----	8 grams.
90.5 -92.5 (mostly 91 -92) -----	46 grams.
92.5 -95 -----	3 grams.
95 -100 -----	2 grams.

Combined all the fractions boiling from 135 to 175 at 18 m.m. and fractionated them into the following fractions at

18 m.m.: up to 135 , 135 -145 , 145 -155 , 155 -165 , 165 -175 . A fair separation resulted on the first fractionation. After three fractionations the temperatures were changed to: 135 -145 , 145 -153 , 153 -165 . After four fractionations most of the 153 -165 had dropped to the 145 -153 fraction but there was not much change in the volume of the 135 -145 fraction. The results of the above fractionation are:

18 m.m.

Up to 135 -----	9 grams.
135 -145 -----	14 grams.
145 -153 (mostly 150 -151) -----	23 grams.
153 -165 -----	6 grams.
Residue-----	9 grams.

2. Preparation of propenyl benzene and dibromo propyl benzene.

If the assumption that the fraction boiling at 157 -159 was correct then it would be transformed to propenyl benzene $C_6H_5CH=CH_2$ by boiling with alcoholic KOH.

Four grams of the allyl benzene was added to a little more than twice the molecular quantity or four grams of KOH dissolved in 80 c.c. of 95% alcohol. This was heated for one hour on a boiling water bath. Then four grams more of KOH were added and the mixture was heated for two hours. The next morning most of the alcohol was distilled off on a water bath. The remaining alcohol was diluted with 250 c.c. of water and the solution made neutral with dilute HCl. This was extracted with ether. The ether solution was dried over $CaCl_2$ for two hours. The ether was distilled off and 25 c.c.

of CHCl_3 and 2 c.c. of bromine were added. After four days a good yield of crystals was obtained. They were dried between filter paper. When dry about a fourth of them was dissolved in 20 c.c.g. warm alcohol. The alcoholic solution was filtered and allowed to stand at ordinary temperature for six days when a good yield of crystals was obtained. They melted at $65-66.5^\circ$. Upon recrystallization from alcohol large needles were formed which melted sharply at 66° . The melting point was checked twice. Hence the crystals were dibromopropyl benzene. The compound boiling at $157-159^\circ$ was allyl benzene $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$.

3. Preparation of dibromopropyl benzene.

Twenty grams of allyl benzene were dissolved in 120 grams of CHCl_3 . Bromine was added in .25 c.c. portions until 10 c.c. were added. This amount of bromine was a little in excess of the theoretical amount or 27 grams. The chloroform solution was allowed to stand for eight days during which time most of the chloroform had evaporated. On distilling practically all came over between 100° and 120° at 5 m.m. The residue crystallized on cooling. The crystals melted at $125.5-126^\circ$ after three crystallizations from alcohol checks from three other crystallizations melted at $126.5-127^\circ$. This compound gave a good test for halogen. Further identification was not attempted.

The fraction boiling at $118-120^\circ$ at 5 m.m. yielded after two fractionations 39 grams of dibromide boiling at $114-115^\circ$ at 5 m.m. This is without doubt ~~allyl~~ dibromopropyl ~~benzene~~ because the allyl benzene absorbed the theoretical amount of bromine. This position of the bromine is without

doubt, because of the structure of allyl benzene. The dibromide boils at 243° - 244° with considerable decomposition. It has a specific gravity of 1.62008 at $20^{\circ}/4^{\circ}$. This does not agree with: Luib. ann 283, 304.

4. Preparation of p-nitro benzoic acid and methyl ester of p-nitro benzoic acid, and preparation of benzoic acid.

In order to identify the fraction boiling at 90.5 - 92.5 at 15 m.m. it was distilled at ordinary pressure. It boiled at 217° - 218° . (G. Errera, Gazette (16) 310° - 375 , E. Merck, Jr. Am. Chem. Society (1912) 2143). A Lassaigne's test was run giving a good test for halogen. Three carius determinations were run which gave the following results:

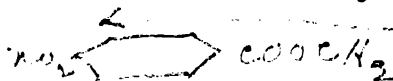
Theoretical % cl.	Found % cl.
22.96	1. 21.36
	2. 21.44
	3. 21.75

From the above data it was concluded that the compound was

chloropropyl benzene, $C_6H_5CH_2CH_2CH_2Cl$. In order to further substantiate this, 10 grams of the compound was gently boiled with a calculated amount of HNO_3 , or 2 grams in three volumes of H_2O . After two days 5 ccq HNO_3 and 15 c.c. of H_2O were added and the solution cooled one more day. Crystals formed when the solution cooled. These were filtered off and washed with H_2O . One gram of p-nitro benzoic was obtained upon recrystallization. Melting point 238° (Beilstein Handbuch). This preparation was repeated and after one recrystallization one gram of p-nitro benzoic acid was obtained. Melting point 237 - 238° . The filtrates from this was evaporated down. The crystals obtained from them were recrystallized. Melting point 237° .

In order to try to oxidise the γ -chloro propyl benzene to benzoic acid with HNO_3 , five grams of the chloride was treated as above with nine grams of HNO_3 in six volumes of H_2O for one day. The crystals formed when solution was cold. They melted at $233^\circ - 238^\circ$ after one recrystallization.

One gram of the nitro benzoic acid was heated with 14 grams of Pcl_5 on a water bath for four hours. Fifteen c.c. of CH_3CH was added and the solution was filtered while warm. During the heating with Pcl_5 the solid mixture changed to a liquid. When the CH_3OH was added the mixture warmed up considerably. On cooling crystals separated out in the shape of needles. These were recrystallized from CH_3OH and melted at 96° . Hence they were Beilstein Handbuch.



Three grams of the chloride were suspended in 200 c.c. of H_2O . Three grams of NaOH were added and the mixture was heated on a water bath. 9.5% KMnO_4 solution was added in 10 c.c. portions until no more KMnO_4 was reduced or (155 c.c.) On acidifying with Hcl no crystals separated out. A few crystals separated out however on evaporation. These were dissolved in a little hot H_2O . This was extracted with ether. The crystals obtained from the ether were recrystallized from a little H_2O . They melted at 120° hence they were benzoic acid.

5. Attempts to identify the high boiling fraction.

The first step in identification of the high boiling fraction was A. Lassaigne's test. The test gave fair results. A cursus determination showed that chlorides were present only as an impurity. The analysis gave 5.534% chlorine. The

whole fraction was treated with one gram of sodium. The mixture was heated for one hour over a small flame and allowed to stand over night. The sodium was decompressed by pouring the mixture into H_2O . The water mixture was acidified with dilute HCl and then extracted with ether. The ether was distilled off. The remaining solution was fractionated once at 19.5 m.m. This gave the following results:

135 -148 -----6 grams.

148 -152 -----14 grams.

152 -155 -----3 grams.

The fraction 148 -152 at 19.5 m.m. boiled at 255° - 260° at ordinary pressure. A carius determination was run on this equation with the following results: I. 3.685% cl, IV.

2.870% cl. Because of the fact that these results were so much lower than the first analysis the fraction was again treated with sodium. Twenty-three grams boiling at 135 -155 at 19.5 m.m. were dissolved in 100 c.c. of ether. One gram of finely chipped sodium was added. The mixture was warmed on a water bath for several hours. After two days the sodium was filtered off and washed with a little ether. The solution was washed with dilute HCl. After the ether was distilled off the compound boiled at 225° - 235° (mostly 230° - 275°) at ordinary pressure. After three fractionations it gave the following division:

225 -235 -----1 gram.

235 -250 ----- none.

250 -277 (mostly 260 -270)-----2½ grams.

277 -282 -----6½ grams.

The 277 -282 fraction gave only a slight trace of halogen.

It is probably diphenyl propane $C_6H_5-CH_2CH_2-C_6H_5$. Boiling point $280^{\circ}-282^{\circ}$ (corr. $281-283$). (V. Meyer and E. Jacobson, Lehrbuch der Organischen Chemie, Page 190).

6. An attempt to condense n-propyl alcohol with benzene in the presence of aluminium chloride.

One mole (140 grams) n-propyl alcohol was mixed with five mols (780 grams) of benzene. One half a mole (133 grs) of aluminium chloride was added as in the other condensations. There was very little rise in temperature. Very few HCl fumes were given off. There was very little change in the color of the mixture except for a light brownish color.

Results of fractionations:

Recovered 710 grams benzene.

" ($87^{\circ}-105^{\circ}$) 65 grams n-propyl alcohol.

$105^{\circ}-210^{\circ}$ ----- $1\frac{1}{2}$ - 2 grams.

$150^{\circ}-210^{\circ}$ (40 m.m.)----- 5 grams.

Tarry residue----- 4 grams.

The fraction boiling at $105^{\circ}-210^{\circ}$ had no definite boiling point. Only one drop came over at $150^{\circ}-160^{\circ}$. There was no evidence of the formation of propyl benzene under the conditions described.

III. Conclusion and Summary.

1. Allyl benzene reacts with benzene in the presence of aluminium chloride to form allyl benzene according to the equation:



2. The formation of considerable quantities of chloro propyl benzene indicates that HCl will add on the double bond of allyl benzene in the presence of aluminium chloride.

3. Unsaturated aliphatic alcohols condense with benzene in the presence of aluminium chloride a great deal easier than saturated aliphatic alcohols, if indeed the latter condenses at all.

4. β dibromopropyl benzene was prepared from allyl benzene.

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