A STUDY
of the
BROMINATION of PARA-CRESOL
IN WATER SOLUTION
and in
HYDROCHLORIC ACID

** **

Thesis

by

Grant V. Jenkins

In partial fulfillment of the requirements

for the degree of Bachelor of Science

in General Science

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

1924

A STUDY OF THE BROMINATION OF PARA-CRESOL IN WATER SOLUTION AND IN HYDROCHLORIC ACID. ALSO DISCUSSION OF THE BROMINATION OF PHENOL IN WATER SOLUTION.

** **

References: No references were available on the bromination of phenol and cresol in water solution. Any credit for the conception of this process, and its future value must go to Mr. H. J. Lucas, of the California Institute of Technology. The design of the apparatus, and the methods used in overcoming difficulties, are products of this laboratory.

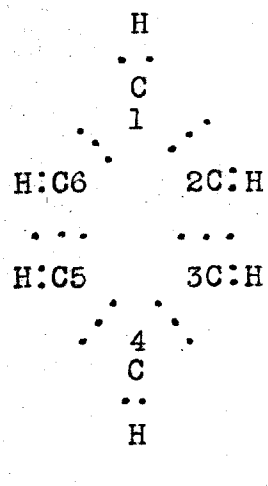
-

STATEMENT OF THE PROBLEM

On the theory of electron displacement, and the effect of side groups on the bromination of the benzene ring, it was proposed to study the bromination of para-cresol in neutral, and in acid solution. Preliminary work was first done on the bromination of phenol in water solution, mainly to master the technic and overcome difficulties encountered. The first consideration of interest was to determine whether the presence of a large concentration of H^+ affected the introduction of Br_2.

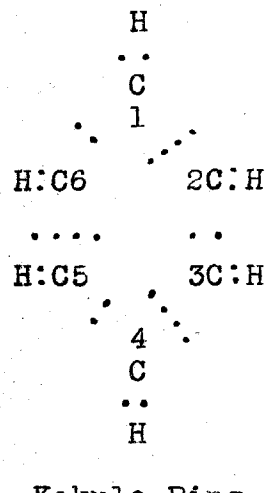
THE PROBLEM

** **



Armstrong and Bayer central theory -

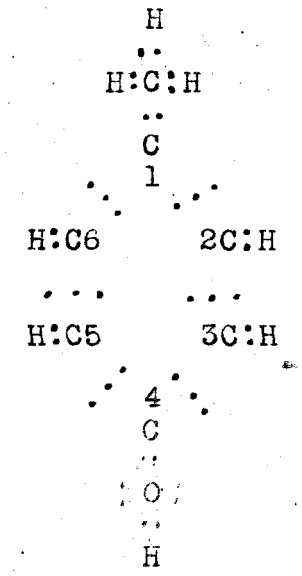
In benzene, C_6H_6, we have thirty electrons which have to be arranged in octets around the six carbon atoms. The simplest arrangement seems to be a ring with the six carbon atoms in contact with a triple electron contact between each two. This arrangement seems to introduce the least strain in the molecule, and gives a symmetrical placement of the electrons. Kekules' conception of the molecule consists of three sets of pairs of carbon atoms, the cells in each pair having four-fold contact with each other, but only double contact with the neighboring pairs.



Kekule Ring

The rate of substitution, ranging from strongly (+) to strongly (-) is: OH, NH_2, Cl, I, Br, CH_3, CO_2H, SO_3H, NO_2 with some question whether I should follow or precede CH_3. In neutralssolution, and because of the comparative influences of the CH_3 and the OH, when para-cresol is brominated with only the required amount of bromine for one substitution in the ring, it is found that

practically all of the replacement is in the 3- position. In other words, the combined effect of the OH in attraction, and the CH_3 in repulsion, causes the BR to substitute for H in the 3- position.



para-cresol

Due to the tendency of the phenols to form salts in strong acid solution by adding H^+ to the OH, it was thought possible that a bromination carried on in 12 N. HCl would give different results than a bromination in neutral solution. With additional H^+ added on the OH its effect of attraction should be lessened, and more Br would go to the 2- position. The results will be discussed later.

After the technic was mastered, and an apparatus designed that would make continuous extraction with a solvent possible, four brominations were carried out. In each case 50 grams of para-cresol was used. Two of the brominations were carried out in neutral solution of water; the other two were done in 12 N. hydrochloric acid. In each case the solution of the brominated products in ether were dried over anhydrous sodium sulfate and distilled in vacuo. The amounts of materials used, time, temperature, length of extraction, and the results of the distillation are given at the back part of this paper.

RESULTS AND RECOMMENDATIONS

***

No definite results can be deduced from this experiment. In the first place considerable difficulty was experienced in getting good seperations. With the bulk of the brominated product distilling at 104° at 20 mm, and with only a small fraction present at athe higher boiling points, it would be unwise to draw conclusions on the bromination in the 2- position which is represented by the higher boiling products, from the data at hand. Many more brominations will have to be carried on before a conclusion can be drawn.

Also, until a method of analysis of the brom-cresol compounds is found, no accurate data can be obtained.

Also, until a preceedure is found by which the brom-cresol compounds can be changed into other derivatives, such as the acetate, benzoate, etc., with boiling points or other physical properties that will permit easy seperation it will be difficult to draw conclusions from the results of the bromination.

I cannot suggest any modification in the apparatus. It worked well for the purpose desired. Details of its construction are found in this paper.

The preparation of brom-para-cresol in water solution. Description of a run, and method used for extraction.

** - **

Fifty grams of para-cresol were dissolved in 4 liters of water in the 12 liter Pyrex flask. Twenty-three cc's of bromine, dissolved in 6 liters of water, was slowly introduced through the seperatory funnel; the complete introduction timed to about one and one-half hours. The solution of para-cresol was vigorously stirred thruout the reaction to minimize the formation of di- and tri-brom compounds due to a local excess of bromine. A flocculent precipitate of brom-para-cresol is immediately formed in the water solution. When all the bromine is introduced into the reaction flask and the reaction is completed, salt is added to excess to lower the solubility of ether in the solution.

After the addition of the salt one liter of ether is added, and the mixture stirred. A total of three liters of ether is added, about two of them in the extraction flask, and the other in the 3 liter Pyrex receiving flask. Enough ice cold water is added through the coil condenser trap to bring the layer of the solution in the extraction flask up to the overflow into the receiving flask. The stirrers must be adjusted so that when they are running, about three inches of ether layer remains in the upper part of the extraction flask. THIS IS IMPORTANT; OTHERWISE WATER WILL BE CARRIED OVER INTO THE RECEIVING FLASK.

The hot water heater must be adjusted for electricity and water flow at a temperature of 50-55°C. The cold water condensers must have a good flow of water, for the ether vapor comes over at a rapid rate, and must be condensed.

With the hot water at the proper temperature, about 20 cc's of ether should be distilled over per minute. The solution in the extraction flask gradually changes color due to the introduction of fresh ether, and the collection of the brom-compounds in the receiving flask. The extraction should continue for at least 24 hours.

At the end of the extraction the stirrers are stopped, and cold water is introduced into the extraction flask (slowly!) until all the ether layer has flowed into the receiving flask. The stop-cock of the separatory funnel is then closed, and the "T" connection from the water condenser to the separatory funnel can be connected directly to a 3 liter bottle for the reception of the excess ether now present in the receiving flask. This excess ether is boiled off until only 400-500 cc's are left in the receiving flask. The brom-para-cresol compounds are soluble in this amount.

The brom-para-cresol compounds in ether are cooled, and dried for several weeks over anhydrous sodium sulfate.

To stop the extraction at any time all that is necessary is to stop the motor, and stop the water heater, which automatically surrounds the ether in the receiving flask with cold water and the whole process ceases.

When the para-cresol was brominated in 12 N. hydrochloric acid the following modifications of the proceedure in water solution were necessary:

Ether is soluble in concentrated hydrochloric acid solution, due to the formation of salt compounds, and therefore the acid had to be neutralized, or nearly so, before the ether was introduced. $NaHCO_3$ was used, and was slowly (CAUTION!) added to the acid immediately after the cresol was brominated. A sludge of bicarbonate and water was used. Considerable diffulty was enountered to prevent foaming, and consequent loss of some of the products of the reaction.

Because of the formation of NaCl by the reaction of the bi-carbonate and the acid, no additional salt was needed. The salt crystals formed in a very fine state thruout the solution, almost like a fine precipitate, but upon standing they were transformed into large crystals.

*****

VACUUM DISTILLATION APPARATUS

** - **

The vacuum distillation apparatus was a regular set-up, consisting of Claysen flask, condenser, receiving flask with five containers, which permitted fractionation without stopping distillation, drying tube containing $CaCl_2$, mercury manometer, water trap, three-way stop-cock, and water vacuum pump. A vacuum as low as 16 mm was obtained. A ceresin bath was used to raise the temperature up to 150°C, and for higher temperatures the direct Bunsen flame was used. A small coil of glass tubing was used with the Claysen flask, and acted as a fractionating column.

-

Some of the minor points of the problem which deserve mention are:

The ether had a bad effect on all rubber parts; the alternate swelling and drying caused the rubber to crack badly, and it was soon rendered worthless. No remedy was found.

The ether recovery was only about 50 per cent, due no doubt to the low temperature at which it boils, and the consequent diffulty of working with it at room temperature.

The sodium sulfate used for drying must be finely divided. About 200 grams was used to dry 500 cc of the ether solution of the brom compounds.

The extraction apparatus was simple to operate, and should be of value in any process where long extraction is desired without much hand labor.

RESULT OF TIME RUN FOR Br^- WHEN ORTHO-BROM-PHENOL WAS KEPT IN THE PRESENCE OF WATER.

* - *

When work on the bromination of phenol and cresol in water solution was first proposed it was thought possible to remove the water that was used for the solvent by boiling, or at least by raising the water to the point where it would steam. It was even proposed to work in vacuo. As is shown in the detailed values of the results obtained this method of removing the excess water was not a success.

It was thought that the continued presence of water or water vapor at room temperature would seriously affect the stability of the brom-phenol molecule, causing part of the product to break down, giving Br^-. To prove whether there was this breaking up of the molecule, two solutions of ortho-brom-phenol in water, one .1N acid and the other neutral, were tested for several days for the presence of Br^- by the standard volumetric analysis of $AgNO_3$ and NH_4SCN, using ferric alum as an indicator. After several day's tests, it was concluded that there was no indication of the decomposition of the brom-phenol compound.

It was found, though, that when a water solution of ortho-bromphenol contained as little as c.o5 grams of Na_2CO_3 to every .163 grams of brom-phenol and was heated to 60°C for 1½ hours, enough AgBr was precipitated on the addition of $AgNO_3$ to be visible.

DETAILED DATA ON BROM-PHENOL and BROM-PARA-CRESOL MADE IN WATER SOLUTION and in 12 N. HYDROCHLORIC ACID SOLUTION.

** **

A
10 grams phenol
300 cc water
3 cc bromine
500 cc water

T° 22°C
time: $\frac{1}{4}$ hour
Solvent: CCl_4

Yield very imperfect - not separated. Tri-brom phenol re-dissolved in water. Tried boiling excess water off and extracting with CCl_4 - but lost much product in escaping steam. Not a practical method of removing water.

-

B
50 grams phenol
1500 cc water
28 cc bromine
2500 cc water

T° 22°C
time: 1 hour
solvent: CCl_4

Gross yield of o, p, di-, tri-brom-phenol was 34 grams. Not a good separation of organic products from the water solution. Tri*brom-phenol (?) formed brown oil mass in water.

-

C
50 grams phenol
2500 cc water
28 cc bromine
5000 cc water

T° 23°C
time: 1 hour
solvent: CCl_4

Less solid precipitate due to larger amount of water present. It was found that CCl_4 was not a suitable solvent, and after this experiment ether was substituted.

-

D
50 grams phenol
2500 cc water
28 cc bromine
5000 cc water

T° 22°C
time: 1 hour
solvent: ether

Continuous extraction apparatus (1922-23 model) used. Extraction time approximately one day (24 hours). Salt added to water solution before ether was added to lower solubility of ether in water.

-

E Duplicate of D.

D and E were mixed, and then distilled in vacuo, and products cataloged under Key Number I.

I Distillation Record D and E

A	84.5° - 86.0°	21 mm	65 grams
B	90° -*93° - 96°	"	6 "
C	124° -*124.8° 126°	20 mm	60 "

71% extraction

-

II 50 grams phenol
2500 cc water
28 cc bromine
5000 cc water

T° 20°C
time: 1 hour
solvent: ether

Successful run with newly designed apparatus (1923-24).

Distillation Record

A	79° - 82°	16 mm	25 grams
B	92° - 120°	17 mm	7 "
C	120° -*122° - 124°	"	35 "
D	124° up	-	4 " recovered from flask

53% extraction

-

III 50 grams para-cresol
4000 cc water
23 cc bromine
6000 cc water

T° 20°C
time: 1½ hours
solvent: ether

Successful run of 1922-23.

Distillation Record

A	101° - 101.5°	18 mm	42 grams
B	104° -*119.4 120.5°	28 mm	6 "
C	130° -*165°	30 mm	7 "

49% extraction

V

50 grams para-cresol
4000 cc 12 N HCl, com.
23 cc bromine
3000 cc 12 N HCl, com.

T° 20°C
time: 1½ hours
solvent: ether
extraction time: 24 hours

1923-24 improved apparatus as shown in drawing.

Distillation Record

A	104° - 105°	20 mm	51 grams
B	108° -*110°- 120°	20 mm	5 "
C	120° - 140°	20 mm	2 "
D	140° - residue	20 mm	16 "

decomposition was rapid at this temperature.

85% extraction.

VI

Duplicate of V

Distillation Record

a	40° - 100°	19 mm	3 grams
A	101° -*104°	20 mm	46 "
B	106° -*112° - 120°	20 mm	7 "
C	120° -*138° - 140°	20 mm	9 "
D	140° residue	20 mm	17 "

same decomposition noticed at this T°.

97 % extraction.

VII

50 grams para-cresol
4000 cc water
23 cc bromine
6000 cc water

T° 20°C
time: 1½ hours
solvent: ether
extraction time: 24 hours

* indicates T° where bulk of distillate came over.

VII, continued

Distillation record

A	101° - 102.5° - *104°	19-20 mm	38 grams
B	106° -*112° - 120°	19-20 mm	8 "
C	152° - 157°	20 mm	16 "
D	residue		13 "

70 % extraction

-

VIII Duplicate of VII

Distillation record

A	101° -*104°	20-21 mm	50 grams
B	120° -*148° - *152°	17 mm	11 "
C	residue		8 "

60 % extraction

-

IX Number VIII refractionated.

Distillation record

a	80° -87.5°	26-27 mm	8 grams
A	96.5° - 98°	22-23 mm	42 "
B	135° - 150°	6-7 cm	11 "

gas, vapor, much bubbling in flask; decomposition (?). The peculiar results of this fractionation have not been explained.

-

Phenol distills at 84°C, at 20 mm.

-

Para-brom-phenol distills at 124.5°- 125° at 20 mm.

-

2Brom-para-cresol (Pomeroy) distills at 135° at 20 mm.

2Brom-para-cresol (Scudder) distills at 136.5 - 138.5° at 21 mm.

-

Para-cresol distills at 99° at 19 mm.

-

3Brom-para-cresol (Hough) distills at 103 - 105.5° at 19-20 mm: Number X.

-

3, 5 di-brom-para-cresol made in CS_2 solution from bromine and para-cresol.

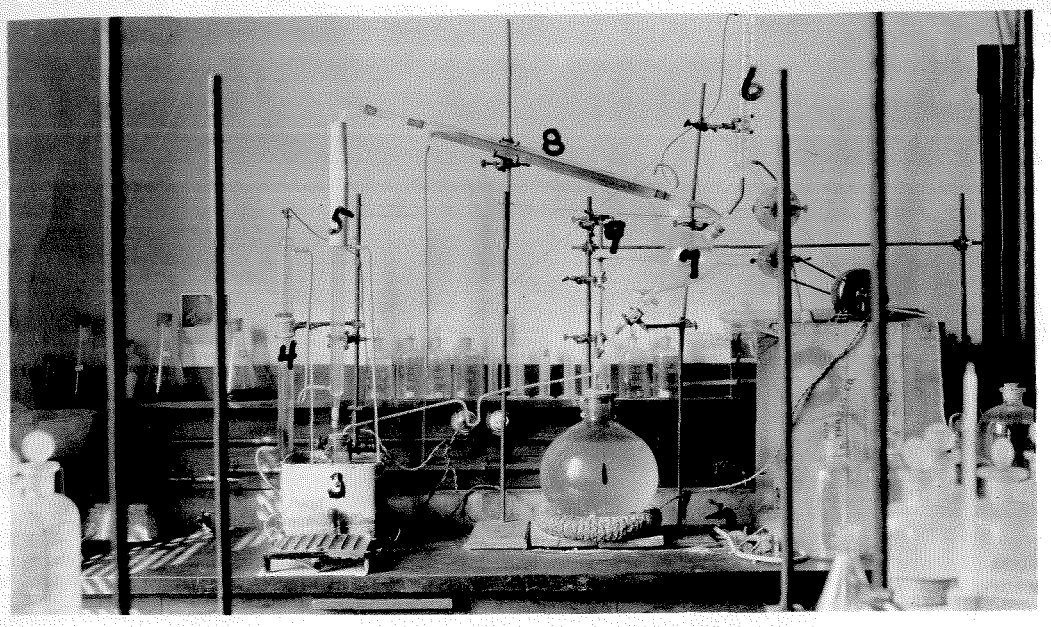
50 grams cresol
200 cc CS_2
46 cc bromine
100 cc CS_2

T° 20°C
time: 1 hour

Distillation record.

XII	A	105° - 120°	22 mm
	B	120° - 130°	22 mm
	C	130° -*134° - *138° - 140°	22 mm
	D	140° - 150°	22 mm
	E_a, E_b, E_c,	150° - *157° -*158.5°	22 mm

-



EXTRACTION APPARATUS

1. 12 l. round bottomed Pyrex flask

2. gravity flow tube with trap from extraction flask to ether recovery flask. Flasks arranged so ether would flow by gravity. Trap introduced to stop vapors of ether from returning to extraction flask.

3. 3 l. round bottomed Pyrex flask where ether is boiled off, but where extracted products are recovered. Kept at 50°C by water heater (4).

4. Coil of nichrome wire in water condenser jacket, regulated by rheostat below (3), and which kept water at 50°C.

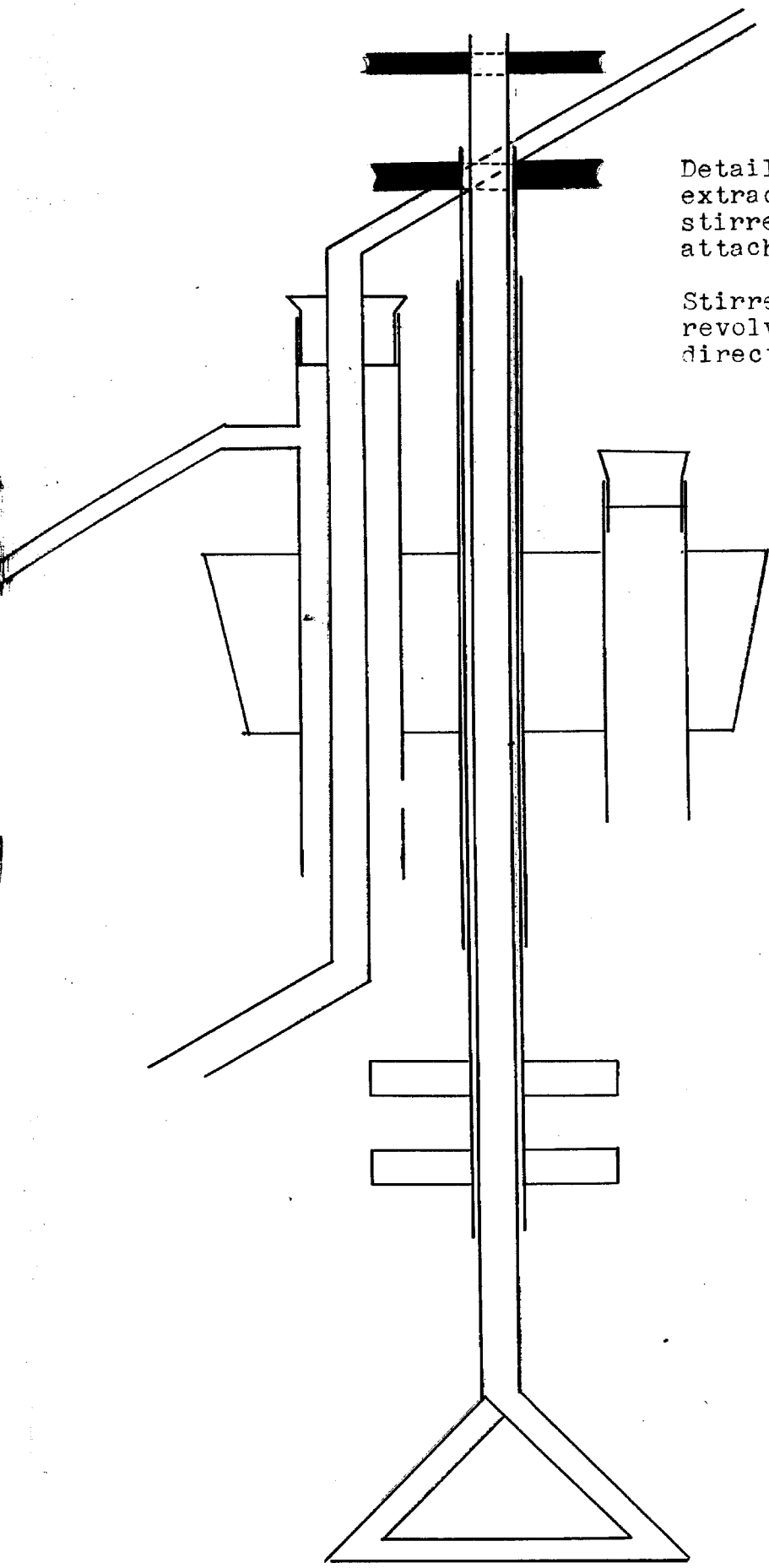
5. Water condenser fed by (4) which served to keep ether vapors hot until they reached condenser (8).

6. Water coil condenser which acted as a trap for ether vapors, and also regulated the pressure of apparatus by its connection with air.

7. 1 l. separatory funnel used to introduce and regulate bromine solution, and also collected ether after extraction was finished.

8. Water condenser to condense ether vapors. Connected with (6) in series with city water mains.

9. Double action stirrer not visible in flask, but run from motor and system of pulleys. Thorough stirring is necessary to break up ether stream and layer.



Detailed drawing of extraction flask stirrer and other parts attached to cork.

Stirrer is arranged to revolve in opposite directions.

APPENDIX

Physical Constants

2 Brom-para-cresol	mp	55° - 56°
	bp	245° - 246° at 760 mm
	bp	136.5° - 138.5° at 21 mm
3 Brom-para-cresol	mp	17° - 18°
	bp	213° - 214° at 760 mm
	bp	103° - 105.5° at 19-20 mm
Phenol	mp	42.5°
	bp	183° at 760 mm
	bp	84° at 20 mm
Para-brom-phenol	mp	63° - 64°
	bp	238° at 760 mm
	bp	124.5° - 125° at 20 mm
Para-cresol	mp	36°
	bp	201.8° at 760 mm
	bp	99° at 19 mm
3, 5 di-brom-para-cresol	bp	157° - 158.5° at 22 mm

*** - ***