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THE CATALYTIC VAPOR PHASE ALKYLATION OF PHENOL

by

Robert Andrew Clendinning

UNION COLLEGE
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A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the require-
ments for the degree of Bachelor of Science in Chemistry.

by Robert A. Clendinning

Approved by Howard E. Sheffer

May 30, 1953

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Gift of Author - 21 Nov. 1953

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INTRODUCTION

The purpose of this research is to study the reaction between ethyl alcohol and phenol over a chemically activated alumina catalyst at several temperatures. The reaction of phenol and ethyl alcohol is also studied over the support used in preparing the activated catalyst to determine the catalytic activity of the support.

An attempt is also made to correlate the data obtained by previous workers at Union College, who have studied the reaction between phenol and methyl alcohol and the reaction between phenol and ethyl alcohol.

THEORETICAL

The reaction between phenols and various alcohols has been studied for many years. There are several commercial processes for the production of various alkylated phenols. In spite of this interest, no definite reaction mechanism has been established.

The most favored mechanism today involves the formation of an alkyl phenyl ether and the subsequent rearrangement of the ether to an alkyl phenol. This view is given some support by the fact that alkyl phenyl ethers are produced in increasing yields as the temperature is lowered. The mechanism of the rearrangement of the alkyl phenyl ether to the alkyl phenol is still in dispute. There are several proposed mechanisms:

(1) An intramolecular rearrangement wherein the alkyl group migrates to the benzene ring, never losing contact with the molecule to which it was originally attached; (2) A dissociation-recombination mechanism wherein the alkyl group splits off the ether, probably as an olefin, and attacks the benzene ring. In this case the rearrangement would be intermolecular in nature; (3) The ether acts as an alkylating agent toward the second molecule. In this case there would be no possibility for the alkyl group to remain attached to the original molecule.

The evidence for these possible mechanisms is conflicting but, on the whole, seems to favor the second of the above mechanisms. For a further treatment of this evidence, see Ref. 1.

EXPERIMENTAL

The method used by this worker is essentially the same as that used by previous workers (Ref. 2,3,4). The reaction mixture, under a nitrogen pressure and a slight suction effect from the gas collection bottle, is forced through a capillary from which it drops into the pre-heater where it is vaporized. As the vapors pass down the stainless steel tube, they enter the catalyst bed. In each three hour run, thirty-two grams of 4-1 catalyst are used, which gives a catalyst bed approximately four inches long. After reaction on the catalyst has taken place, the vapors pass through the post-heater and the products are collected in a three neck five hundred milliliter flask.

The gaseous products (mostly ethylene) pass from the flask and are collected over water in a graduated twenty liter bottle. The method previously used, i.e., absorption of the ethylene by silver nitrate (Ref. 5), was found to be too time consuming, so it was decided to collect all of the gas produced during the run. A pressure equalizer was attached to the collection bottle to minimize the suction effect referred to above.

The temperature is measured by means of a chromel-alumel thermocouple and a Leeds-Northrup Student Potentiometer. The thermocouple fits a stainless steel tube inside of and concentric with the main reaction tube. By moving the thermocouple up and down in the tube, the temperature may be determined at any desired position. The temperature is maintained in the pre-heater, catalyst bed, and post-heater by means of three variacs.

At the end of each run, approximately two liters of nitrogen are passed through the reaction chamber, thus sweeping any vapors down into the collection flask. The nitrogen is collected in the same bottle as the ethylene in case any gaseous products are also swept through.

ETHYLENE GAS ANALYSIS

As mentioned before, all the ethylene produced in a six hour run as well as the nitrogen used for sweeping the catalyst bed, is collected over water in a graduated twenty liter bottle.

The ethylene present is determined by absorption with bromine in carbon tetrachloride. The gas (or an aliquot) is led from the large collection bottle into a Milligan bottle containing the bromine-carbon tetrachloride solution, where the ethylene reacts with the bromine to form ethylene dibromide. The non-reactive gases are led out of the Milligan bottle into a smaller graduated collection bottle, and thus the amount of ethylene is determined by subtraction. To insure complete bromination of the ethylene, it was decided to pass the gas back and forth through the Milligan bottle several times.

Care must be taken to insure the absence of any leaks throughout the system since the method of analysis depends on the collection of all the gas produced during the run. This effect will be pointed out later in the discussion.

ANALYSIS OF PRODUCT

The crude product is treated with sodium hydroxide and extracted with ether (see Ref. 2,3,4). The ether extract, which contains the phenolic ethers, is dried, the ether distilled off, and the phenolic ethers distilled. Because of the small amount of ethers present, it was decided that a rough separation into several boiling ranges was sufficient.

The alkaline layer of phenols is acidified with acid, the water layer extracted with benzene, and the benzene roughly distilled off. The phenols are now fractionally distilled in a column about four feet long, packed with stainless steel helices. Under total reflux, the column has approximately thirty theoretical plates. A plot of temperature of distillation versus volume of distillate is made (see section on graphs) and several fractions are chosen for identification.

The fractions are identified by making the phenoxyacetic acid and/or the phenyl urethane derivatives. This experimenter was more successful with the phenyl urethane derivatives than with the phenoxyacetic acid derivatives. Both derivatives are made according to directions given in Ref. 6.

GRAPHS

The following graphs represent the fractional distillation of the phenolic components of Runs PE-2 and PE-3. The volume of distillate should not be interpreted as the actual volume of the product since some benzene is present in both cases. The distillation of the benzene is not shown on either curve. The curves start where the distillate solidified on cooling which occurred at approximately 170°C . The numbers refer to the fractions taken. It should be noted that the distillation was continued, in both cases, until diphenyl (which was added to the pot to insure complete distillation of the phenols) was distilled over. The information in the table of results is taken from these graphs.

Distillation: Phenolic Components PE-2

Temp. °C

Vol. Distillate (ml.)

I

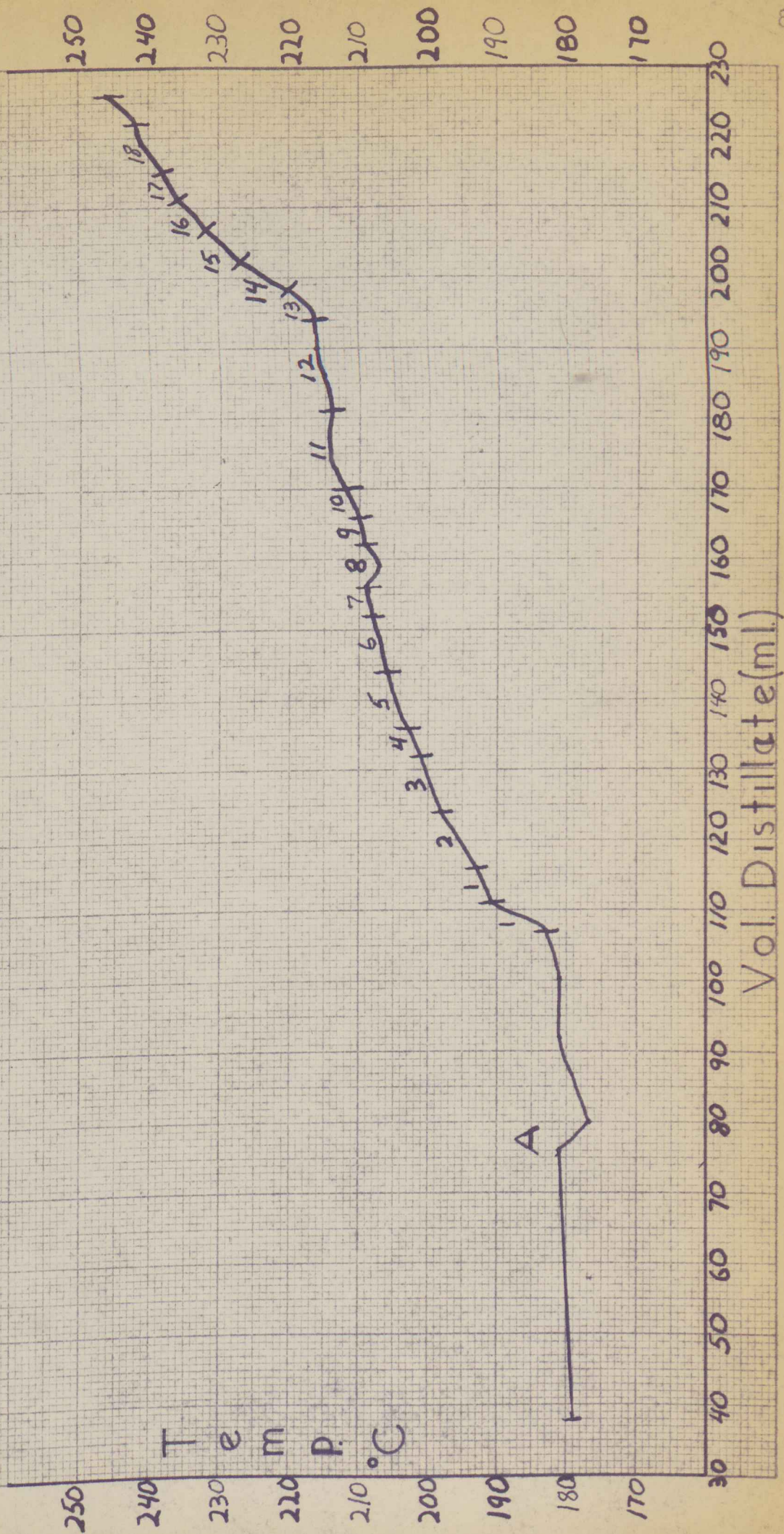
8 9 10 11+12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36

160 170 180 190 200 210 220 230 240 250

10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

7.

Distillation: Phenolic Components PE-3



DISCUSSION

In the following table the results of this year's work are tabulated. In addition to the two runs shown in the table, a third run was made using a catalyst which had been activated by heating for eight hours at 500°C. The results of this run are not tabulated since the only product obtained was three percent by weight of the feed of phenols. Ethylene gas was also given off. Due to faulty absorption by the silver nitrate, it was not analyzed. Nearly all of the phenol was recovered. From this run, it can be seen that the activity of the catalyst is not due to the alumina support but is actually due to the material on the support.

From the table we see that, in a run using chemically activated alumina, the meta isomer has been obtained and identified for the first time, in addition to the ortho and para isomers. The amount of meta isomer increases with increasing temperature. The actual increase is probably not as great as shown in the table due to contamination of the meta isomer by the para isomer.

The reaction seems to have gone farther at the higher temperature as indicated by the fact that 67% of the phenol was converted at 426°C while 62% was converted at 356°C. This receives support since all the products increased in amount at 426°C except the phenolic ethers and the higher phenols. If the mechanism actually goes through a phenolic ether, it would be expected that less would be formed at the higher temperature. The decrease in amount of the higher phenols is discussed more fully in the section, Summary of Results. It might be mentioned here that in Run PE-2, 2,4-diethyl phenol was identified and the 2,6-diethyl phenol was tentatively identified as being among the constituents of this group.

RESULTS

Run Number	FE	2	3
Time	Hrs.	6	6
Temperature	°C.	356	426
Contact Time	Sec.	3.81	3.49
Catalyst: Number		4-1	4-1
Feed	Mol:Mol	1:1	1:1
Analysis: Alkene	wt. %	1.8	3.9
Phenolic Ethers	"	3.0	1.56
Phenol	"	24.8	22.0
o-ethyl phenol	"	14.2	16.3
m-ethyl phenol	"	2.5	8.55
p-ethyl phenol	"	1.7	2.07
Higher phenols	"	8.8	5.40
Losses (accountable) ¹	"	23.0	9.2
Losses (unaccountable) ²	"	20.2	31.0
Calculated Water in Product	"	6.6*	7.7*
Alcohol Converted	Mol %	52.3*	59.1*
Alcohol Converted to Alkene	"	8.8	21.0
Phenol Converted	"	62.0	67.0
Phenol Converted to Phenolic Ethers	"	3.8	1.82
Phenol Converted to o-ethyl phenol	"	26.0	27.6
Phenol Converted to m-ethyl phenol	"	4.6	14.5
Phenol Converted to p-ethyl phenol	"	3.1	3.5
Phenol Converted to di-ethyl phenols	"	13.2	7.5
o-ethyl/m- & p-ethyl phenol ratio	Mol/Mol	3.35	1.53

*estimated from ethylated products and ethylene

¹includes losses in run, distillation

²includes losses in extraction, formation of diethyl ether, etc.

The alcohol converted was estimated on the basis of the number of moles of ethylated products and ethylene produced. The estimate is made by adding these two factors and dividing by the total number of moles of ethyl alcohol passed through the reaction chamber. In this calculation, two ethyl groups are assumed to be present in the higher phenols.

The water is estimated by making the assumption that a mole of water is produced for every mole of ethyl alcohol that reacts. The number of moles of ethyl alcohol that react is estimated as outlined in the previous paragraph.

The amount of alkene produced increases as the temperature increases, probably due to the dehydrating effect of the catalyst. However, the amount reported in Run P3-2 is suspected to be low due to a leak in the lead gasket of the reaction tube. This suspicion is borne out when this run is compared with runs by previous workers.

It might be mentioned here that information from the boiling points of the phenolic ethers indicates that the majority of this fraction consisted of partially alkylated phenolic ethers, not phenetols, in both runs.

Other effects in connection with these runs will be discussed under the Summary of Results.

SUMMARY

The reaction between phenol and ethyl alcohol over a chemically activated alumina catalyst at 356°C. and 426°C. has been studied. The main products are the ortho, meta, and para ethyl phenols. Over 60% of the phenol and over 50% of the alcohol have been converted in each run. Other products include small amounts of phenolic ethers, alkenes, and higher phenols.

The reaction between phenol and ethyl alcohol has also been studied over an alumina catalyst which was activated by eight hours heating at 500°C. This is the support used in preparing the chemically activated catalyst used in the other runs. Almost no catalytic activity was noted with the plain alumina and it can be safely said that the catalytic activity in the other runs is due to the material on the alumina.

SUMMARY OF RESULTS OF MY WORK AND THAT OF PREVIOUS WORKERS AT UNION COLLEGE

In the following table, the results of previous workers on this project are summarized along with the runs done this year. The data appears here as it appears in the respective theses and no attempt has been made to change it in any way.

Examining numbers one, two, three, and four, it is hard to draw conclusions since the losses in numbers two, three, and four are so high. However, it will be assumed here that the losses in these runs are distributed proportionately among the products. Also, since the contact times are nearly the same (with the possible exception of number one), the effect of temperature can be shown.

The amount of phenol converted increases as the temperature increases, but the increase is not as great as that noted in subsequent runs. The amount of mono alkyl phenols is correspondingly increased while the amount of higher phenols is decreased, as the temperature increases. The generally low yields of higher phenols here in comparison with subsequent runs may be explained on the basis that there is less time for a second alkylation to take place with these low contact times. As might be expected, the amount of phenolic ethers decreases with increasing temperature. The ratio of ortho alkyl phenol to meta and para alkyl phenol appears to decrease slightly as the temperature is increased.

In examining numbers five, seven, and eight (approximately equal contact times), the effect of temperature may be clearly seen again. The amount of phenol converted increases and, correspondingly, the amount of mono alkyl phenols increases, especially the meta isomer. The yield of alkene also increases with increasing temperature, if we assume

SUMMARY OF RESULTS

Number	1	2	3	4	5	6	7	8
Operator								
Run Number	3	1	2	3	1	2	2	3
Alcohol	MeOH	MeOH	MeOH	MeOH	EtOH	EtOH	EtOH	EtOH
Time	3	3	3	3	6	5	6	6
Temperature	325	327	361	421	325	318	356	426
Contact Time	2.72	2.34	2.28	2.09	3.58	2.84	3.81	3.49
Catalyst : Number	4-1	4-1	4-1	4-1	4-1	4-1	4-1	4-1
Feed	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1

Analysis:								
Alcohol	0.0	-	-	-	-	0.0	-	-
Alkene	0.0	-	-	-	-	1.8	1.8	3.9
Water	-	-	-	-	-	11.8	-	-
Phenolic Ethers	13.8	12.8	6.4	3.2	5.0	12.7	3.0	1.6
Phenol	40.3	41.3	41.9	34.6	29.1	31.4	24.8	22.0
o-alkyl phenol	13.6	6.6	10.2	13.7	15.4	11.7	14.2	16.3
m-alkyl phenol	7.1	3.3	5.3	8.0	6.9	6.0	2.5	8.6
p-alkyl phenol	8.4	1.7	3.5	1.6	13.3	5.5	1.7	2.1
Higher phenols	0.0	-	-	5.5	4.2	7.3	8.8	5.4
Residue	16.0	34.3	32.7	33.4	21.2	12.2	-	-
Total Losses	-	-	-	-	-	-	43.2	40.2
Calculated Water in Product	100%	-	-	-	-	-	6.6%	7.7%
Alcohol Converted	0.0	-	-	-	-	100%	52.3%	59.1%
Alkene Converted to Alkene	46.4	44.9	44.1	53.3	17.7	9.6	8.8	21.0
Phenol Converted to Phenolic Ethers	17.0	14.8	7.4	3.7	56.5	54.0	62.0	67.0
Phenol Converted to o-alkyl phenol	15.7	7.6	11.8	15.8	-	2.1	3.8	1.8
Phenol Converted to m-alkyl phenol	6.2	3.8	6.2	9.2	17.7	13.1	26.0	27.6
Phenol Converted to p-alkyl phenol	-	-	-	-	8.0	6.8	4.6	14.5
Phenol Converted to di-alkyl phenols	-	-	-	-	-	-	3.1	3.5
o-alkyl/m & p-alkyl phenol ratio	1.9	2.0	1.9	1.7	2.2	1.9	13.2	7.5

estimated from ethylated products
and ethylene
assumed by Lencoux

the low value in number seven to be due to the leak in the gasket as noted in the discussion part of this thesis. The amount of higher phenols appears to be decreased by the increase in temperature. This effect might also tend to increase the amount of mono alkyl phenols slightly. Again the amount of phenolic ethers decreases with the increase in temperature.

The apparent contradictions in number six to the above conclusions may be explained on the basis of the lower contact time. Thus the amount of phenol converted might be expected to be less and hence the amount of mono alkyl phenols would also be less. As noted in the previous runs, less higher phenols would be expected since there would be less time for the second alkylation to take place. The greater amount of phenolic ethers is also to be expected here since there is less time for the reaction to take place. This might be considered evidence for the mechanism that the reaction goes through the ether rather than the direct alkylation of the ring by the alcohol.

The ratio of ortho alkyl phenol to meta and para alkyl phenol appears to decrease slightly with increasing temperature as has been noted in the previous runs, with the exception of number seven. Possible explanations for the high ratio in number seven are: (1) some meta isomer may have been distilled in the ortho isomer range due to the closeness of the boiling points of the ortho and meta isomers; or (2) proportionately more losses were incurred in the meta and para isomers than in the ortho isomer since a leak in the seal of the distillation column was noted in number seven.

In examining the eight runs collectively there are several generalizations that can be drawn: (1) Increasing the contact time with the

temperature constant, decreases the amount of phenolic ethers and increases the amount of phenol converted, particularly to the mono alkyl phenols. This is to be expected since the longer the molecules are in contact with the catalyst, the greater possibility there is for a reaction of the type described in the theoretical section of this thesis to take place.

(2) An increase in the contact time, combined with an increase in temperature, increases the amount of phenol converted and decreases the amount of phenolic ethers even more than the increase in contact time alone. (3) The ratio of ortho alkyl phenol to meta and para alkyl phenol appears to decrease slightly as the temperature is increased, showing that less of the ortho isomer is obtained at higher temperatures. The relatively high increase in meta isomer observed in numbers seven and eight is apparently somewhat offset by a relatively smaller increase in the para isomer and only a moderate increase in the ortho isomer.

(4) The yields of higher phenols seems to be rather sensitive to the contact time and the temperature. At the two lower temperatures studied, an increase in contact time seemed to increase the yield of higher phenols probably because there is more time for the second alkylation to take place. However, at the higher temperature, the temperature effect seems to be more important and the yield is decreased. (5) In general, alcohols which are capable of forming alkenes over the catalyst used, will yield more alkene at the higher temperature. (6) It is important to note that apparently not all the alcohol is reacted, as was previously assumed. The amount of alcohol reacted appears to increase with increasing temperature and increasing contact time, as might be expected.

SUMMARY OF DERIVATIVES

The following table summarizes the work that has been done in identifying the products by means of derivatives. The procedure for preparing the derivatives can be found in Ref. 6 while the literature values of the melting points can be found in Ref. 6,7,8,9. As noted in the analytical section of this thesis, this worker was more successful in preparing the phenyl urethane derivatives than in preparing the phenoxyacetic acid derivative.

In the second table the yields of the derivatives before recrystallization, the literature and observed melting points, and the fraction taken for identification are given for this year's work. The melting points of the phenoxyacetic acid derivative are taken after recrystallization. The phenyl urethane derivatives were not recrystallized.

DERIVATIVES MADE THIS YEAR

Phenoxyacetic Acid

Run	Fraction	Lit. m.p.	Obs. m.p.	% Yield
PE-2	19 (ortho)	140-141	129-132	21
PE-2	28 (meta)	76-77	72-75	-
PE-3	6 (ortho)	140-141	121-123	54

Phenyl Urethane

Run	Fraction	Lit. m.p.	Obs. m.p.	% Yield
PE-2	22 (ortho)	141	122-125	40
PE-2	28 (meta)	139	135-137	37
PE-2	29 (para)	120	116-118	69
PE-2	31 (2,4-)	96-99	92-95	59
PE-3	6 (ortho)	141	112-116	36
PE-3	12 (meta)	139	123-130	32
PE-3	13 (para)	120	116-120	58

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