CONDENSATION OF TERT-BUTYL ALCOHOL WITH PHENOL IN THE PRESENCE OF ANHYDROUS ZINC CHLORIDE UNDER THIRTY DEGREES TEMPERATURE

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE

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1938


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THESIS

Submitted to the Faculty of
Michigan State College in
partial fulfilment of the
requirements for the degree
Master of Science

by
Albert H Agett
Organic Chemistry
1938

6-29-54
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ACKNOWLEDGMENT

The writter takes this opportunity to express his sincere appreciation for the assistance and guidance given by Dr.R.C.Huston.

INTRODUCTION

In 1916 Huston and Freedman (1) condensed benzyl alcohol and benzene by useing anhydrous aluminum chloride as the condensing agent.

In 1920 (2) benzyl alcohol and phenol were condensed by the same method.

In 1929 (3) benzyl alcohol and para-cresol were also condensed by the use of anhydrous aluminum chloride as the condensing agent.

In 1934 Huston and Fox (4) condensed tert-butyl and tert-amyl alcohols with benzene.(same method)

In 1936 tert-butyl and tert-amyl alcohols were condensed with phenol.(5).

To investigate the use of zinc chloride as a condensing agent below thirty degrees temperature the author has attempted to condense tertiary butyl alcohol with phenol.

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11 HISTORICAL

Previous workers have used anhydrous zinc chloride as a condensing agent and as a catalyst in many instances. In all cases that were investigated an elevated temperature was required to bring about the desired reaction.

Liebmann (6) condensed benzyl alcohol with phenol in the presence of anhydrous zinc chloride. The reaction took place rapidly and with a fair yield.

Kippernberg (7) brought about the condensation of an alcohol and an amine. Here again an elevated temperature was required to bring about the reaction in the presence of anhydrous zinc chloride.

Fisher and Roser (8) (9) condensed alcohols with aromatic bases. This reaction took place only at elevated temperatures and required a long period of time.

Liebermann(10) condensed butyl, benzyl and amyl alcohols with phenol. Finding also that the higher homologues of phenol failed to give the ferric chloride tests. An elevated temperature was required to initiate the reaction.

Merz and Weith (11) also produced diphenyl ether by the action of anhydrous zinc chloride at 110° on phenol.

Auer (12) prepared ethyl phenol by heating absolute alcohol (ethyl) and phenol in the presence of anhydrous zinc chloride.

In the crotonization of aldehydes and ketones Perkins (13) discovered that in a liquid medium acetaldehyde was converted into crotonaldehyde with zinc chloride at a temperature of 97°.

Prieb (14) condensed benzaldehyde with nitromethane in the presence of anhydrous zinc chloride to give the nitro derrivatives of phenyl ethylene.

Frank and Kohn (15) found that hot para-aldehyde was converted into mono-molecular aldehydes at 100°.

Knownagin (16) acetylated aldehydes in the presence of anhydrous zinc cholride at a very high temperature.

Sabateir and Mailhe (17) used zinc chloride as a dehydrating agent, especially in the dehydration of alcohols to give ethers and unsaturated (usually)

hydrocarbons. It was also found that it was impossible to use zinc chloride to dehydrate methyl alcohol to give di-methyl ether as gaseous products are produced through a very complicated reaction and a certain amount of hexamethylbenzene is also formed.

The author was unable to find any references in which anhydrous zinc chloride had been used successfully as a condensing agent at reduced temperatures.

DISCUSSION

The condensation of tertiary butyl with phenol was attempted by the authors (19). No alkylated phenol was isolated by this method. Many different methods were used to bring about this reaction at the desired temperature but they were all unsuccessful. It was found, however, that by the addition of a small quanity of anhydrous aluminum chloride to the reaction mixture that the zinc chloride was activated and the reaction took place. The percent yield of the para isomer compares favorably with that of the aluminum chloride condensations with less gummy material being formed. Upon purifying the para isomer it was noticed that there was a low and a high boiling fraction that could not be any of the original reactants. During the course of the investigation these fractions were proven to be the ortho and the dialkylated phenols which apparently exist in equilibrum with the para isomer, but in very small quanities. Attempts were made to produce the ortho and the dialkylated isomers by heating the para isomer in the presence of the aluminum chloride zinc chloride mixture (same amounts as used in condensations)

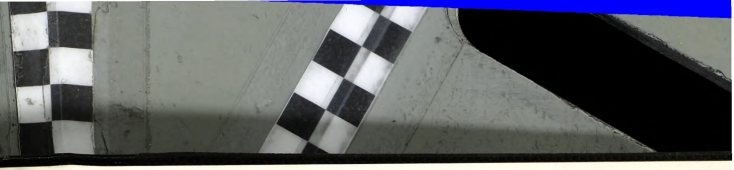
but only the ortho-tertiary butyl phenol was isolated.in very small quanities.The dialkylated product was not obtained in this procedure although it was found in small amounts when tert-butyl alcohol and phenol were condensed in the presence of the zinc chloride aluminum chloride mixture.When the same method was used with aluminum chloride alone (20) both the ortho and the dialkylated phenols were isolated in small quanities (see tables).When the ortho isomer was treated with aluminum chloride only the para tertiary butyl phenol could be isolated.The same procedure was also followed useing anhydrous zinc chloride as the equilibrum producing agent,but no ortho or dialkylated phenols were isolated.With phosphoric acid as the equilibrum producing agent no ortho or dialkylated phenols were isolated.However when tertiary butyl alcohol and phenol were condensed in the presence of phosphoric acid (21) a small yield of ortho tertiary butyl phenol was found but no dialkylated isomer was isolated .

The structure of the alkylated phenols were proven by comparison with those produced by Perkins,Dietzler,and Lundquist(20).In addition

Swayzee (22) condensedortho bromo phenol with tert-butyl alcohol useing the aluminum chloride method.The author upon the bromination of the 4-tertiary butyl phenol found that the product formed was identicâl in Melting Point and Boiling Point to that of Swayzee's above.A mixed melting point was run with no depression. A bromine determination was made (23) (see tables) on both compounds and close agreement with the theoretical were obtained.One atom of bromine being attached to the ring.

A carbon and hydrogen determination (24) was run on the ortho alkylated phenol and the calculated results agree favorably with the theoretical (see tables).The orhto tertiary butyl phenol was then bromine determination made (23).It was also found to have only one atom of Br attached to the ring.Since the melting point and the boiling point of this compound does not agree with that of 2-bromo 4-tertiary butyl phenol and since there are no other likely possibilties it can be safely stated that it is 2-tertiary butyl phenol.Also when the ortho tertiay butyl phenol was treated with aluminum chloride it rearranged almost quantitively to the 4-tertiary butyl phenol.

Carbon and hydrogen determinations(24) were made on the 2,4 ditertiary butyl phenol and the calculated results were in agreement with the theoretical (see tables)



The author also attempted to alkylate para-bromo phenol with tertiary butyl alcohol in the presence of anhydrous aluminum chloride, anhydrous zinc chloride and aluminum chloride mixture, and in the presence of phosphoric acid. In all three cases no alkylated phenols were recovered. Apparently the ortho position under these conditions is not receptive to alkylation.

Tertiary butyl bromide and phenol were condensed in the presence of metallic Sodium (25). The only alkalyated phenol that was isolated was the para isomer and no ortho or dialkalyated were obatained.

In order to facilitate the separation of the ortho isomer from the para isomer it was found that it was very conveinient to use a 5% solution of KOH. The para tertiary butyl phenol being soluble and the ortho tertiary butyl phenol insoluble in this solution (see tables).

EXPERIMENTAL

A.

Condensation of Tertiary Butyl Alcohol with Phenol in the Presence of Zinc Chloride and Aluminum Chloride Under Thirty Degrees Temperature.

Eighteen and five-tenths grams (.25 mole) of Tertiary butyl alcohol and 23.5 grams (0.25 mole) of phenol were treated with 80 ml. of petroleum ether in a five hundred ml. round bottomed three necked flask equipted with mecury sealed mechanical stirrer, and a condenser which carries both a therometer which reaches into the reaction mixture and a bent tube for the outlet of HCl gas. This apparatus was placed in the hood. Then seventeen grams (.125 mole) of Zinc Chloride was added to the mixture and stirred for one half an hour. Then to this mixture was added three grams of anhydroud aluminum chloride. No rise in temperature was noted. After the addition of the aluminum chloride the stirring was continued for four or five hours. During this time only a very little amount of HCl gas was given off. The comtents became a slight pink in color and upon standing overnight became quite dark. at which time it was decomposed with ice water and HCl. The hydrolyzed product was then extracted three times with

ether and dried over $CaCl_2$.The ether was removed by distillation and the residue fractionated.The first fraction was collected from 90°-120° @ 14 mm.pressure and was found to be mostly unchanged phenol and ortho tertiary butyl phenol.The second fraction was collected at 120°-135° @ 14 mm. pressure and was found to be almost pure para tert-butyl phenol.The third fraction was collected at 135°-150° @ 14mm. pressure and was found to be mostly 2,4 ditertiary butyl phenol.These three fractions were purified by fractional distillation.The para tertiary butyl phenol was recrystallized from petroleum ether and was to be a 38% yield .M.P.97.5°;B.P.120°-122° @ 14 mm. pressure.The ortho tertiary butyl phenol was found to be a slightly yellow colored liquid upon purification.Yield 1.5%;B.P.115°-117° @ 23 mm pressure.The 2,4 ditertiary butyl phenol was purified by fractionation.It crysatllized as a white solid with M.P. 53° and B.P. 143°-145° @ 23 mm pressure.Less than 1% yield was obtained.

B.

Reaction of Para Tertiary Butyl Phenol with Zinc Chloride and Aluminum Chloride.

Seventy-five grams (.5 mole) of pure tert butyl phenol (para isomer) were placed in a 500ml. modified Claisen flask fitted with a capillary, thermometer, and a condensing flask. Thirty-four grams of of anhydrous zinc chloride and six grams of anhydroud aluminum chloride was added cautiously to the warmed para tertiary butyl phenol. A small amount of HCl was given off at this time and some iso-butylene. The reaction was carried out under reduced pressure, water pump, and the mixture was heated for three hours at 35 mm pressure. At the end of the three hour period the heat was gradually increased and about twenty grams of phenol was distilled fractionally from the mixture. A solution made up of five ml. of distilled water and eleven grams of sodium carbonate was then added to the residue and filtered immediately, while hot. Upon purifiaation by fractional distillation obtained 54.5 grams (73%) yield of para tertiary butyl phenol M.P. 97°. One and five tenths grams (2%) of 2,4 ditertiary butyl phenol was obtained M.P. 54°.

C.

Condensation of Tertiary Butyl Alcohol with Para Bromo Phenol in the Presence of Anhydrous Zinc Chloride and Aluminum Chloride.

The procedure the same as in A above and upon purifiaction obtained 35.5 grams (82%) of para bromo phenol and 5 grams (3%) of an unidentified compound. B.P. 125°-127° @14mmm pressure.

D.

Condensation of Tertiary Butyl Alcohol and Para Tertiary Butyl Phenol in the Presence Of Zinc Chloride and Aluminum Chloride.

The procedure the same as in A above. Upon purification recovered thirty grams (80%) of para tertiary butyl phenol. No other alkalyated phenol was isolated.

E.

Condensation of Tertiary Butyl Alcohol and Phenol in the Presence of Anhydrous Zinc Chloride Under Thirty Degrees Temperature.

The procedure the same as in A above with the exception that 17 grams of anhydrous (fused) Zinc Chloride was used as the condensing agent. No alkalyated phenols were isolated. Ninety % (21 grams) of para teritary butyl phenol was recovered.

F.

Condensation of Tertiary Butyl Alcohol with Phenol in the Presence of Anhydrous Aluminum Chloride.

The procedure the same as in A above. Upon purification a 41% yield of para tertiary butyl phenol was obtained. M.P. 97.5°; B.P. 120°-122° @ 14 mm. pressure. The ortho tertiary butyl phenol upon purification was 1.5% yield of a slight yellow liquid with a B.P. 115°-117° @ 23 mm. pressure. The 2,4 ditertiary butyl phenol was purified by fractional distillation and crystallized as a white solid with a M.P. 53.5° and B.P. 143°-145° @ 23 mm pressure. A 5 % yield of the pure product was obtained.

G.

Reaction of Para Tertiary Butyl Phenol in the Presence of Anhydrous Aluminum Chloride.

The procedure the same as in B above. Thirty-four grams of anhydrous aluminum Chloride was added. A great deal of HCl was evolved at this time. The filtrate was fractionated and obtained 58% (43.5 grams) of para tertiary butyl phenol, five grams (6.6%) of 2,4 ditertiary butyl phenol, two grams (2.6%) of ortho tertiary butyl phenol.

H.

Reaction of Tertiary Butyl Alcohol with Para Bromo Phenol in the Presence of Anhydrous Aluminum Chloride.

Eighteen and five-tenths grams of (.25 mole) tertiary butyl alcohol and 43.5 grams (.25 mole) of para bromo phenol was treated with 80 ml. of petroleum ether in a 500 ml. round bottomed three necked flask. The procedure the same as in A above. Upon hydrolysis, extraction, and purification obtained 39 grams of para bromo phenol and no alkalyated product was identified.

I.

Condensation of Tertiary Butyl Alcohol and Para Tertiary Butyl Phenol with Anhydrous Aluminum Chloride.

The procedure is identical to that in A above. Upon hydrolysis, extraction and purification twenty grams (80%) of para tertiary butyl ph nol were recovered. Five grams (1.5%) of 2,4 ditertiary butyl phenol were obtained M.P. 53.5°.

J. Reaction of Para Tertiary Butyl Phenol with Tert. Butyl Alcohol in the presence of Anhydrous Zinc Chloride.

The procedure the same as in A above .25 mole of the reactants being used. No dialkalyated phenols were isolated. Twenty-two grams (92%) of para tertiary butyl phenol recovered.

K.

Condensation of Tertiary Butyl Alcohol with Phenol in the Presence of Phosphoric Acid. (26)

Eighteen and five-tenths grams (.25 mole) of tertiary butyl alcohol and 23.5 grams (.25 mole) of phenol and 200 grams of phosphoric acid were placed in a 500 ml. roung bottomed flask fitted with a mecury

mecury sealed mechanical stirrer and reflux condenser. The flask was then placed on the steam bath and heated for eight hours at 100° with constant stirring. At the end of this period the phosphoric acid was siphoned off and the residue was fractionally distilled. Obtained 19 grams (80%) of para tertiary butyl phenol, M.P. 95°; .5 grams (2%) of 2,4 ditertiary butyl phenol, M.P. 53.5°.

L.

Condensation of Tertiary Butyl Alcohol with Para Bromo Phenol in the Presence of Phosphoric Acid

The procedure the same as in K above. Fourty-three grams of para bromo phenol (.25 mols) was used. Upon purification 95% (41.5 grams) of para bromo phenol was recovered. No alkalyated phenol was obtained.

M.

Reaction of Tertiary Butyl Bromide and Phenol in the Presence of Metallic Sodium.

Eleven and five-tenths grams of (.5 mole) metallic sodium was suspended in one hundred mls. of toluene in 500ml. round bottomed three necked flask

fitted with a mecury sealed mechanical stirrer and reflux condenser. Fourty-seven grams (.5mole) of phenol were added carefully and the mixture stirrered until the reaction was completed. Then 68.5 grams (.5 mole) of tertiary butyl bromide added slowly by means of a separatory funnel. The reaction mixture was stirred for six hours and allowed to stand overnight. Upon purification 42.5% (20 grams) of para tertiary butyl phenol were isolated, M.P. 97.5°. No other alkalyated phenol was obtained.

N.

Bromination of Para Tertiary Butyl Phenol

Twenty-three grams (.25 mole) of para-tertiary butyl phenol was disolved in sixty mls of carbon tetra chloride in a two hundred ml. round bottomed three necked flask, to which was fitted a mecury sealed mechanical stirrer, reflux condenser fitted with a thermometer reaching below the surface of the liquid, and a separatory funnel. Fourty grams (.25 mole) of Bromine was added by use of the separatory funnel. During the addition of the Bromine the mixture was cooled with an ice and salt mixture and kept around 10°. The mixture was then allowed to come to room temperature with stirring for four hours after the Bromine was

added. It was allowed to stand overnight and then it was purified by fractional distillation under reduced pressure. Obtained a white crystalline solid, B.P. 121-123° @ 16mm/pressure and M.P. 45°.

O.

Bromination of Ortho Tertiary Butyl Phenol

The procedure indentical to that of N above. Upon purification a white colorless solid M.P. 55-56° and a B.P. 145-148° @ 14mm. pressure was obtained.

TABLE OF RESULTS

ALCOHOL	PHENOL	CONDENSING AGENT	PRODUCT	% YIELD	M.P.	B.P.
TERT/BUTYL	phenol	$ZnCl_2$(17gr.).$AlCl_3$(3gr.)	p-tert.butyl phenol	38.0%	97°	120-122°/14mm
			2,4 ditert.butyl phenol	41.8%	54°	143-144°/23mm
			o-tert.butyl phenol	41.0%	liquid	115-117°/23mm
----------	p-tert.butyl phenol	above	p-tert.butyl phenol	73.0%	97°	120-122°/14mm
			2,4 ditert.butyl phenol	2.0%	53.5°	143-145°/23mm
			o-tert.butyl phenol	None	--------	----------
tert.butyl	p-bromo phenol	above	para bromo phenol	82.0%	62.5	230°/760 mm
			unidentified product	3.0%	solid	125-127°/14mm
Tert.butyl	p-tert.butyl phenol	above	p-tert.butyl phenol	87.0%	96.5°	122-123°/14mm
			2,4 ditert.butyl phenol	None	----------	----------
			o-tert.butyl phenol	None	----------	----------
TERT/Butyl	phenol	AlCl3 (17gr .125 m)	p-tert.butyl phenol	41.0%	97.5°	120-123°/14mm
			2,4ditert.butyl phenol	5.0%	53.5°	143-144°/23mm
			o-tert.butyl phenol	1.5%	liquid	115-117°/23mm
---------	P-TERT.Butyl	AlCl3 (17gr .125m)	p-tert.butyl phenol	52.0%	97°	120-122°/14mm
			2,4 ditert.butyl phenol	6.5 %	54.0°	144-145°/23mm
			o-tert.butyl phenol	2.5 %	liquid	116-117°/23mm
tert.butyl	p-bromo phenol	above	p-bromo phenol	75.0%	63.0°	230°/760 mm
			No Condensation	-------	----------	----------
tert.butyl	p-tert.butyl	above	p-tert.butyl phenol	80.0%	97.0°	120-123°.14mm
			2,4 ditert. butyl phenol	1.5%	53.0°	140-145°/24mm
----------	p-tert.butyl	$ZnCl_2$ (17gr)	p-tert.butyl phenol	89.0%	97.0°	120-125°/14mm
			No Condensation	-------	----------	----------
tert.butyl	phenol	$ZnCl_2$ (17gr)	No Condensation	-------	----------	----------
tert.butyl	phenol	H_3PO_4 (200)	p-tert.butyl phenol	80.0%	96.5%	120-122°/14mm
			2,4 ditert.butyl phenol	2.0%	52.5%	142-145°/23mm
			o-tert.butyl phenol	None	----------	----------
tert.butyl	p-bromo phenol	H_3PO_4	No Condensation	------	----------	----------
TERT.Butyl Bromide	phenol	Metallic Na	o-tert.butyl phenol	--------	----------	----------
			P-tert.butyl phenol	42.5%	98.0°	120-125°/14mm
			2,4 ditert.butyl phenol	------	----------	----------

TABLE OF RESULTS
Cont.

SOLUBILITY OF ALKYLATED PHENOLS IN 5% KOH

COMPOUND	SOLUBILITY (5%KOH)
p-bromo o-tert.butyl phenol	insoluble
Ortho tert.butyl phenol	insoluble
o-bromo p-tert.butyl phenol	soluble
Para tert.butyl phenol	soluble

PERCENT CARBON AND HYDROGEN

COMPOUND	% C THEO.	% C CALC.	% H THEO.	% H CALC.
P-tert.butyl phenol	80.00	79.85	9.33	10.250
O-tert.butyl phenol	80.00	78.35	9.33	10.305
2,4 ditert,tert.butyl phenol	81.55	82.01	10.67	10.790

PERCENT BROMINE

COMPOUND	Calc. % Br	THEO. % Br
2 bromo 4 tert.butyl phenol M.P.	36.38	34.93
2 tert.butyl 4 bromo phenol M.P.	35.85	34.93

SUMMARY

1. Tertiary butyl alcohol will not condense in the presence of zinc chloride at or below 30° as with aluminum chloride.

2. Tertiary butyl alcohol and phenol will condense in the presence of zinc chloride and aluminum chloride mixture to give para tertiary butyl phenol, ortho tertiary butyl phenol, and 2,4 ditertiary butyl phenol.

3. Ortho and 2,4 ditertiary butyl phenol apparently exist in equilibrum with para tertiary butyl phenol when in the presence of zinc chloride and aluminum chloride mixture. It is possible to isolate them from this reaction mixture.

4. Ortho tertiary butyl phenol in the presence of aluminum chloride rearranges almost quanitatively to give para tertiary butyl phenol.

5. Para bromo phenol will not condense with tertiary butyl alcohol in the presence of aluminum chloride, zinc chloride, zinc chloride and aluminum chloride mixture, or in the presence of phosphoric acid.

SUMMARY Cont.

6. Apparently the para position is strongly favored when both the ortho and para positions are open for alkalyation.

7. The ortho alkalyated phenols are insoluble in 5% KOH while the para alkalyated isomers are soluble in this solution.

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